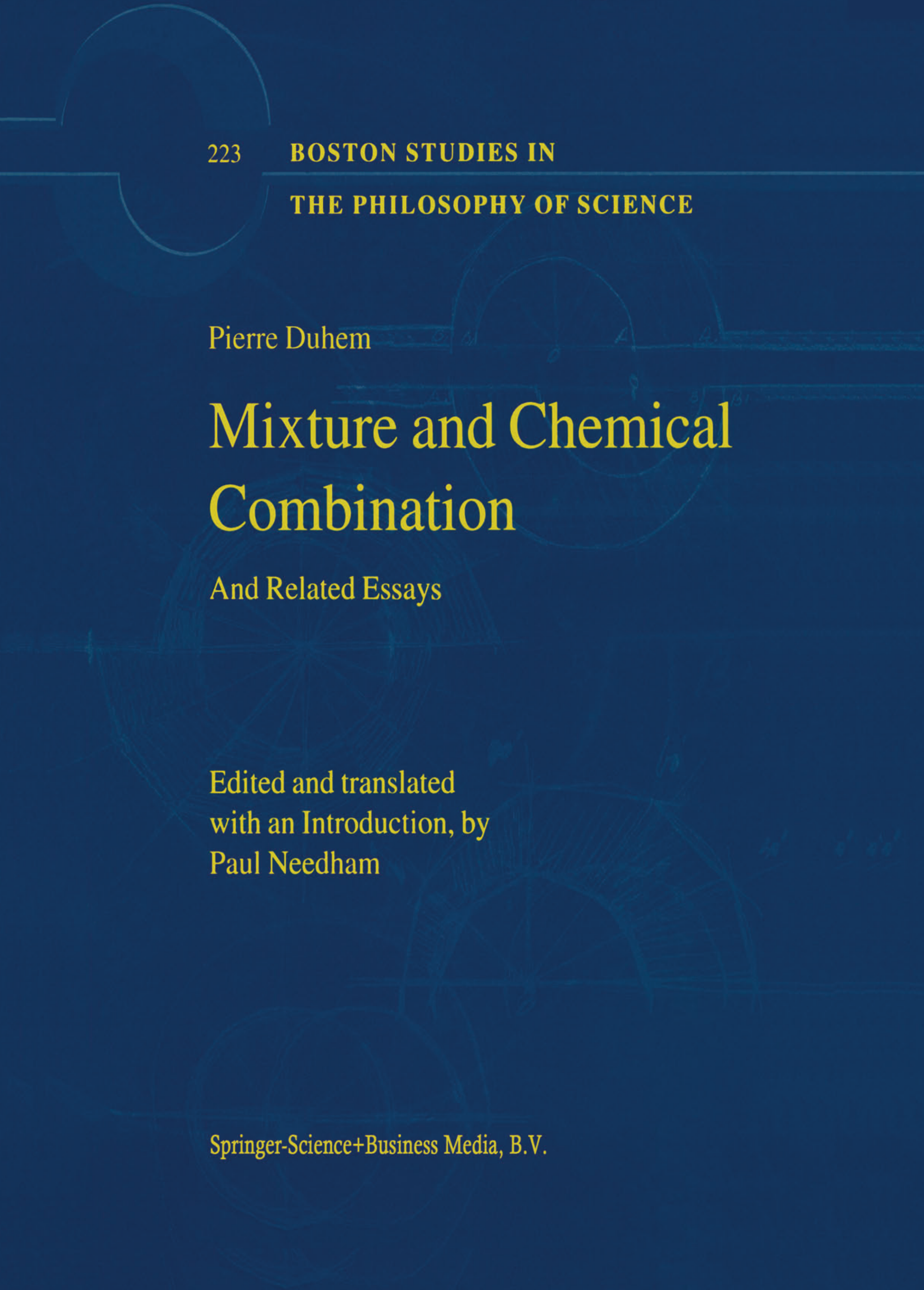

223 BOSTON STUDIES IN
THE PHILOSOPHY OF SCIENCE

Pierre Duhem

Mixture and Chemical Combination

And Related Essays

Edited and translated
with an Introduction, by
Paul Needham

Springer-Science+Business Media, B.V.

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VOLUME 223

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INTRODUCTION

Alongside the scientific work which gained him lectureships in physics at Lille (1887) and Rennes (1893), and the chair of physics at Bordeaux (1894, changed to chair of theoretical physics in 1895), Duhem began to publish articles on philosophical and historical topics related to his scientific interests in 1892. Many of these appeared in the Catholic journal *Revue des questions scientifiques*, and he was to draw on them in books published in the first years of the new century. English translations of all or part of these books have begun to appear in recent decades,[1] as well as a selection of articles, including some from *Revue des questions scientifiques* published during the 1890s (Duhem 1996). The present volume, which continues this work, focuses on issues related to chemistry, and contains translations of *Le mixte et la combinaison chimique* (1902) together with a number of related articles from *Revue des questions scientifiques* and other sources.

The question of chemical structure is taken up in one of the first of Duhem's *Revue des questions scientifiques* articles, "Atomic Notation and Atomistic Hypotheses" (1892b), where he retraces developments during the course of the 19th century from the establishment of the law of constant proportions by Proust around 1803. The greater part of this 1892 article is integrated either verbatim or with only minor linguistic changes into *Le mixte et la combinaison chimique* (henceforth *Mixture and Chemical Combination*), which elaborates the earlier account and adds chapters dealing with the pre-19th century history of the notion of mixture as well as more detailed interpretations and an assessment of what Duhem considered to be the way forward. A translation of this earlier article is therefore not included in the present selection. (The translation referred to under Duhem (1892b) in the list of references indicates the passages adapted in *Mixture and Chemical Combination.*)

It is difficult to conceive of modern chemistry without its notions of molecular structure. But this did not fall within the compass of the line of development Duhem advocated. He was critical of the atomic theory, both in the 1892 article and the 1902 book. It might help to put this into perspective by saying that it is only since the turn of the 20th century that the molecular nature of chemical substances has become a matter of universal consensus, and its general character is still a matter of dispute. The reductionist way in which the corpuscular doctrine is often interpreted has been vigorously criticised in recent philosophy of chemistry, and the

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[1] Duhem (1903), (1905-6), (1906), (1908), (1915), (1985).

standard chemist's conception is not without its critics.[2] Although Duhem seems to have been inordinately stubborn in ignoring pointers to corpuscular microstructure, there is something of value both in his critical attitude towards the naive way in which molecular conceptions have been introduced and in the way he developed his alternative approach.[3]

Duhem readily acknowledged that from Dalton's postulates, "it is easy to deduce the fundamental laws of chemistry" (1892b, p. 441). He did not dispute that it "agrees well with the primary laws and the primary notions of chemistry" (1892b, p. 443), but questioned whether it provides any explanation of them. He considers the elaborations in the form of ascribing atoms *atomicities*, added with a view to explaining aspects of chemical structure that came to light several decades into the 19th century, to be entirely gratuitous, and shows them to build on so many *ad hoc* devices as to render them completely devoid of explanatory value.

It might be thought, on the strength of his derogatory remarks on explanation in Ch. 1 of *Aim and Structure* (Duhem 1906), that Duhem should not think there is anything exceptional in a theory not providing any explanation of the phenomena with which it deals. A standard interpretation of this work has it that Duhem held the object of theory formation to be the classification of phenomena *as opposed to* the explanation of phenomena. Duhem's rhetorically excessive diatribes against explanation might better be seen, however, as directed specifically at the Cartesian tradition of seeking explanation by reduction to *a priori* principles, which in his view was continued long after Descartes' time in the form of insistence on explanations in terms of simple mechanical forces. This comes across clearly in his 1896 paper, "The Evolution of Physical Theory" (translated here as Essay 2), where he refers to the policy of searching for mechanical explanations upheld by the British school of physicists in the 19th century as "new Cartesianism" (1896, p. 492). (This continuity of tradition is not mentioned in *Aim and Structure*, presumably because it does not sit well with the nationalistic distinction between the "broad and shallow" mind of the British which he contrasted with the "deep and narrow" mind of the French—see Duhem 1906, Pt. I, Ch. IV.) Moreover, when presenting his own favoured theories and approaches, he has no qualms about making explanatory claims—something which is well illustrated by a number of passages in the works translated here. This would suggest that the charge that the

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[2] See, for example, van Brakel (1986), (1997) and (2000, Ch. 5) Scerri (1991), (1993) and (1994). The writings of R. G. Woolley raise some questions about the nature of modern conceptions of molecules; see, for example, Woolley (1978), (1988), (1991) and (1998). A useful review of recent discussion is Hendry (1998).

[3] Truesdell (1984) places Duhem in a tradition of rigorously developing the foundations of thermodynamics which is an active field of research today; see also Pradas (1991). Prigogine has always acknowledged Duhem as the first to appreciate the importance of Clausius' notion of non-compensated heat in the development of the thermodynamics of irreversible processes for which he has himself become famous. See Kondepundi and Prigogine (1998, p. 87 and *passim*), and Brouzeng (1987, pp. 121-34), (1991).

atomic theory lacks explanatory value is a negative criticism directed specifically against that particular theory.

But if Duhem rejected atomism as the basis of understanding chemical structure, what does he offer in its place? The reference to notation in the title of the 1892 article might suggest a mere form of words without substantial referential content—in a word, instrumentalism.[4] Whether an interpretation along these lines is borne out by a consideration of all the threads in Duhem's argument is a question which merits further attention, however. The precise role assigned to convention is crucial here. Dalton's atomism was not received by his contemporaries as the uncontroversial assumption demanded by the laws of constant and multiple proportions that it is usually presented as being in school chemistry today. Wollaston thought Dalton had no grounds whatsoever for claiming as he did that his assumption about water, to the effect that its formula is HO, is "very probable"; it is a convention for which the question of correctness does not arise beyond a certain point (it would be wrong to include a symbol for sulphur in the formula for water, for example). There were, in fact, no grounds for assigning a compound a particular compositional formula, as opposed to any other featuring the same elements, until Cannizzaro published his method in 1858. Despite this, the term "conventionalist" has come to be associated specifically with those who, like Wollaston, recognised the limitations of what they could reasonably claim to know and sought to articulate their claims accordingly. It by no means follows that conventionalists declined to make any truth claim simply because they shrank from making the particular kind of truth claims Dalton advocated. The issue is far more delicate.

Duhem is rather clear about exactly what is involved in the conventional aspect of compositional formulas. This accords with the great stress laid on articulating the precise meaning of scientific claims in his general philosophy, which is much concerned with the representation afforded by a physical theory as a result of a correspondence between a concept and a physical magnitude. A simple illustration is provided by the "correspondence between the concept of warmth and the algebraic magnitude that we call the temperature. ... [B]y virtue of the correspondence established between these two ideas, the one becomes the *symbol* of the other" (Duhem 1992a, p. 143; 1996, pp. 3-4). In general,

> The physical concept which we are concerned to represent possesses a certain number of fundamental properties. The magnitude intended to symbolise it should present a certain number of essential features for representing these properties. But every magnitude that introduces these features can be taken as a symbol of the physical concept that concerns us. (Duhem 1892a, p. 144; 1996, p. 4)

Temperature, as he goes on to point out, introduces the characteristics that equally warm bodies have the same temperature and a greater value of temperature is

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[4] As Ariew and Barker put it in their Introduction, "Duhem's rejection of atomism was based on his instrumentalism (or fictionalism)" (Duhem 1996, p. xi).

assigned to a warmer body, and "every magnitude which introduces these two characteristics can be taken as *temperature*" (loc. cit.).

A discussion in a paper on the foundations of thermodynamics published in the same year (1892c, pp. 284-9) makes it quite clear that Duhem's intention was not to offer a strict empiricist interpretation of the relations of being as warm as and being warmer than, as required by the instrumentalism that some of the logical positivists were to espouse. The import of the warmth relations not only extends far beyond what is discernible by the senses; it even contradicts them. They apply to temperatures far above and below the range of human experience. And within this range, the senses inform us about surface regions with a certain extension for a certain duration, whereas the warmth relations apply to subregions of these regions for indefinitely shorter and longer intervals, to say nothing of the interiors of bodies. Moreover, wooden and metal bodies judged from the circumstances to be at equilibrium are counted as equally warm, despite our experiences to the contrary when we touch them. What Duhem had in mind was something other than an operational interpretation of these relations.

If several magnitudes, as he says, represent the same concept of temperature, their differences cannot be significant. Thus, it would be incorrect to say that by heating a body from 10°C to 20°C its temperature is doubled; for although 20 is twice 10, 10°C is the same as 50°F, and 20°C the same as 68°F, but 68 is not twice 50. It is a mistake to conclude that features of the numbers used to represent a concept necessarily reflect a feature of that concept. Duhem points out that "we do not understand what statements such as ... body A is seventeen times warmer than body B or is three times less warm than body B" (1892a, p. 142; 1996, p. 3). Duhem knew that properties of numbers used to represent qualities may well not represent, or may misrepresent, properties of the qualities themselves, and was wary of drawing conclusions from properties of the number system. The modern theory of measurement, whose founding fathers were only just beginning to write on the subject as Duhem was writing on chemical structure,[5] clarifies the degree of arbitrariness Duhem was talking about in terms of scale types. A scale type is characterised by the kind of transformations of scale that are considered to preserve the physical features of the underlying concept. Empirical temperature is measured by a type of scale called an interval scale, which can be interconverted to an equally acceptable scale by a linear transformation, like that used in converting degrees Celsius to degrees Fahrenheit, and any features not preserved by the transformation are purely conventional aspects of a particular scale without physical significance.

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[5] Helmholtz (1887) and Hölder (1901). The contemporary development of measurement theory took off with the critique of Hölder's account in Suppes (1951). For a historical review, see Diez (1997). Miller (1971, p. 229) makes the point that "Duhem's axiomatic outlook which characterised this discussion of the first law [of thermodynamics] was indeed pioneering for physics and to some extent anticipated the major axiomatic research in mathematics." Duhem's views on the import of measurable concepts were distinctly modern.

Conventionalism is, however, usually understood to involve a far more radical position than the mere recognition of certain conventional aspects of scientific descriptions such as those involved in scales of measurement. It is usually taken to involve an instrumentalist stand, allowing for no substantial theoretical truth, and correspondingly no ontological commitment in Quine's sense, i.e. no reference of items designated by the predicates of the theory. Ariew and Barker, in their Introduction to Duhem (1996), seem to regard Duhem as a conventionalist in this sense when they describe him as holding the view that "Theoretical propositions are not true or false but 'convenient' or 'inconvenient'" (p. xi). The question is whether Duhem is correctly interpreted as a conventionalist in this sense, as distinct from merely acknowledging that laws accepted as true delimit the import of physical concepts only up to a certain degree as with any measurable property. It seems pretty clear that the care with which Duhem does specify the conventional element in his treatment of formulas leaves no room for charges of conventionalism, and is comparable with what he says about temperature.

A critic who charges the atomist with overlooking elements of convention and declines to embrace the truth claims of the atomist may, nevertheless, want to make claims about what is true, then. He might adopt the view that matter is ultimately continuous, although it seems divisible into discrete portions on a sufficiently large scale. Again, he might prefer to keep an open mind regarding the ultimate nature of matter, aware that the application of mathematical analysis incurs postulates—such as those going beyond infinite divisibility (denseness of the rational numbers)—whose literal physical interpretation may be difficult to justify. Mathematical analysis was not called upon in the development of the notion of chemical formulas that ensued once limitations of compositional formulas came to light and which Duhem discusses. It remained, nevertheless, an issue for him since, as he makes clear in the final two chapters of *Mixture and Chemical Combination*, he saw the way forward in chemistry as building on the links with physics established in the newly emerging field of physical chemistry, and in particular, with thermodynamics which is couched in the language of mathematical analysis.

In this connection, it is interesting to note what he says about the consequences of trying to follow the path of viewing matter as discrete on the microscopic level.

> we are entirely free to represent a body, which our senses perceive as continuous, either by a continuous distribution of matter in a certain space, or by a discontinuous collection of very small atoms.
>
> The latter mode of representation has been adopted by many theoreticians of physics. Poisson, in particular, employed it is systematic fashion because he believed he saw there the expression of the real constitution of bodies. Without wishing here to examine all the objections which confront this way of dealing with Physics, there is at least one that we can draw attention to now. The formulas to which it immediately leads always involve extensive sums of a very large number of disjoint, very small masses in very close proximity. To render these formulas manageable in Analysis and, at the same time, to extract from them results which can be translated into experimental language, it is necessary to replace these sums, by means of a calculus

> of approximation, with integrals over continuous space, *spreading out*, as it were, the putative disjoint masses in some such way that their matter fills the intermediate spaces. In this way the continuity which was first rejected is now restored to matter after the event. Now this conversion of sums to integrals is a very delicate and very tricky mathematical operation. It is difficult to bring it to a successful conclusion without avoiding tedious procedures. Besides, it always entails many entirely gratuitous hypotheses about the order of magnitude of molecules and their separations. (Duhem 1911, Vol. I, pp. 13-4)

Speaking of the 2-volume treatise from which this passage is taken, Truesdell comments "I have not found in its more than a thousand pages a word against molecules" (Truesdell 1984, p. 41). This might be construed as compatible with the thoroughgoing instrumentalist interpretation. But another view of the matter is suggested by thermodynamicists' comments on their own subject. Around the time Duhem wrote his 1911 treatise, we see laws of thermodynamics being described as "free from all hypothetical assumptions as to the molecular condition of the participating substances" (Findlay 1915, p. 8). More recently, Denbigh puts it by saying that "[t]hermodynamics ... is independent of the fine structure of matter" (Denbigh 1981, p. 4), expressing more succinctly an attitude of non-commitment which is a natural reading of Duhem's choice of representations.

Others more boldly assert "mass is incidental to chemical reactions whose main consequence is the change in the number of molecules of the various reacting species" (Kondepudi and Prigogine 1998, p. 371). But this must be reconciled with the fact that the theory is formulated in terms of continuous magnitudes. In particular, functions of state are treated in thermodynamics as functions of the amount of each component; the internal energy, for example, is a function $U(S, V, N_1, \ldots, N_r)$ of the entropy, S, the volume, V, and a measure of the amount of each component, N_i. These amounts of each component might be thought of, in accordance with the atomic view, as numbers of molecules, or such numbers divided by Avogadro's number.[6] But the fact remains that theory allows the internal energy to be differentiated with respect to the variable N_i, yielding the important concept of the chemical potential of the ith component. And this presupposes that N_i ranges over the real numbers, and not merely the integers or the rational numbers as the atomic interpretation suggests. Accordingly, adopting the atomic interpretation in thermodynamics rather than the neutral stance means not treating the theory literally but taking an instrumentalist view of at least certain aspects of it. Adopting the atomic interpretation is therefore no less instrumentalist than adopting the continuous interpretation: neither interpretation is actually combined with the relinquishing of all the commitments of the other.

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[6] As, for example, suggested by (Callen 1985, p. 9): "a simple system has a definite chemical composition which must be described by an appropriate set of parameters. One reasonable set of composition parameters is the numbers of molecules in each of the chemically pure components of which the system is a mixture. Alternatively, to obtain numbers of more convenient size, we adopt the mole numbers, defined as the actual number of each type of molecule divided by Avogadro's number."

It remains to be seen how adopting an instrumentalist or non-committed stance to part of the theory and a realist view of the remainder might be rigorously articulated. But this serious problem is the issue Duhem is pointing to in the above passage. Quine was later to argue that what he called ontological commitment to the literal truth of the theory we actually use cannot be shunned, as Church (1958) nicely explains, unless it can be shown how talk of the entities referred to can be replaced by another theory which makes do without them but which still serves the same general purposes adequately. Duhem is clearly charging the atomist with much the same intellectual dishonesty that Church diagnoses. Atomism may be unproblematic to the chemist displeased with "the physicists who had never been 'satisfied with the hard, indivisible ball of specific substance and definite mass which has served chemistry so well' ... [and whose] meddling with the atoms led to a situation that only a 'few chemists can understand'."[7] But Duhem is not arguing from such an over-simplified viewpoint.

The challenge to a straightforward interpretation of thermodynamics as a science of continuous matter, which Duhem seems to acknowledge in his 1911 treatise, derived in large part from the refinements extending the import of chemical formulas. The question is at what stage does the atomic view become indispensable? The continuous view of matter was hardly challenged by the laws of constant and multiple proportions; but can this view be sustained once we leave the simple notion of compositional formulas and broach the features of chemical structure required by isomerism? This phenomenon was first recognised by Gay-Lussac who, as editor of *Annales de Chimie*, noted that Wöhler's compositional analysis of cyanic acid, published in 1824, was the same as Liebig's analysis of fulminic acid, published there in 1823. After similar discoveries Berzelius in 1832 proposed calling "substances of similar composition and dissimilar properties isomeric, from the Greek *ἰσομέρης* (composed of equal parts)" (Leicester and Klickstein, p. 265). The fixed proportion of elements in a given compound required by the law of constant proportions therefore provides in general only a necessary feature of a given compound; it is not sufficient to characterise it. Isomers were differentiated by physical properties such as melting and boiling points, solubility in various solvents, etc., and by the chemical reactions in which they participated as reactants or products. The French chemists, led by Jean Dumas (1800–84), tackled the problem of isomerism by seeking a characterisation of compounds in terms of these chemical reactions. Duhem traces the development of compositional formulas, which merely reflect the proportions of the constituent elements, into structural formulas, which build on certain systematic aspects of the chemical reactions involving the compound in question.

The basic idea was that of substitution. Starting from an archetypal substance, substitution reactions are naturally thought of as resulting in the replacement of

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[7] Quoted from Edward Divers' presidential address, first published in *Proceedings of the British Association for the Advancement of Science*, (1902), 557-75, by Gavroglu (1997, pp. 289-90).

definite parts of one reactant with parts of another. Substances resulting from the substitution of parts of the archetypal substance were all said to belong to the same type, which was named after the archetypal substance itself. Thus, replacement of hydrogen in water results in substances belonging to the water type. The doctrine was elaborated to take account of additional factors. Duhem describes these details with admirable clarity in the book translated here, and they will not be described in this introduction. The present discussion is confined as far as possible to the question of interpretation.

The type theory led to the development of structural formulas in which subgroups are indicated by collecting letters within parentheses, or in the form of a two-dimensional diagram in which collections of letters are linked by short straight lines. The subscripts of the original compositional formulas are taken to be a device indicating a number of elemental units. Thus, the compositional formula C_2H_6O, for example, contains two units of carbon, six of hydrogen and one of oxygen, which might be arranged $(CH_3)_2O$ to distinguish dimethyl ether from its isomer ethyl alcohol, whose structural formula is written C_2H_5OH.

This may suggest to the modern reader an atomic interpretation, substitution effecting a replacement of one or more atoms in a molecule by a group of atoms. But Duhem's presentation of structural formulas certainly does not presuppose the atomic interpretation. As we have said, his account of compositional formulas does not require an interpretation as a listing of the number of atoms of each kind in a molecule. How can he resist the atomic interpretation of structural formulas based on types? For substitution would seem to involve one part of something being replaced by another. Duhem argues on two fronts. On the one hand, he offers a critique of the atomic hypothesis in the final section of the 1892 article "Notation atomique et hypothèses atomistiques" which, as already noted, was to the general effect that the elaboration of Dalton's view by the ascription of atomicities gave no real explanation. This critique is taken over in *Mixture and Chemical Combination*. And on the other hand, he offers an alternative proposal to the general effect that the Aristotelian theory of mixture provides the basis of an adequate interpretation. Although some of Duhem's formulations in "Notation atomique et hypothèses atomistiques" clearly suggest that this idea was well-formed in 1892, this interpretation is first explicitly developed in the text that appeared as the 1902 book.

Duhem's critique of atomism is directed against the theories of Charles Adolphe Wurtz (1817–84), professor of chemistry at the *École de médecine* in Paris from 1853 and at the Sorbonne from 1874. Wurtz came in for a good deal of criticism from Marcelin Berthelot (1827–1907), who dominated chemistry in France until the beginning of the new century and with whom Duhem came into conflict. Berthelot raised the standard positivist charge that appeal to atoms or molecules which no one can see is mystical. But like other critics of atomism, his objections were not confined to this positivist insistence on observability. The idea of a structureless atom seems incapable of explaining anything.

> Physical forces, as well as chemical forces, will allow testing in the atom only movements of the whole, without the possibility of internal vibrations; these can exist only in a system formed of several parts. It results then that there cannot be in the interior of an indivisible atom any reserve of hidden energy. Such are the rigorous consequences of the atomic theory.[8]

And as we now know, the atoms that came to be sanctioned by the scientific community are not the structureless atoms to which the 19th century critics of atomism objected, but structures whose constituents are described by continuous functions over space and time. Duhem's objections to atomism were all of this theoretical or conceptual character; nowhere, to the best of my knowledge, does he raise the positivist objection that atoms cannot be seen. Any such reliance on simple observation would, in any case, hardly fit in with his well-known holistic ideas about conducting of experiments and performing observations which he describes at length in his 1906 book.[9]

The Aristotelian theory of mixture is first presented in Ch. 1 of *Mixture and Chemical Combination* as standing in contradiction with the atomism of antiquity. In the last two chapters it is suggested that modern (i.e. 19th century) chemistry, in the eyes of a thermodynamicist, can be seen as extending and developing the Aristotelian view rather than contradicting it. Duhem does not claim this as an original insight, but merely to be following Sainte-Claire Deville (1818–81), who is said to have maintained that "A chemical formula does not describe what really now subsists in the compound, but what can be found potentially, and can be taken out by the appropriate reactions" (1902, p. 151). Whereas the atomist treats what appears to be a homogeneous substance as merely an appearance because the limitations of our perceptual abilities to not allow us to discern atoms, the Aristotelian treats it as really homogeneous. "[I]f combination has taken place," Aristotle says, "the compound *must* be uniform—any part of such a compound being the same as the whole, just as any part of water is water" (*De gen. et corr.*, I.10; 328a10-2). On this view, no parts of a mixture contain the original ingredients, which cannot actually occur in the mixture but are potentially recoverable.

Duhem confines himself to these "two contradictory opinions of the nature of a mixt" in *Mixture and Chemical Combination* (p. 15). But it is now usual to distinguish three schools of thought among the ancients on the nature of mixture. Shortly after Aristotle (384–322 BC) established his peripatetic school, the Stoics, so called after their meeting place in Athens at the painted colonnade (Gr. *stoa*), established a school which flourished from *c.* 300 BC to *c.* AD 200. Although their interests in the later part of this era focused on ethical matters, questions of physics, metaphysics and cosmology dominated in the earlier period. Unfortunately, little manuscript material survives from this period, and our chief sources today are

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[8] From Marcelin Berthelot, *Origines de l'Alchimie*, quoted by Nye (1972, p. 9).

[9] This theme is developed in Needham (1998) and Needham (2000).

reports from the later period. It is clear, nevertheless, that one of their major concerns was the problem of mixture, on which their view differed both from the atomists' and Aristotle's. The *De mixtione* of Alexander of Aphrodisias (fl. c. AD 200)[10] contains an exposition and critique of Chrysippus' (*c*.279–206 BC) version of the Stoic theory of mixture, which Alexander found distinctly inferior to Aristotle's. To see how such a third view is possible, it must be appreciated that there is a further general issue about the nature of matter, in addition to the question of homogeneity, on which different stands can be taken, namely the question of whether two quantities of matter can occupy the same place. It was because Aristotle, in agreement with the atomists, held this to be impossible that he was led, in the light of the homogeneity assumption, to the view that the original ingredients of a mixture are not actually, but only potentially, present. The contradiction of which Duhem speaks might be understood as arising from a disagreement on the issue of homogeneity—although this is not, as we will see, where Duhem actually locates the point of conflict. At all events, there is clearly a possibility of disagreement on the principle on which Aristotle was in agreement with the atomists, namely the impossibility of cooccupancy, and this is the line the Stoics took. They agreed with Aristotle and against the atomists that there was good reason to deny the real homogeneity of mixtures, but held that cooccupancy is possible. Accordingly, the Stoics could, like the atomists, hold that the original ingredients are present in a mixture.

Duhem himself does not seem to have made any such sharp distinction between these two antiatomist views. There is no mention of the Stoics in *Mixture and Chemical Combination*, and the Stoic view is, as far as I am aware, first mentioned quite late in his writings in Vol. I, Ch. V, §IX of *Le système du monde*, which appeared in 1913, in a short 7-page discussion largely filled with translations of passages from Alexander's *De mixtione*, and containing no reference to his 1902 book. The omission of the Stoic theory from the earlier book is somewhat puzzling, and it is tempting to speculate that Duhem saw no real difference in the two views. But no explicit argument to this effect is to be found there, or anywhere else in Duhem's work. There is, however, a definition of "mixture or combination" in the same section of the *Traité d'energetique* from which the last quotation was taken, and the relevant passage is translated here as Essay 8. This definition is taken, in its essentials, from an earlier formulation of Duhem's (1892c, pp. 271-3), and is specifically contrasted with the view held by "many physicists" who regard the impenetrability of matter as impossible. Thus, Duhem was clearly aware of the cooccupancy issue when writing *Mixture and Chemical Combination*. Nevertheless, when at the end of this section from the *Traité d'energetique* he refers to his 1902 book, it is in connection with the question of the opposition between, on the one hand, the "atomic and Cartesian school" and the "peripatetic doctrine" on the other. He apparently considered this opposition to be jointly

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[10] Translated into English in Todd (1976).

exhaustive of the possible positions. Note that the Cartesian view takes matter to be continuous, and not ultimately comprised of indivisible atoms, but agrees—as Duhem stresses (1902, Pt. I, Ch. 2)—with atomism in excluding cooccupancy. It would seem, then, that he still considered the alternative to the atomic view to be one which, in accordance with the Aristotelian view, has it that the original ingredients exemplify substance kinds which are no longer exemplified by any part of the mixture, even though, as the 1911 definition suggests, he held that the original matter which exemplifies the original substance kinds cooccupies the same region of space in contradiction with Aristotle's view.

The important point about the Aristotelian view for Duhem, then, is the doctrine of generation and corruption: the original ingredients do not actually exist in the mixt. It seems that what he advocated was actually a fourth view, Aristotelian in so far as it upholds the doctrine of the merely potential existence of the original ingredients in a mixt, and Stoic in so far as it accepts the possibility of cooccupancy.[11] It is interesting to note, in connection with Duhem's divorcing of the Aristotelian doctrine of the potential presence from the issue of the continuity of matter, that Fritz Paneth (1931) was later to take up a similar idea on the basis of the atomic theory of matter, although this is somewhat obscured by differences in terminology. Paneth proposed to address the issue with an unhappy distinction between conceptions of elements as "basic" and "simple," which was to be understood in conjunction with a "transcendental" view of elements in compounds.

There are further deviations from the view Aristotle actually maintained. What Duhem explicitly acknowledged is that his view supplements Aristotle's, insisting that there is no inconsistency:

> [I]n all that is supposed by chemical mechanics regarding the generation and destruction of chemical compounds, we find nothing that does not accord with the analysis of the notion of mixt given by Aristotle. Of course, the law of conservation of mass and the law of definite proportions are invoked there; but in complementing and making more precise the results of the Stagirite, these laws do not modify its character. According to Aristotle, and following contemporary thermodynamicists, the elements do not actually exist any more within the mixt; they exist only as a possibility. (1902, p. 172).

What he fails to mention is that in *De gen. et corr.* I.10, Aristotle outlines a further kind of mixing process in addition to that involved in the formation of what Duhem calls mixts. This second kind of mixing involves the "overpowering" of the one ingredient, making it transform entirely into the other kind of ingredient (see Joachim 1904). It transpires (*De gen. et corr.* II.4) that this second kind of mixing process is the basis of the transmutation of the elements. What motivated Aristotle in distinguishing such a kind of process was the quest to explain ordinary observable phenomena such as the evaporation of water, and not alchemical dreams of

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[11] The relation of the Stoic to the Aristotelian view, and the emergence of Duhem's distinctive conception, is discussed in greater detail in Needham (2002).

converting base metal into gold. Even as late as the eighteenth century it seems that the conversion of ice to (liquid) water, and this to steam, were taken to involve a change of substance. Duhem tells us in "Theories of Heat" (translated here as Essay 1) that Joseph Black understood his discovery of the phenomenon of latent heat to involve a chemical reaction between ice and caloric producing (liquid) water. But such phenomena were understood since Lavoisier (who took it that he was analysing water by reducing steam over carbon), and certainly by Duhem, to involve a phase transition of one and the same substance. Now this doctrine of the transmutation of the elements seems to create considerable tension in Aristotle's scheme, and so it is just as well that it is dropped from any modern adaptation of the philosopher's ideas on generation and corruption. But Duhem makes no mention of this aspect of Aristotle's theory.

Duhem's use of the term "energetics" in the title of his 1911 treatise derives, he tells us, from a paper by one of the earlier figures in the development of thermodynamics, J. Macquorn Rankine (1820-72):

> The system of general laws of Physics is known today under two names: the name of *Thermodynamics* and the name of *Energetics*.
>
> The name *Thermodynamics* is closely linked to the history of this science. Its two most essential principles, the principle of Carnot and the principle of the conservation of energy, were discovered by studying the motive power of heat engines. The name is still justified by the fact that the two concepts of *work* and *amount of heat* are continually featured in the arguments in which this doctrine is developed.
>
> The name *Energetics* was introduced by Rankine.[12] Since the idea of *energy* is the first that this doctrine had to define, and it was to this that the majority of other notions employed there were connected, this name seems no less well chosen than the name *Thermodynamics*.
>
> Without deciding whether it is more appropriate to regard the one or the other of these terms as more preferable, we will employ both as mutually equivalent. (Duhem 1911, Vol. I, p. 3)

There is no suggestion here that energy is taken to be the only fundamental concept with which the theory deals, nor even that it is one of a few to which all the other familiar terms of science can be reduced. Wilhelm Ostwald (1853–1932), who also used the term "energetics" for a general theory of chemistry, seems to have thought of it in a reductionist manner, claiming that it renders not only the notions of atom and molecule unnecessary, but even that of matter. Duhem certainly did not think the notion of material bodies redundant, as is abundantly clear from the section of the 1911 treatise translated here. But nor does he seem to have had any kind of reductionist project in mind. His leading idea was rather that progress in science was continually bringing to light defects in previously established theories and presenting the problem of how the exceptions could be accommodated in yet more general theories. Duhem rose to the challenge by seeking to extend the traditional

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[12] J. MACQUORN RANKINE, "Outlines of the Science of Energetics," *Glasgow Philosophical Society Proceedings*, Vol. III, no. 6, 2 May, 1855.—J. MACQUORN RANKINE, *Miscellaneous Scientific Papers*, p. 209.

principles of mechanics so that they could encompass the new phenomena rather than saving them by adding restrictions limiting their range of application. This attitude comes across particularly clearly in two of the papers in the present selection.

In "On Some Recent Extensions of Statics and Dynamics" from 1901 (Essay 7), he reports a "wide-spread opinion regarding the phenomena of friction," according to which "the equations of Mechanics, written without mention of friction, are general; but in teaching our theories, we apply them to very abstract bodies, [which are] very different from those presented to us in experience. We treat perfectly rigid, perfectly polished solids, whereas natural solids are always more or less deformable, more or less rough, from which the discrepancies between the predictions of Mechanics and the results of observation arise." Duhem's attitude is rather that "[t]hese discrepancies all disappear if, instead of applying the equations of Mechanics to very simplified abstractions in order to represent, even roughly, the properties of natural bodies, we take account of the roughness and deformations of these bodies in making the application" (Duhem 1901, pp. 143-4). This implies, of course, that he is not content to defend laws by claiming they deal with ideal objects; he wants to see them sufficiently well articulated to deal with the real objects of the world. Although superficially a technical article, with its arrays of mathematical equations, this 1901 paper was published in the *Revue des questions scientifiques* and was therefore intended for a general readership. In fact, the general strategy illustrated should be apparent to the reader without any detailed knowledge of the traditional divisions of mechanics into dynamics, which deals with the accelerations actually produced by forces, and statics, which deals with situations in which counteracting forces result in a stable equilibrium. The general issues dealt with in the paper are introduced as bearing on the evolution of theories of physics, making the paper an illuminating complement to the predominantly historical treatment of the same subject in the earlier paper "The Evolution of Physical Theories from the Seventeenth Century to Our Day" (1896). Duhem refers the reader to this latter paper at several points in *Mixture and Chemical Combination*, and it is also included in this selection as Essay 2.

The second paper pertinent to the non-reductionist spirit in which Duhem pursued his research is of a quite different character. It too is referred to in *Mixture and Chemical Combination* and is included in this volume. Presented as a review, the prime subject of "Thermochemistry: in Connection with a Recent Book of Marcelin Berthelot" is a book authored by the man usually portrayed as Duhem's arch fiend, Marcelin Berthelot, who has already been mentioned above. Berthelot's highly productive and broad-ranging research gave him an authoritative position in French chemistry which, like Dumas' before him, led to a career in politics. In this role he eagerly pursued the anti-clerical policies of the third republic, becoming minister of education for 1886-7, and even foreign minister for 1895-6. One of his major contributions to science was the synthesis of a large number of organic compounds from inorganic raw materials, repudiating the claim of vitalism that a special life force is required for their production. He was instrumental in changing the direction of research in organic chemistry from one dominated by the pursuit of analysis to one equally or more concerned with the synthesis of new substances. There is no mistaking the importance accorded the role of synthesis in Duhem's account of 19th century chemistry. But Berthelot's influence interfered with the progress of Duhem's career. Being the precocious student that he was, Duhem submitted his doctoral thesis on thermodynamic potentials on 20 October 1884, before completing his first degree. The thesis was rejected, however. It enlarged upon the ground-breaking monograph-length paper of J. Willard Gibbs (1839–1903), "On the Equilibrium of Heterogeneous Substances," which had been published in an obscure journal in two parts in 1876 and 1878, as well as work of Massieu and Helmholtz. Duhem (1886)—presumably his unsuccessful thesis—contained (pp. 33, 141f.) the basic theorem known to every student of thermodynamics as the Gibbs-Duhem equation (to the effect that the thermodynamic magnitudes for substances in a mixture cannot vary independently[13]). The introduction to the book contained a critique, based on general thermodynamic principles, of Berthelot's law of maximum work, formulated in 1873, which has it that at constant temperature and pressure, substances will react with one another by following that process which is most exothermic—i.e. which evolves most heat. This was Duhem's undoing.

Berthelot was, together with the Danish chemist Julius Thomsen (1826–1909), a pioneer of thermochemistry, constructing the calorimeter known as "Berthelot's bomb." Valuable though this was, the law of maximum work is of restricted value, being essentially an application of the principle of the conservation of energy. The more general principle governing chemical reactions under constant temperature and pressure involves a thermodynamic potential called the Gibbs free energy, usually symbolised by G. This potential takes entropy into account as well as energy. In purely mechanical contexts, equilibrium corresponds to a state of minimum energy. Thermodynamic considerations show that the minimum energy requirement is not one that holds generally, however, but only under the restriction of constant entropy. Equilibrium is also characterised as a state of maximum entropy, but again, not without qualification, the general principle being that a system moves spontaneously to a state of maximum entropy under the constraint that the energy is constant. Now, constant energy or constant entropy are not typical of the conditions usually encountered in laboratory studies of chemical reactions, and the information in these characterisations is more usefully expressed in terms of independent variables such as temperature and pressure or volume by Legendre transformations yielding appropriate thermodynamics potentials. Of these, the potential most

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[13] Duhem's contribution was to give an elegant derivation of the theorem by an application of Euler's theorem on homogeneous functions. See Miller (1963) for a translation of the "clear and concise" presentation in Duhem's textbook, *Traité Elémentaire de la Mécanique Chimique Fondée sur la Thermodynamique* (4 vols., 1897-9).

frequently applicable to chemical contexts is the Gibbs potential, G. Reactions proceed spontaneously at constant temperature and pressure when accompanied by a total reduction in G, i.e. when the change in the Gibbs free energy, ΔG, is negative. According to classical thermodynamics, this has two components:

$$\Delta G = \Delta H - T\Delta S, \tag{1}$$

showing that an emission of heat (corresponding to a negative value of the change in enthalpy, ΔH) is conducive to reaction, but also allowing that the heat absorbed in an endothermic reaction can be offset by a sufficiently large increase in entropy, ΔS, whose effect is magnified at higher absolute temperature, T. Consequently, it is by no means necessary that all reactions proceed exothermically, as Berthelot's law requires, except at the absolute zero of temperature, where the law does hold for all reactions.[14] (The thermodynamic potential Duhem introduces on p. 367 of "Thermochemistry" and symbolised by "F" is the closely related Helmholtz free energy. The condition that $\Delta F = \Delta U - T\Delta S$ be negative for spontaneous reactions, where U denotes the internal energy, applies under conditions of constant *volume* and temperature.)

Doubts about Berthelot's law were voiced outside France by van 't Hoff in his *Etudes de dynamique chimique* (1884). In a review of this work Svante Arrhenius—who like Duhem encountered opposition to his thesis from his own university in Uppsala—wrote

> What a difference between the present champions of thermochemistry and the author! The former anxiously seek to avoid the physical phenomena which are said to interfere with chemical reactions, but confront them at every turn. The author takes a completely different line. Following Horstmann's ideas, he removes the Janus aspect that the thermochemists persist in putting on nature. The physical heat phenomena are merely simple, more well-known, special cases of the chemical heat phenomena. From the mathematical formulas for the connection between heat flow, temperature and chemical reaction he found the following, extremely general, law: "Every equilibrium relation between two material systems changes by reducing temperature for the benefit of the system whose production gives rise to heat." From this it follows that at normal temperatures Berthelot's "principe du travail maximum" only holds in most cases, and holds for all cases only at absolute zero. Since the reviewer has arrived at the same conclusion, which is supported by an unparalleled amount of experimental data, from completely different grounds, he can only agree completely with the author's view in this case. (Arrhenius 1885, pp. 364-5)

The force of this critique became more generally accepted outside France as the relevance of Gibbs' work—inaccessible not merely by reason of being published in an obscure journal; it was written in a concise style calling for what was then a rare combination of knowledge of chemistry and mathematical techniques—was gradually absorbed into the scientific community. Instead of spearheading the development and

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[14] See Callen (1985, pp. 277-9) for a concise account of the inadequacies of the law of maximum work.

application of Gibbs' work, however, Duhem's thesis was sunk by the committee of Lippmann, Hermite and Picard under the watchful eye of Berthelot.[15]

Readers unfamiliar with chemical thermodynamics may find some of the things Duhem says in the final chapter of *Mixture and Chemical Combination* less strange if they bear in mind that equation (1) is quite general and not restricted to the formation of compounds. It governs changes in any kind of mixture, and in particular, the stability of solutions. The contrast between compounds and solutions established by the law of constant proportions is thus diminished by subjecting them to the same general principles

A projected series of articles which Duhem was to write for the journal *Revue des deux mondes* was promptly called to a halt after the first contribution "Theories of Heat" (Duhem 1895, translated here as Essay 1) at the instigation of higher powers, which Duhem's biographer Jaki (1984) suggests was also Berthelot's work. When the opportunity arose for a review of Berthelot's thermochemical researches, Duhem was remarkably restrained, allowing the force of sound methodology to carry the day.[16] But most importantly, his argument against the idea that Berthelot can defend his principle by restricting its scope specifically to chemical, as distinct from physical, processes illustrates Duhem's general strategy of seeking a more general principle rather than retreating to the safety of restrictions. The irony of the opponent of vitalism resorting to insulating the scope of chemistry from the encroachment of physics needs no further comment. Note, however, that Duhem's purpose was not to reduce chemistry to physics. His argument was rather that chemical reactions are one kind of phenomena among others which call for a changing and broadening of the older principles of physics. The criticisms he offered of the prejudice in favour of reduction to mechanical models may well be seen in the light of this aim.

The historical survey "Theories of Heat" is included in the present selection, of course, on its own merits. Duhem's interest in chemistry was mediated, as we have seen, by his interest in thermodynamics—a subject which grew out of attempts to capture the notion of heat and ancillary concepts. An account of this history at the hand of the same author therefore nicely complements the purely chemical background to thermodynamics provided by *Mixture and Chemical Combination*. Duhem himself refers the reader to "Theories of Heat" in the final chapter of this book.

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[15] (Duhem 1886) is a work with the same title as the thesis, and published shortly after by Hermann, Paris. As Jaki (1984, p. 51) points out, "[s]ince it would have been impossible to turn within the summer months of 1885 a thesis, allegedly faulty in all its essentials and unreliable in all its details and inferences, into a masterpiece which ultimately earned a place in the series 'Landmarks of Science', the thesis and the book should be considered identical." Duhem later submitted a thesis to the faculty of mathematics (Duhem 1988) dealing with applications of thermodynamic potentials, which was accepted in 1888 by a committee comprising Bouty, Darboux and Poincaré.

[16] But for a different opinion, see Dolby (1984).

Duhem's other papers on chemical subjects aimed at a general readership are included for completeness. "The Phase Law" (1898) is, like "Thermochemistry," a piece occasioned by the review of a newly published book in which Duhem takes the opportunity to cover the essential background for the lay reader. The phase rule was one of the simple results of Gibbs' obscure paper on heterogeneous systems whose far-reaching consequences played a major role in convincing chemists of the relevance of thermodynamics to their subject. Duhem wrote a lengthy piece for the newly started American *Journal of Physical Chemistry* in 1898, where he displays his instinct for rigorous argument. The usual demonstrations of the phase rule presuppose that each substance present in the system under consideration is present in every phase. But this condition is patently not satisfied by a range of well-known systems to which the rule had in fact been applied. True to form, Duhem develops his own proof from more general conditions justifying the application of the rule to these cases too. The book reviewed by Duhem in "The Phase Law" is a non-technical, descriptive work illustrating the kind of application that so impressed the chemists of the day. Duhem carefully presents some well chosen examples, and explains concepts employed elsewhere in this collection.

The science of heterogeneous equilibria has been called a "Dutch science" (Daub 1976, p. 747) in recognition of the experimental work of the Dutch physical chemists which did more than anything to bring Gibbs' theories into the light of day. The tradition was established by Bakhuis Roozboom (1854–1907) who, with the assistance of van der Waals (1837–1923), published his first results in 1887. A good account of how the phase rule was brought in to solve his mystery is given in Daub's 1976 article commemorating the centenary of the publication of the first part of Gibbs' paper. It is, unfortunately, typical of the awareness of Duhem's contribution to the subject that Daub says "Prior to this time [1887], the only scientist to pay heed to Gibbs' thermodynamics was James Clerk Maxwell" (p. 747, fn. 1), and the only relevant work of Duhem's that he mentions is his contribution, mentioned above, in the *Journal of Physical Chemistry* to the debate on the rigorous derivation of the phase rule (Daub 1976, p. 750).

Duhem's 1899 paper, "A New Science: Physical Chemistry," is something of a propaganda piece specifically aimed at a French readership where he argues for the significance of the new discipline. It appears now as a strange mixture of historical background and industrial application. Disinterest and lack of investment in the latter, he suggests, cost France a considerable price in missed economic opportunity.

Duhem refers the reader to this paper at the beginning of his 1900 review of van 't Hoff's lectures, which contains a particularly clear account of the laws of Moutier and van 't Hoff which spelt doom for the principle of maximum work. But the review is especially noteworthy for taking up the form of chemical isomerism called stereoisomerism, in which van 't Hoff, along with Pasteur and Le Bel, was one of the pioneering figures. No account of stereoisomerism is given in the 1892 article "Notation atomique et hypothèses atomistiques," which must strike the modern reader as a remarkable omission from a work claiming that the atomic theory plays no explanatory role in accounting for the facts of chemical structure. For the van 't Hoff–Le Bel hypothesis of a tetrahedral molecular structure to explain the only difference in pairs of stereoisomers—that they rotate the plane of polarised light in opposite senses—was well known by then. This form of isomerism is taken up in *Mixture and Chemical Combination*, however, with the comment that the van 't Hoff–Le Bel hypothesis complements the essentially topological account of chemical structure afforded by type theory with "a new element taken from geometry" (1902, p. 128). The 1900 article supplements this rather austere remark with a challenge to the advocate of van 't Hoff's picture of molecular shape to provide a coherent and informative account of the elements standing at the apexes of the tetrahedron. Mere pictures, Duhem seems to be saying, are not the stuff of articulate theories.

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I have sought to reduce adjustments to a minimum and to give as literal a translation as possible, although Duhem's very long sentences have often been broken down. His division into paragraphs is retained, even though many of them comprising just one or two lines would normally be integrated into larger paragraphs in modern English. Page numbers of the original are given in square brackets, except for the number of the first page of articles, which is given in the reference to the original name and place of publication accompanying each article. Together with the retention of the original paragraphs, this should facilitate comparison with the original and following references in the secondary literature. Remarks in square brackets are my own comments. I have usually translated the French word "corps" with "substance," but occasionally "body" where this seemed more appropriate. The reader should be aware that these two English words usually correspond to the same word in the original. An exception occurs in the discussion of Aristotle at the beginning of "The Evolution of Physical Theories" (Essay 2), where Duhem follows traditional philosophical usage and understands "substance" to denote the Aristotelian concept of what cannot be predicated of any other thing. In addition, Duhem occasionally uses the French word "substance" in the sense that the English word "substance" is used here as the usual translation of "corps," for example on p. 26 of the review of van 't Hoff's book. When quoting, Duhem often uses a construction which I render in the form:

"...," says so-and-so, "...,"

although Duhem does not break off the quotation, as I have done here, in order to insert "says so-and-so." In all such cases, the boundary between quoted material and what I take to be the insertion of Duhem's words is my own interpretation. The actual placing of footnotes giving sources of quotations may strike the reader as eccentric; but I have tried to adhere to Duhem's practice as far as possible. Duhem wrote chemical formulas with subscripts rather than the modern convention of using subscripts, thus, "H^2O" rather than "H_2O." The latter convention is followed here. Finally, Duhem's usual practice of using the title "Mr." when referring to other scientists has not, on the whole, been followed in the translation. An exception is the essay "Thermochemistry," where it seems to be an integral part of the polemical critique of Mr. Berthelot.

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Mixture and Chemical Combination

An Essay on the Evolution of an Idea

Preface

The following pages first appeared in the *Revue de philosophie*,[1] and it is for philosophers that they were intended. Consequently, in the course of the development of science, the evolution of a notion, that of a *mixt*, we have wanted to emphasise the principle directions which have, through more than three centuries, guided the theories of physics. As an alternative to atomistic, Cartesian and Newtonian theories, these views now seem to have given way to a voice which was abandoned in the sixteenth century, the peripatetic method.

Although this book was not written with this intention, we would be pleased if chemists were also to find in it matters for reflection.

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[1] [*Revue de Philosophie*, 1 (1900), 69-99, 167-97, 331-57, 430-67, 730-45. The book here translated was originally published as *Le mixte et la combinaison chimique: Essai sur l'évolution d'une idée*, C. Naud, Paris, 1902; and reprinted by Fayard, Paris, in 1985.]

PART ONE

The Origins of the Chemical Revolution

CHAPTER 1

MIXTS ACCORDING TO THE ATOMISTS AND ACCORDING TO THE PERIPATETICS

Throw [11] a little sugar into a glass of water. After a short time, the solid, white crystalline body which constitutes the sugar has disappeared. The glass contains no more than a homogeneous liquid, transparent like water, but with a different taste. What is this liquid? The vulgar call it sugared water. The chemist says that it is a solution of sugar in water. These two descriptions correspond to two essentially distinct opinions.

Let us forget for the moment all chemical theory and analyse this simple operation of the preparation of a glass of sugared water.

Is there still any sugar or any water in the glass? No: the sugar has been eradicated; we have seen it gradually disappear. The liquid enclosed in the glass is no longer water—that is to say, that highly mobile, all but tasteless liquid, which provides the rain which fuels the springs which makes up the rivers—but a new liquid, more or less syrupy, whose sweet taste is reminiscent of that of the sugar which has served to form it. The glass therefore no longer contains either the water or the sugar which we had mixed there, but a new body, a *mixt*[1] formed at the expense of the two *elements*.

Nevertheless, even though the mixed substance, the sugared water, is no longer either water or sugar, it can be destroyed and the water and sugar from which it was formed regenerated. Warm it gently. It will evaporate [12] and we can, if we wish, condense the vapour and collect a water similar in every respect to that we had poured into our glass. During the evaporation, the sugared water disappears, depositing a white solid that we recognise as sugar. If the sugared water no longer *actually* contains the water and sugar from which it was formed, it can, by ceasing to exist, reproduce the water and sugar; it contains them *potentially*.

What in general, then, is a mixt? Some bodies, the one different from the other, are brought into contact. Gradually, they disappear, they cease to exist, and in their place a new body is formed, distinguished by its properties from each of *the*

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[1] [Duhem's substantive *mixte* is consistently translated with the old chemical term "mixt."]

elements which produced it by their disappearance. In this mixt, the elements no longer have any actual existence. They exist there only potentially, because on destruction the mixt can regenerate them. And the characteristics which determine the mixt belong not only to the body as a whole, but also to each part, however small, that the mind can cut out of the homogeneous body. Moreover, these characteristics are to be found in all mixts, both in what we today call mixtures[2] and that for which we reserve the name *chemical combination.*

This is, it seems, the clear, certain and obvious lesson that one is able to draw from the experience of the majority of people.

Not at all writes the chemist who, furthermore, loudly proclaims his empiricism and professes only to teach the facts! Such a notion of mixt, far from offering any certainty, is but a vulgar illusion, a gross deceit of our dull senses. It is unworthy of a mind capable of any reflection and contrary to the principles of sound physics.

Our eyes are too feeble to see an object one twentieth of a millimetre long, yet isn't it the witness of the eyes that you rely upon in order to affirm that water is a homogeneous and continuous fluid? [13] Take one of the microscopes that physicists have devised and perfected. Already in this liquid which you thought everywhere identical with itself, you see a multitude of unsuspected objects swimming before your eyes, and still the microscope has only made your sight one or two thousand times more powerful. How would it be if you were given, like the fabled Lynceus, limitless power of visual penetration? This water, which seems to you to fill in continuous fashion the volume of the containing glass, you would see as a collection of small solid bodies, separated from one another, which roll over one another without change of size or figure when the water is deformed and flows.

Each drop of water is thus composed of a multitude of *molecules.* The same holds for each small crystal of sugar. When sugar is put into the presence water, the molecules of sugar are not destroyed nor altered, but like prisoners who break away from their common chain, they are dissolved and, without breaking or modifying the molecules of water, they slip between them. The sugared water is therefore not at all homogeneous, with the smallest part possessing the same properties as the whole. The apparent homogeneity is only an illusion of our senses, which are very indelicate when it comes to perceiving the intimate structure of bodies. In sugared water, the water and the sugar subsist, juxtaposed, but not confounded. Sugared water might be called a mixture of sugar and water for the same reason that the contents of this sack is said to be a mixture of wheat and straw. In forming it, the sugar and water have no more ceased to exist in order to form a new body than the grain and straw have ceased to exist when the beater has thrown them higgledy-piggledy into the sack. Distillation which separates the water from the sugar no more regenerates the elements at the expense of the mixed body than the fan

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[2] [Duhem's substantive *mélange* is consistently translated as "mixture."]

recreates the wheat and the straw. It simply sorts molecules of different natures which the dissolution has jumbled together.

These two ways of conceiving the relation [14] of a mixture to the mixed bodies are both ancient. The Greek atomists regarded the homogeneity of a mixt as a mere appearance. The deficiencies of our senses alone prevent us from recognising the juxtaposition of the mixed elements. In the immortal lines in which the thoughts of the philosophers have been transmitted to us, Lucretius gave expression to his doctrine of mixts.[3] Having described the branching and entangled molecules which comprise the tissue of solid bodies, the small, smooth globes free of all bonds which roll over one another in the midst of liquids, the pointed particles which constitute gases, he analyses the intimate structure of sea water. Among the smooth round bodies which give rise to its fluidity and which, when isolated, compose fresh water, other bodies are dispersed, also rounded, permitting them to follow the movements of the liquid, but rough and capable, because of their unevenness, of wounding the tongue and producing the experience of a bitter taste. These rough elements adhere to the soil, while smooth particles of water easily pass through the pores. Thus, sea water changes to fresh water by filtration on passing through the ground:

> Sed quo amara vides eadem, quæ fluvida constant:
> Sudor uti maris est; minime id mirabile habendum,
> Nam quod fluvidum est, e lævibus atque rotundis
> Est: at lævibus atque rotundis mista doloris
> Corpora; nec tamen hæc retineri hamata necesse'st:
> Scilicet esse globosa, tamen cum squalida constent;
> Provolvi simul ut possint et lædere sensus.
> Et quo mista putes magis aspera lævibus esse
> Principiis, und'est Neptuni corpus acerbum;
> Est ratio secernundi, seorsumque videndi.
> Humor dulcit, ubi per terras crebrius idem
> Percolatur, ut in foveam fluat, ac mansuescat.
> Linquit enim supra tetri primordia viri
> Aspera, quo magis in terris hærescere possunt.[4]

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[3] Lucretius, *De rerum natura,* lib. II, vers. 390-476

[4] [lines 464-477, translated by Cyril Bailey as follows: "But because you see that some things which are fluid, are also bitter, as is the brine of the sea, it should be no wonder. ... For because it is fluid, it is of smooth and round particles, and many rugged painful bodies are mingled in it; and yet it must needs be that they are not hooked and held together: you must know that they are nevertheless spherical, though rugged, so that they can roll on together and hurt the senses. And that you may the more think that rough are mingled with smooth first-beginnings, from which is made the bitter body of the sea-god, there is a way of sundering them and seeing how, apart from the rest, the fresh water, when it trickles many a time through the earth, flows into a trench and loses its harshness; for it leaves behind up above the first-beginnings of its sickly saltness, since the

To this doctrine the peripatetics objected that a mixed body is really distinct from the bodies from which it is formed. In producing the [15] mixt, the elements cease to exist. The mixt only comprises them as a potentiality; when decomposed, it can regenerate them. The exposition that we have just given of the two contradictory opinions of the nature of a mixt is hardly more than a paraphrase of what Aristotle says.[5]

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rough particles can more readily stick in the earth." *Titi Lucreti Cari De rerum natura libri sex*, edited with prolegomena, critical apparatus, translation, and commentary by Cyril Bailey, © 1947 Clarendon Press, Oxford; p. 261. Reproduced by permission of Oxford University Press.]

[5] Aristotle, Περὶ γενέσεως χαὶ φθορᾶς [*De generatione et corruptione*], Bk. I, chap. x.

CHAPTER 2

THE NOTION OF A MIXT IN THE SEVENTEENTH CENTURY

We [17] follow the fortunes of these two opinions through the course of the history of chemistry.

Throughout the middle ages, the peripatetic doctrine regarding the generation and corruption of mixed bodies was taught in the schools. Was it accepted by the alchemists? It would be difficult to fathom, under the obscure language which concealed their true thoughts; less capable of abstraction, more imaginative than the scholastics, they were undoubtedly inclined towards the views of the Epicureans. But without investigating this question, we are content to take up chemistry at the time of the scientific renaissance.

At this time, we see philosophers of nature coming back into vogue, on account of their faithfully upholding, during the course of several centuries, the Epicurean idea that apparently continuous mass is an assemblage of small bodies of various forms, and that the various arrangements of these small bodies must explain the properties of the various mixts which the chemist studies.

We find this idea clearly expressed by Bacon[1], who indicates within these limits the aim of the new physics:

"It is necessary to illuminate the texture and true constitution of bodies, from which all the peculiar properties and occult powers in things derive, and, as one [18] says, their specificity, and from which the laws of all power of alteration and transformation derive.

"For example, it is necessary to investigate, in all kinds of bodies, what the volatile part is, and what the tangible essence is: and whether the volatile part is considerable and swollen, or meagre and reduced ...; and in the same way, to study the tangible essence, which contains no less variety than the volatile part, its hairs, and its fibres and its equally variable texture; and again the disposition of the volatile part in the mass of the body, the pores, pipes veins and cells and the rudiments of organic bodies."

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[1] Bacon, *Novum organum*, pars ædificans.

These ideas gained more force with Gassendi's attempt to oppose scholastic physics with atomic physics; they triumphed with Descartes.

Descartes defined with admirable clarity the characteristics which he attributed to material in order to make intelligible all the phenomena that our experiences reveal. Let us quote, in particular, this passage[2]:

"Now since we are taking the liberty of fashioning this matter as we fancy, let us attribute to it, if we may, a nature in which there is absolutely nothing that everyone cannot know as perfectly as possible. To this end, let us expressly suppose that it does not have the form of earth, fire, or air, or any other more specific form, like that of wood, stone, or metal. Let us also suppose that it lacks the qualities of being hot or cold, dry or moist, light or heavy, and of having any taste, smell, sound, colour, light, or any other such quality in the nature of which there might be said to be something which is not known clearly by everyone. But on the other hand, let us not also think that this matter is the 'prime matter' of the philosophers, which they have stripped so thoroughly of all its forms and qualities that nothing remains in it which can be clearly understood. Let us rather conceive it as a real, perfectly solid body which uniformly fills [19] the entire length, breadth and depth of this huge space in the midst of which we have brought our mind to rest. Thus, each of its parts always occupies a part of that space which it fits so exactly that it could neither fill a larger one nor squeeze into a smaller; nor could it, while remaining there, allow another body to find a place there. Let us add that this matter may be divided into as many parts having as many shapes as we can imagine, and that each of its parts is capable of taking on as many motions as we can conceive. Let us suppose, moreover, that God really divides it into many such parts, some larger and some smaller, some of one shape and some of another, however we care to imagine them. It is not that God separates these parts from one another so that there is some void between them: rather, let us regard the differences he creates within this matter as consisting wholly in the diversity of the motions he gives to its parts. From the first instant of their creation, he causes some to start moving in one direction and others in another, some faster and others slower (or even, if you wish, not at all); and he causes them to continue moving thereafter in accordance with the ordinary laws of nature."

Furthermore, Descartes says in another place[3]:

"The only principles which I accept, or require, in physics are those of geometry and pure mathematics. [...] I recognise no matter in corporeal things apart from that

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[2] Descartes, *Le Monde ou le Traité de la Lumière*, chap. VI. [*The World or Treatise on Light*, extracts translated by John Cottingham, Robert Stoothoff and Dugald Murdoch, *The Philosophical Writings of Descartes*, Vol. I, Cambridge University Press, 1985; pp. 90-1. Reproduced by permission of Cambridge University Press.]

[3] Descartes, *Principia Philosophiæ*, pars secunda, art. LXIV. [*Principles of Philosophy*, part two, art. 64, in *The Philosophical Writings of Descartes*, Vol. I (note 2), p. 247. Reproduced by permission of Cambridge University Press.]

which the geometers call quantity, and take as the object of demonstrations, i.e. that to which every kind of division, shape and motion is applicable. Moreover, my consideration of such matter involves absolutely nothing apart from these divisions, shapes and motions."

The shapes which Descartes attributes to the small parts of bodies often differ very little from those attributed by Epicurus, in agreement with Lucretius. In [20] one of the writings which he published following the *Discourse on Method*, by way of exemplifying this method, he describes these shapes thus[4]:

"First, I suppose that water, earth, air and all other bodies which surround us are composed of several small parts of various shapes and sizes which are never so well arranged nor so precisely joined together that there are not several intervals around them. These intervals are not empty, but filled with that very subtle matter, by the mediation of which I have shown above the action of light is communicated. And in particular, I also suppose that the small parts of which water is composed are long, smooth and slippery, like small eels, which, although they are joined and interwoven, neither become knotted nor ever fasten onto one another in such a way that they cannot easily be separated. And contrary to nearly all these, the parts, both of earth and even of air, and of most other bodies, have very irregular and uneven shapes, and are of such kind that they cannot be so little interlaced but that they fasten onto and bind with one another, as do the different branches of shrubs which grow together in a hedge. And when they bind together in this way, they compose bodies as hard as earth, wood and suchlike. Whereas if they had simply rested one on the other, being hardly intertwined and perhaps not at all, and being so small that they could be moved and separated by the agitation of the subtle matter that surrounds them, then they would occupy much space, and compose liquid bodies which are very rare and light, such as oils and the air."

These hypotheses are taken up again in the books of the *Principles*[5] and *Treatise on Light*[6].

Descartes obtained bodies by mixing together three elements which, as he conceived them, [21] bore very little resemblance to the mixts conceived by Aristotle. The Stagirite had compared them with the mixture of wheat and straw that was raked together in the air. Could Descartes, without contradicting himself, imagine the mixture of the two elements otherwise than as a juxtaposition of small shaped parts of which these elements are composed? Could he conceive of the mutual penetration of two of these particles that he regarded as identical with the extension they themselves occupied? Already in the *Treatise on Light* he had informed us that "each of its parts always occupies a part of that space which it fits so exactly that it could neither fill a larger one nor squeeze into a smaller; nor could

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[4] Descartes, *Les Météores,* chap. I, art. III.

[5] Descartes, *Principia Philosophiæ*, pars quarta, passim.

[6] Descartes, *Le Monde ou le Traité de la Lumière*, chap. III and IV.

it, while remaining there, allow another body to find a place there." In a letter to Henry More[7], he maintains yet more clearly the impenetrability of material as a necessary consequence of the essence that he attributed to it: "It is not possible to conceive that one part of an extended thing penetrates an equal part, unless one understands by that that the part of its extension which it has in common with the latter is removed or annihilated; but what is annihilated does not penetrate anything else; that demonstrates, in my opinion, that impenetrability belongs to the very essence of extension, and not to the essence of any other thing."

A solution cannot therefore be, according to this view, anything other than an interposition of particles of the dissolved body with particles of the solvent; and it is this Descartes[8] allows regarding the water of the sea. Among the elongated, smooth, flexible particles, slippery as eels, which ordinarily constitute fresh water, are found little, pointed and rigid sticks which constitute sea salt. The shape and size of these two elements which constitute sea water explain all the properties as one would wish. Descartes shows how [22] evaporation easily carries off the fresh water which leaves behind the sea salt. He shows likewise[9], following the example of Lucretius, how filtration through soil retains the larger and stiffer sticks to which the sea owes its salinity, and allows only the tenuous, fleeting particles which constitute fresh water to pass through.

This example well illustrates to what extent Descartes was inspired by the physics of the atomists. He did not, however, adopt their ideas[10]. Not only are the particles which compose bodies not, for him, indivisible *atoms*; there is also *subtle matter* filling the intervals left between the particles, so that there is no vacuum in nature.

This doctrine, according to which vacuum is impossible in nature, was harshly criticised by Pascal. Huygens followed suit, declaring that vacuum is necessary for the movement of small corpuscles. This was soon to become the general opinion of physicists, whose principles thenceforth accorded with those taught by Epicurus and Lucretius. But just as Descartes had preserved intact the notion of a mixt as conceived by the Greek atomists in his philosophy, this notion was not in any way affected by the failures of the Cartesian physics.

One Jean Rey, a doctor of medicine living in Bugue, Périgord, and contemporary of Descartes, was an expert in natural philosophy. Mr. Brun, apothecary in Bergerac, established that lead and tin increase in weight when burnt in air, and was so surprised by his discovery which he believed unknown that he wrote to the doctor in

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[7] Descartes, *Epistolæ*, Amsterdam edition (1714), pars prima, epist. LIX. [Letter to More dated 15 April, 1649.]

[8] Descartes, *Les Météores*, chap. I, art. VIII, and chap. III.—*Principia Philosophiæ*, pars quarta, art. XLVIII.

[9] Descartes, *Les Météores*, chap. III, art. VIII, and chap. III.—*Principia Philosophiæ*, pars quarta, art. LXVI.—*Epistolæ*, pars secunda, epist. I and II.

[10] Descartes, *Principia Philosophiæ*, pars quarta, art. CCII.

Bugue: "I entreat you with all my heart to engage in searching for the cause of so unusual an effect, and I would be obliged if your efforts could illuminate this marvel for me." [23] Jean Rey[11], who had already established the previously unknown fact that the air is heavy, replied in these terms: "Resting on foundations already laid down, I therefore reply to this question and triumphantly uphold that the addition of weight comes from the air in the vessel, which is dense, heavy, and not in any way made sticky by the violent and prolonged heat from the furnace. This air mixes with the lime (aided by frequent agitation) and attaches to the smallest parts in the way that sand thrown and stirred into water is made heavier by making it wet and adhering to the smaller grains."

It is clear that Jean Rey imagined, as did the atomists, that the mixt is formed from the air and the chalk of tin.

According to the reply just heard, Jean Rey is a precursor of Lavoisier. The anti-phlogiston revolution assures the glory of his name, but the friendship of Mersenne did not prevent him remaining unknown to his contemporaries and his *Essays* had no influence on the development of chemistry.

The same cannot be said of the writings of Boyle and Lémery.

When discussing the theory of mixtures, Robert Boyle does not hesitate to declare that the opinion of the ancient atomists, adopted in his time by the "chemists," if not the most probable, is at least more probable than that of the peripatetics. Still, he brings a correction to this opinion of the chemists. But this correction is conceived in the spirit of the Epicurean doctrine.

"Now in this general notion of mistion it does not appear clearly comprehended," he says[12], "that the *miscibilia* or ingredients do in their small parts so retain their nature and remain distinct in the compound, that they may thence by the fire be taken again asunder: [24] for though I deny not that in some mistions of certain permanent bodies this recovery of the same ingredients may be made; yet I am not convinced that it will hold in all or even in most, or that it is necessarily deducible from chymicall experiments, and the true notion of mistion. ... I will not peremptorily deny, but that there may be some clusters of particles, wherein the particles are so minute, and the coherence so strict, or both, that when bodies of differing denominations, and consisting of such durable clusters, happen to be mingled, though the compound body made up of them may be very differing from either of the ingredients, yet each of the little masses or clusters may so retain its own nature, as to be again separable, such as it was before. As when gold and silver being melted together in a due proportion[13] *aqua fortis* will dissolve the silver, and leave the gold untoucht; by which means, as you lately noted, both the metals may

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[11] *Essays de* Jean REY, *docteur en médecin, sur la recherche de la cause par laquelle l'Estain et le Plomb argmentent le poinds quand on les calcine;* Bazas, 1630; Essay XVI.

[12] Robert Boyle, *The Skeptical Chymist,* part II. [Dent, 1911 reprint of the 1661 edition, pp. 86-8]

[13] [Boyle's text has at this point the parenthetical comment "(for in every proportion, the refiners will tell you that the experiment will not succeed)" which Duhem does not indicate that he omits.]

be recovered from the mixed mass. But [...] there are other clusters wherein the particles stick not so close together, but that they may meet with corpuscles of another denomination, which are disposed to be more closely united with some of them, than they were among themselves. And in such case, two thus combining corpuscles losing that shape, or size, motion, or other accident, upon whose account they were endowed with such a determinate quality or nature, each of them really ceases to be a corpuscle of the same denomination it was before; and from the coalition of these there may emerge a new body, as really one, as either of the corpuscles was before they were mingled, or, if you please, confounded: Since this concretion is really endowed with its own distinct qualities, and can no more by the fire, or any other known way of analysis, be divided again into the corpuscles that at first concurred to make it, than [25] either of them could by the same means be subdivided into other particles."

First, in this treatise from which we have quoted the essential passage, we see two kinds of mixed bodies distinguished. The one has ingredients which can be separated by fire and all sorts of solvents; the other is formed of corpuscles so intimately arranged that no means of analysis available to the chemist is able to distinguish them. They are not truly *simples*. Several elements contribute to their formation. But they are *indecomposable*, and among the substances that the chemist is not able to resolve, Robert Boyle does not hesitate to place gold and silver. Thus was established, it might be mentioned, the notion of a *simple substance* that Lavoisier and his contemporaries were to set out.

When he published the last edition of Lémery's *Cours de Chymie*[14], Baron wrote: "Of all the works that Lémery has published, there is none that does him more honour and contributes more to the great reputation that he has acquired than his *Cours de Chymie*. Most nations are agreed and recognise the value of this work. It has been translated into nearly all the European languages. When it first appeared, in 1675, it got off, following the review of M. de Fontenelle, as a work of elegance and delight. Editions followed one another almost year by year. It was, in the words of the celebrated historian of the Académie, a completely new science which sees the light of day, and which stirs the mind's curiosity."

This work, whose influence was both extensive and profound, was closely linked to Cartesian physics, the main hypotheses of which Lémery [26] adopted, although he stoutly declares "I entertain no opinion that is not founded on experience."

Descartes thought of all bodies as a network or tissue with knots in which *subtle matter* circulated. The flexible particles of liquid, the branched molecules of

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[14] *Cours de Chymie*, content la manière de faire les opérations qui sot en usage dans la médecine par une méthode facile. Avec des raisonnements sur chaque opération, pour l'instruction de ceux qui veulent s'appliquer à cette science, par M. Lémery, de l'Académie des Sciences, docteur en médecine.

New edition, revised, corrected and augmented with a large number of notes, by Mr. Baron, doctor of medicine, and member of the Royal Academy of Sciences, Paris, 1757.

solids and gases, and finally the *third element*, were the three principles of material things, the irreducible ingredients which comprised the so-called principles of the chemists. Lémery followed Descartes' opinion at this point without hesitation:

"The first principle that can be admitted for the composition of mixts," he says, "is a universal spirit which, being prevalent everywhere, produces different things according to the various matrices or pores of the earth in which it finds itself engulfed. But since this principle is somewhat metaphysical, and does not fall under the senses, it is as well to establish it from the senses: I will report that which is generally in use."

"Since the chemists have found five kinds of substance in the course of analysing divers mixts, they have concluded that there are five principles of natural things, water (which is called *phlegm*), spirit (called *mercury*), oil (called *sulphur*), salt, and earth (called *dead* or *black earth*[15])."

"The name *Principle* should not be taken in a sense altogether exact in chemistry, because the substances to which this name has been given are principles only from our point of view and because we cannot go further in the division of bodies, but it is well understood that the principles are repeatedly divisible in an infinity of parts, which might more justly be called principles."

The principles of the chemists were compound although indecomposable substances which are, however, able to unit with one another in such an intimate manner that the resulting mixt is in its turn indecomposable, according to what Boyle was first to put forward: "The five principles are easily found in animals and vegetables, but not [27] so easily in minerals; there are some, such as gold and silver, from which it is not possible to extract two, nor effect any separation, whatever is said by those who investigate with much care salts, sulphurs and the mercuries of the metals. I would like to believe that all the principles are included in the composition of these mixts, but it is not important that these principles remain in their first state and that they may be extracted; because it might be that these substances called *principles* are so united the one within the other that it is not possible to separate them without destroying their shape. But it is only by virtue of their shape that they are called *salts*, *sulphurs* and *spirits*."

The shape of the particles which compose each of the substances employed by the chemist makes intelligible the various properties of these substances:

"Since the nature of a thing so obscure as that of a salt cannot be better explained than by attributing to the parts which compose it such shapes as correspond to all its effects, I shall maintain that the acidity[16] of a liquid consists in the pointed parts of salt put in motion. And I think no one will dispute whether an acid has points, since that is shown by everyone's experiences. It is only necessary

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[15] *terre damnée*.

[16] Until Rouelle [1703-1770], the two words *salt* and *acid* could sometimes correspond to the same concept; a distinction was made between *acid salts* and *alkaline salts*.

to taste an acid to be convinced, for it pricks the tongue as does any material cut and finely pointed. But a demonstrative and convincing proof that acids are composed of pointed parts is that not only do all acid salts crystallise into tapering, pointed forms; but all the dissolutions of various materials made by acid liquids take this shape in their crystallisation. These crystals are composed of points differing from one another in length and size, and this diversity must be attributed [28] to the greater or lesser sharpness of the points of the various sorts of acids."

"Likewise, this different in subtlety of the points is what makes one acid penetrate and dissolve well one mixt that another is not able to rarefy. Thus, vinegar dissolves lead, which aqua fortis cannot, and aqua fortis dissolves quicksilver which vinegar is not able to penetrate, and so on."

"As for alkalis, they are recognised by pouring an acid on them, which immediately, or soon after, gives rise to a violent effervescence persisting until the acid can no longer find bodies to rarefy. This effect makes it reasonable to conjecture that alkalis are rigid and brittle matter, whose pores are so shaped that the acid points entering into them shatter and disperse all that opposes their movement ..."

"There are as many different alkalis as there is matter with different pores, and this is the reason why an acid will ferment one kind of matter and not another. For there must be an appropriate proportion between the acid points and the pores of the alkali."

These few extracts suffice to give an idea of the explanations which abound in Lémery's *Cours de Chymie.* Descartes would certainly have recognised this chemistry, where matter is attributed only divisibility, shape and movement, as the daughter of his philosophy. But Lucretius is equally entitled to claim paternity for his master Epicurus.

CHAPTER 3

THE NOTION OF A MIXT IN THE EIGHTEENTH CENTURY UP TO THE CHEMICAL REVOLUTION: THE NEWTONIAN SCHOOL

Physics [29] underwent a profound transformation in the eighteenth century. No longer content to consider division, shape and movement in matter, attractive and repulsive action between the various particles of bodies was countenanced. It had been Cartesian or Epicurean; now it was Newtonian.

What Newton accomplished in the domain of natural philosophy is one of the most profound revolutions known to the history of the human mind.

Newton succeeded, in his book entitled *Philosophiæ naturalis principia mathematica,* in deducing from a single law the movements of heavy bodies on the surface of the earth, the displacements, relative to the earth, of the moon, the sun, the planets, the satellites and the comets, and finally the ebb and flow of the sea. The statement of this law of universal gravitation is remembered by everyone.

When this work had been accomplished, Newton applied himself to the study of the effects of light. By means of devices which are always quoted as models of the experimental method, he had obtained results regarding the colours of the prism or thin films which have remained classics. In his *Opticks* he described these results and the experimental procedures which furnished them. He avoided dabbling with any hypotheses concerning the nature of light, or the influence [30] exerted on it by bodies it encounters or traverses. But the conjectures that he carefully eliminated from the body of the work crop up in the *Questions* with which it finishes.

In Question XXIX, Newton asks himself "Are not the rays of light very small bodies emitted from shining substances? For such bodies will pass through uniform mediums in right lines without bending into the shadow, which is the nature of rays of light. They will also be capable of several properties, and be able to conserve their properties unchanged in passing through several mediums, which is another condition of the rays of light. Pellucid substances act upon the rays of light at a distance in refracting, reflecting, and inflecting them, and the rays mutually agitate the parts of those substances at a distance for heating them; and this action and reaction at a distance very much resembles an attractive force between bodies."[1]

Pursuing these considerations, Newton shows how the principal optical phenomena might be explained by a mutual attraction exerted at insensible, but nonzero, distances, between the smaller parts of bodies and the small projectiles which constitute rays of light.

Having reached this point, the genius of Newton embraced a vaster field. Considering the collection of phenomena studied by physicists and chemists, he asked himself whether all these phenomena might not be reduced to mutual attractions and repulsions. Among these actions, one will be sensible at large distances: the attraction which produces universal gravitation. The others are insensible, unless the corpuscles between which it is exerted are extremely close together, as with the actions of material particles on the light particles. The XXXIst and last question [31] of *Opticks* is devoted to the exposition of this vast hypothesis, the sketch of an immense work which took physicists more than a century to realise.

"Have not the small particles of bodies certain powers, virtues, or forces, by which they act at a distance, not only upon the rays of light for reflecting, refracting, and inflecting them, but also upon one another for producing a great part of the phenomena of nature? For it is well known, that bodies act one upon another by the attractions of gravity, magnetism, and electricity; and these instances shew the tenor and course of nature, and make it not improbable but that there may be more attractive powers than these. For nature is very consonant and conformable to her self. ... The attractions of gravity, magnetism, and electricity, reach to very sensible distances, and so have been observed by vulgar eyes, and there may be others which reach to so small distances as hitherto escape observation."[2]

It was to attractions of this kind that he was obliged to attribute the cohesion of solids, the rising of liquids in capillary tubes and the round shape of drops of mercury. Analogously, repulsive forces explained the elasticity of gas.

"And thus[3] nature will be very conformable to her self and very simple, performing all the great motions of the heavenly bodies by the attraction of gravity which intercedes those bodies, and almost all the small ones of their particles by some other attractive and repelling powers which intercede the particles."[4]

The great physical theory would not be complete if it were to neglect the traits of chemical phenomena. And far from omitting such effects, Newton devoted the greater part of the [32] XXXIst question to them. According to the hypotheses he

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[1] [Sir Isaac Newton, *Opticks or a Treatise of the Reflections, Refractions, Inflections & Colours of Light*, based of the fourth edition, 1730, Dover, 1952, pp. 370-1. Henceforth *Opticks*.]

[2] [*Opticks*, pp. 375-6.]

[3] [Duhem writes *"Si toutes ces choses sont comme nous l'avons supposé"*—If everything is as we have supposed; the English edition has "And thus."]

[4] [*Opticks*, p. 397.]

developed, when two substances combine, this combination is the result of attractions which are exerted at small distances between the particles of the two bodies. "For when salt of tartar runs *per deliquium*, is not this done by an attraction between the particles of the salt of tartar, and the particles of water which float in the air in the form of vapours? And why does not common salt, or salt-petre, or vitriol, run *per deliquium*, but for want of such an attraction?"[5]

This is not the place to follow the immense development of the doctrine of molecular attraction in physics. In chemistry itself, this notion only interests us in so far as it concerns the motion of a mixt.

Certainly, the doctrine of molecular attraction diverges essentially, in its fundamental principles, from the Epicurean and the Cartesian doctrines. Rather than explaining all natural phenomena by shape and movement, a third irreducible element, force, is invoked, and both Epicureans and Cartesians recoil in horror at the intervention of this *occult quality*.

Nevertheless, like the Epicureans and the Cartesians, the Newtonians supposed bodies to be composed of particles distinct from one another. In fact, the Newtonians were not obliged to formulate precise and detailed hypotheses about the shape of these particles, since they could attribute, on the basis of various laws, attractions and repulsions which their predecessors explained by the shape of particles. In this way, they avoided the naive and infantile reasoning invoked by Descartes, Boyle and Lémery, and they rejoiced in their superiority.

Why do various parts of solid bodies adhere so strongly to one another? In order to explain the durability of solid bodies, the Epicureans invoked the entanglement of small hooks and the [33] ramifications borne by the atoms "which," Newton observed, "is begging the question." The Cartesians imagined that the particles of bodies are glued together by rest. "To compose a body as hard as can be imagined," Descartes[6] said, "I think that it is enough if all its parts touch, without any space between them, and without any being in motion. For what paste or cement could be conceived beyond this, for holding the parts together better?" This cement made of rest, Newton replies, is an occult quality, or rather, pure nothing. "I had rather infer from their cohesion, that their particles attract one another by some force, which in immediate contact is exceeding strong, ... and reaches not far from the particles with any sensible effect."[7]

Descartes, we have seen, assimilated[8] gases to bundles of small twigs whose branches are placed one on top of the other. Boyle insisted on this hypothesis:

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[5] [*Opticks*, p. 377.]

[6] Descartes, *Le Monde ou le Traité de la Lumière*, chap. III.

[7] [*Opticks*, p. 389.]

[8] Descartes, *Les Météores*, chap. I, art. III.

"[T]he particles of air," he said[9], "must be as well sometimes considered under the notion of little springs, which remaining bent, are in their entire bulk transported from place to place; as under the notion of springs displaying themselves, whose parts fly abroad, whilst, as to their entire bulk, they scarce change place: as the two ends of a bow, shot off, fly from one another; whereas the bow it self may be held fast in the archer's hand." Newton was repelled by the puerility of these hypotheses: "[The] vast contraction and expansion [of the air] seems unintelligible, by feigning the particles of air to be springy and ramous, or rolled up like hoops, [34] or by any other means than a repulsive power."[10]

In the same way, instead of explaining the substitution of one body by another in a chemical reaction like Lémery, as a certain proportion of points and pores, Newton attributes the displacement to the relative size of the attractions brought into play: "When salt of tartar *per deliquium*, being poured into the solution of any metal, precipitates the metal and makes it fall down to the bottom of the liquor in the form of mud: Does not this argue that the acid particles are attracted more strongly by the salt of tartar than by the metal, and by the stronger attraction go from the metal to the salt of tartar?"[11]

The study of such substitutions enables the metals to be arranged in order of the magnitude of attraction which they exert on an acid such as aqua fortis: "A solution of iron in *aqua fortis* dissolves the *lapis calaminaris* [cadmia], and lets go the iron, or a solution of copper dissolves iron immersed in it and lets go the copper, or a solution of silver dissolves copper and lets go the silver, or a solution of mercury in *aqua fortis* being poured upon iron, copper, tin, or lead, dissolves the metal and lets go the mercury; does not this argue that the acid particles of the *aqua fortis* are attracted more strongly by the *lapis calaminaris* than by iron, and more strongly by iron than by copper, and more strongly by copper than by silver, and more strongly by iron, copper, tin, and lead, than by mercury?"[12]

This passage has inspired all those chemists, from Geoffroy to Bergmann, who have constructed tables of affinities.

Newton therefore rejects, more often than not, the adventitious hypotheses concerning the shape of molecules which have condemned the Epicureans and the [35] Cartesians; but he did not avoid them altogether. In order to explain the colours of thin films by *fits of easy reflection* and the *easy transmission*[13], he was

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[9] R. Boyle, *New experiments physico-mechanical, touching the spring of the air; and its effects made for the most part in a new pneumatical engine,* experiment I. [*The Works of the Honourable Robert Boyle in Five Volumes,* 1744. Vol. I, "New experiments ...," p. 10.]

[10] [*Opticks*, p. 396.]

[11] [*Opticks*, p. 380.]

[12] [*Opticks*, pp. 380-1.]

[13] [Question 29, *Opticks*, p. 372.]

constrained to attribute a particular shape to luminal projectiles. Buffon[14], one of the more fervent, if not more competent, admirers of Newton, upheld against Clairaut this hypothesis: The particular laws of molecular attraction are all only simple modifications of the universal law of attraction, inversely proportional to the square of the distance; they appear different only because at very small distances, the shape of the atoms which attract themselves does as much or more than the mass for the expression of this law. This view was accepted and developed by Macquer[15], by Guyton de Morveau[16], by Monge[17], and by Bergmann[18].

Based on the vast synthesis of the doctrines of Newton and Leibniz, P. Boscovich, avowed opponent of the Atomists and the Cartesians, rejected Buffon's views. For him, the elementary particles between which molecular attractions and repulsions are exerted are without extension, and consequently without shape. But under the influence of forces which strain at nearby and remote material points, they are able to form groups, kinds of structures. Newton had already countenanced the existence of these kinds of arrangements when he wrote in his *Opticks*: "Now the smallest particles of matter may cohere by the [36] strongest attractions, and compose bigger particles of weaker virtue; and many of these may cohere and compose bigger particles whose virtue is still weaker, and so on for divers successions, until the progression end in the biggest particles on which the operations in chymistry, and the colours of natural bodies depend, and which by cohering compose bodies of sensible magnitude."[19] Following this idea of Newton's, Boscovich allowed that material points, the elements of every body, are able to arrange themselves in more or less complex molecular structures. These complex molecules differ from one another by their exterior shape, the distribution of material points within this figure, and the actions exerted by the one on the other. The peculiarities of these molecules explain the various properties of solids, liquids and gases, and these explanations present considerable analogies with those proffered by the Epicureans and the Cartesians.

The three great Atomist, Cartesian and Newtonian schools were therefore led to conceive of the notion a mixt in the same way.

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[14] Buffon, *Mémoires de l'Académie des Sciences pour* 1745 (parus in 1749).—Clairaut, *ibid.*—Buffon, *Histoire naturelle, générale et particulière, servant de suite à l'histoire de la Terre et d'introduction à l'histoire des minéraux. Supplément*, t. I, Paris, 1774.

[15] Macquer, *Dictionnaire de chimie*, deuxième édition. Paris, 1778, art. *Affinité.*

[16] Guyton de Morveau, *Digressions académiques*, Dijon, 1772.—*Encyclopédie méthodique. (Chimie, Pharmacie et Métallurgie)*, t. I. Paris 1786, art. *Affinité*; t. II. Paris, 1792, art. *Attraction.*

[17] Monge, *Encyclopédie méthodique. Dictionnaire de physique*, t. I. Paris, 1793, art. *Affinité* et *Attraction.*

[18] Bergman, *Opuscula*, dissertatio XXXIII, §1.—*Traité des affinités électives*, Paris 1788, p. 2.

[19] [*Opticks*, p. 394.]

CHAPTER 4

THE NOTION OF A MIXT IN THE EIGHTEENTH CENTURY UP TO THE CHEMICAL REVOLUTION: THE EMPIRICIST SCHOOL

Alongside [37] these schools, a fourth arose after the seventeenth century, the empiricist school.

Fontenelle has left an intriguing catalogue of differences which frequently arose between chemists of the empirical school and those he calls chemist-physicists.

"Monsieur du Clos," he says[1], "continued this year with the examination that he had begun of the *Essays on chemistry* of Mr. Boyle ... Mr. du Clos, as great a chemist as Boyle, but perhaps with a more chemical turn of mind, did not find it necessary, nor even possible, to reduce this science to principles as clear as shape and movement, and he had no difficulty in accommodating a certain specious obscurity which had become well established. For example, if some Brazil wood is boiled in some alkaline sulphurated salt, an intense crimson colour is produced, which is lost and suddenly degenerates into a yellowish one by mixing with aqua fortis, spirit of saltpetre or several other mineral liquors. Mr. du Clos attributes this beautiful red to the excitement of the sulphurated salts, and Mr. Boyle to the new texture of the particles which form the surface of the liquid. Chemistry resolves substances into certain crude and tangible principles, [38] salts, sulphurs, etc. by visible operations. ... But physics, by delicate speculations, acts on the principles as chemistry does on substances; it resolves them into other principles yet more simple, into small bodies infinitely varied in shape and movement: that is the principal difference between physics and chemistry ... The essence of Chemistry is more confused, broader; it resembles more the mixts where the principles are more confused with one another. The essence of Physics is more distinct, simpler, clearer, seeking to return to first beginnings. The other does not go to the bottom."

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[1] Fontenelle, *Histoire de l'Académie royale des Sciences,* t. I. Depuis son établissement en 1666 jusqu'à 1686. Année 1669. Physique, Chimie. Paris, 1733.

The portrait of the chemist that Fontenelle has outlined for us would certainly meet with the approval of Jean-Joachim Beccher, of Speyer. What cannot be found in his strange book on *Subterranean physics*[2]? Theological arguments by which he proves that the devil has reached the centre of the earth in his fall; stories of boundless incredulity, such as the anecdote about a maidservant who swallowed some frogs eggs and threw up six live frogs; the meaningless comparisons which made him think of metals as male minerals and stones as female minerals; important chemical observations and above all, violent diatribes against those who philosophise on chemistry.

Nevertheless, submitting either to current fashion or the influence of Boyle, whose small springs[3] he criticised, but whom he admired and befriended, Beccher dealt carefully with the atomists and the Cartesians. Sometimes, however, he seems to share the opinion of the Cartesians. At the beginning of his work[4], commenting [39] on the text *Deus creavit cælum et terram*, he maintains that all material is composed of *sky* and *earth*. It is the *sky*, and not the air, that is the principle of rarefaction and condensation. The air does not possess the elastic force that is attributed to it because the air itself cannot be rarefied or condensed without the elasticity of the sky. Evidently, Beccher's *sky* has close affinities with the *subtle matter* of Descartes. Just as in 1699, the chemist from Speyer composed all things of *sky* and *earth*, the Cartesian Lémery had in 1675 composed all things of *subtle matter* and *earth*.

Beccher treated the Atomists and Cartesians leniently, reserving all his venom for the Peripatetics. Let us examine, he says[5], the doctrine of Aristotle's pupils regarding the mistion[6] of minerals. What does it teach? What everyone already knows. What does it provide us with? With names and covers to put on realities, after having emptied them. It tells us that minerals are *mixts* that are formed from *elements*, that they have *constitutions* and *qualities*. Who doesn't know that? But how are these mistions made and how are all the different kinds of minerals produced? That is the difficult question, where the efforts of our artful people stumble. Why is tin able to form a non-fragile alloy with lead, but not with silver?

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[2] Joh. Joachimi Beccheri, Spirensis germani, Sacr. Coes. majest. consil. et med. Elect. Bav., *Physica subterranea* profundam subterranearum genesin ex principiis hucusque ignotis ostendens, 1699, 2nd. edition, 1738.

[3] "Roberto Boyle præ omnibus nostro sæculo palmam concederem, si misso suo *elaterio*, chymica experimenta ulterius continuasset: et in exponendis istis non tam materiam *concludendi*, quam in singulis dubitandi, tractare sibi propsuisset." (Beccher, *loc. cit.*, Sectionis quartæ caput primum.)

[4] Beccher, *Physica subterranea* liber primus. Sectio prima: de Creatione universi Orbis. Caput primum: De Creatione Coeli.

[5] Beccher, *Physica subterranea* liber primus. Sectionis quartæ caput primum: De necessitate Physicæ circa Mixtionem.

[6] [Since Duhem's *mixte* and *mélange* have been preserved in the English as 'mixt' and 'mixture', respectively, his *mixtion*, which appears for the first time here will be tracked in the English by 'mistion', even though this is, unlike the French, an antiquated term.]

It would be easy to give you a reason: they are contrary substances with different constitutions. But if you ask them in what the constitution of substances consists and in what respect they differ, then they are speechless. Aqua fortis dissolves metals; that is because, these philosophisers say, it possesses the *dissolving quality*. Certainly; and furthermore: *quantum est quod aliquid quantum dicitur*,[7] equally begging the question. But why does aqua fortis dissolve all metals with the single exception of gold? Here all philosophy is in confusion! How more noble is Spagyric[8]! It takes [40] as theses truths established in practice—experiences. To the phenomena of mistion and the characteristics of mixts it assigns true causes and solid grounds. It continuously reveals new combinations. Yet for all the sagacity, subtlety and meticulousness of this science, you will find not a word on it in the books of the philosophers. They feed only on ideas, abstractions and vain fancies; they only cling to names, happily ignoring their ignorance.

Elsewhere, we see Beccher hurl this whim at the Peripatetics[9]: "They say to you that qualities change, which everyone knows. But why have they changed, and how? Here, deep silence reigns. They would not succeed in explaining for you even if they sweated with their Aristotle for the whole of eternity."

Beccher's principal glory is his having had as a disciple the chemist who created the phlogiston theory, the medical doctor who conceived animism, the illustrious Georges-Ernest Stahl.

Like his master, Stahl[10] rejected the peripatetic theory of mixts. But it is fair to add that, in contradistinction to his master, his rejection was based on reasons and not on jokes. The peripatetic theory was connected, it seemed to him, with the contention that matter is infinitely divisible—a contention which he could not accept[11].

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[7] [It is the size it is because it is the size it is said to be]

[8] This name was used for a long time as a synonym for *Chemistry*.

[9] Beccher, *Physica subterranea* liber primus. Sectionis quartæ caput tertium: Generalia quædam Axiomata de Mixtione continet.

[10] Georgi Enesti Stahlii, Consil. Aulici et Archiatri Regii, *Fundamenta Chymiæ* dogmaticæ et experimentalis, et quidem tum communioris physicæ mechanicæ, pharmaceuticæ ac medicæ tum sublimioris sic dictæ hermeticæ atque alchymicæ; olim in privatos auditorum usus posita, jam vero indultu auctoris publicæ luci exposita. Norimbergæ, 1723.

[11] Stahl, *Fundamenta Chymiæ*, pars III: "... Intellixit quidem, quod ipsi concedendum, quod si quantitas hujusce modi aggregati quovismodo imminuatur, ut sensibilis tantum pars remaneat, ibi illa pars adhuc tota sit mixta, et hæc pars per guttulas imo singulæ guttulæ in minores ulterius proportiones divisæ, tamen sint mixtæ, denn mag etwas zertheilen, so klein man will, so bleit doch das mixtum noch da; interim exemplum ipsum explicandæ mixtionis indoli nimis crassum est atque ineptum: Und ist daher darauf gefallen, das man ein Ding in infinitum secundum lineas mathematicas zertheilen könne."

A large part of Stahl's works are written in this bizarre mixture of German and barbaric Latin. One understands that Buffon was able to write "M. Macquer and M. de Morveau the first of our chemists to have spoken French. This science was therefore born when one began to speak

While [41] maintaining the excellence of the experimental philosophy, Stahl treated Cartesian and Atomist physics with respect: "Although the mechanical philosophy," he says[12], "is well adapted to explain all things, it is in the study of physico-chemical questions that it has been most daringly applied. I do not scorn moderate usage of this method; however, in order not to be blinded by preconceived views, it should be remembered that it [the mechanical philosophy] does not throw away a day on such questions. We should not be surprised. Most of the time it views these assertions with suspicion. It licks the surface and the skin of things, leaving the kernel intact. Concerning the shape and movement of particles it rests content to extract a very general and fairly abstract explanation of the phenomena. But it does not worry about knowing what mixts, compounds, and aggregates are, nor what their nature is, nor what are the properties of these sorts of bodies, nor in what they differ from one another."

In fact, Stahl had certainly meditated on the physico-mechanistic theories of Descartes, Boyle and Lémery, and he adhered to the essential principles of these theories.

At the beginning the second part of his work[13], he divides all bodies into fluids and solids, and ascribes to them a constitution which he borrows practically word for word from Lucretius. He corrects this doctrine only by the introduction of the Cartesian *subtle matter.*

Fluid bodies are not continuous, but contiguous: they are formed from separated, solid particles which are capable of movement. These [42] particles are small globes with smooth surfaces. They are all endowed with the same motive force by which they tend to fall with the same heaviness if the fluid is homogeneous; that is why the surface of liquids is always parallel to the horizon.

Fluid bodies condense when the pores which separate their particles become narrower, and dilate when the pores become larger. In the first case, a subtle matter which fills the pores is driven out, and in the second case the subtle matter penetrates the dilated pores.

The hardness of solid bodies is not due to the juxtaposition and lack of movement of the particles. Rather, solid bodies are formed from branched particles which are intertwined with one another in such a way that it would be very difficult to separate them. When one of the particles is displaced, it caries along with it all the others.

The chemist who accepts these principles could not fail to admit the theory which is common to the Epicureans and the Cartesians regarding the constitution of mixts, and so did Stahl.

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it." (Buffon, *Histoire naturelle, générale et particulière*, servant de suite à la théorie de la Terre et d'introduction à l'histoire des minéraux.—Supplément, tome I^{er} Paris, 1774.)

[12] Stahl, *Fundamenta Chymiæ*, pars I. Préambule daté de 1720.

[13] Stahl, *Fundamenta Chymiæ*, pars I, tractatus I, Proemium.

"Dissolution," he says[14], "is merely the division of bodies into very thin and smooth parts which force themselves into the pores of the menstruation, by way of forming a single fluid. But this division of the parts which constitute the whole could not be brought about if the liquid which is supposed to dissolve or to divide does not penetrate the pores of the bodies to be dissolved. It evidently follows that all dissolving must be the formation of parts which, by their shape and dimensions, fit into the pores of the dissolving bodies. A given liquid is therefore not able to dissolve all bodies, but only a certain ones."

"Besides, any body whatsoever is assembled and woven from particles which are not all alike, but on the contrary very dissimilar. These particles have very different shapes and [43] dimensions, and the variation of the texture, the position and the disposition of these particles confer on a given body diverse pores. One easily concludes that there should exist various menstrua whose smallest parts can penetrate the pores of these bodies."

"This granted, it is easy to understand why aqua fortis dissolves metals, but not wax or sulphur ..."

Doesn't it seem as though this page were taken from Lémery's *Cours de chymie*?

Particles of diverse *principles*, united in very intimate fashion, constitute a first class of bodies to which Stahl appropriately reserves the name of *mixts*[15]. Thus, *iron* is formed from salt, sulphur and mercury, but in certain proportions, and *acid salt of sulphur* is formed from salt and water. The union of principles in mixts is so intimate and so strong[16] that it is extremely difficult, if not impossible, to separate them. The mixt totally disappears without the decomposition of one chemical compound into another. Gold, for example, will be completely dissolved in the state of a tincture, will be totally amalgamated with mercury, will pass over entirely to the state of saline composition, and will become totally volatilised. Quicksilver treated with other saline materials will become "with all its weight" a salt. It will be possible to entirely revive it, and by whatever reagents it is precipitated, fixed, and extracted, it would be very easy to make it release the material with which it was united, and restore it to its first form of quicksilver, by means of contrary acids and alkalis, and even by means of very intense fire.

When the corpuscles of two or more [44] mixts are united together, they form a *compound* body[17]. The corpuscles of mixts which constitute a compound do not adhere to one another as strongly as the molecules of elements within a mixt.

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[14] Stahl, *Fundamenta Chymiæ*, pars II; sectio I; caput II: De solutione et menstruis.

[15] Stahl, *Fundamenta Chymiæ*, pars II.—Tractatus II: Doctrinæ chymicæ. Pars I, sectio III: De objecto chymiæ, Membrum I: De corruptione chymica.

[16] Stahl, *Fundamenta Chymiæ*, pars II.—Tractatus I; sectio III: De combinatorium mixtorum.

[17] Stahl, *Fundamenta Chymiæ*, pars II.—Tractatus II: Doctrinæ chymicæ. Pars I, sectio III: De objecto chymiæ, Membrum I: De corruptione chymica.

Further, compounds may be separated into their elements or exchange elements between one another.

Finally in order to form an extended body of sensible magnitude by joining with one another, the molecules of one and the same mixt or one and the same compound constitute an *aggregate.*

It is clear that the German empirical school is definitely united with Stahl in their view of a mixt arising from the doctrines of the atomists and the Cartesians.

The French empiricist school readily acknowledged the great names of Beccher and Stahl. But it could with good reason claim as its leader a chemist whose originality made him the equal of his German counterparts, and who was the first to precisely fix the notions of base, acid and neutral salt—Guillaume-François Rouelle, demonstrator in the Jardin du Roi.

Rouelle hardly published anything except short notes. But the writings of his pupils have preserved his thoughts for us. In particular, a faithful reflection is to be found in the articles written for the *Encyclopaedia* of Diderot and d'Alembert by a friend and disciple of Rouelle's, himself a talented chemist, de Venel.

In his courses where Rouelle's talents as a manipulator, as well as his eccentricities and violence of language, attracted a large audience, he extolled the virtues of empirical chemistry and maligned the theoreticians of chemistry. The rather puerile explanations of Lémery and his followers were consigned to the rubbish dump under his sarcasm. "Fortunately it is no longer necessary," said Venel[18], "to combat the intertwinings, interpenetrations[19], [45] crooks, whorls[20], and other chimeras of the chemists of the last century." The new Newtonian chemistry did not fare any better under his criticism. One can judge from the bitter attacks of one of his students[21] against "the system of affinities, a beautiful fantasy more likely to amuse our scholastic chemists than to advance science," attacks which are "but an insipid copy[22] of the expressions which escaped from a celebrated man[23] in the heat of discourse by which he compromised his reputation at the same time as he was establishing it by the real service he nevertheless rendered to chemistry."

In the course of proclaiming the excellence of purely empirical chemistry, and affirming "that chemistry is only a collection of facts[24] without, for the most part, any connection between them or dependencies of the one on the other," Rouelle's disciples could not help conceiving of the act of mistion and the constitution of a mixt in a certain manner. The idea that they formed was borrowed from Stahl, that

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[18] De Venel, article *Mixte et Mixtion* in the *Encyclopedia* Diderot and d'Alembert.

[19] *introsusceptions.*

[20] *spyres.*

[21] Monnet, *Traité de la Dissolution des Métaux,* Amsterdam, 1775.

[22] Macquer, *Dictionnaire de Chemie,* second edition, Paris, 1778. Article *Affinité* (in a note).

[23] An allusion to Rouelle.

[24] Monnet, *Traité de la Dissolution des Métaux,* préface.

is to say, in the last analysis, from Lémery, Boyle and the Epicureans. Is this not evident to whoever reads the following passage[25]?

"A mistion is not made by the mere *juxtaposition*, but by the superficial adhesion, of principles, as the aggregation is brought about by pure adhesion of the integral parts of chemical individuals. Fortunately it is no longer necessary to combat the intertwinings, interpenetrations, crooks, whorls, and other chimeras of the chemists of the last century."

"A mistion is not carried out nor occurs except between the solitary, unique, individual parts of the principles, *fit per minima*[26] ..."

"The cohesion of mixture[27] is very intense; the knot that holds together the principles of mixts is very strong. [46] It resists all mechanical forces. ... Even the most universal of chemical agents, fire, with all the known energy of its dissociative action, acts in vein on the most perfect *mistion*, on a certain order of chemically compound bodies."

At the time when Lavoisier's discoveries were determining the antiphlogiston revolution from which modern chemistry emerged, two schools contend for the knowledge of the only true method. One, lured by the example of celestial mechanics, tries to bring all reactions under a chemical mechanics based on the hypothesis of affinity. The other mocking at this haste with which it is desired to reduce to a system facts still hardly known, proclaims the exclusive dominion of experience in the study of combinations and decompositions. But both agree on one point. Chemist-physicists and empirical chemists conceive of the constitution of a *mixt* in the same way. And the notion which they accept is, in its essentials, that which was formed by the atomists of ancient Hellas—that which was transmitted by Epicurean and Cartesian philosophers.

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[25] De Venel, article *Mixte et Mixtion* in the *Encyclopedia* Diderot and d'Alembert.

[26] [it takes place through the smallest parts]

[27] *cohésion mixtive.*

PART TWO

From the chemical revolution to our time

CHAPTER 1

SIMPLE SUBSTANCES

The [49] antiphlogiston revolution accomplished by Lavoisier is the starting point for the discoveries which constitute modern chemistry. The discoveries seem to have had as their principal effect and, according to most chemists, as their true object, the triumph, in completeness and precision, of the atomic notion of a mixt.

Although it contributed indirectly to this work in making possible all the subsequent research, the law of the *conservation of mass* in chemical combination did not have any direct influence on the notion of a mixt. It did not do the same as the theory of combustion and the creation of a new chemical nomenclature intimately connected with this theory, because they fixed the notion of a *chemically simple substance.*

The ancient alchemists supposed that all substances were formed from the same elements, few in number, but variously combined. Given this point of departure, the transmutation of the various substances that nature offers us seemed possible. For many substances, this transformation was easily accomplished. It was never senseless to think along these lines.[1]

The scientific renaissance was at first careful not to condemn these attempts. Bacon[2] assigns [50] as the purpose of the new physics: "to give to silver the colour of gold or a more considerable weight ..., or transparency to some non-diaphanous stone, or tenacity to glass."

However, the continual and resounding failures of the alchemists, persevering with the transmutation of metals, was to open[3] the eyes of the physicists. Without denying that all substances might be composed of the same elements few in number, Boyle[4] was the first who dared proclaim that, in certain cases, elementary corpuscles might unite in a particularly intimate fashion, and "form a new body

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[1] pour beaucoup de corps, cette transmutation s'accomplissait aisément; il n'était nullement insensé d'en poursuivre pour tous l'achèvement.

[2] Bacon, *Novum Organum*, pars ædificans.

[3] *désiller.*

[4] Boyle, *The sceptical Chymist*, Part. II. [The following quotation is essentially the latter part of the longer extract quoted in Pt. 1, Ch. 2, here translated directly into modern English from Duhem's French rendering, which is somewhat different from his earlier translation.]

endowed with an individuality as real as that of the elementary corpuscles before their union; neither fire, nor any known method of analysis, can further divide this body in such a manner as to separate the corpuscles which have combined to form it; nor can the same methods subdivide these [corpuscles] into other particles."

We have seen Lémery, then Stahl, then de Venel adopt Boyle's idea and apply it to metals which preserve their individuality through the hottest fires and the most complicated chemical transformations. It is this idea that inspired the school of Lavoisier to define the chemically simple substance.

It is no longer a philosophical question whether material is reducible to a single principle or a small number of principles present in all substances. All cases of a substance which has resisted all known means of analysis are called *simple substances*, and the chemist declares himself satisfied when he has resolved a substance into a certain number of such simple substances.

Such a substance is always merely *provisionally* simple; indecomposable today, it might yield tomorrow to another method of analysis. Potash and caustic soda were such substances until the day came when the voltaic pile allowed Humphrey Davy to realise the [51] predictions of Lavoisier and isolate potassium and sodium.

"We would contradict all we have just revealed," says Lavoisier[5], "if we were to devote ourselves to the great discussions of the principles constituting bodies and of the elementary molecules. We are here content to regard as simple all those substances that we have not been able to decompose, all that we obtain as the last result of chemical analysis. Perhaps those substances which are simple for us will one day be decomposed in their turn, and we are probably close to this time for siliceous clay and for the fixed alkalis; but our imagination should not outstrip the facts, and we have not had to say more than nature teaches us."

Much later, Lavoisier writes[6]: "All that can be said about the number and nature of the elements is confined, in my opinion, to purely metaphysical discussions, which propose to resolve indefinite problems that are susceptible of infinitely many solutions, none of which accords, in all probability, with nature. I will therefore be content to say that, if by the term 'element' we intend to designate the simple and invisible molecules of which bodies are composed, it is probable that we know nothing of them. But if, on the other hand, we attach to the term 'element' or 'principle of bodies' the idea of the last term reached by analysis, all the substances that we are still unable to decompose by any means are for us elements. This does not assure us that substances that we regard as simple might not be composed of two or more principles, but since [52] these principles are never separated, or rather since we have no means of separating them, they behave as far as we are concerned

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[5] Lavoisier, *Mémoire sur la nécessité de réformer et perfectionner la nomenclature de la Chimie*, read to the Public Assembly of the Royal Academy of Science on 18 April, 1787.—In: *Méthode de nomenclature chimique*, proposed by de Morveau, Lavoisier, Berthollet, and de Fourcroy, Paris, 1787.

[6] Lavoisier, *Traité élémentaire de Chimie*, Discours préliminaire (3rd. edition, vol. I, p. xvi).

like simple substances and we should not suppose them to be compounded until such time as observation and experience have furnished us with proof to that effect."

"We cannot therefore claim," Lavoisier says in another place[7], "that what we today regard as simple is in fact so. All we are able to say is that such a substance is a recognised term of contemporary chemical analysis, which according to our present state of knowledge cannot be further subdivided. Presumably the earths will soon cease to be counted as simple substances ..."

The provisional and empirical character of the definition of simple substance leaves the field free to the philosopher whose hypotheses, more powerful than the practice of chemical analysis, claim to decompose substances which have resisted all reagents. Some of these hypotheses on the unity of material have long enjoyed favour, such as the theory of Prout, which has it that all substances are formed from condensed hydrogen and which stole the adherence of the illustrious J.-B. Dumas. Moreover, the interest that they have engendered, in these latter years, by research relating to *agentaurum* clearly shows that chemists have retained, with Bacon, the hope "of giving to silver the colour of gold or a more considerable weight." Certainly, the idea of simple substances that these chemists created differs little from the notion of a mixt decomposable only with difficulty, defined by Boyle, Lémery and Stahl.

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[7] Lavoisier, *Traité élémentaire de Chimie*, 3rd. edition, vol. I, p. 194.

CHAPTER 2

THE LAW OF DEFINITE PROPORTIONS

Those [53] who have read the authors of the seventeenth century and, particularly, the eighteenth century, will be quite surprised to hear that Proust is credited with establishing the law of definite proportions. All these authors seem to admit, and several formally state, the following truth: when two substances combine together, the mass of the one stands in a fixed relation to the mass of the other.

Jean Rey had already asked himself[1] "Why doesn't the lime of tin increase in weight to infinity when fire which will always provide dense and heavy air for increasing it is continued indefinitely"? And he maintained that "Nature, by its inscrutable wisdom, has here set up barriers that it will never pass ... It is religious in so far as it stops at the limits that have once been prescribed. Our lime is of this condition: The dense air is attached to it and will adhere little by little to the most meagre of its parts. Thus its weight increases from beginning to end, but when all has been taken on, it does not take up any more. Do not continue your calcination with this hope; it will be in vain."

Newton[2] knew that a definite amount of aqua fortis was required to dissolve a definite amount [54] of a given metal, iron for example, and that a greater amount of aqua fortis is required to dissolve a certain mass of iron than the same mass of copper, and a greater amount to dissolve a certain mass of copper than the same mass of silver.

The proportion which must exist between the masses of the ingredients that are made to react in order to obtain a definite compound Stahl[3] calls *natural weights, pondus naturæ*. "Spirit of nitrate only takes hold of spirit of wine when the mass of the second is in a given relation to the mass of the first. And it really seems that this is the natural weight, because if you add a greater amount of spirit of wine, it will not produce any more spontaneous combination nor any more heating."

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[1] Jean Rey, Essays sur la recherche de la cause par laquelle l'estain et le plomb augmentent de poids quand on les calcine. Essay XXVI.

[2] Newton, *Opticks*, Question XXXI.

[3] Stahl, *Fundamenta Chymia*, pars II. — Tractatus II: Doctrinæ chymicæ. Pars I, sectio II: De compositionibus. — Articulus I. Volatilium.

But the idea suggested by Jean Rey, Newton and Stahl takes on a singular force as a result of Rouelle's researches into the formation of neutral salts. To form a neutral salt from a definite mass of a base it is necessary to combine a mass of acid which stands to the former in a fixed relation. If an excess of acid is added, it will mix with, it will "aggregate" with, the salt formed. It will not enter into the constitution of the salt. Can a clearer statement of these principles be imagined than the following due to Venel[4]?

"An essential characteristic of a *mistion*, one which is very more general because it is without exception, is that the principles which combine to bring about the formation of a *mixt* combine in a certain fixed proportion, a certain numerical quantity of determinate parts, which constitute in artificial mixts that which chemists call the *point of saturation* ... The general observation about the proportion of ingredients of a mistion is a dogma of eternal truth, of absolute, not to say conceptual,[5] truth. We call *mixts* or non-*simple*, truly chemical, substances, [55] those which are so essentially, so necessarily, composed according to a definite proportion of the principles, that not only the removal or the *addition*[6] of a certain amount of such and such principle would change the essence of the substance; any excess whatsoever of a principle is inadmissible in mixts, be it natural or artificial, and the removal of a portion of a certain principle is, by the definitions presented above, the actual decomposition, the chemical destruction, of a portion of the mixt. So if a given amount of nitrous acid is separated from a given amount of saltpetre, there does not remain a saltpetre less laden with acid, but a mixture of saltpetre, perfect as before, and a fixed [amount] of alkali, which is the other principle of saltpetre, absolutely naked, to which the acid with which it was joined has been entirely removed."

These lines were written in 1765. Whoever has read them is not surprised to hear Lavoisier affirm[7] "that 72 parts by weight of oxygen are required to saturate 28 of carbon and that the gaseous acid which is produced has a weight precisely equal to the sum of the weights of carbon and oxygen that were used to form it" and teach[8] that "water is composed of oxygen and the base of an inflammable gas in the proportion of 83 parts to 15." Nor is he surprised to see Bergmann devote himself to careful, numerical analyses which presuppose an implicit belief in the fixed composition of the substances analysed.

Must we not therefore admit that the law of definite proportions was completely known and accepted since the time of Rouelle? That in contesting it, Berthollet was taking an inexplicable step backwards? That Proust's only merit was to demonstrate

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[4] De Venel, art. *Mixte et Mixtion* from Diderot and d'Alembert's *Encyclopaedia*.

[5] nominale.

[6] suraddition.

[7] Lavoisier, *Traité élémentaire de Chimie*, 3rd. edition, vol. I, p. 68.

[8] Lavoisier, *Ibid.*, p. 94. [In the Dover edition of the English translation of the Elements (p. 89) the figure 85 rather than Duhem's '83' is given.]

anew what was known before? We would be allowing ourselves to be carried by appearances. We would allow to pass, misunderstood, one of the most profound transformations that the notion of mixt has undergone, [56] that which has led chemists to distinguish a physical mixture from a chemical combination.

Let us return to the *Essays* of Jean Rey and to the reply[9] made by the doctor from Périgord to the following question: *Why doesn't lime increase in weight to infinity?* "For (he said) why doesn't the lime increase indefinitely, when the fire can be indefinitely continued, which will always provide the dense and heavy air to increase it?[10] I develop this difficulty, which could tie up someone of lesser subtlety, by remarking that all material which increases by the addition of another is either solid or liquid, and that the mixture is made between them in [one of] three ways. For either solid material is mixed with solid, or liquid with liquid, or one of these with the other. The mixing and growth which occur in the first two ways have no bounds. Mix some sand with some other sand, and you will always augment it by [simply] adjoining them endlessly. Mix some wine with some other wine, and you will always [simply] adjoin them and never be finished. It is not the same with the third way, when one adds and mixes a liquid material with a solid. Such mixed addition does not always increase, certainly not to infinity. Nature, by its inscrutable wisdom, has here put up the barriers that it never crosses. Mix some water with sand or flour, and they cover themselves totally down to the smallest of their parts. Pour in more, they will not take up more of it. Withdraw them from the water, they only carry what adheres to them and which just suffices to encircle them. Plunge them back a hundred times and they do not come out better charged. Let them rest therein, and they will leave the surplus and go to the bottom by themselves. Nature is so religious that it stops at the limits once prescribed. Our lime is in this condition ..."

Isn't the idea expressed in this page of Jean Rey's, albeit rather naively, that which we find [57] in Newton's *Opticks*, there rendered precise by the hypothesis of molecular attraction?

According to Newton[11], when a particle of a body which exerts an attraction on the particles of another body is surrounded by a certain number of particles, its action ceases to make itself felt on the other particles of the same kind from which it is now too distant. It is thus *saturated* and the combination comes to an end. "[W]hy does not Salt of Tartar draw more Water out of the air than in a certain proportion to its quantity, but for want of an attractive Force after it is satiated with Water? ... And is it not from the like attractive Power between the Particles of Oil

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[9] Jean Rey, *Essays sur la recherche de la cause par laquelle l'estain et le plomb augmentent de poids quand on les calcine*, Essay XXVI.

[10] [Despite the quotation marks, what Duhem writes between them is not exactly the same as what he writes as the first quotation in the second paragraph of this chapter.]

[11] Newton, *Opticks*. Question XXXI.

of Vitriol and the Particle of Water, that Oil of Vitriol draws to it a good quantity of Water out of the air, and after it is satiated draws not more [...]?"[12]

The number of particles of the second body that hold a particle of the first body is all the larger as the attraction exerted by the first body on the second is more intense. We can therefore judge the force of attraction of a first body on a second by the mass of this second body that is necessary to saturate the first. We have seen that particles of aqua fortis were more energetically attracted by iron than by copper, by copper than by silver or quicksilver. "[I]s it not for the same reason that Iron requires more *Aqua fortis* to dissolve and saturate it than Copper, and Copper more than other Metals [...]?"[13]

Newton therefore compares the limitation that is observed in chemical reactions to saturation which manifests itself in the most ordinary phenomena of dissolution such as when sea salt is dissolved in water.

Chemists of the [58] empirical school indicated their agreement yet more clearly.

"A fixed proportion," Stahl says[14], "is always required between the solvent and the substance to be dissolved. Thus, a pound of camphor, for example, always requires at least two pounds of menstruum. Similarly, a definite amount of aqua fortis dissolves only a fixed amount of silver. A definite amount of water dissolves only a fixed amount of salt."

And de Venel[15], interpreting the ideas of Rouelle, writes following the passage reported above: "All the menstrua enter into real mistion with substances that they dissolve, but the energy of all menstrua is limited by the dissolution of a definite amount of the dissolved substance. Water, once *saturated* with sugar, does not dissolve any new sugar. Sugar thrown into a perfectly saturated sugar solution remains unchanged, under the same degree of heat, in its state of a concrete body. This last circumstance makes manifest the dogma that we are propounding, but it is only possible to observe when the energy of various menstrua is tested on concrete or substantial bodies. For it is not the same thing when tried on liquids, and some excess of *dissolved alkali* poured onto spirit of vinegar, for example, shows no sensible sign that any part of the liquid would be rejected from the mistion. But it really is so, and chemistry has some simple means of demonstrating [the presence], in similar cases, [of] the least surplus or superfluous portion of one of the principles. And this surplus portion is not more united with the mixt despite swimming in the same liquid. Because two liquids capable of perfectly mixing with one another, and which actually mix very perfectly, are not in mistion together ..."

"It is evident that all these unions of aqueous liquids are true, pure, aggregations. [59] A certain amount of water is united by the bond of a true mistion to a definite

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[12] [*Opticks*, p. 377.]

[13] [*Opticks*, p. 381. The words "and saturate," corresponding to Duhem's "et saturer," are not in the English version.]

[14] Stahl, *Fundamenta Chymia*, pars II.—Tractatus I.—Sect. I, chap. I: De natura fluidi et solidi.

[15] De Venel, art. *Mixte et Mixtion* from Diderot and d'Alembert's *Encyclopaedia*.

amount of salt, and constitutes an aqueous liquid which is a true mixt. That is shown, among other things, by the fact that when a portion of the water is removed, a portion of the mixt perishes. In place of an *aqueous saline mixt*, a concrete body, a crystal of salt, is obtained called a *lye*, *lixivium*. But all the water that might be superadded to this lye as such does not draw together with it any more than with an aggregation. It is the water which unites with the water, and that is why this mixture has no limits, no proportions."

Now the amount of sugar that may dissolve in a given amount of water is fixed by the given conditions. But it changes when the conditions change and depends, in fact, on a range of circumstances. It increases when the temperature is raised (and de Venel knew that, because he was careful to say that the dissolving of which he spoke was left *under the same degree of heat*). It varies if some foreign bodies are mixed with the water, for example spirit of vinegar.

These are the facts that the most common observation teaches the empiricists—facts which were, however, easily seen to accord with the various chemical theories which arose during the course of the eighteenth century.

Stahl, who clung to Lémery's ideas, thought that a solid substance dissolves in a menstruum when the pores of the menstruum are of such a shape and size as to be able to accommodate the molecules of the solute[16]. Dissolution therefore ceases when the pores of the menstruum, blocked up with solute molecules, are no longer able to receive any more.

But heat enlarges the pores of various substances, while cold tightens them[17], and that is due to the different movements of the molecules of ether, movements which are the essence of heat and cold. [60] It is therefore clear that, in a given menstruum, a given solid becomes more soluble when the degree of heat is raised and less soluble when the degree of heat is lowered.

It is also clear that if a foreign substance is mixed with the solvent, a new liquid is obtained whose pores would not be disposed in the same way as in the first liquid. A given solid would not have the same degree of solubility in the new menstruum as in the old.

Newtonian theories lead to similar conclusions.

The number of sugar molecules that a molecule of water can retain in its neighbourhood does not depend solely upon the attraction exerted by the water molecule on the sugar molecules grouped around it. It depends also on the attractions by which the other molecules of the solvent attract these sugar molecules, and consequently on the nature of the solvent molecules. On mixing water with a foreign body, the solubility of sugar would vary in such water.

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[16] Stahl, *Fundamenta Chymia*, pars II.—Sect. I, Chap. IX: De præcipitatione.—Tractatus I, Sect. I, Chap. II: De solutione et menstruis.

[17] Stahl, *Fundamenta Chymia*, pars II, Proemium.

The number of sugar molecules amassing around a water molecule under the combined action of all the forces which attract them would depend on whether these molecules were stationary or animated by a rapid movement. Now it is a rapid movement of the ultimate particles of bodies that Newton, like Descartes, attributes to heat. The solubility of sugar in water therefore varies with the temperature.

Viewing the rapid movement of particles as constituting the essence of heat was a remnant of Cartesian physics in Newton's philosophy—a remnant which was to disappear with the work of Black and Crawford. Heat was regarded as the effect of an imponderable fluid, present in all bodies, to which the new chemical nomenclature assigned the name *caloric*. Molecules of caloric were, like molecules of other substances, endowed with attractive and repulsive action, effective [61] only at very small distances. The limit of chemical combination is a state of equilibrium between the forces emanating from the molecules of material and the forces emanating from caloric.

"Metallic substances," Lavoisier says[18], "increase in weight during their calcination in proportion to the oxygen that they absorb. At the same time they lose their metallic state and are reduced to an earthy powder. Metals in this state should not be considered as entirely saturated with oxygen because their action on this principle is balanced by the force of attraction exerted on it by the caloric. In the calcination of metals, the oxygen responds in fact to two forces, to that exerted by the caloric and that exerted by the metal. It only tends to unite with the latter because of the difference in these two forces—the excess of the one over the other."

"Metals do not all have the same degree of affinity for oxygen. Gold and silver, for example, and even platinum, cannot remove it from caloric, whatever the degree of heat. As for the other metals, they are charged with greater or lesser amounts, and in general, they absorb it until the principle is in equilibrium with the force of the caloric which retains it and that of the metal which attracts it. This equilibrium is a general law of nature in all combinations."

The determination of the amount of sugar that is able to hold in suspension a definite amount of water united with a definite amount of caloric was no more a problem of statics. It was not necessary to press further for a solution to this problem in order to predict that the amount of sugar capable of dissolving in this amount of water depends on the amount of caloric found to be contained there.

"These phenomena of solution by caloric," [62] Lavoisier says[19], "are always involved to a greater or lesser extent with solution in water. This is convincing when it is seen that water cannot be poured onto salt in order to dissolve it without employing, in reality, a mixed solvent of water and caloric. Thus, several different cases can be distinguished according to the nature and mode of existence of each salt. If, for example, a salt is scarcely soluble in water, but very much so in caloric, then

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[18] Lavoisier, *Traité élémentaire de Chimie*, IIIrd. part, chap. VII, §VI (3rd. edition, vol. II, p. 127).

[19] Lavoisier, *Traité élémentaire de Chimie*, IIIrd. part, chap. V, §I (3rd. edition, vol. II, p. 39).

this salt will clearly be scarcely soluble in cold water, but very soluble, on the other hand, in hot water."

In their immortal *Memoir on Heat* of 1783, Lavoisier and Laplace[20] sketched the solution to such problems of chemical statics and thereby obtained the important laws regarding the dissolution of salts or the formation of ice within slightly acid water.

Now Stahl compared the saturation of water by salt or sugar with the saturation of aqua fortis by iron or copper. If, in order to saturate a definite amount of water, it is necessary to mix an amount of sugar which depends on the temperature and the foreign bodies added to the solution, why doesn't the mass of copper dissolved by a given amount of aqua fortis depend of the temperature, the dilution of the aqua fortis, and all the circumstances of the reaction? In order to form a saturated compound, the elements combine in a proportion which is fixed when the conditions in which the combination is accomplished are also fixed. But if the conditions vary, the constitution of the saturated compound may vary and should in general vary. It might be that, in certain cases, a compound has a definite composition, independent of the circumstances in which the compound is formed. But such cases are certainly exceptional. Fixing the particular characteristics [63] by which such a case can be recognised; discovering, in the non-exceptional cases, which influence that each of these conditions of the reaction exerts on the composition of the product obtained—this is the aim of the *chemical statics* whose method Lavoisier and Laplace outlined.

This is the doctrine that Berthollet presented in 1799, at the Institute of Egyptology[21], defended during the course of several years[22] with just as much sagacity in his theoretical deductions as there was skill in his experimental determinations, and developed with an admirable clarity in his *Essay on Chemical Statics*[23].

"We must," Berthollet says in this work, "find in the combination the laws that we have observed in the chemical action which produces dissociation ... Struck by having found determinate proportions in several combinations, chemists have often thought it a general property of combinations to be constituted of definite proportions, so that, according to them, when a neutral salt receives an excess of acid or alkali, the homogeneous substance which results is a solution of neutral salt in a portion of free acid or alkali."

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[20] Lavoisier and DE LAPLACE, *Mémoire sur la chaleur*, read at the Academy of Sciences on 18 June, 1783. (*Mémoires de l'Académie des Sciences pour* 1780. Paris, 1784.)

[21] Berthollet, "Recherches sur les lois de l'affinité," *Mémoires de l'Institut pour* 1799, pp. 1, 207 and 229.

[22] Berthollet, "Observations relatives à différents mémoires de Proust," *Journal de physique*, Vol. LIX, pp. 347,352; 1804.

[23] Berthollet, *Essai de Statique chimique*, 1st. part, p. 61, Paris, 1806.

"It is a hypothesis having as its only foundation a distinction between a combination and a solution, and in which the properties which cause a separation are confounded with the affinity which produces the combinations. But it is necessary to recognise the circumstances which can determine the separations of the combinations in a certain state, and which limit the general law of affinity."

Berthollet's theory was the natural corollary of all that had been taught by chemists of the eighteenth century, both Newton's disciples as well as the followers of the empiricist school, regarding chemical saturation. [64] Denying this theory, maintaining that each chemical combination has a composition which is fixed, specific and rigorously independent of the conditions in which this combination took birth, would be to produce a profound revolution in the notion of a mixt.

S.-L. Proust was sufficiently bold to attempt such a revolution, and fortunate enough to achieve it.

In 1799 Proust[24] remarked that if natural copper carbonate is dissolved in an acid and then precipitated by an alkaline carbonate, the amount of copper carbonate obtained is exactly equal to the natural carbonate employed at the start. Therefore, this transformation neither gains nor loses any trace of carbonic acid or copper oxide in the salts tested. The copper carbonate prepared in the laboratory therefore has the same composition as the copper carbonate formed in the bowels of the earth by processes certainly very different from those employed by the chemist.

Generalising this discovery, Proust did not hesitate to affirm that all chemical combinations are characterised by an absolutely fixed, specific combination independent of the conditions in which the combination is formed. All the cases of combination with variable composition that have been thought to occur are, in fact, impure combinations containing an excess of one of the components, or a mixture of two distinct combinations of the same elements.

"These eternally invariable proportions," Proust says[25], "these constant attributes that characterise the true compounds of art, or those of nature, in a word the *pondus naturæ* so well understood by Stahl; all this, I say, is no more in the power of the chemist than the law of election which governs all combinations."

A [65] discussion arose between Proust and Berthollet. "This discussion[26], one of the more memorable of which science has kept in memory, went on from 1799 to 1806, and was pursued by both parties with a power of argument and a feeling of respect for the truth without ever overstepping the conventions." It terminated with a victory for Proust's ideas.

What an upheaval in the principles maintained up to then by all chemists! The saturation of a chemical combination is no longer analogous to the saturation of a solution. The concentration of a saturated solution depends of the temperature,

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[24] Proust, "Recherches sur le Cuivre," *Annales de Chimie*, Vol. XXXII, p. 26, 1799.

[25] Proust, "Recherches sur le Cuivre," *Annales de Chimie*, Vol. XXXII, p. 30, 1799.

[26] Ad. Würtz, *La Théorie atomique*, p. 5.

foreign bodies, and all the circumstances in which the act of dissolution is accomplished. On the other hand, the raising or lowering of temperature, and the presence or absence of foreign bodies, may favour or disturb the production of a chemical combination, but it can have no effect on the composition of this combination. According to the experimental conditions, it is possible to produce some water or not to form any, but on all the occasions when water is formed, this water comes from a certain mass of hydrogen and a mass of oxygen eight times greater.

Henceforth, two categories of mixts were distinguished from one another: the *chemical combinations* and the *physical mixtures*. The law of definite proportions, inapplicable to physical mixtures, but holding rigorously of chemical combinations, was to be the criterion which permits them to be distinguished.

CHAPTER 3

CRUDE CHEMICAL FORMULAS AND EQUIVALENT MASSES

Not [67] only has each chemical combination a perfectly definite composition, but also the compositions of the various chemical combinations are not entirely independent of one another. Such was the result of work undertaken by Richter at the end of the eighteenth century[1].

Mix a neutral solution of barium nitrate with an equally neutral solution of sulphate of potash. Neutral barium sulphate is precipitated and the solution too remains perfectly neutral, containing some potassium sulphate without any excess of acid or alkali. This fact, or rather, this law of the continuity of neutrality in the double decompositions of salts, of which many examples analogous to the preceding could be cited, was still, in 1777, unknown to Wenzel. It is the basis of Richter's researches.

Let us analyse the observation which we have just reported.

Sufficient barium nitrate was decomposed that the barium obtained exactly neutralised the sulphuric acid of the potassium sulphate. At the same time, the nitric acid provided by the decomposition exactly neutralises the potassium of the potassium sulphate. [68] Therefore if we take the masses of the sulphuric acid and nitric acid which neutralise the same mass of barium, these masses of sulphuric and nitric acid also neutralise the same mass of potassium.

More generally, let us consider a series of acids A_1, A_2, A_3, ... and a series B_1, B_2, B_3, ... of bases. A neutral salt formed by the acid A_1 and the base B_1 contains a mass m_1 of acid and a mass n_1 of base. Suppose, on the one hand, that, in order to neutralise the mass m_1 of the acid A_1, masses n_2, n_3, ... of bases B_2, B_3, ... are required, respectively; and on the other hand, masses m_2, m_3, ... of acids A_2, A_3, ... are required to neutralise the mass n_1 of the acid B_1. Now if a neutral salt is formed by means of acid A_p and base B_q, it is certain that the mass of the acid and the mass of the base will be in the proportions of m_p to n_q.

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[1] Richter, *Anfangsgründe der Stöchyometrie oder Messkunst chemischer Elemente*, 1792-1793.—*Mittheilungen über die neueren Gegenständen der Chemie*, 4th. volume, 1795.

Thus, among the numerous salts that can be formed by combining each of the acids $A_1, A_2, A_3, \ldots$, with each of the bases $B_1, B_2, B_3, \ldots$, it suffices to analyse all those that can be formed by combining a single acid A_1 with each of the bases $B_1, B_2, B_3, \ldots$, together with all those that can be formed by combining the single base B_1 with the acids $A_1, A_2, A_3, \ldots$, in order that the composition all the others should be known in advance.

Berthollet who, via Fischer, knew of the discovery of Richter and who, with Guyton de Morveau, had been among the first to grasp its significance, assessed it in these terms[2]: "The preceding observations seem to me to lead necessarily to the consequence that my researches on the laws of affinity have only indicated, but that Richter has positively established, the knowledge that the different acids in corresponding proportions reach a neutral state of combination with bases. This conclusion may have considerable utility in verifying experiments which have been made on the proportions of elements in salts and even for determining [69] on what experiments have yet to pronounce for establishing the most certain and easy method for carrying out this most important objective for chemistry."

It is clear that the law discovered by Richter can be formulated thus:

Consider a series of acids and bases

$$A_1, A_2, A_3, \ldots, B_1, B_2, B_3, \ldots$$

Each of these substances can be put into correspondence with one of the numbers in the series

$$m_1, m_2, m_3, \ldots, n_1, n_2, n_3, \ldots$$

In all cases where one of these acids—say A_p—is combined with one of these bases—say B_q—the mass of the acid entering into combination would stand to the mass of the base as m_p is to n_q.

Taken in this form, the law immediately suggests the idea of an analogous law, applicable not only to neutral salts formed by the union of acids and bases, but to all combinations of simple substances. This law, which Richter had already applied to the combinations of oxygen with metals, can be stated thus:

Let $C_1, C_2, C_3, \ldots$ *be the various simple substances of chemistry. Each of these substances can be put into correspondence with an appropriate number so as to obtain a set of numbers* $p_1, p_2, p_3, \ldots$ *If two substances* C_m, C_n *enter a combination, either alone, or with one or more other substances, the masses of these two substances which are combined always stand to one another in the same relation as the numbers* p_m, p_n.

Precise as this law is, it is clear that it is not complete and that it calls for a modification.

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[2] Berthollet, *Essai de Statique chimique*, vol. I, p. 134, 1803.

When two substances C_m, C_n are combined, the masses of the two entering into combination stand, according to the preceding law, in a definite, unique relation, that of the two numbers p_m, p_n.

Now, the two substances C_m, C_n might form several combinations. In each of these, [70] the composition is perfectly definite, but the composition varies from the one to the other. Lavoisier observed this for oxygen compounds of sulphur and nitrogen, Richter for the oxides of iron and mercury, and in his conflict with Berthollet, Proust demonstrated it for various substances. These facts are irreconcilable with Richter's law unless it is given the appropriate correction.

This correction, known as the *law of multiple proportions*, is the work of John Dalton.

We will not detail here the history, which is quite uncertain, of Dalton's discovery[3]. But we will return to the ideas which have suggested it. Let us state the consequence of this discovery in the form that it has acquired with the progress of chemistry.

Let C_1, C_2, C_3, ... *be the various simple substances; each of these substances can be put into correspondence with an appropriate number, called the* PROPORTIONAL NUMBER, *in such a way as to obtain a table of proportional numbers:* p_1, p_2, p_3, ... *If the substances* C_1, C_2, C_3, ... *enter a combination together, the masses of these substances which are combined stand to one another as* $\lambda\, p_1$, $\mu\, p_2$, $\nu\, p_3$, ..., λ, μ, ν ... *being* INTEGRAL NUMBERS.

For example, to hydrogen, oxygen, nitrogen and chlorine it is possible to assign the numbers 1; 16; 14; 35.5. When nitrogen is combined with oxygen to form the various nitrogen oxides which chemistry has discovered, the masses of nitrogen and oxygen which are combined stand to one another as $\lambda \times 14$ and $\mu \times 16$, λ being equal to 1 or 2 and μ to one of the numbers 1, 2, 3, 4, 5, 7. When nitrogen is combined with hydrogen, the masses of the two substances which unite to form ammonia stand to one another as 14 and 3×1. When oxygen is combined with hydrogen to form water, the masses of the two gas reagents stand to one another as 16 and 2×1. In hydrochloric acid, the [71] masses of hydrogen and chlorine stand to one another as 1 and 35.5. In the oxygen combinations of chlorine, the masses of chlorine and oxygen stand to one another as $\lambda \times 35.5$ and $\mu \times 16$, λ being equal to 1 or 2 and μ to one of the numbers 1, 2, 3, 4, 5, 7.

Dalton and his contemporaries were not content with the introduction of the words *integral numbers* in the statement of the previous law; they would say *simple integral numbers*. But this restriction, coming right at the beginning of chemistry, became less and less tenable as chemistry developed and extended its researches. In particular, the progress of organic chemistry has led to the attribution of integral

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[3] This history is to be found in Ad. Wurtz, *La Théorie atomique*; this book, together with preface which Würtz put at the beginning of the *Dictionnaire de Chimie*, should be read by anyone who is interested in the history of chemical doctrines.

numbers λ, μ, ν ... of large values and the character of simplicity which they were at first attributed has disappeared. How, for example, can it be retrieved in the formula of a paraffin where the masses of the combined carbon and hydrogen stand to one another as λ times the proportional number of carbon and μ times the proportional number of hydrogen, and where λ, μ have the following values: $\lambda = 27$, $\mu = 56$?

The law we have stated is the foundation on which the use of *chemical formulas* rests.

Rather than repeatedly writing the proportional number of each simple substance, it is represented by a letter or a symbol. Thus the letter H represents the proportional number 1 of hydrogen, the letter O the proportional number 16 of oxygen, and the symbol Cl the proportional number 35.5 of chlorine. A table placed at the beginning of treatises on chemistry presents the number represented by each of these symbols and the simple substance to which it relates, as for example in this table:

Hydrogen	$H = 1$,
Oxygen	$O = 16$,
Sulphur	$S = 32$,
Nitrogen[4]	$N = 14$,
Chlorine	$Cl = 35.5$

Suppose, given this table, that we [72] want to represent the composition of any substance, for example that of a body formed from nitrogen, oxygen and hydrogen. The masses of nitrogen, oxygen and hydrogen contained in the body will stand to one another as $\lambda \times 14$, $\mu \times 16$ and $\nu \times 1$, λ, μ, ν being three integral numbers. Now we attribute to the substance the symbol $N_\lambda O_\mu H_\nu$, which will be its chemical formula. Thus, nitric acid is obtained by combining nitrogen, oxygen and hydrogen in the proportion of the numbers 14, $48 = 3 \times 16$ and 1, in view of which it has the chemical formula NO_3H.

Is the formula of a compound determined absolutely and without any equivocation when it is known, first, what the composition of the substance is and, second, what the proportional numbers of the elements which it contains are? Certainly not.

For example, instead of saying that the masses of nitrogen, oxygen and hydrogen that are contained in nitric acid stand in the relation 14, 3×16 and 1, we can say

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[4] [Duhem's use of the symbol "Az," corresponding to the French "azote," has been systematically changed to "N."]

that they are as 2 × 14, 6 × 16 and 2 × 1, in which case the formula for nitric acid will be $N_2O_6H_2$. Again, we could say that they are as 3 × 14, 9 × 16 and 3 × 1, in which case the formula for nitric acid will be $N_3O_9H_3$.

Thus, *without changing the proportional numbers which correspond to various simple substances, it is possible to assign the same compound several different formulas; each of these formulas are obtained from the most simple of them by multiplying the numbers which figure in it by the same number.*

But there is more. The proportional number of a simple substance is not determined absolutely and without equivocation. Instead of taking the number 16 as the proportional number of oxygen, we might adopt the number 8. We can, with this new number, as well as with the former, write the chemical formulas of substances which contain some oxygen; only these formulas will not be the same. The masses of nitrogen, oxygen, and hydrogen which are contained in nitric acid stand to one another as 14, 6 × 8 and 1; the new formula of nitric acid [73] will then be NO_6H. We could equally take the number 32 as the proportional number of oxygen; the masses of nitrogen, oxygen and hydrogen contained in nitric acid standing as 2 × 14, 3 × 32 and 2 × 1, we must give nitric acid the formula $N_2O_3H_2$.

Thus, *the proportional number of each simple substance can be replaced by another, obtained by multiplying or dividing the first by an integral number.*

The principles that we have reviewed cannot suffice for the creation of a chemical notation exempt from confusion. Those who, given hydrogen has the proportional number 1, accept the number 16 as the proportional number of oxygen, would attribute to water the formula H_2O, while those who accept the number 8 as the proportional number of oxygen write the formula of water as HO or H_2O_2, whereas the latter formula represents, for the former chemists, hydrogen peroxide.

In order to avoid confusion, it is necessary to introduce a new convention into chemical notation. All chemists have implicitly accepted and employed this convention, but Laurent seems to be the first to have explicitly formulated it[5].

The convention is as follows: *Proportional numbers of the various simple substances are chosen in accordance with the way* ANALOGUES *of chemical compounds are represented by analogous formulas.*

An example will show immediately how this convention allows for the restriction of the indeterminacy in chemical notation.

Supposing the proportional number of hydrogen is 1, what proportional number should we take for sulphur? Sulphur admits as proportional numbers any of the numbers 8, 16, 32, 48, 64, ... For each of these numbers a different formula corresponds to hydrogen sulphide: HS_2, HS, H_2S, H_3S, H_4S ... If the preceding convention is not invoked, the choice [74] between these different formulas remains free. But if the preceding convention is accepted, a rule is immediately imposed:

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[5] Laurent, *Méthode de Chemie*, pp. 3, 10, 16. Paris, 1854.

hydrogen sulphide is analogous to water; we must assign a formula like that of water.

If we had adopted the number 8 as the proportional number of oxygen, we would have given water the formula HO; it would then be necessary to give hydrogen sulphide the formula HS and attribute to sulphur the proportional number 16. Had we adopted the proportional number 16 for oxygen, then we would give water the formula H_2O, and we would have to give hydrogen sulphide the formula H_2S and attribute sulphur the proportional number 32.

Thus, from the fact that oxygen and sulphur, in union with hydrogen, give rise to analogous compounds, it follows that the proportional numbers of these two substances need not be chosen arbitrarily. When the proportional number of the one is chosen, the proportional number of the other has thereby been fixed. This is a conclusion that we can generalise by saying:

When two simple substances can, by combining with the same third substance, give rise to two compounds analogous to one another, if the proportional number of one of the simple substances is fixed, the proportional number of the other is thereby found to be fixed without ambiguity.

These two proportional numbers, thus linked to one another, are said to be *equivalents* with one another. Thus, the number 8 for oxygen and the number 16 for sulphur are equivalent proportional numbers for oxygen and for sulphur. The same holds for the number 16 for oxygen and the number 32 for sulphur.

Will the convention that we have formulated allow us to ban all ambiguity from chemical notation? Will it lead us to adopt a unique system of proportional numbers, all equivalent with one another? Will it assure the concordance of symbols used by different chemists?

Such an agreement comes up against a first difficulty. [75] If it is to result from the previous convention, it is first of all necessary that all chemists agree to regard the same chemical compounds as mutual analogues. Yet such an agreement might well not obtain.

All geometers are agreed in regarding all right angles as equal, or in declaring that only one perpendicular can be drawn to a point taken outside a straight line from this line. Agreement on this point is necessary, since we have in effect defined what it is to be a right angle, and what it is to be a perpendicular. From these definitions it follows, by a logical deduction, that all right angles are equal, and that from a point only one perpendicular can be drawn on a line. So if someone were to deny one or other of these statements, it would be possible, by an appropriate series of syllogisms, to drive him back to a contradiction.

On the other hand, if one of two chemists affirms an analogy between two substances which the other denies, I do not have the right to say to the other that what you say is certain, and to the other, that what you say is absurd. My judgement about the disagreement which divides them cannot be reasonably formulated in such rigorous terms. I can only say to the one that I approve of your opinion, and to the other, that I am not of the same opinion.

The compounds which come into question for comparison are not, in fact, at all like the figures treated in geometry, beings of reason, abstractions that our minds combine by means of other abstractions and which can be adequately defined by saying in what manner they are made up. They are, it is true, abstractions, for when a chemist speaks of water or hydrogen sulphide, he does not intend to speak of any particular mass of water, nor of any particular mass of hydrogen sulphide. But, drawn from the observation of concrete bodies and particulars by an intuitive generalisation, these abstractions cannot be defined. What is understood by water or hydrogen sulphide can no more be defined *more* [76] *geometrico* than can what is understood by horse or frog. These notions are susceptible of *description*, but not of *definition*.

Similarly, the notion of analogy arises from an unanalysable intuition. It is one of those indefinable notions that Pascal has attached to the comprehensive[6] rather than the geometric mind. It must be accorded a scientific value, however, if the name of science is not to be withheld from studies such as comparative anatomy. It is impossible to mark with a precision that excludes all ambiguity the characteristics by which two substances are counted analogous or not. In the complete absence of definitions, I lack the base for constructing arguments which are likely to convince someone who denies an analogy which I accept and who accepts an analogy which I deny. In the absence of any definition, the appreciation of chemical analogies remains relative, personal and variable from one chemist to another, from one school to another.

Certainly, there are analogies so striking that no sensible chemist will fail to mistake them. There are substances which present such similarities that no one hesitates to compare them. Thus, who would for example imagine separating the acids hydrogen sulphide, hydrogen selenide and hydrogen telluride from one another, or the acids hydrogen chloride, hydrogen bromide and hydrogen iodide?

But it is not always so. A chemist might, with Dumas, find a certain analogy between hydrogen sulphide and hydrogen chloride. If he gave hydrogen chloride the formula HCl, he must give hydrogen sulphide the formula HS. Someone else might deny the analogy of the two acids and, while preserving the formula HCl for hydrogen chloride, attribute hydrogen sulphide another formula, for example H_2S. Again, logic gives us no means of cutting short their quarrel.

In any case, if logic is impotent to [77] compel two chemists to agree on the characteristics of chemical analogy, it does at least oblige one chemist to be self-consistent with these characteristics.

Suppose, for example, that, at the beginning of a treatise, a chemist has stated the following rule: We will regard as analogies those compounds which form

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[6] *l'esprit de finesse.*

isomorphous crystals. He is obliged to regard permanganates and perchlorates, which are isomorphous, as analogous and to give the same formula to perchloric acid and permanganic acid. And if, in the course of his treatise, we see he has given permanganic acid the formula Mn_2O_7 and perchloric acid the formula ClO_7, we are in the right when we say to him: You sin against logic. Either cease regarding isomorphism as a certain mark of chemical analogy or see to it that you give the same formula to permanganic acid and perchloric acid. You can chose between these two paths, but you are obliged to make a choice.

Such is the only means of conviction at our disposal to settle discussions which arise about fixing chemical formulas. It seems to be very limited; but its power is, in reality, much greater than at first appears, since it is rare that a mind is entirely self-consistent!

Suppose that two chemists, confronted with two compounds, are in agreement in deciding that two compounds are analogues or asserting that they are not. Does it follow that the proportional numbers of all simple substances, and the chemical formulas of all compound substances would be fixed without room for a single divergence? Not necessarily, and here a new difficulty comes to the fore which we must examine.

Here are a certain number of simple substances which form compounds whose analogy is indubitable. With J.-B. Dumas, we classify the one close to the other in the same natural family; for example, fluorine, chlorine, bromine and iodine. The [78] condition that we have imposed to represent analogous compounds by analogous formulas fixes the proportional number of fluorine, bromine and iodine if we give a proportional number to chlorine. If, for example, we have taken 35.5 as the proportional number of chlorine, the proportional numbers of fluorine, bromine and iodine, *equivalent* with 35.5 for chlorine, are 19, 80 and 127.

Here now is another family of simple substances which give rise to compounds standing in close analogy; they are, for example, oxygen, sulphur, selenium, and tellurium. Again, if we have adopted a certain proportional number for oxygen, we are obliged to attribute to sulphur, selenium, and tellurium well determined proportional numbers, *equivalent* with that taken for oxygen.

But the choice of proportional number for oxygen is, so far, arbitrary. I can take the number 8 for oxygen, and then the proportional numbers for sulphur, selenium, and tellurium *equivalent* with that are determined as 16, 40 and 64. The formula of water would be HO and those of the acids hydrogen sulphide, hydrogen selenide and hydrogen telluride would be written HS, HSe and HTe, respectively. I can, however, take 16 as the proportional number of oxygen; the respective *equivalents* of sulphur, selenium, and tellurium would then be 32, 80 and 128. The formula of water would be H_2O, and those of the acids hydrogen sulphide, hydrogen selenide and hydrogen telluride would be written H_2S, H_2Se and H_2Te.

Here we have an indeterminacy. Can it be made to disappear? The convention thus far invoked is impotent if there is no connection between the chlorine family and the oxygen family; if two compounds cannot be found which are recognised as analogues by all chemists, one of which contains fluorine or chlorine, while the other contains, in the same way, oxygen or sulphur.

When the convention of which we have thus far made use became illusory, because two [79] simple substances whose proportional numbers we wish to compare are never found in analogous compounds, many chemists appealed to another convention, the *rule of Avogadro and Ampère.*

To understand the origins of this key rule, it is necessary to go back to the origins of modern chemistry. Lavoisier had, in fact, already observed[7] that in order to produce an explosive mixture which forms water, it is necessary to introduce into a bottle "one part of oxygen gas, and then two parts of hydrogen gas."—To carry out the synthesis of water according to the method he employed together with Meusnier[8], "one should take the precaution of being supplied with a sufficient supply of very pure oxygen gas ... Double the amount of hydrogen gas is prepared with the same care ..." In 1805, Gay-Lussac and de Humboldt confirmed this view, proposed fortuitously by Lavoisier. They showed that the volumes of hydrogen and oxygen which combine to form water, measured at the same temperature and pressure, are exactly in the relation of 2 to 1. In 1809, Gay-Lussac[9] understood this observation. He saw that when all the measurements are taken at the same temperature and pressure, there is a simple relation not only between the volumes of the two gases which combine, but also between the sum of the volumes of the gases entering into combination and the volume occupied by the combination itself, taken in the gaseous state.

This law is the experimental foundation of the rule of Avogadro and Ampère.

We will examine the ideas which led Avogadro and Ampère to propose this rule later[10]. For the moment, we will seek to present it in a form which is independent of all schemes concerned with the nature of chemical combination. [80] This, we believe, is what we will achieve by presenting it in the following form:

Suppose that the proportional numbers for hydrogen, nitrogen and oxygen are taken to be 1, 14 and 16, respectively. The formula of nitric acid is then NO_3H. This formula may be interpreted in the following manner: When combining 14 grammes of nitrogen, $3 \times 16 = 48$ grammes of oxygen and 1 gramme of hydrogen, $14 + 48 + 1 = 63$ grammes of nitric acid are obtained, and 63 grammes is then said to be the *molecular mass* of nitric acid. In general, if the proportional number of each element in a compound substance is replaced by an equal number of grammes, and this number of grammes is multiplied by the integers which occur as the exponent of the symbol of the same element, and finally if the products thus

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[7] Lavoisier, *Traité élémentaire de Chimie*, 3rd. edition, vol. I, p. 95.

[8] Lavoisier, *Ibid.*, p. 98.

[9] Gay-Lussac, *Mémoires de la Société d'Arcueil*, vol. I, 1809.

[10] [Chapter 8.]

obtained are added together, then the number of grammes obtained is the molecular mass of the compound considered. Without lingering on the ideas which have led to the choice of this word, ideas which will be taken up later, we will take it for the moment as a simple notation.

Let us consider various compounds that chemists agree in regarding as mutual analogues, for example hydrogen chloride, hydrogen bromide and hydrogen iodide, and take, for each of them, a mass equal to its molecular mass: 36.5 grammes of hydrogen chloride, 81 grammes of hydrogen bromide and 128 grammes of hydrogen iodide. Suppose, finally—what actually holds for the substances just mentioned—that these compounds can, without decomposing into their elements, be volatilised and brought to the neighbourhood of the state that physicists call the *state of a perfect gas*. We state that at the same temperature and pressure the various masses of gas occupy the same volume. So, instead of using chemical analogies to establish a dependence between the formulas of hydrogen chloride, hydrogen bromide and hydrogen iodide, it is possible to [81] assign formulas such that the molecular masses of the various gases occupy the same volume under the same conditions of temperature and pressure.

But this criterion offers the advantage of being applicable to compounds which do not stand in any chemical analogy. Water and hydrogen chloride, for example, are not analogous compounds, but may be attributed formulas such that in the state of a perfect gas, the molecular mass of water and the molecular mass of hydrogen chloride occupy the same volume when brought to the same temperature and subjected to the same pressure. Hence, if chlorine is attributed the proportional number 35.5, and consequently, hydrogen chloride the formula HCl, water must be represented by the symbol H_2O and oxygen inevitably takes 16 as its proportional number.

We have just applied the rule of Avogadro and Ampère to a particular case; the rule can be stated in general in the following way:

The chemical formulas of various compound substances are fixed in such a way that the molecular masses of these substances, brought to the state of a perfect gas, occupy the same volume for the same conditions of temperature and pressure.

This rule does not, it is true, apply to all compounds, but only gaseous compounds, and even then, only to those which can be brought to the neighbourhood of the perfect [gas] state without decomposition. Despite this restriction, the compounds to which it applies are sufficiently numerous to allow some kinds of bridges to be established between the various families of simple substances and settle most of the contentious cases regarding the fixation of the equivalent proportional numbers.

In any case, this result can only be obtained if all chemists recognise the rule of Avogadro and Ampère. The rule has the character of a simple convention, and it may be accepted or rejected without sinning against logic.

In the schools of chemistry, some take the [82] former view, others the second. Rather than establishing agreement between the various chemical notations, the rule of Avogadro and Ampère became the object of ardent controversy which has barely faded today.

This seems to indicate a return to the only convention accepted by all chemists, to that which Laurent formally stated, and to ask whether this rule does not suffice to fix proportional numbers. Among simple substances one can, as Dumas was the first to show, form natural groups or families. Substances which compose the same group give rise to a number of combinations which stand to one another in close analogy, so that within the same family, Laurent's convention applies without exception. But aren't there links of analogy between simple substances belonging to two different families, albeit less numerous and much looser, but recognised by all chemists and allowing the establishment of an equivalence between proportional numbers of substances of the first family and proportional numbers of substances of the second family? At the very least, it will suffice if two analogous compounds can be found one of which contains a substance of the first family which is replaced, in the other, by a substance of the second family.

The chemist is particularly helped in the search for analogies capable of linking together the substances of two different families by a law discovered in 1819 by Mitscherlich, the law of *isomorphism*.

The phosphate and arsenate of the same base usually provide the clearest and least contestable chemical analogies. The two salts crystallise with exactly the same shape. Not only does a solution of phosphate and a solution of arsenate deposit crystals of the same form; if the two solutions are mixed, crystals are obtained in which the arsenate and the phosphate are intimately mixed, not in any definite proportions, and the mixed crystals [83] have the same form as the pure crystals of arsenate and phosphate. This is the remarkable property that is expressed by saying that the arsenate and the phosphate of the same base are *isomorphs*.

Isomorphism is not unique to arsenates and to phosphates; Mitscherlich found it in various groups formed by combinations which provide close analogies. Thus, the sulphates of the magnesium series form hydrates in analogous manner by forming isomorphous crystals.

These observations facilitate the statement of the following rule: *All cases where combinations form isomorphic crystals are chemically analogous and, consequently, should be represented by the same formula.*

The work of Mitscherlich and his successors continued to bring striking confirmation of this law. In all the cases where two combinations show the characteristics of isomorphism, it is recognised that the two combinations present, from the point of view of chemistry, a very great resemblance. Isomorphism is regarded by all chemists as a sure and reliable sign of chemical analogy.

From 1826, it was brought into use by Berzelius in revising and modifying the system of proportional numbers that he had proposed in 1812.

In 1813, he gave the anhydride of sulphur the formula SO_3 and the anhydride of chromium the formula CrO_6; but the chromates are isomorphous with the corresponding sulphates and provide close analogies. The anhydride of chromium should therefore take a formula like that of sulphuric acid and be written CrO_3. Henceforth, the oxide of chromium should be written Cr_2O_3 and, because of the isomorphism of the alum of chromium with ordinary alum and alum of iron, alumina and the peroxide of iron should be written Al_2O_3 and Fe_2O_3. It is thus that the *sesquioxides* have gained the right to be cited in chemistry.

Later, [84] Regnault[11] showed how the isomorphism of certain compounds facilitated the resolution of certain controversial cases which involve the determination of proportional numbers.

All chemists agree in giving the suboxide of copper the formula Cu_2O and the corresponding sulphide the formula Cr_2S. But some write the formulas AgO, AgS for the oxide and sulphide of silver, while others attribute to them the formulas Ag_2O, Ag_2S. "The natural sulphide of silver," Regnault says, "is isomorphous to the natural subsulphide of copper Cu_2S; the two sulphides seem to be replaceable in complete proportion, for example in fahlerz. We have said that this isomorphism only exists between substances presenting the same chemical formula, and we are frequently dependent on this law to establish the equivalences of simple substances. But silver sulphide is an exception if we write its formula AgS. This consideration has led several chemists to give silver sulphide the formula Ag_2S, and Ag_2O to our protoxide of silver. This view is confirmed by several other circumstances ... But if the formula for silver sulphide is written Ag_2S and, in consequence, that of our protoxide of silver Ag_2O, it is necessary to write the formula of soda Na_2O and not NaO, because we have seen that silver sulphate was isomorphous with the sulphate of anhydrous soda. The salts of potassium and lithium being isomorphous with the corresponding salts of soda when they contain the same amounts of water of crystallisation, it is necessary to formulate potash as K_2O and the oxide of lithium Li_2O, etc."

Considerations of this kind allow linking up by relations of equivalence the proportional numbers of most of the simple substances.

All chemists agree in attributing hydrochloric acid the formula HCl; if the proportional [85] number of hydrogen is arbitrarily taken to be unity, the proportional number of chlorine is found to be fixed and equal to 35.5. In the same way the proportional numbers of the substances in the chlorine family—fluorine, bromine and iodine—are also fixed.

Chemists have for a long time drawn attention to the analogy which exists between the oxygen compounds of chlorine and the oxygen compounds of nitrogen, particularly between chlorates and nitrates. In demonstrating that these salts are isomorphous, Mallard established this analogy beyond dispute. Now this analogy

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[11] Regnault, *Cours élémentaire de Chimie*, 2nd edition, vol. II, p. 346.

fixed the proportional number of nitrogen, equal to 14, and by this intermediary, the proportional numbers of the substances of the nitrogen family—phosphorous, arsenic, antimony and bismuth—were also fixed.

Between each of the two preceding families of simple substances and the family of oxygen, it is possible to find some analogies.

The fluoroxytungstanates and the fluoroxyniobiates offer close analogies with fluorotungstates and fluoroniobates. Marignac has shown that all of these salts are isomorphs of one another. A relation of equivalence is thereby established between the proportional numbers of fluorine and the proportional number of oxygen, the latter necessarily taking on a value of 16, which gives equivalent numbers to sulphur, selenium and tellurium with values 32, 80 and 128, respectively.

On the other hand, the sulphoarsenate of cobalt (cobaltine), the sulphoarsenate of nickel (gersdorffite) and the sulpho-antinomate of nickel (ullmannite) resemble iron sulphide (pyrites) and manganese sulphide (hauerite) so much that it is hard to tell them apart. Numerous phenomena of isomorphism, studied by Retgers, are manifested in this series of compounds. From that a single equivalence was obtained between the proportional numbers of arsenic and antimony, on the one hand, and on the other, the proportional number of sulphur, the latter in agreement with the value of 32 already found by another route.

Not only can the various families of metalloids thus be linked with one [86] another; from the metalloids it is equally possible to pass to the metals.

Analogy, together with isomorphism, of perchlorates and permanganates fixes the equivalent of manganese, and analogy, together with isomorphism, of sulphates and chromates fixes the equivalent of chromium.

From manganese and chromium it is possible, following the route already trodden by Berzelius, to pass to iron; iron is linked to nickel, to cobalt, to magnesium and to calcium; from calcium, by the intermediary of barium, one can pass to lead. The facts of isomorphism are provided between iron sulphate and the sulphates of copper; and besides, we have seen with Regnault how to pass from copper to silver and from silver to the alkaline metals. Many equivalences are thus found to link up in a rational way with the two proportional numbers of hydrogen and chlorine.

Does this mean that all substances are to be found encompassed by this network of analogies, woven by isomorphism, some links of which we have just described? The facts of chemistry known so far do not allow that they be tightened in such a way as not to be eluded by some groups of substances. In order to link the carbon family with other families of metalloids, we find only the quasi-isomorphism of sodium nitrate and calcium carbonate, indicating a rather faint analogy between these substances. Mercury, whose salts are not isomorphic with any other compounds, remain isolated among the metals.

But the rule of Avogadro and Ampère, so lively contested, takes on a unique authority in the light of this minute analysis of chemical analogies. All the controversies were in fact settled by the law of isomorphism in the same sense that they would be by applying that rule. Confirmed by an immense number of examples, it is obvious to all sensible chemists. It would be puerile not to make use of it to resolve the few doubtful cases that the determination of [87] *equivalent proportional numbers* might still present. The table of these numbers is thus found to be definitely fixed. Today, all treatises on chemistry have at their head a table entitled the *atomic weights* of the elements.

CHAPTER 4

CHEMICAL SUBSTITUTION

We [89] have just seen how chemists brought a confused and indefinable notion, the notion of chemical analogy, into correspondence with a representation of a mathematical clarity, the *chemical formula* or, to speak more precisely, the *crude chemical formula.*

We will now witness the development of a new notion, that of *chemical substitution.* Tied first to the notion of chemical analogy to the point of being merged with it, it has gradually been separated from it until it has become absolutely independent. Like chemical analogy, it is one of the confused, indefinable notions which are intuitive and unsettled.[1] Like chemical analogy, it will be represented by a symbol endowed with a mathematical clarity, by a certain arrangement of signs which constitute the *developed chemical formula* or *formula of constitution.*

When a zinc plate is immersed in a solution of copper sulphate, the copper is precipitated and the copper sulphate contained in the solution is replaced by zinc sulphate. This substitution of one metal by another in a salt solution is the oldest known phenomenon of substitution. For a long time, these phenomena of substitution were regarded as the marks of chemical analogy. Zinc was a substance [90] analogous to copper, which it substitutes in copper sulphate yielding a substance analogous to this latter salt.

The substitution of one substance by another in a chemical compound was thus regarded as a mark of chemical analogy, both between the substances which substitute one another and the compounds which are derived from one another by this substitution. The masses of the two substances which are susceptible to substitution of the one by the other must, then, be proportional to equivalents of these two substances. Two compounds, the one of which is derived from the other by substitution, must be represented by similar formulas.

Thus, in the example that we have just cited, 32.50 grammes of zinc replaces 31.75 grammes of copper. The equivalent numbers of zinc and copper must therefore

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[1] qui se sentent, mais ne se concluent pas.

stand to one another as 32.50 and 31.75. Copper and zinc sulphates must be represented by analogous formulas.

Progress in chemistry has modified this view. The fact that one of two compounds is derived from the other by substitution is no longer regarded as a mark of chemical analogy between these chemical compounds. The masses of two substances one of which substitutes the other are not always proportional to the equivalent numbers of these two substances as these are generally accommodated today under the heading of *atomic weights*.

Thus, a strip of copper immersed in a solution of silver nitrate precipitates the silver and yields copper nitrate. 31.75 grammes of copper substitutes 108 grammes of silver. Dalton, Wollaston, Gay-Lussac, Gmelin and Dumas considered that the equivalents of copper and silver stand in the same relation as the numbers 31.75 and 108. They regarded silver nitrate as analogous to copper nitrate and gave these two substances similar crude formulas: $AgNO_6$, $CuNO_6$.

Silver nitrate is today no longer regarded as analogous to *cupric* nitrate; for [91] reasons indicated above, the salts of silver are regarded as analogous to *cuprous* salts each of which contains, for the same amount of acid, twice as much copper as the corresponding cupric salts. Silver nitrate and cupric nitrate are no longer represented by similar formulas. The one is given the formula $AgNO_3$, and the other the formula CuN_2O_6. The equivalent numbers (atomic weights) adopted today for copper and silver are not proportional to the numbers 31.75 and 108, but to the numbers $31.75 \times 2 = 63.50$ and 108.

This separation between the notion of substitution and the notion of chemical analogy was the result of slow progress. We will briefly outline the history of this development.

The first attempt to separate the idea of chemical substitution from the idea of chemical analogy consisted in showing that two elements to which chemists attributed roles so absolutely different that they were placed, so to say, at two antipodes of chemical classification, namely chlorine and hydrogen, were susceptible to substitution of the one by the other. This discovery, one of the most surprising and most fruitful to be made in chemistry, was due to J.-B. Dumas.

In the course of passing a current of chlorine through alcohol, Liebig obtained a liquid which he named *chloral*, a name which, without prejudging the composition of the compound, recalls the circumstances of its formation. In 1834, Dumas returned to the study of this reaction and determined the composition of chloral exactly. The result of this determination was that chloral differs from alcohol in having five equivalents[2] less of hydrogen and three equivalents more of chlorine.

It required the genius of Dumas to grasp in this single result the trace of the phenomenon of substitution [92] because this phenomenon was masked, concealed

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[2] We continue to employ the word *equivalent* in the sense of what is today called *atomic weight* or *atom*. The advantage of this substitution will soon be seen.

by a further phenomenon. Dumas drew the following law from the fact which he studied by a bold induction:

When a substance can be regarded as a hydrate—and this is precisely the case with alcohol—the chlorine begins by taking away the hydrogen from the water which it contains without being combined in the compound which results from this reaction. If the action of the chlorine continues to take effect on the partially dehydrogenated substance thus obtained, the chlorine displaces the remaining hydrogen, *substituting it* equivalent for equivalent. If instead of taking a hydrated substance, chlorine is made to react with an anhydrous substance, then the phenomenon of substitution takes place right away.

It is difficult to conceive today exactly how audacious Dumas had to be to take such a stance. At that time, the electrochemical theory of Berzelius reigned uncontested. According to this theory, chemical combination is a manifestation of the attraction that positive electricity exerts on negative electricity. Among simple substances, some are positively electrified—hydrogen and the metals—and the others are negatively electrified; these are the metalloids. In a combination, the positive charge of a metal is attracted by a force which keeps the metal within the combination. Another metal more strongly charged with positive electricity than the first, and consequently more energetically attracted than the first, could displace it and take its place. But where electropositive hydrogen is held in place by attraction, electronegative chlorine can only be repelled. It is therefore impossible that chlorine would come to occupy the place of hydrogen in a combination. The substitution of one of these elements by the other is an absurdity.

Following Dumas's struggle with the reigning theory, a chemist, Laurent, who was disposed to follow the logical consequences of an idea to their ultimate conclusion became interested. Taking the denial of electrochemical ideas even further than Dumas, he [93] maintained that not only is chlorine able to substitute hydrogen equivalent for equivalent; what is more, the compounds which are transformed from one to another by similar substitutions are analogues of one another. He based this claim on a comparison of chlorine derivatives of naphthalene with hydrogen carbide which had created them.

Supported by Laurent's idea, Dumas presented an incontestable argument in 1839: the discovery of trichloroacetic acid.

A small amount of crystallisable acetic acid is introduced into a flask filled with dry chlorine and exposed to sunlight. After a certain time, the walls of the flask are covered with crystals. These crystals are shown upon analysis to have a composition which differs from that of acetic acid by having three equivalents less of hydrogen and three equivalents more of chlorine. Like acetic acid, the substance which constitutes these crystals is a monobasic acid. It neutralises bases forming salts whose constitution and properties completely resemble the constitution and properties of corresponding acetates. In summary, despite the radical difference in the elements which are substituted for one another, it is impossible to find two substances more alike than acetic acid and trichloroacetic acid.

In 1844 Melsens completed the beautiful discovery of Dumas. Just as chlorine could replace the hydrogen in acetic acid, so could hydrogen freed from contact with a sodium amalgam transform trichloroacetic acid to acetic acid by an inverse substitution.

This last evidence showed that two elements, no matter how different in view of the totality of their chemical properties, can substitute for one another in a combination without notably changing the properties of this combination, just as two metals can replace one another without profoundly changing the properties [94] of the salt within which this substitution takes place.

The idea of substitution, at first intimately connected with the idea of the existence of a chemical analogy, both between the simple substances which replace one another and between the compound substances derived from one another by substitution, took a first step in the direction of progress. The analogy of simple substances which are replaced was no longer required by chemists as a necessary condition for regarding the replacement as substitution. It remained to take a new step, and count the idea of substitution totally independent of any analogy between the two compounds derived from one another by the chemical reaction considered. This step was due to Regnault. Based on studies of the chlorine derivatives of chlorohydric ether and Dutch liquid oil, he extended the notion of substitution to the point of regarding substances whose chemical properties were profoundly different as derivatives by substitution.

The notion of *chemical substitution* was thus constituted as a new notion, independent of the notion of *chemical analogy*.

The two notions are distinct, but have a characteristic in common. Chemical substitution can no more be defined than can chemical analogy. Thus, when two chemists dispute concerning the same reaction whether it is to be seen as a substitution or not, it is not possible to throw the one or the other back onto a contradiction by a sequence of syllogisms.

When, for example, Dumas suggested trichloracetic acid is derived from acetic acid by the substitution of chlorine for hydrogen, Berzelius refused to accept the idea. He regarded trichloracetic acid as a compound with a character totally different from acetic acid. Certainly, this resistance might be regarded as unwise; it might be objected that the Swedish chemist's theory is strange and sterile, whereas Dumas's view is natural and fruitful. [95] But can it be said to be absurd, as a geometer who professes a false theorem can said to be absurd? No; that would go beyond the rights of logic. His obstinacy might be puerile and unreasonable, but it is not contradictory.

We have seen that the first action of chlorine on alcohol consists, according to Dumas, in taking away two equivalents of hydrogen. A compound is formed, discovered by Liebig who called it *alcool deshydrogenatum* or, abbreviated, *aldehyde*. Neither Liebig nor Dumas were certain whether to consider aldehyde as a derivative by substitution of alcohol. What substance in fact replaced the hydrogen taken away? Today, chemists regard aldehyde as a derivative of alcohol by substitution of one equivalent of oxygen for two substances, H and OH. They have put forward very good reasons in support of this view, and it would not be sensible to stick to the old view of Liebig and Dumas. However, there could be no accusation of *absurdity*.

CHAPTER 5

CHEMICAL TYPES

Two [97] compounds the one derived from the other by substitution are not necessarily analogues; they are not necessarily endowed with the same *chemical function*. Potassium chloride, a neutral salt, is derived from hydrochloric acid by substitution of potassium for hydrogen. Nitrogen chloride, which is not basic at all, is derived from ammonia by substitution of hydrogen by chlorine. Dumas proposed that the expression *chemical type* be used to denote the characteristic, distinct from analogy and chemical function, which relates two substances derived the one from the other by substitution. All compounds derived, immediately or mediately, from one another by some route of substitution of one element by another belong to the same chemical type.

But should the notion of type be limited to compounds which are derived from one another by the substitution of one simple substance by another simple substance, for example, by the substitution of chlorine for hydrogen? Evidently not; chemical facts, already classic during the epoch when Dumas created the notion of chemical type, showed that this notion should not be constrained by this feature.

Gay-Lussac studied the combinations of cyanogen. This compound gas, formed from carbon and nitrogen united in equivalent proportions, acts in a range of circumstances as a simple substance, chlorine. It forms combinations with metals [98] which often have close analogies with chlorides. The formulas of these substances become similar if the complex whole CN which constitutes cyanogen is represented by a single symbol, Cy. For example, potassium chloride is represented by the formula KCl, and potassium cyanide could be represented by the formula KCy.

Salts of ammonia are entirely analogous, in virtue of their chemical properties, to the salts formed by potassium and sodium. They are often isomorphic. Their formulas should be alike if the group or *radical* NH_4, to which Ampère drew the attention of chemists and Berzelius called ammonium, was replaced by a single symbol, Am. It can be said that this group of compounds functions as a simple substance, like an alkaline metal.

Chemical analogy and chemical function are preserved in compounds under replacement of chlorine by cyanogen, and of potassium or sodium by ammonia.

Isn't it natural to say that a parallel replacement equally preserves chemical type when it constitutes a substitution, even a substitution of a simple substance by a compound group—by the group CN for the element Cl, by the group NH_4 for the element K or the element Na?

Dumas therefore widened the notion of chemical type by allowing that the type is conserved not only by substitution of one element by another, but also by the substitution of an element or of a group of elements by a group of elements. Dumas demonstrated the legitimacy of this extension with the observation that by the action of nitric acid on a large number of organic substances, the group NO_2 replaces hydrogen exactly like chlorine does.

This generalisation of the notion of type was soon to receive a striking confirmation by the discovery of ammonia-based compounds, made by A. Wurtz in 1849.[1]

On [99] treating cyanic acid with potash, ammonia is obtained. Treating ether cyanide in the same way with potash, Wurtz obtained a volatile liquid endowed with a piquant odour analogous to that of ammonia, turning litmus blue, combining directly with hydracids to form salts very similar to salts of ammonia, and combining with oxyacids with the elimination of water to form yet more combinations highly analogous to corresponding ammonium salts. Wurtz regarded this base as ammonia NH_3 in which an equivalent of hydrogen disappears, making room for a complex group formed from hydrogen and carbon, the group C_2H_5, to which chemists have given the name *ethyl*. He called this base *ethylamine*.

The ethyl group is not the only group formed from carbon and hydrogen which can replace an equivalent of hydrogen in ammonia. By a procedure analogous to that by which he prepared ethylamine, Wurtz obtained a host of other analogous bases: methylamine, which is ammonia with the group CH_3, which he called *methyl*, replacing an equivalent of hydrogen; *propylamine*, where the group *propyl* C_2H_7 replaced an equivalent of hydrogen in ammonia ... All these bases belong to the same type, the *ammonia type*, whose importance was thus made clear. At the first attempt, Wurtz made a considerable extension with this type, attaching to the group of ammonia substitutes most of the volatile alkaloids which constitute organic chemistry.

Hofmann's work, coming directly after Wurtz's, contributed considerably to making the notion of the ammonia type precise and corroborating the theory of types.

Reacting ammonia NH_3 with hydroiodic acid yields a combination which is ammonium iodide NH_4I. The action of a base on this substance regenerates the ammonia.

If, on the other hand, ammonia is treated, in the way Hofmann did in [100] 1850, with ether hydroiodide whose formula is C_2H_5I, a salt is obtained which

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[1] [Duhem's spelling "Würtz" has been changed throughout to the more usual "Wurtz."]

stands to the ethylamine of Wurtz as ammonium iodide does to ammonia. It is ammonium iodide with hydrogen replaced by the group C_2H_5, therefore having the formula $N(C_2H_5)H_3I$, and is *ethylammonium iodide*. Treating this substance with a base yields the ethylamine of Wurtz.

The action of ether hydroiodide on ammonia produces not only ethylammonium iodide, however. A salt derived from ammonium iodide by substitution of *two* equivalents of hydrogen by *two* C_2H_5 groups is also produced. It is the iodide of *diethylammonium* with a formula $N(C_2H_5)_2H_2I$. Treated with a base, this iodide yields a substance analogous to ethylamine, but which is derived from ammonia by the substitution of *two* groups C_2H_5 for *two* equivalents of hydrogen. This is diethylamine with formula $N(C_2H_5)_2H$.

Again, the same reactions yield an iodide of *triethylammonium*, $N(C_2H_5)_3HI$, and a *triethylamine*, $N(C_2H_5)_3$, which derive, respectively, from ammonium iodide and ammonia by the substitution of *three* C_2H_5 groups for *three* equivalents of hydrogen.

Not only did these researches enrich the ammonia type by the discovery of the amines twice and three times substituted; they revealed a series of combinations belonging to another group, the type hydroiodide of ammonia or ammonium iodide, NH_4I. We have seen how the action of ether hydroiodide on ammonia forms substances which are derived from it by substitution of one, two or three equivalents of ammonia [*sic*[2]] by one, two or three ethyl groups. Moreover, this same action produces a substance in which the four equivalents of hydrogen in ammonium iodide are replaced by *four* ethyl groups, namely *tetraethylammonium* iodide, $N(C_2H_5)_4I$.

Gerhardt [101] introduced a new extension of the ammonia type by attaching substances which form the class of *amides*. Amides were studied by Dumas, who envisaged them as dehydrated salts of ammonia. If, for example, the elements of water, H_2O, are removed from acetate of ammonia, acetamide is obtained. Here is how Gerhardt related the amide substances discovered by Wurtz:

What is the ethyl group, C_2H_5, which we have seen replaces an equivalent of hydrogen in ammonia to form ethylamine? It is what remains when one equivalent of oxygen and one equivalent of hydrogen are removed from alcohol, whose formula is C_2H_6O. Alcohol is therefore ethyl C_2H_5 plus hydroxyl OH. Take in the same way acetic acid, with formula $C_2H_4O_2$, and remove the hydroxyl group OH. A radical remains with the formula C_2H_3O, a radical which Gerhardt named *acetyl*. Now for Gerhardt, acetamide is the substance $N(C_2H_3O)H_2$ which is derived from ammonia by substitution of one equivalent of hydrogen by the acetyl group.

More generally, if one equivalent of hydrogen in ammonia is replaced by a group which, when united with OH, forms an alcohol, we have an amine. If, on the other

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[2] [presumably hydrogen, as it was in the almost identical text of §III of Duhem's "Notation atomique et hypothèses atomistiques," *Revues des question scientifiques*, 31 (1892), 391-457.]

hand, it is replaced by a group which, when united with OH, forms an acid, we have an amide.

This idea of Gerhardt's was later to find a powerful confirmation in the discovery of the *alkylamides*. An equivalent of hydrogen in ammonia is replaced by the remainder of an alcohol, for example by the ethyl group, and another equivalent of hydrogen by the remainder of an acid, for example the acetyl group, and the result is a substance whose properties are intermediate between or, rather, are akin to, those of ethylamine and those of acetamide. Such a substance would be an alkylamide.

By attaching amides to the ammonia type, [102] Gerhardt illuminated well the fundamental principle on which we have insisted: that various substances do not need to be analogues nor fulfil the same functions in order to belong to the same type. In fact, while amines are bases which offer close analogies with ammonia, it is by no means the case that amides share the alkaline properties of ammonia.

At the time when the work of Wurtz and Hofmann created a host of compounds, some belonging to the ammonia type, others to the ammonium iodide type, the researches of Williamson concerning the formation of ether by the action of sulphuric acid on alcohol was to emphasise the importance of another type, the *water type*.

Williamson showed in 1851 that the properties of alcohol and ether are easily interpreted if alcohol is regarded as water H_2O in which an equivalent of hydrogen is replaced by the ethyl group, and ether is regarded water in which two equivalents of hydrogen are replaced by two ethyl groups. So alcohol might be represented by the formula $(C_2H_5)HO$ and ether by the formula $(C_2H_5)_2O$.

Numerous proofs can be given in support of this view. One cannot do better, it seems to me, than to cite the most striking which consists of treating sodium ethoxide with the iodide of an alcoholic radical, for example with methyl iodide. The substance thereby obtained is analogous to ether and called a mixed ether; it is water in which one equivalent of hydrogen has been replaced by the ethyl group, C_2H_5, and the other equivalent of hydrogen has been replaced by the methyl group, CH_3. The formula of this substance is therefore $(C_2H_5)(CH_3)O$.

Williamson was not satisfied with creating the water type by adding to it alcohol, ether and the mixed ethers; he put in a large group of acids, bases and salts from the chemistry of minerals. Nitric acid, $(NO_2)HO$, is water with an equivalent of hydrogen replaced by the *nitryl* group NO_2. Potash, [103] KHO, is water in which an equivalent of hydrogen has been replaced by an equivalent of potassium. Silver oxide, Ag_2O, is water in which two equivalents of hydrogen have been replaced by two equivalents of silver. Silver nitrate, $(NO_2)AgO$, is water in which one equivalent of hydrogen has been replaced by a nitryl group, while the other equivalent of hydrogen has been replaced by an equivalent of silver. This takes us back to ideas Davy and Dulong had put forward regarding the constitution of salts—ideas which Liebig and Wöhler have clearly expressed in the course of studying the combinations of benzoic acid.

The water type was soon enriched by Gerhardt with a new category of substance the possibility of which Williamson had conceived. What, for Williamson, is alcohol? It is water where an equivalent of hydrogen has been replaced by the ethyl group. What is ether? It is water where two equivalents of hydrogen have been replaced by two ethyl groups. What is acetic acid? It is water where one equivalent of hydrogen has been replaced by an acetyl group, C_2H_3O. Cannot, therefore, a substance which stands to acetic acid as ether stands to alcohol, be conceived as a substance which stands to water where *two* equivalents of hydrogen have made way for *two* acetyl groups, and which would therefore have the formula $(C_2H_3O)_2O$? The realisation of this substance was provoked by an unexpected discovery.

In 1850, all chemists believed, with Gerhardt, that monobasic acids cannot exist in the anhydrous state. All known anhydrides were associated with polybasic acids. Now, reacting dry chlorine with dry silver nitrate, a chemist produced anhydrous nitric acid. The chemist in question, whose discoveries always seem to have had the task of questioning and reversing received ideas—to the great profit of science—was Henri Sainte-Claire Deville.

Confronted by this fact, Gerhardt did not hesitate to abandon his old ideas. He sought to interpret Sainte-Claire Deville's discovery. For [104] him, the nitric anhydride stands to nitric acid as ether stands to alcohol: it is water whose *two* equivalents of hydrogen have been replaced by *two* nitryl groups NO_2. Its formula is $(NO_2)_2O$. In 1851, Gerhardt based on this interpretation a strictly general method for producing anhydrides of monobasic acids. Should, for example, acetic acid anhydride be required, then react silver acetate, $(C_2H_3O)AgO$, with acetyl chloride, $(C_2H_2O)Cl$. What is produced is the substance whose existence was predicted by Williamson. Odet and Vignon were later, by means of Gerhardt's method, to reproduce the nitric anhydride of Sainte-Claire Deville.

Gerhardt was not satisfied with enlarging the water type by adding the class of monobasic acid anhydrides; he defined new types, such is the *hydrochloric acid type*.

Water contains two equivalents of hydrogen. It might happen that just one of these equivalents is replaced by an equivalent of a simple substance, as in potash, or by a group of elements, as in alcohol, nitric acid and acetic acid. It is also possible that both equivalents of hydrogen are simultaneously replaced, and then in various ways. The two equivalents of hydrogen might be replaced by two equivalents of an element, as in silver oxide. One of them might be replaced by a simple substance and the other by a group of elements, as in silver nitrate, potassium acetate and sodium ethoxide. They might be replaced by two identical groups of elements, as in ether, nitric anhydride and acetic anhydride. They might, finally, be replaced by two different groups of elements, as in the mixed ethers, acetic ether and nitric ether.

Things are completely different with hydrochloric acid. It contains only a single equivalent of hydrogen which, in substitution phenomena, is always replaced at one go by an equivalent of a simple substance or by a group of elements. When this

[105] equivalent of hydrogen is replaced by an equivalent of sodium, we have sodium chloride; by the group NH_4, then we have ammonium chloride; by the group C_2H_5, then we have ethyl chloride; by the group C_2H_2O, then we have acetyl chloride.

Hydrochloric acid, *water*, *ammonia* and *ammonium iodide* are, after Gerhardt, the principal types under which all chemical combinations came to be regimented. The nomenclature is, however, far from being complete. There is, in particular, one type that Gerhardt does not mention and which has taken on a major importance since Kékulé has taught us to see most organic combinations as derived from it, namely the *methane type*, represented by hydrogen protocarbon CH_4.

Mineral chemistry provides us with still more types. We leave them aside, thinking that the preceding suffices to give a clear conception of what chemists in the middle of the nineteenth century understood by chemical types and the way in which this notion has developed. We are impatient to take up a new notion, rich in consequences, the notion of a *condensed type*.

CHAPTER 6

CONDENSED TYPES, VALENCY AND DEVELOPED FORMULAS

Williamson [107] had related monobasic acids to the water type; they were represented as water in which one equivalent of hydrogen has been replaced by a certain group of elements, by an acid radical. Thus, nitric acid was water in which an equivalent of hydrogen has been replaced by the nitryl group, NO_2. Acetic acid is water in which an equivalent of hydrogen has been replaced by the acetyl group C_2H_3O. Such substitution involves the replacement of one of the two equivalents of hydrogen contained in water. The other can, in turn, be replaced by an equivalent of a metal such as potassium, sodium or silver; salts are formed in this way.

In this case, an acid contains only a single equivalent of hydrogen which a metal can replace to form a salt. So a given acid and a given metal can only form a single salt. But this is not always the case. Take sulphuric acid and make it react with potash. It forms two different salts, according to the circumstances. One of these salts contains one equivalent of hydrogen and one equivalent of potassium; the other contains two equivalents of potassium and contains no hydrogen. It is this that leads us to say that sulphuric acid is dibasic.

Similarly, ordinary phosphoric acid [108] can yield three different salts with potassium. The first of these salts contains an equivalent of potassium and two equivalents of hydrogen; the second, two equivalents of potassium and one equivalent of hydrogen; and the third, three equivalents of potassium and no hydrogen. Ordinary phosphoric acid is *tribasic.*

But how can acids such as sulphuric and phosphoric acid belong to the water type? How can we understand the circumstance that after one substitution, which removes an equivalent of hydrogen from water, there remain yet two or three equivalents of hydrogen in the water replaceable by a metal? At first, it seems difficult, if not impossible. Williamson resolved the difficulty.

How have we imagined the formation of a monobasic acid, nitric acid for example? We have supposed that water H_2O loses an equivalent of hydrogen and that this equivalent of hydrogen is replaced by the group NO_2. Let us now take the formula of water H_2O not once, but twice. From each of these formulas let us remove an equivalent of hydrogen, which will leave us two hydroxyl groups OH; for the *two* equivalents of hydrogen removed the group SO_2 is substituted *a single time*. We will have a formula $(SO_2)(OH)_2$ which will represent the composition of sulphuric acid. Two equivalents of hydrogen remain in this formula coming from water from which it was derived, two equivalents of hydrogen resembling entirely the single equivalent contained in nitric acid. Depending on whether both equivalents or just one are replaced by the same number of equivalents of potassium, the neutral sulphate $(SO_2)(OK)_2$ or the acid sulphate $(SO_2)(OK)(OH)$ of this metal is obtained. The double basicity of sulphuric acid is therefore brought out by this formula.

Similarly, phosphoric acid is obtained by taking the formula of water H_2O three times, removing one equivalent of hydrogen from each of these H_2O groups [109] and substituting these *three* equivalents of hydrogen with a *single* PO group. The formula $(PO)(OH)_3$ of the compound thereby obtained clearly shows the triple basicity of phosphoric acid.

Thus the polybasic acids belong to the water type, although to the water type several times condensed, thanks to the intervention of a group of elements susceptible of alone substituting for several equivalents of hydrogen removed from several different H_2O groups. The dibasic acids are thus reduced to the water type twice condensed; two hydroxyl groups OH are tied together by a single group. The tribasic acids are reduced to the water type condensed three times; three hydroxyl groups OH are tied together by a single group.

"Mr. Williamson has written that in two lines[1]; but how rich in developments this simple statement was!" Williamson's idea, issuing from the notion of basicity, was soon to lead to one of the greatest discoveries which have been made in chemistry, the discovery of glycol.

In 1854 Berthelot concluded an important work on the ethers of glycerol with the following words: "These facts show us that glycerol presents, vis-à-vis alcohol, precisely the same relation that phosphoric acid presents vis-à-vis nitric acid. In fact, while nitric acid only produces one series of salts, phosphoric acid produces three: the ordinary phosphates, the pyrophosphates and the metaphosphates ... Similarly, while alcohol only produces a single series of neutral ethers, glycerol gives rise to three distinct series of neutral combinations."

The facts observed by Berthelot were exact; the interpretation that he proposed was erroneous. The three series of ethers of glycerol derive from one and the same glycerol, and not three different glycerols, comparable to orthophosphoric, pyrophosphoric and metaphosphoric acid. [110] These three series of ethers are comparable, not with orthophosphates, pyrophosphates and metaphosphates, but with three series of salts that are produced by ordinary phosphoric acid in virtue of its triple basicity. Orthophosphoric acid, we have seen, is formed from three hydroxyl groups OH joined together by the PO group. If in one of the OH groups

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[1] Ad. Wurtz, *La Théorie atomique*, p. 145.

an equivalent of hydrogen is replaced by an equivalent of potassium, the result is the acidic orthophosphate of potassium; if in two of these groups, the neutral orthophosphate of potassium; if in three of these groups, the basic orthophosphate of potassium. Similarly, glycerol belongs to the water type three times condensed; it is formed from three hydroxyl groups OH tied together by the group C_3H_5. In each of these hydroxyl groups, hydrogen can be replaced by an acid group, for example by an acetyl. Depending on whether such a substitution is effected in one, two or three of these groups, we will have three different acetyl ethers of glycerol.

This was the interpretation that A. Wurtz proposed in 1855 of the facts observed by Berthelot.

Alcohol and glycerol are comparable to nitric acid and phosphoric acid. Alcohol is a single alcohol as nitric acid is a single acid. Glycerol is a triple alcohol as phosphoric acid is a triple acid. In order to confirm this view, what was required was to form a substance which would stand to alcohol as sulphuric acid stands to nitric acid, and would be a double alcohol as sulphuric acid is a double acid. Wurtz sought to form this substance, intermediate between alcohol and glycerol, and succeeded; it is glycol, discovered in 1856.

In what way should we proceed to obtain a substance which is a double alcohol based on Williamson's ideas on the constitution of polybasic acids and Wurtz's on the constitution of glycerol? We should look for a group composed of carbon and hydrogen which is capable of substituting for [111] two equivalents of hydrogen and tying together two hydroxyl groups. Now there exists a substance, composed of carbon and hydrogen, which seems to present the required characteristics, namely the gas ethylene, whose composition is represented by the formula C_2H_4. This substance combines with two equivalents of chlorine to form a liquid oil well known under the name *Dutch liquid oil.* Dutch liquid oil $C_2H_4Cl_2$ can be regarded as hydrochloric acid twice condensed by substitution of ethylene for two equivalents of hydrogen. The ethylene group therefore looks like one of the groups, analogous to SO_2, which can substitute for two equivalents of hydrogen.

Let us therefore take ethylene as our point of departure. Combining it with bromine or iodine yields the bromide or iodide of Dutch liquid oil; if this is saponified[2] with silver oxide, the compound $C_2H_4(OH)_2$ is obtained. This is the substance which is a double alcohol, intermediate between alcohol and glycerol, sought by Wurtz; it is glycol.

The discovery of a new substance might have important consequences in the practical domain. But from the point of view of the science of chemistry, this discovery has no interest if it is not the occasion of the demolition of a false theory and the confirmation of a new, correct theory or the suggestion of a new theory. The importance of a new fact is measured by the evolution that it imprints on ideas. In the light of this rule, there are, in chemistry, few substances whose discovery has

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[2] [Saponification refers to hydrolysis with alkaline substances.]

been so important as that of glycol. The modern chemical notation hangs on it—to what extent we will now examine.

The discovery of glycol made everyone appreciate the characteristic possessed by certain groups, such as ethylene, of replacing two equivalents of hydrogen taken from two different HCl or from two different H_2O, and tying together the remaining two equivalents of chlorine or the two remaining OH groups. This characteristic was already indicated by Williamson as belonging to the SO_2 group and [112] as explaining the double basicity of sulphuric acid. He made a profound distinction between the groups which we have just cited and groups such as the nitryl group NO_2, the ethyl group C_2H_5 and the acetyl group C_2H_2O. These can only substitute for one equivalent of hydrogen taken either from hydrochloric acid or water. The latter substitutions generate products belonging to the same group from which they come, of the hydrochloric acid type or the water type. On the other hand, substitutions of the former kind generate products which do not belong to the same type from which they came, but to a twice condensed type—the doubly condensed hydrochloric acid type or the doubly condensed water type. Picking up again, under a more precise form, an expression already employed by Milon and by Malaguti, Wurtz called the first groups *monatomic* groups, and the second *diatomic* groups. Later, he proposed the replace these terms by *univalent* and *bivalent* groups, respectively. Adopting these latter expressions, we therefore say that NO_2, C_2H_5 and C_2H_2O are univalent groups, and that SO_2 and C_2H_4 are bivalent groups.

The PO group which we encountered in studying phosphoric acid and the group C_3H_5 which we have cited in connection with glycerol possesses the property of being able to substitute for three different equivalents of hydrogen taken from three different HCl's or three different H_2O's. They therefore yield combinations which belong not to the hydrochloric acid type, or to the water type, but to the triply condensed hydrochloric acid type or the triply condensed water type. The group PO and the group C_3H_5 in phosphoric acid and in glycerol are therefore *trivalent* groups.

Let us pursue the consequences of these ideas.

How did Williamson come to compare the water type with the doubly condensed water type? He considered nitric acid which contained a single equivalent of hydrogen replaceable by an alkaline metal and which produces a single series of salts [113] with such metals. Secondly, he considered sulphuric acid which contained two equivalents of hydrogen each of which could be replaced by an alkaline metal so as to produce two series of salts according as the metal replaces one or two equivalents of hydrogen. From this comparison the idea was born that if nitric acid derives from water by substitution, then sulphuric acid should be derived by substitution of two times H_2O, and so appeared the doubly condensed water type.

Let us now compare the action of water on metals with the action of hydrochloric acid. Hydrochloric acid contains a single equivalent of hydrogen which can be substituted by an equivalent of a metal such as potassium or sodium. On reacting with each of these metals, a single salt is formed—potassium or sodium chloride. Water, on the other hand, contains two equivalents of hydrogen each of which can be replaced by a metal such as potassium or sodium. If a single equivalent of hydrogen is replaced by the metal, a first series of compounds is obtained, the hydroxides such as potash KOH or soda NaOH. If two equivalents of hydrogen are replaced by the metal, a second series of compounds is obtained, the oxyanhydrides K_2O and Na_2O which are analogues of silver oxide Ag_2O.

Isn't this comparison between hydrochloric acid and water entirely analogous to that which exists between a monobasic acid and a dibasic acid? Are we not led to regard water as belonging to the doubly condensed hydrochloric acid type, as deriving from two groups HCl by substitution of a single equivalent of oxygen for two equivalents of chlorine? And then, with Odling and subsequently Wurtz, will we not repeat for chlorine what we have said about the group of compounds NO_2, C_2H_5 and C_2H_3O, or for oxygen what we have said about the group of compounds SO_2 and C_2H_4? Shall we not say that, in hydrochloric acid, chlorine is a *univalent element*, and [114] that in water, oxygen is a *bivalent element*?

Similarly, ammonia might be regarded as belonging to the triply condensed hydrochloric acid group. It is derived from three HCl groups by substitution of one equivalent of nitrogen for three equivalents of chlorine. In ammonia, nitrogen is a *trivalent element.*

Methane might be regarded as belonging to the quadruply condensed hydrochloric acid type. An equivalent of carbon is substituted for four equivalents of chlorine taken from four different HCl's. In methane, carbon is a *quadrivalent element.*

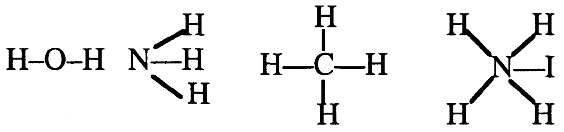
Ammonium iodide might be regarded as derived, by substitution of an equivalent of iodine for an equivalent of hydrogen, from the *ideal* substance NH_5, which would be ammonium hydride. This might be associated with the five times condensed hydrochloric acid group. It would be derived by substitution of a single equivalent of nitrogen for five equivalents of chlorine taken from five different HCl's. In this substance, nitrogen is a *quinquivalent* element.

All the types of which we have spoken are thus found to be reduced either to the hydrochloric acid type or the one, two, three, four or five times condensed hydrochloric acid type. There are still other types which can all be reduced to the hydrochloric acid type condensed a certain number of times.

This said, let us consider any chemical type formed by the union of two elements or two groups of elements a and b. If it is the hydrochloric acid type, a will be Cl and b will be H. If it is the water type, a will be O and b will be H_2; and so on. If the type corresponds to the hydrochloric acid type condensed n times, each of the two groups a and b is said to be n-valent in the compound $a\ b$, or, when united in forming the compound $a\ b$, *the two groups a and b exchange n valencies,* and the formula of the compound is written by drawing n lines between the two symbols a and b.

Thus, in hydrochloric acid, one equivalent [115] of hydrogen exchanges one valency with one equivalent of chlorine, and the formula for hydrochloric acid is written H–Cl. In water, an equivalent of oxygen exchanges two valencies with two equivalents of hydrogen, and the formula for water is $H_2 = O$. In ammonia, an equivalent of nitrogen exchanges three valencies with three equivalents of hydrogen, and the formula for ammonia is $N \equiv H_3$. In methane, an equivalent of carbon exchanges four valencies with four equivalents of hydrogen, and the formula for methane is $C \underline{\equiv} H_4$. In ammonium iodide, an equivalent of nitrogen exchanges five valencies with five equivalents of hydrogen, and the formula for ammonium iodide is $N \overset{=}{\equiv} H_4I$.

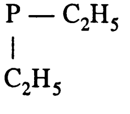
That oxygen, nitrogen, carbon and nitrogen again have replaced the chlorine of two, three, four and five HCl groups is represented still more clearly by writing



Each line marks the place of one equivalent of chlorine replaced by substitution and indicates the equivalent of hydrogen that was united with it.

Let us now consider a combination belonging to the type *a b*; it is formed by the substitution of an element or a group of elements A for the group *a*, and an element or a group of elements B for the group *b*. Again, the two groups A and B are said to exchange *n* valencies in the compounds AB, and the formula for the compound is written by putting *n* lines between the symbols A and B.

Take, for example, triethylphosphine; it is a substance derived from ammonia by substitution of one equivalent of phosphorus for one equivalent of nitrogen and three ethyl groups C_2H_5 for three equivalents of hydrogen. One equivalent of phosphorous is therefore said to exchange three valencies with the group $(C_2H_5)_3$ in this substance and the compound is written [116] $P \equiv (C_2H_5)_3$.[3] Or better, the equivalent of phosphorus is said to exchange a valency with each of the three groups C_2H_5, giving trimethylphosphine the formula



$$\begin{array}{l} C_2H_5 \\ | \\ P - C_2H_5 \\ | \\ C_2H_5 \end{array}$$

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[3] [The text actually reads $P \equiv (C_2H\ )_3$, with the "5" missing (although there is a space there). The "5" is not missing from the corresponding place in "Notation Atomique," *Revue des questions scientifiques*, 31 (1892), 391-457; p. 429.]

Clearly, the type to which a combination belongs is now represented by the number of valencies that are exchanged between the two parts whose union is supposed to generate this combination.

This method of representation presents a first advantage which is immediately apparent.

Consider the ammonium type. A certain number of combinations are put into this type, for example phosphorus protochloride, that can be derived from ammonia by substitution of an equivalent of phosphorus for an equivalent of nitrogen and three equivalents of chlorine for three equivalents of hydrogen. But evidently, ammonia can equally be regarded as derived from phosphorus protochloride by the inverse substitutions. In general, each of the combinations that we have put into the ammonia type could be chosen as the typical combination from which all the others are derived by substitution. The choice from all the combinations belonging to a given type of one which gives the type a name is therefore somewhat arbitrary.

The arbitrary importance given to one combination among all those belonging to the same group is avoided by the valency notation. All combinations belonging to the same type are now marked with the same characteristic, without having to make any play a particular role. And this common characteristic is precisely what is considered essential for the type, namely the condensation to which it is necessary to subject the hydrochloric acid type to obtain the type in question.

But [117] the introduction of the notion of valency offers other, more considerable, advantages.

There is something arbitrary and indeterminate in the operation by which a combination is related to a given type, namely the way in which it is split into two parts. It is also in general possible to relate a given combination to several different types or even to relate it to a given type in several different ways.

Consider methylamine, for example. It can be regarded as ammonia in which an equivalent of hydrogen has been replaced by a methyl group CH_3, and it is then put into the ammonia type. It can equally be regarded as methane in which an equivalent of hydrogen has been replaced by the group NH_2, and it is then put into the methane type.

Take a slightly more complicated case, methylammonium iodide. This can be regarded as ammonium iodide in which an equivalent of hydrogen has been replaced by the group CH_3, and it is put into the ammonium iodide type. It can be seen as methane where an equivalent of hydrogen has given way to the group NH_3I, and it falls under the methane type. Finally, it can be considered as hydroiodic acid whose equivalent of hydrogen is replaced by methylammonium $NH_3(CH_3)$, in which case it has been derived from the hydrochloric acid type.

Take yet another example, potassium nitrate. This substance comes, if you like, from water where one equivalent of hydrogen has been replaced by the group NO_3, and the other by an equivalent of potassium, so that it derives from the water type. It also comes, if you prefer, from potassium chloride whose chlorine has been replaced by the group NO_3, and it therefore derives from the hydrochloric acid type. Finally, it might be regarded as ammonium iodide where four equivalents of hydrogen have been replaced by two equivalents of *bivalent* oxygen and where the equivalent of iodine has been replaced by the group OK, [118] and it is now related to the ammonium iodide type.

One among these various ways of envisaging a given compound should be chosen which fixes the type to which it would belong. But the consequences of this obligation to make a choice are not entirely happy. In fact, each of these different types to which a compound can be attached has the advantage of illuminating the relations that the compound has with certain substances, but also has the drawback of casting a shadow over the relations that it has with other substances.

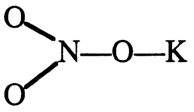
Take, for example, methylammonium iodide. In linking it to the ammonium iodide type, we bring out its relations with the compounds of ammonia, but we conceal its links with methyl alcohol and the ethers derived from that. In linking it with methane, we illuminate the latter relations, but obscure the analogies of the compound with the salts of ammonia.

It is here that the new notation based on the notion of exchange of valency comes into play to advantage. It gives us the means of avoiding the arbitrary and defective choice between the various types to which a given compound might be linked.

What, in fact, makes a compound eligible for a determinate type? It is the taking of one particular element or group of elements which belongs to the compound, and stating how this element or group of elements exchanges valencies with the remainder of the compound (that is to say, the degree of condensation to which the hydrochloric acid type is subjected) and how the exchanges are brought about (that is to say, in what way the hydrochloric acid type has been brought to this degree of condensation). When, for example, I say that potassium nitrate belongs to the *water* type (that is to say, to the *hydrochloric acid* type *twice* condensed), where one equivalent of hydrogen is replaced by the group NO_2 and the other by an equivalent of potassium, I say that potassium nitrate contains an equivalent of bivalent oxygen which exchanges one [119] valency with the group NO_2 and another valency with potassium. When I regard the same substance as derived from *ammonium iodide* (or, what comes to the same thing, from *hydrochloric acid* condensed five times) by substitution of the group OK for an equivalent of iodine and two equivalents of oxygen for four equivalents of hydrogen, I say that, in potassium nitrate, nitrogen is a quinquivalent element which exchanges one valency with the group OK and the other four with two equivalents of oxygen. When I link potassium nitrate with the *hydrochloric acid* type, I intend to express that the salt contains an equivalent of univalent potassium which exchanghas es its single valency with the group NO_3.

But doesn't what just been said immediately suggest the idea of *making clear the number of valencies of each of the elements which figure in the compound and the way in which these valencies are exchanged with one another?*

Thus, for potassium nitrate, we note that nitrogen is quinquivalent in this compound, that potassium is univalent and each of the equivalents of oxygen is bivalent; moreover, two of these equivalents of oxygen each exchange two valencies with two valencies of nitrogen; and the third equivalent of oxygen exchanges one of its valencies with the fifth of nitrogen's valencies and the other with the single valency of potassium. Potassium nitrate will therefore be represented by the following symbol:[4]



This symbol does not link potassium nitrate with any type in particular, but it makes clear all the types to which the salt might belong. The various ways of envisaging potassium nitrate lead, in fact, to writing the salt as

$$K—O—NO_2$$

if it is to be linked to the water type, or writing it as

$$O_2 \equiv N—OK$$

if [120] it is to be linked with the ammonium iodide type, or writing it as

$$K—NO_3$$

if it is to be linked with the hydrochloric acid type. And it is easily seen that all that can be expressed by each of these formulas is completely expressed by the symbol that we wrote first. This symbol is the *developed formula* or the *constitutional formula* of potassium nitrate.

The purpose of the developed formula of a compound substance is therefore to show clearly all the types to which the compound might be linked and all the substitutions by which it can be derived from each of these types, without giving preference to any one of them.

The fruitfulness of such a notion is immediately apparent.

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[4] [The two leftmost oxygens should presumably each be connected to the nitrogen with a double line, as they are in the corresponding diagram in "Notation Atomique," p. 433.]

When the formula of a compound is known, it is immediately apparent which substances it can give rise to by way of substitution, so the reactions to which the substance will give rise can be classified, and sometimes predicted.

Moreover, comparing the developed formulas of a given substance with others shows by which substitutions it would be possible to pass from the one to the other. Now the chemist has at hand general methods which, in a great number of cases, permit the bringing about of a given substitution with considerable reliability. Therefore, when the constitutional formula of a substance is known, he will very often be in a position to reproduce substances by means of other substances which are already available; in other words, to effect a *synthesis*.

This ability of a developed formula to indicate the route by which it is possible to synthesise a given substance is one of the great and admirable accomplishments of modern chemical notation. It has led to innumerable discoveries and enriches industry each day with new products. To give examples of such syntheses would be appropriate in a study of pure chemistry, but would not be appropriate here. [121] Let us cite just two syntheses from among the more remarkable in the way they were predicted to meet the needs of their time, but which have become quite common today: the synthesis of acetic acid by Grimaux and Adam, and the synthesis of indigo by Bäyer.

CHAPTER 7

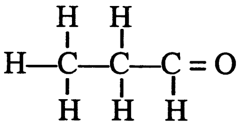
ISOMERS AND STEREOCHEMISTRY

Leaving [123] aside the practical import of the developed formula, its fecundity manifests itself with so bright a light that it would be puerile to delay demonstrating it. There is another consequence, it too theoretical, to which the new notation leads us, and it is to this consequence which we would now wish to pay particular attention.

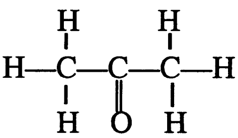
Two substances might have the same crude formula but different developed formulas. They would then be two distinct substances, although of the same composition. To obtain them, different reactions are necessary to produce different substitutions. Such substances are *isomers* of one another.

The isomerism between two substances can itself be of two different kinds.

Take the two substances whose developed formulas are:



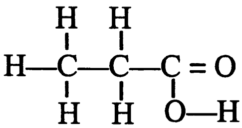
$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & \mid & & \mid & & & & \\ H & - & C & - & C & - & C & = & O \\ & & \mid & & \mid & & \mid & & \\ & & H & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & \mid & & & & \mid & & \\ H & - & C & - & C & - & C & - & H \\ & & \mid & & \Vert & & \mid & & \\ & & H & & O & & H & & \end{array}$$

The first is *propionaldehyde*, the second is *acetone*.

When the former is submitted to the action of an oxidant, [124] the hydrogen that is linked to the equivalent of carbon which already carries an equivalent of oxygen will be replaced by the OH group and we obtain a substance with the developed formula



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & \mid & & \mid & & & & \\ H & - & C & - & C & - & C & = & O \\ & & \mid & & \mid & & \mid & & \\ & & H & & H & & O & - & H \end{array}$$

which contains the group OCOH characteristic of the organic acids. This is an acid, *propionic acid.*

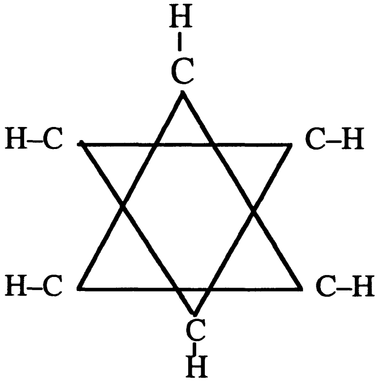
When acetone is submitted in the same way to an oxidant, nothing similar is produced because the equivalent of carbon which exchanges two valencies with oxygen is not directly united with an equivalent of hydrogen. Acetone submitted to the action of an oxidant divides into acetic acid and formic acid.

This is the first form of isomerism. Between the two isomers there is a *difference of chemical function*: placed in analogous circumstances, they give rise to different reactions, undergoing different substitutions.

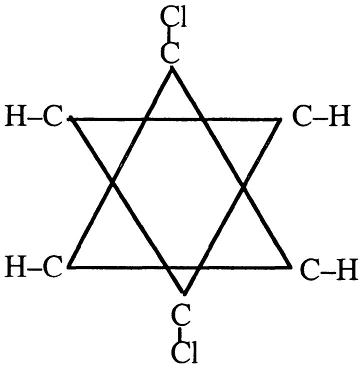
There is a completely different case of isomerism, where two compounds formed from the same elements, but arranged in different fashion, can always undergo similar substitutions, so that in chemically analogous conditions, the two compounds give rise to analogous reactions. But these analogous reactions do not form identical products. They produce substances which differ in the totality of their physical properties, and are once again isomers just like the substances which were used to form them.

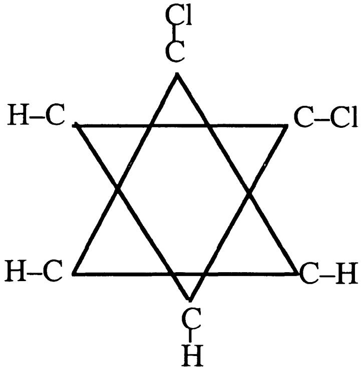
The derivatives of benzene provide, as Kékulé has shown, striking examples of this *isomerism of position.*

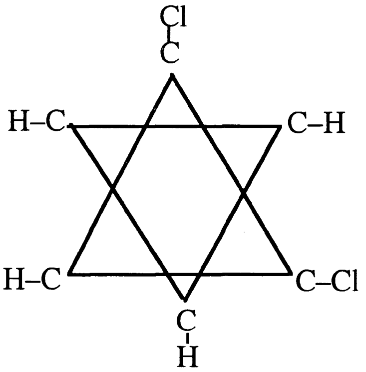
Benzene, whose crude formula is C_6H_6, is formed from six equivalents of quadrivalent carbon [125] united with six equivalents of monovalent hydrogen. It is given the developed formula:



Suppose two equivalents of hydrogen are substituted by, for example, two equivalents of chlorine. Depending on how the substitutions were carried out, we can be led to attribute the product obtained one or other of the following three formulas:







These three formulas represent three different *dichlorobenzenes* which chemists distinguish by the prefixes *ortho*, *para* and *meta*. The three dichlorobenzenes differ from one another in various of their physical properties: densities, fusion points, boiling points, etc. But their chemical properties are similar; placed in analogous conditions, they undergo analogous reactions. For example, it is possible to substitute two equivalents of chlorine in each of them by two OH groups and obtain three isomeric *diphenols*. It is possible to substitute [126] two equivalents of chlorine by two NO_2 groups and obtain three isomeric *dinitrobenzenes*. In all cases where two equivalents of hydrogen in benzene are substituted by two identical elements or two identical groups of elements, the products of this double substitution fall under three isomeric forms, the forms *ortho*, *para* and *meta*, thus offering one of the most striking and best studied examples of isomerism of position.

According to the principles that have just been stated, to enumerate all the possible isomers of a substance whose crude formula is given is to enumerate and present all the distinct representations that can be formed with a definite number of equivalents of various simple substances, each with a known valency. This is then a simple mathematical problem that Leibniz has called *analysis situs*;[1] Cayley and G. Brunel have shown how the problem can be resolved geometrically. The successes of the method are one of the great triumphs of the chemical notation based on the notion of valency: above all, they have contributed to overturning the prejudice with which this notation has long clashed.

Despite its fecundity, more surprising by the day, the notation of valencies encountered one special category of isomers that it remained unable to represent.

Take a tartrate, the tartrate of sodium, for example. The substance occurs in two varieties, identical in most of their physical and chemical properties, but clearly opposite with respect to a certain optical characteristic. If a tank containing a solution of the one variety is placed in the trajectory of a ray of polarised light, the plane of polarisation of the ray is rotated about the ray, *from left to right*, at a certain angle. If the same ray is intercepted by the same tank containing an equally concentrated solution of the other variety, the plane of polarisation is [127] again rotated about the ray, at the same angle, but *from right to left. The solutions of the two varieties of sodium tartrate have the same ability to rotate, but in contrary senses; the former is the dextrorotatory* or *right* tartrate, and the second variety is the *lævorotatory* or *left* tartrate.

Right sodium tartrate and left sodium tartrate can both be obtained in crystalline form by evaporation from their respective solutions. The crystals offer, at first sight, the greatest resemblance. If, however, they are examined with care, as Pasteur did, it is not long before it is recognised that a crystal of right tartrate does not have the shape of a solid superimposable on a crystal of left tartrate. The facets which bound the crystals of the two varieties are so structured that there exists between the two kinds of crystal exactly the same relationship as that between a right and left hand. A crystal of left tartrate is identical with the image of a crystal of right tartrate viewed in a mirror.

A number of examples of the kind of isomerism presented in connection with sodium tartrate are known in organic chemistry.

Now the single notion of valency is unable to represent this kind of isomerism. Sodium tartrate, for example, cannot provide two different developed formulas. Whatever substitution is performed on the substance, the equivalents of carbon, oxygen, hydrogen and sodium are always found in the same number and interrelated in the same way.

Is it not possible to substitute for the notation based solely on the notion of valency a more complete, more penetrating, notation which, without losing the advantages of the old notation, provides different schemas corresponding to two isomers endowed with inverse rotatory abilities, to what were frequently called

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[1] ["Analysis situs" is a former name for topology.]

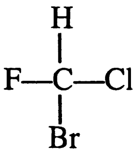
optical antipodes? This is the problem that Le Bel in Paris and J. H. Van 't Hoff in Amsterdam tackled simultaneously twenty-five years [128] ago.

Obviously guided by Pasteur's crystallographic work, they sought to construct symbols for the constitution of each of the two optical antipodes such that the symbol for the one would be the reflection in a mirror of the symbol of the other. To succeed, they did not need to rest content with notions employed up to that time in the establishment of formulas of constitution where only the nature of the various elements and the valencies that they exchange were taken into consideration. Reflect one of the old formulas of constitution in a mirror; the image and the object will present the same elements and exchange the same links between one another. From the point of view of *analysis situs*, the given formula and its reflection will be identical. Le Bel in Paris and Van 't Hoff were therefore obliged, in all necessity, to complement the elements of representation employed up to that time and used in *analysis situs* with a new element taken from geometry. That is what they did.

Instead of representing the four valencies with which an equivalent of carbon is endowed in most organic combinations by four lines issuing from a point, they represented them by four lines issuing from the four corners of a *tetrahedron*.

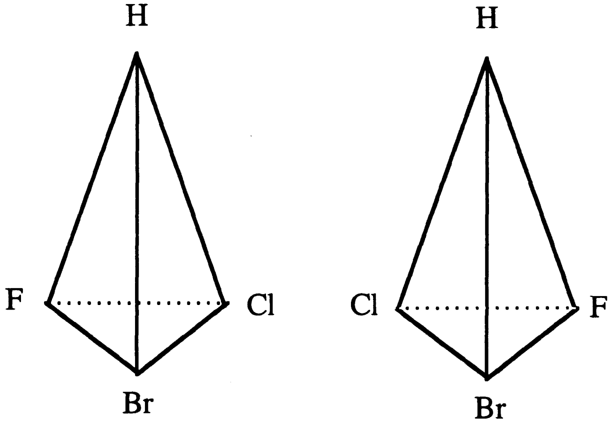
Then it is easily seen that all substances where at least two of valencies of tetrahedral carbon are saturated by identical elements or identical groups of elements will be represented by a schema which is exactly superimposable on its mirror image. But it is not the same if the four valencies of tetrahedral carbon are saturated by four different elements or groups. In that case, when properly disposing the symbols of the four elements or groups of elements over the four corners of the tetrahedral, two figures are obtained which are symmetrical with one another but not superimposable.

Suppose, for example, that the four [129] valencies of an equivalent of carbon are saturated by, respectively, an equivalent of each of the four monovalent substances: hydrogen, fluorine, chlorine and bromine. We are dealing with fluorochlorobromomethane, to which the old notation would attribute the following developed formula



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{F}{-} & \mathrm{C} & {-}\mathrm{Cl} \\ & | & \\ & \mathrm{Br} & \end{array}$$

which does not entail any isomerism. The *stereochemical* notation, on the other hand, can equally represent the compound by two symmetric, but non-superimposable, formulas which are as follows:



The two formulas can represent the optical antipodes, and there do in fact exist two fluorochlorobromomethanes endowed with inverse rotatory powers.

The use of a tetrahedric symbol for the representation of tetravalent carbon therefore facilitates, in certain cases, the construction of two symmetric but non-superimposable symbols for two substances of the same composition and the same constitution. Does this procedure provide a satisfactory representation of the phenomena of isomerism where the two isomers are perfectly similar in all respects except their [130] ability to rotate equally but inversely? To respond positively to this question is precisely to establish the following two laws:

1. In all cases where a chemical compound occurs in two forms which are optical antipodes of one another, stereochemistry can represent the constitution of the substance by two symmetric but non-superimposable schemas;
2. In all cases where stereochemistry represents the constitution of a substance by two symmetric but non-superimposable schemas, the substance occurs in two isomeric forms which are optical antipodes of one another.

The verification of the first law presents hardly any difficulties, and might be said to be contemporaneous with the introduction of stereochemistry or, more precisely, that it was what gave rise to stereochemistry. It is because it is possible to put into correspondence two symmetric but non-superimposable schemas with each pair of optical antipodes discovered in chemistry that Le Bel and Van 't Hoff have proposed stereochemistry as a general theory.

The verification of the second law is more difficult, although more conclusive for the theory; and this verification itself comprises two parts.

In the first place, every substance endowed with the ability to rotate and, in consequence, represented by a stereochemical symbol non-superimposable on its symmetric counterpart, presupposes the existence of a second substance having a symbol with precisely this symmetry standing as an optical antipode of the first. If therefore chemistry provides us with a substance endowed with the ability to rotate the plane of polarisation from left to right, such as glucose, which is also called *dextrose*, it should equally provide us with a substance, isomeric to the first and turning the plane of polarisation from right to left. All *dextrose* presupposes a *lævulose*. The search for the optical antipode of any substance endowed with rotatory power should, sooner or later, succeed. Research along these lines had already been undertaken by Pasteur; after the work [131] of the great crystallographer, the coupling of a large number of optical antipodes has been completed.

In the second place, every substance whose constitutional formula can, in stereochemistry, take on two symmetric but non-superimposable arrangements, should be endowed with the ability to rotate and occur in two isomers, the one dextrorotatory and the other lævorotatory. Now, it very often happens that the reaction which gives rise to such a substance does not yield any substance endowed with rotatory power, but a substance lacking this power which is, appropriately, said to be *inactive*. Such facts pose grave objections to the theory of stereochemistry which it must resolve. Aided by the ideas created by Pasteur, this it has been achieved to great effect.

It can happen that the inactive substance is, in fact, a mixture of equal proportions of the two optical antipodes. Evaporation of a solution of such a substance often yields not a single kind of crystal, but equal weights of two kinds of crystal, those of the one kind being symmetric with those of the other but not superimposable. It suffices to sort the crystals and separate those of the same kind from one another, and redissolve them in isolation, obtaining two solutions endowed with the power of rotation, the one the inverse of the other.

It can happen that the inactive substance obtained is a chemical combination which the two antipodes seek to form when united in equal amounts. In this case, evaporation of the solution does not yield two kinds of crystal; the crystals obtained are all of the same shape, and this shape is identical with its mirror image. Pasteur has already shown that inactive substances known as *racemates* result from the combination of a right tartrate with the same amount of a left tartrate. From this the name *racemic compound* is given to inactive substances generated by the combination of two optical antipodes [132] of equal masses. Splitting inactive substances that stereochemistry implies should be regarded as racemic combinations into their two optically inverse components is the aim pursued by adherents of the new doctrine. They persevere in their efforts towards their goal with extremely ingenious methods, and success has frequently crowned their endeavours. By their success, the notation of stereochemistry has gained the characteristic of fecundity which alone fully justifies the use of a scientific symbolism. Not only has it served to methodically classify well-known truths; it has even been the instrument of discovery.

CHAPTER 8

THE ATOMIC THEORY: CRITIQUE OF THIS THEORY

We [133] have just expounded the fundamental principles of modern chemistry, and nothing in this exposition has led to the intervention of the doctrines of the atomists, either in confirmation or refutation. The original experimental laws have been taken as the basis of this science, the law of the conservation of mass, the law of definite proportions, the law of equivalent proportions and the law multiple proportions. Certain notions like those found in natural sciences are associated with these laws, the notion of *chemical analogy* and the notion of *chemical substitution*, and numerical and geometrical symbols have facilitated the expression of these notions in a form perceptible to the imagination and giving chemical classification an admirable clarity. But nothing has constrained us to pronounce on the nature of mixts, and to chose between the disciples of Epicurus and the partisans of Aristotle.

It should not be concluded that those whose discoveries have created and developed modern chemistry were not at all concerned with atomic doctrines.

A certain number of chemists, and not the lesser figures, prudently distanced themselves from these doctrines. Richter did not borrow anything from them; it was rather Pythagorean inclinations which led him to bring in his remarks on the numerical values of equivalent masses, [134] and remarks in the same spirit are to be found in certain of Dumas's writings and above all in the work of Mendeleev. Others among the creators of chemical science seem to have meticulously avoided all hypotheses about the nature of mixts and not wanted to concede anything taken from any other source than experience. But many expect Epicurean hypotheses to interpret the already familiar laws or to lead to the discovery of new principles.

Already in 1790 Higgins considered that the atoms of elements which enter into combination have fixed masses and build groups of definite numbers to form a molecule of the compound. He mixed with this fundamental conception, it is true, several inadmissible hypotheses, leaving to John Dalton the honour of creating the modern atomic theory.

Did the atomic theory serve to guide Dalton in the discovery of the law of multiple proportions? Or did the results of experience, on the contrary, have precedence in the order of his researches over the hypothetical interpretation provided by the Epicurean doctrines? There is a problem in settling this dilemma[1]. However it might be resolved in one or other sense, Dalton's thought remains perfectly clear.

Simple substances are formed of *atoms*. The atoms of the same simple substance are all alike; they have the same mass. The atoms of two different simple substances have different masses, and their masses stand to one another as do the equivalents of simple substances. Thus, for the various simple substances, the equivalents measure the *atomic masses* and can be attributed this name.

All compound substances are reducible to *molecules*. The molecules of a given compound are all identical with one another; each is formed from a certain number, necessarily whole, of atoms of each simple substance which combine to bring about the formation [135] of the compound. The chemical formula of a combination simply expresses which atoms and in what number they are united in a molecule of the combination. Thus, to say that the formula of hydrochloric acid is HCl is to say that the molecule of hydrochloric acid contains one atom of hydrogen and one atom of chlorine. To say that the formula of water is H_2O is to say the molecule of water contains two atoms of hydrogen and one atom of oxygen. The similarity between two formulas represents not only the wholly subjective analogy of two chemical compounds; it denotes the similar structure of their molecules, the objective source of chemical analogy.

Such are the ideas that Dalton put forward and developed from 1803 to 1808, and that Thomson and Wollaston were to penetrate in the public domain. Soon they were to be found in lots of writings on chemistry. In 1813 Amedeo Avogadro adopted them, as did Ampère in 1814; the structures characteristic of each compound formed by elementary atoms of the compounds they called *integral molecules*, a term already employed by Haüy to designate the solids whose association constitutes a crystal. They taught that at the same temperature and under the same pressure, the unit of volume of all gases contains the same number of integral molecules. This is the form in which the statement of the law which played such a large part in the fixation of chemical formulas was first to be found.

The structure that the atoms of the various simple substances form when they unite to generate a molecule of a compound substance is identical with the integral molecule whose repetition produces a crystal. Therefore similar structures, which characterise analogous compounds, should form similar crystals. Thus, the preceding hypotheses are very naturally linked to the law of isomorphism, and it was so that Mitscherlich understood the great principle with which he enriched the science of chemistry. Witness the statement which he gave: "The same number of atoms, combined in the same manner, [136] produce the same crystalline shape; and this same crystalline shape is independent of the chemical nature of the atoms and determined only by the number and relative position of the atoms."

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[1] On the history of Dalton's works, see Ad. Wurtz, *La Théorie atomique*, pp. 17 ff.

All the notions, all the principles that contribute to fixing the *crude formula* of a chemical compound find their interpretation in the atomic theory. And so it is with the notion of valency, the basis of the *developed formula.*

Each atom possesses one or more *atomicities*. The atomicity is that by which an atom is able to attach to another atom; or, rather, in order that two atoms join, it is necessary that a certain number of atomicities of the first and an equal number of atomicities of the second are joined to each other.

There are atoms which only possess one atomicity: the atoms of chlorine, bromine, iodine, hydrogen, potassium, etc. Evidently, each of these atoms can unite with only one atom of the same class. When such a union is effected by fusing the single atomicity of one of these atoms with the single atomicity of the other, these two atoms exhibit no more free atomicity; they are *saturated.*

There are atoms which possess double atomicities: oxygen and calcium are cases in point. The oxygen atom can join with two atoms of hydrogen, each single atomicity of which will saturate one of the atomicities of oxygen to form water. The calcium atom can be combined with two atoms of chlorine to form calcium chloride. But an atom of oxygen will be combined with a single atom of calcium because each, having two atomicities to saturate, will need only the two atomicities of the other.

When an atom of hydrogen is found in a compound substance, its single atomicity saturates one of the atomicities of the remainder of the compound. Chlorine, which also exhibits a single atomicity will be equally apt to saturate the single atomicity by saturating itself. A chlorine atom and a hydrogen atom [137] could, therefore, substitute one another in such a molecular structure.

On the other hand, for an oxygen atom which possesses two atomicities to be saturated, being placed in a molecular structure requires that the part of the structure which is displaced to make way for it releases two atomicities. For such an introduction of an oxygen atom to become possible, it is not sufficient the remove a single atom of hydrogen from the molecular structure; this operation disengages only one atomicity. It is necessary to remove two hydrogen atoms or two chlorine atoms. Oxygen therefore possesses the property that a single one of its atoms substitutes for two hydrogen atoms or two chlorine atoms.

These examples suffice to show how the phenomenon of substitution is accounted for in the theory of the constitution of matter. What we have called the *number of valencies* of an element is now the number of atomicities possessed by the atom of the elementary substance. The lines which represented exchanges of valencies in our developed formulas represent in reality how atomicities of the various atoms collected in a molecule are pairwise saturated.

All that we have just said is very general; we have spoken about the atomicities possessed by an atom without going into the precise nature of these atomicities. It is, in fact, easier to describe how the atomic school introduces atomicity into the phenomena of substitution than to show how it explains this peculiar property of the atom. Most of the chemists of this school avoid pronouncing on the nature of this I know not what that fuses two atoms together and which has, perhaps, the flaw of resembling too much the classic crooks with which Lucretius had armed his corpuscles.

Some physicists, however, make no attempt to emulate this prudent reserve and have attempted to say in what atomicity consists. Father A. Leray regards [138] atoms as polyhedra and the atomicity which they possess stands in relation to the facets which form their boundaries. J. Thomson, developing the ideas of Lord Kelvin, considers that atoms are *rings of turbulence* born within a perfect fluid, the *ether*. The knots by which these rings can wrap around one another differ according to the shape, simple or complex, of these rings. From these arise the various atomicities that can be exhibited by atoms of chemical elements. All these hypotheses have a common characteristic which, it seems, is inevitable: it is the shape of the atom to which they attribute atomicity.

It is again to the shape of the atom that the power of rotation is attributed if stereochemistry is interpreted according to the atomic doctrines. The carbon atom is regarded as having a tetrahedral shape or as exhibiting more or less the same elements of symmetry as a tetrahedron.

It therefore seems that modern chemistry possesses certain and fruitful methods which allow it to analyse the structure of chemical molecules, the arrangement of atoms within these molecules and the very shape of these atoms. "It is the path which chemistry has recently entered[2], and so rapid has been the progress accomplished in this direction during the last twenty years! that obscurities in the arduous problems of the intimate structure of chemical molecules—problems that Gerhardt had declared inaccessible—are dissipated!"

Premature triumph! The symbols employed in modern chemistry—crude formulas, developed formulas, stereochemical formulas—are precise instruments of classification and discovery as long as they are regarded only as the elements of a language, of a notation, appropriately conveying to the eyes, under a particularly striking and precise form, the notion of analogous compounds, substances derived from one another, optical antipodes. When, on the other hand, it is regarded as a reflection, [139] as a sketch of the structure of a molecule, of the arrangement of atoms, of the shape of each of them, this leads to insoluble contradictions.

Let us examine, for example, the difficulties encountered when seeking to substitute the notion of valency with the notion of atomicity envisaged as an intrinsic property of the atom which is a consequence of its shape.

The number of valencies possessed by a given element in a given combination is a definite number. Thus, chlorine, bromine and iodine are univalent in hydrochloric, hydrobromic and hydroiodic acids; oxygen is bivalent in water; nitrogen is trivalent in ammonia; carbon is quadrivalent in methane. But it does not follow that the

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[2] Ad. Wurtz, *La Théorie atomique*, p. 189.

number of valencies of an element would be an entirely determinate number, in absolute fashion, in abstraction from the combination in which this element is introduced and the way it is involved. The number of valencies of an element may vary according as it is part of one combination or another. Carbon, quadrivalent in methane or carbon dioxide, is bivalent in carbon monoxide; and nitrogen, trivalent in ammonia, is quinquivalent in ammonium iodide. Moreover, when two equivalents of the same element occur in the same combination, they may do so with different valency numbers. In ammonium nitrite, for example, the equivalent of nitrogen which comes from ammonia is quinquivalent and that which comes from nitrous acid is trivalent. Ethylcarbylamine contains two equivalents of quadrivalent carbon and one equivalent of carbon which exhibits only two valencies.

This variation in the number of valencies of an element with the combination in which it occurs is therefore an undeniable fact. It is not without a little embarrassment that chemists have envisaged valency or atomicity as an elementary property of the atom.

Take, [140] for example, the nitrogen atom. It should, according to the circumstances, exhibit trivalency or quinquivalency. Whatever the desired interpretation that might be given to valency or atomicity, nitrogen must in any case exhibit first of all three atomicities, which we call *atomicities of the first order*, and which are those fixed by three atoms of hydrogen in ammonia. Then, it exhibits two other atomicities, which might be called *atomicities of the second order*, and it is these which fix the elements of hydroiodic acid in the formation of ammonium iodide.

An atomicity of the second order of the nitrogen atom could not arise from the same cause, or act in the same manner and in the same proportions as, an atomicity of the first order. For otherwise, if the five atomicities were absolutely identical, reasons of symmetry would render absurd the existence of compound such as ammonia where three of these atomicities would be satisfied while the other two would be free. We must therefore accept that there is an essential difference between an atomicity of the first order of a nitrogen atom and an atomicity of the second order of the same atom, whatever the origin and nature of this difference might be.

Now, is this essential distinction that we have been obliged to establish between atomicities of the first order and atomicities of the second order admissible, bearing in mind that we want to regard these atomicities as intrinsic properties of the nitrogen atom?

Take ethylamine. In this substance, the ethyl group C_2H_5 is fixed by an atomicity of the first order of the nitrogen atom. If this substance is combined with hydroiodic acid, its elements will be fixed by atomicities of the second order, and we obtain ethylammonium iodide.

Now take ammonia, in which nitrogen's three atomicities of the first order are saturated by three hydrogen atoms. [141] If it is combined with ethyl iodide, iodine will be saturated by one of the atomicities of the second order and the ethyl group will be fixed by the other and we thus obtain a substance whose composition is the same as in the preceding example.

These two substances of the same composition are formed in different ways. In the one, the ethyl group is fixed by an atomicity of the first order and in the other it is fixed by an atomicity of the second order. Since these two atomicities of different orders cannot be identical, the two compounds cannot be identical either, and the two reactions that we have described should give two isomeric ethylammonium iodides.

But experience shows that the products of these reactions are not two different isomers, but one and the same substance.

Facts of this kind—and they are numerous—are difficult to explain on the view that isolated atoms possess a determinate number of atomicities, whatever the property might be in virtue of which these atomicities might be explained.

A response has, it is true, been made to these objections and this should be discussed. It consists in denying that the number of valencies of an element can vary according to the compound in which it is ensconced. Several chemists formulate this negation as follows:

The number of valencies of a given element is strictly invariable. The nitrogen atom, for example, always has five equivalent valencies; the carbon atom always has four.

Each of these atomicities can be saturated by an atomicity borrowed from another atom. Thus, in ammonium iodide, the five atomicities of the nitrogen atom are saturated by five atomicities taken from four hydrogen atoms and one iodine atom. In carbonic gas, the four atomicities of carbon are saturated by their union with two diatomic atoms of oxygen. In these [142] conditions, nitrogen appears to us pentatomic, and carbon tetratomic.

But an atomicity belonging to a given atom might equally well be saturated by another atomicity belonging to the same atom. Two such atomicities, saturated by one another, become inactive in the various reactions in which the atom takes part, and the atom seems to exhibit two atomicities less than it actually possesses. In ammonia, for example, two atomicities of the nitrogen atom are saturated by one another, and the atom displays no more than three atomicities with which three hydrogen atoms are fixed, so that in ammonia, nitrogen *seems* triatomic. In carbon oxide, two atomicities of the carbon atom are united with one another and the oxygen can only saturate two atomicities of the carbon atom which *seems* diatomic.

The number of valencies of an element, fixed in reality, is thus variable in appearance. But in its apparent variation, it always augments or diminishes by two or a multiple of two, so that a given element exhibits an apparent number of valencies which are variable according to the compound in which the element is ensconced, but which is always even, or always odd. Nitrogen should, according to this system, always exhibit an uneven number of valencies, and the apparent number of valencies of carbon should always be even.

A superficial examination of the chemical domain seems to suggest that this rule is confirmed by facts: "For the elements," Wurtz says[3], "changes in saturation capacity, that is to say, the progression of atomicity, take place more often according to two different modes, sometimes following the series of even numbers, sometimes following the series of odd numbers ... This distinction between the elements of even atomicity and the elements of odd atomicity is not without importance, at least for some of them ... But it [143] must be added that this rule is subject to exceptions."

Some of these exceptions have better characterisations.

The works of Marignac have drawn attention to the isomorphism of the fluorooxytungstanates with the fluorotungstanates. Now, the former compounds derive from the latter by substitution of a single equivalent of oxygen for a single equivalent of fluorine. The valencies that saturated this equivalent of fluorine before the substitution must be saturated after the substitution by the equivalent of oxygen. How is this incontestable statement to be reconciled with the previous hypothesis that attributes to fluorine an invariably odd number of valencies and to oxygen an invariably even number of valencies?

In accordance with all chemical analogies, the law of Avogadro and Ampère requires that nitric oxide be attributed the formula NO. A single equivalent of nitrogen is united there with a single equivalent of oxygen. Necessarily, the apparent number of valencies in the compound is the same for nitrogen and oxygen. Yet the previous hypothesis requires that nitrogen has an uneven number of valencies and oxygen an even number.

The examples of compounds which are exceptions to the rule under discussion can be multiplied. "Chlorine[4], quadrivalent in the peroxide ClO_2, is quinquivalent in chloric acid $ClO_2(OH)$. Manganese, bivalent in $MnCl_2$ and MnO, sexivalent in potassium manganate $MnO_2(OK)_2$, is septivalent in the permanganate $MnO_3(OK)$. Tungsten, quinquivalent in the pentachloride WCl_5, is sexivalent in the hexachloride WCl_6. Uranium, bivalent in the bichloride UCl_2, is trivalent in uranyl chloride UOCl and quinquivalent in the pentachloride UCl_5. Vanadium is trivalent in the bichloride $VaOCl_2$ and quinquivalent in vanadyl chloride $VaOCl_3$."

The [144] theory according to which each atom possesses an invariable number of atomicities, but is capable of self-saturation, is therefore in flagrant disagreement with the facts.

Thus the modern chemical notation, based on the notion of valency, and so improperly called *atomic notation*, is shown to be an admirable instrument of classification and discovery as long as it is not viewed as more than a figurative representation, a schema of divers ideas which have been dealt with in the manner of

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[3] Ad. Wurtz, *La Théorie atomique*, p. 186.

[4] Ad. Wurtz, *La Théorie atomique*, p. 188.

chemical substitution. But searching for an image of the arrangement of atoms and the structure of molecules only leads to obscurity, incoherence and contradiction.

Is there nothing in this immense edifice of modern chemistry, in the construction of which Epicurean hypotheses have played a considerable role, which serves to prop up these hypotheses? There is a foundation of atomic doctrines whose existence must not be misunderstood, but whose solidity should not be exaggerated: the law of multiple proportions.

In acetylene, 1 gramme of hydrogen is combined with 12 grammes of carbon. In all cases of a compound containing hydrogen and carbon, the masses of these two substances ensconced there stand to one another as n and $m \times 12$, m and n being two whole numbers. Again, in each chemical compound which contains carbon and hydrogen, the mass of the former stands to the mass of the latter in a relation which can be written $12 \times \frac{m}{n}$, where $\frac{m}{n}$ is a *commensurable number*. Such is the teaching of the law of multiple proportions.

In Dalton's time, the preceding proposition was stated in terms of the condition that the two whole numbers m and n be *simple numbers*. This restriction would not be imposed today, when chemists attribute to the numbers m and n for a substance such as cetyl hydride the values $m = 16$ and $n = 34$; or for a paraffin, they write $m = 27$ and $n = 56$.

What, [145] then, is the exact sense of the truth that we have just stated? Is it a truth which is drawn, by induction, from the facts of experience? It is easy to verify that such a law is not and cannot be verified by experience, and that it would always be absurd to demand of it a verification by the experimental method.

It is the peculiarity of the experimental method to possess a sensibility ever more sharp but always limited, to provide information affected by errors which will diminish without end, but will never vanish. No method of measurement gives the exact value of the quantity to be measured, but only two limits between which this value certainly lies. No procedure of chemical analysis, however subtle it might be supposed to be, can give us the exact relation between the mass of carbon and the mass of hydrogen in a chemical compound. It brings to our knowledge only two numbers A and B between which the proportion lies.

Now, between two given numbers A and B, no matter how close they may be, it is possible to insert an infinity of numbers such as $12 \times \frac{m}{n}$, where $\frac{m}{n}$ is a commensurable number. An infinity of numbers $12 \times i$, where i is an incommensurable number, can equally well be inserted. Is the proportion of the mass of carbon to the mass of hydrogen in the compound considered of the first kind or of the second? Experience cannot settle the matter. The law of multiple proportions can be neither verified nor gainsaid by the experimental method. It eludes the grasp of this method.

Whether we accept or reject the law of multiple proportions, we can be just as certain that the facts will not catch us out. Does this mean that we are entirely free to affirm or deny this law? Is it permissible, should we find some advantage from the point of view of chemical notation, to call this an arbitrary convention? Several [146] authors today would not attribute to it any other value.

If the law of multiple proportions is a purely arbitrary convention, a simple decree of our pleasure, the same would, of necessity, go for all those propositions which are founded upon it, and for all the notions which only have sense because of it. The notion of condensed type and the notion of valency entailed by the use of developed chemical formulas would lose all significance if the law of multiple proportions were withdrawn. Which sane person, therefore, would dare to assert that this fruitful notation, mother of discoveries which have transformed science and changed the face of industry, is but a pure play of the mind? Are we equally free to conceive or not to conceive the ideas that it has implemented? Are the propositions on which it rests neither true nor false, but absolutely arbitrary and conventional?

"Nature keeps reason powerless and prevents it overreacting beyond this point." We must recognise that in stating the law of multiple proportions, which, by nature, transcends experience, the chemist intends to state a proposition having some foundation in reality, and the power and fecundity of the chemical system whose base is the law of multiple proportions is the *a posteriori* justifying base of the postulate.

Can we press further? Can the real objective foundation of the law of multiple proportions be made precise? It is this question to which the atomic theory responds with striking simplicity. If in all chemical compounds which contain carbon and hydrogen the masses of carbon and hydrogen stand to one another as $m \times 12$ and n (m and n being two whole numbers), it is because the masses of the atoms of carbon and hydrogen stand to one another as 12 and 1, and all molecules containing carbon and hydrogen necessarily contain a whole number of atoms of each of the two substances.

Clearly, [147] the response is satisfactory and can pass as a victory for the atomic theory, a victory all the more marked as the interpretation of the law of multiple proportions was not conceived after but was, on the other hand, contemporary with the law and presided, perhaps, at its discovery.

Is this victory decisive? Were this the case, it would be necessary that the interpretation of the law of multiple proportions provided by the atomic theory was not only a plausible and appealing interpretation, but also the only interpretation possible. Now who would dare to go so far as to vouch for this interpretation and affirm that no other explication could ever be provided? Moreover, when it is shown with what ease, with what clarity, all the principles of modern chemistry can be gathered in an exposition where the name and idea of the atom are banished, and what difficulties, what contradictions, suddenly appear as soon as the principles are interpreted in accordance with the atomic doctrines, the unique success of the atomic theory is seen to be but an apparent victory, without a future. This theory cannot provide knowledge of the true, objective foundation of the law of multiple proportions. Such a foundation is yet to be discovered. Finally, when everything has been taken and weighed exactly, modern chemistry does not plead in favour of the Epicurean doctrines[5].

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[5] The reader aware of the laws of crystallography would without difficulty see that all that has been said here about the law of multiple proportions and its interpretation by atomic hypotheses can be repeated literally for the law of rational indices and its interpretation either by the integrated molecules of Haüy, or by the lattice of Bravais.

CHAPTER 9

CHEMICAL MECHANICS: FIRST ATTEMPTS

The [149] tableau of modern chemistry that we have so far traced is incomplete. Some thirty years ago a new branch cropped up. To grow, it was obliged to come out of the old moulds where, for three centuries, the doctrines of chemistry have run, cracking the thick crust of atomic, Cartesian and Newtonian hypotheses. Today, having achieved its complete development, it looks like a descendent of the old peripatetic stock, made younger and enlivened with a new vigour. This vigorous and abstruse subject is Chemical Mechanics.

Water is a substance whose composition is completely definite. The mass of oxygen it contains is eight times greater than the mass of hydrogen it embodies. According to its crude formula, two equivalents of hydrogen are combined there with one equivalent of oxygen. According to the developed formula, each of the two valencies of the bivalent oxygen is saturated by a valency of univalent hydrogen. We see clearly from this information which substitutions link water with acids, with bases and with alcohols. The place of water in the chemical classification is distinguished with perfect clarity. Do we know all that we can legitimately desire to know about this substance?

Under given conditions of temperature and pressure, hydrogen and oxygen are mixed. [150] Will these two substances combine to form water? If they combine, will the combination be total or partial? If partial, what rule fixes the limit? Some water is placed in definite circumstances. Will it remain unaltered? Will it resolve itself into its elements? If it is subject only to partial decomposition, up to what point will it dissociate? These questions crop up, inevitably and insistently, in the consciousness of the chemist. How incomplete his science would be if, having precisely classified the chemical compounds according to their analogies and exactly demarcated the substitutions by which these substances can be derived from one another, he could not predict in which circumstances a definite reaction would occur, and in which circumstances a definite substance will be generated or destroyed.

To all these questions, however, the chemical doctrines that we have expounded so far have not a word to say in response.

Why this silence? Whence comes the powerlessness that this resounding silence engenders?

At the same time that the hypotheses of the atomists, long scorned by chemists, were returning to favour, taking hold of the discoveries which issued in the notion of chemical substitution and seeming to gain by the day confirmations ever more numerous and striking, one man dared to challenge these hypotheses as a cause of sterility. He was bold enough to declare that the laws which govern combination and decomposition will not be discovered by searching under chemical reactions for unions and separations of atoms. He dared to maintain that, to build chemical mechanics, it was necessary to consider the mistion from the simple and obvious point of view which Aristotle had suggested. The measurable physical changes which accompany the act of mistion must, he said, be studied; then, with the aid of thermodynamics, it will be possible to fix the conditions which assure the formation or destruction of various combinations.

This [151] man, whose views seemed oddly routine and retrograde to those filled with enthusiasm for the atomic doctrines, but who today must be admired and whose scientific and philosophical perceptiveness celebrated, is Henri Sainte-Claire Deville.

"Whenever the desire arises," said Sainte-Claire Deville[1], "to imagine, or to draw, atoms or groups of molecules, I cannot see that anything is achieved other than a crude reproduction of a preconceived idea, of a gratuitous hypothesis—in short, of sterile conjectures. These representations have never inspired a serious experiment; they are always produced not to test, but to seduce. And these illustrations which are so popular today present a more serious danger to the young in our schools than has been thought. The way they strike the eyes and satisfy the mind is deceitful. They induce belief in a real interpretation of the facts and make us forget our ignorance. Knowing our ignorance is a prerequisite for wanting to understand."

What, then, do the chemical formulas express? The arrangement of simple, indestructible atoms within the molecules of compound substances! Not at all: the substances which enter into combination cease to exist within the combination; "It cannot be accepted[2] that sulphuric acid and potassium as we know them in the free state are simultaneously present in potassium sulphate." A chemical formula does not describe what really and actually subsists in the compound, but what can be found potentially, and which can be taken out by appropriate reactions. "When a solution of sulphuric acid is saturated with a solution of potash, by mixing them in suitable proportions, one may wonder what has become of the elements after the combination. A first hypothesis, the oldest, [152] would have us accept that the acid and the base subsist in the salt, as expressed by the rational formula SO_3, KO of

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[1] H. Sainte-Claire Deville, *Leçons sur l'Affinité*, presented before the Société chimique, 28 February and 6 March, 1867. (*Leçons de la Société chimique*, année 1866-1867, p. 52.)

[2] H. Sainte-Claire Deville, *loc. cit.*, p. 22.

potassium sulphate. Another hypothesis would have us believe that the elements are arranged in such a way as represented by an absolutely unknown system SO_4 which is united with potassium. None of these hypotheses is necessary ... At bottom, rational formulas explain nothing. They simply indicate the possibility of extracting from a complex chemical system elements which are less complex by means of certain procedures suggested by experience. Thus, in decomposing sulphates by heat, sulphuric acid is separated from a base. In decomposing these same sulphates by a pile, they are transformed to a metal deposited at the negative pole, and to sulphuric acid and oxygen (SO_4) which are discharged at the positive pole."

Mix hydrogen and chlorine; in diffuse light, the mixture is slowly transformed to hydrochloric acid. Chemists have tried to represent this transformation as a play of atoms. For some, both the free atoms H and Cl are joined to form HCl molecules. For their successors, on the other hand, a double substitution operates which yields two HCl molecules. But for the prudent observer who rejects the chimeras of the atomists, there is simply a change from one substance to another substance endowed with different properties, and this change is accompanied by certain measurable effects, for example the release of a certain amount of heat.

The disappearance of a substance or a collection of substances and the appearance of another substance endowed with different properties; the conservation of mass of the system during the transformation; change, by contraction or dilation of the volume which it occupies; the release or absorption of a certain amount of heat; such, in short, is all that attentive observation reveals to us in a chemical reaction, [153] all that we can and need analyse and measure.

But aren't all these characteristics to be found in a collection of transformations—the dissolving of a salt in water, in the changing of white phosphorus to red phosphorus, in the fusion of ice, in the vaporisation of water—the study of which, forsaken by chemists, has been abandoned by the physicist? "There will therefore be a simple phenomenon of change of state there[3] ... In fact, combination and dissolution could not be characterised merely by a change of state. The change of state is itself characterised by the production of some physical property existing in the compound that is not found in the same degree in the mixture where the combination proceeds. So all or nearly all the relative changes of state of cohesion are found when relative changes of state of affinity are studied. The general character is the gain or loss of latent heat."

The rules which determine whether a definite chemical reaction does or does not occur are stated in the formulas where only the measurable elements of the reaction figure: the pressure under which it proceeds, the temperature, the change in volume that it determines and the amount of heat that it releases or absorbs. But these elements are also those which the experimenter studies and measures in the course of any change of physical state. Is it not therefore to be expected that rules of the same

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[3] H. Sainte-Claire Deville, *loc. cit.*, p. 5.

form determine the necessity or impossibility of a chemical reaction, the necessity or impossibility of a fusion, of a vaporisation, of an allotropic modification, of a dissolving? Is it not to be expected that physical mechanics and chemical mechanics do not constitute separate sciences, proceeding by different methods based on different principles, [154] but a single science, the mechanics of change of state? "If the combination[4] particularly affects what we call the chemical properties of substances, if dissolution sensibly alters only physical properties, in a word, if combination and dissolution is identical with one and the same phenomena of which they represent the extremes, it is clear that all difference ceases to exist between physical properties and chemical properties of material. Both are under the absolute domination of heat and, in virtue of that, mechanical agents. Modern experiments tend to allow a more and more prominent influence to these in the results obtained in physics and chemistry, two sciences which tend more and more to merge into one another and with mechanics."

In announcing the birth of a doctrine which issued in thermodynamics, embracing at the same time the laws of locomotion[5] and those which govern the various physical phenomena, as well as those which preside over chemical reactions, H. Sainte-Claire Deville was a prophet. He glimpsed the advance of work which was to become the scientific crowning of the nineteenth century.

But he was not equal to foretelling that so general a science was possible, that it was on the point of being completed. To demonstrate this possibility, to make it plausible that this event is near at hand, it would be necessary to outline some chapters of the new discipline, it would be necessary to stun minds with the close analogy which exists between chemical mechanics and physical mechanics. H. Sainte-Claire Deville succeeded in analysing chemical equilibria produced in the course of partial decompositions or *dissociations*.

The carbonate of lime decomposes when its temperature is raised and carbonic gas is released. Liquid water and solid arsenic transform into vapours when heated. H. Sainte-Claire Deville perceived a close analogy[6] between the two phenomena. [155] The point of decomposition of carbonate of lime is analogous to the boiling point of water and arsenic: neither the one nor the other of these points is invariable. Just as the boiling point of a solid or liquid body depends on the pressure of the vapour over the body, so the point of decomposition of carbonate of lime depends on the pressure of carbonic gas in the vessel where the reaction occurs. Under atmospheric pressure, arsenic cannot be fused; the point of fusion of this substance is higher than its boiling point. When warmed, it passes directly to the vapour state

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[4] H. Sainte-Claire Deville, *loc. cit.*, p. 64.

[5] *mouvement local.* [Cf. Duhem's *L'Évolution de la mécanique*, (Paris, 1903), Ch. 1, "Peripatetic Mechanics," where *mouvement* is introduced as a general concept of change of which change of place, *mouvement local*, is a special kind.]

[6] H. Sainte-Claire Deville, *Leçons sur la Dissociation*, presented before the Société chimique, 18 March and 1 April 1864.

before being liquefied. But if the pressure of the arsenic vapour is increased, the fusion point remains almost invariable while the boiling point rises, eventually above the former, so it is possible to fuse arsenic in a closed vessel. The same holds for carbonate of lime; it cannot be fused in the open air, because under atmospheric pressure the point of fusion is much higher than the point of decomposition. But if the pressure of the carbonic gas is increased, the point of decomposition finally rises above the point of fusion. This explains the celebrated experiment of James Hall who succeeded in fusing carbonate of lime at red heat in a resistant and hermetically closed receptacle.

The precise experiments of H. Debray were soon to confirm these views of H. Sainte-Claire Deville. At a given temperature, the vaporisation of a solid or liquid body stops when the vapour produced has acquired a certain pressure. This *saturated vapour pressure* depends only on the temperature and increases with it. Similarly, at a given temperature, the decomposition of calcium carbonate stops when the carbonic gas emitted attains a certain pressure; this *dissociation pressure* is absolutely fixed at a given temperature, and varies with temperature, increasing with it[7].

Following [156] H. Debray, the disciples of H. Sainte-Claire Deville paid particular attention to the study of chemical equilibria, and soon, thanks to the discoveries of Troost, those of Hautefeuille, of Isambert, of Gernez and of Ditte, it was established that the most characteristic chemical reactions, as well as allotropic modifications and polymerisations, give rise to equilibrium phenomena whose laws are identical with the laws of change in physical state, the laws of fusion and of vaporisation.

But this was no more than a corollary to the ideas of Sainte-Claire Deville, ideas whose scientific and philosophical plenitude remained for a long time misunderstood. Frequently stated in quite obscure form, sometimes sullied by blending with views that they were intended to supplant, they were never entirely accepted even by the disciples of the master. Besides, they could only be freely developed by reversing two other theses of chemical mechanics. One, the theory of *maximum work*, was born before Sainte-Claire Deville's research on dissociation. The other, the theory of *dynamic equilibria*, is contemporaneous with this research.

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[7] The interpretation of James Hall's experiment and the notion of dissociation [156] pressure derived from it has been given in very clear fashion by Georges Aimé in a thesis submitted in 1834. The writings of George Aimé remained unknown and were without influence on the work of Sainte-Claire Deville and his disciples. (Georges Aimé, *De l'influence de la pression sur les actions chimiques*, Thesis of Paris, 1834. Reprinted in the *Mémoires de la Société des Sciences physique et naturelles de Bordeaux*, fifth series, vol. V, 1899.—P. Duhem, "Un point d'histoire des sciences: la tension de dissociation avant H. Sainte-Claire Deville," *Mémoires de la Société des Sciences physique et naturelles de Bordeaux*, fifth series, vol. V, 1899, and *Journal of Physical Chemistry*, vol. III, p. 364, 1899.)

The theory of maximum work resulted from the union of doctrines, first introduced into physics by Newton, in the law established in the middle of the nineteenth century expressing the equivalence between heat and work.

According to Newton, the atoms which are the ultimate elements of material are attracted or repulsed by forces effective only at short distance. Furthermore, these atoms are agitated, executing movements of very [157] small amplitude but with very great speed, and it is these internal movements which produce in us the sensation of heat. When a system under transformation maintains an invariable temperature, the kinetic energy of these movements remains constant. It increases or diminishes when the temperature rises or falls. As early as 1780, Lavoisier and Laplace, in their imperishable *Mémoire sur la Chaleur*, remarked that this kinetic energy plays the role in the mechanical theory of heat played by *free caloric* in the theory which regards heat as a fluid. Whenever *latent caloric* is lost by a system in the course of a modification, the mechanical theory recovers the equivalent in the work that the various forces applying to the atoms carry out during the modification. So when a modification takes place without change of temperature, and consequently without tangible variation in the heat, the amount of heat released by the modification measures the work accomplished by both internal and external forces which determine the modification.

By the middle of the nineteenth century the caloric hypothesis had been left in ruins by the instinctive foresight of Robert Mayer and the experimental research of James Prescott Joule which made precise the definition of the mechanical equivalent of heat and determined its value. The mechanical theory of heat was brought into favour, and the ideas formulated by Lavoisier and Laplace were taken up again, in particular by Clausius. They inspired the celebrated[8] paper of the great physicist published in 1850.

These ideas found an immediate application in chemical mechanics.

Molecular forces compete with external forces in arranging atoms within substances. The various forces are brought into play, according to the laws of mechanics, to produce both physical changes of state and chemical reactions. Newton had already stated this principle, Lavoisier [158] and Laplace developed it, and Berthollet tried to deduce from it a chemical statics.

Now, a known theorem says that any ensemble of bodies taken at rest cannot be put into motion by the action of certain forces unless they do positive work. An ensemble of bodies at rest in a certain state can therefore only experience a change of state if the change transmits positive work from the external forces and the molecular forces. But according to the ideas of Lavoisier and Laplace which Clausius took up, if the change of state is accomplished at a constant temperature, this work is measured by the amount of heat released by the ensemble of bodies. We are thus

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[8] R. Clausuis, *Poggendorff's Annalen*, vol. LXXIX, 1850.—*Théorie mécanique de la Chaleur*, first edition, vol. I, mémoire I.

led to state the following principle: *All change of physical or chemical state which itself begins in an ensemble of bodies maintained at a constant temperature is accompanied by a release of heat.*

This principle which, long after its discovery, was called the *principle of maximum work*, was stated in 1853 by the Danish chemist Julius Thomsen[9]. He was led to it from Clausius's ideas along lines similar to those that we have just traced.

We are mistaken. This principle is the one to which Thomsen was logically led by the considerations that he developed; but it is not the principle that he stated. That principle is the one obtained by replacing the words *all change of physical or chemical state* in the one we have just written with Thomsen's words *all purely chemical reactions.*

The correction is fundamental. It was necessary. It is all too clear, in fact, that the principle of maximum work is known not to apply to changes of physical state. Each day we see, at invariable temperature, ice fuse, water vaporise, and, moreover, spontaneous modifications which absorb heat. On pain of being [159] continually and formally contradicted by experience, the law of maximum work must be restricted to purely chemical mechanics.

But this restriction, which is indispensable if contradiction by the facts is to be avoided, was illogical. The hypotheses from which the law of maximum work emerged require that this law has an unlimited import and tolerates no separation whatever between physical mechanics and chemical mechanics. Berthollet said as much, and it was impossible to misunderstand him. The theory of changes of state based on the hypothesis of molecular attraction therefore experienced another setback. It had already been contradicted by chemistry when at Berthollet's hands it denied the law of definite proportions. Renewed by its union with the mechanical theory of heat, it was now contradicted by physics.

It was irreconcilable with the hypotheses which led to its formulation, but it is possible, after all, that once this useless scaffolding was abandoned, the law stated by Julius Thomsen might be in accord with the facts and it would be appropriate to examine whether such an agreement is to be found or not.

A grave difficulty arises immediately for this examination, however, and seems to render it illusory. The law of maximum work presupposes knowledge of how to distinguish a physical phenomenon from a chemical phenomenon. It claims to be applicable only to chemical phenomena, and so before deciding whether it is confirmed or contradicted by a change of state, it must be decided that this change of state is chemical and non-physical. Now, where is the characteristic to be found which allows such a decision to be taken? Berthollet had already insisted on the absence of any such characteristic, and the law of maximum work was still quite

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[9] J. Thomsen, "Die Grundzüge eines thermo-chemischen Systems," *Poggendorff's Annalen*, vol. LXXXVIII, 1853;—vol. XCII, 1854.

new to science when the work of Sainte-Claire Deville and his school made evident to everyone the correctness of Berthollet's idea. In the absence of any line of demarcation between physical modifications and chemical modifications, the experimental [160] critique of the law of maximum work becomes empty and useless. A host of reactions condemn this law without further ado for anyone who takes them to be purely chemical, but are irrelevant for those who claim that some part of the transformation is physical.

This state of confusion cannot be supported in the true spirit of science. It is very favourable to those who look for subterfuges to escape conflict with the facts. But it will not do to save the law of maximum work.

A mixture of oxygen and hydrogen can be transformed into water vapour, and water vapour can be dissociated into oxygen and hydrogen. Is it a distinctly chemical reaction, free from any admixture of physical modification? At a sufficiently high temperature a state of chemical equilibrium is established within a mixture of oxygen, hydrogen and water vapour, and if the pressure is increased somewhat without raising the temperature, a certain amount of oxygen and hydrogen are combined, and this combination releases some heat in accordance with the principle of maximum work. If, however, the pressure is decreased somewhat without changing the temperature, a certain amount of water vapour would be decomposed, and this decomposition would absorb some heat, contrary to the principle of maximum work. If the proponents of the principle of maximum work accept the favourable witness of the first experiment, on what grounds do they base the rejection of the refutation inflicted by the second?

Thus, the discoveries of Sainte-Claire Deville and his disciples demolish the chemical statics which had been produced by the union of the mechanical theory of heat with the Newtonian hypotheses[10].

During the eighteenth century, while the Newtonian hypotheses [161] of astronomic attraction and molecular attraction completely took hold of physics, a small school of scholars remained faithful to the Cartesian and atomic doctrines and would accept nothing in their theories which could not be reduced to shape and movement. This school was centred in Switzerland around the illustrious Bernoulli family.

Lesage, who tried to explain universal attraction by the impact of ethereal particles on material molecules, belonged to this school. So too did Pierre Prévost, friend and executor of Lesage's will.

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[10] The reader who wants to enquire further into the details of the law of maximum work might look into the following writings: P. Duhem, *Introduction à la Mécanique chimique*, Gand. 1893.—"Thermochimie, à propos d'un livre récent de M. Marcelin Berthelot" *Revue des questions scientifiques*, 2nd. series, vol. VI, 1897 and Paris, 1897 [translated in this volume as "Thermochemistry"].

Pierre Prévost was particularly preoccupied by the theory of heat. In imitation of what Newton imagined for light, Prévost regarded[11] heat as composed of small projectiles which bodies throw into space the more vigorously the warmer they are. These projectiles warm the bodies into which they penetrate. When two bodies are in the presence of one another they attain, at the end of a certain time, a certain state of equilibrium where neither of them is warmed nor cooled. It is not that either of the bodies discontinues to throw out calorific projectiles towards the other or to receive them from the other, but a regime is established where each of the bodies receives, in a given time, as many heat corpuscles as it emits. This is the hypothesis of *dynamic equilibrium* which was to meet with singular fortune in chemical statics.

Among the most important of the doctrines which assured the renown of the Swiss atomic school it is appropriate to put the explication of the properties of gases proposed in 1726 by Jean Bernoulli the older and developed in 1738 by his son Daniel Bernoulli in the 10th. section of his *Hydrodynamics*. According to the Bernoullis, the force of expansion of gases is due neither to Descartes' branching particles nor to Boyle's small springs nor to Newton's molecular repulsions. Atoms of gas [162] are agitated by continuous and rapid movements and rebound after striking the walls of the vessel which encloses the aeriform fluid. The molecular bombardment produces a pressure endowed with all the properties recognised by experimentalists.

When in the middle of the nineteenth century the progress of the mechanical theory of heat revived the interest of physicists in atomic hypotheses, the explication of the properties of gases conceived by Bernoulli was taken up and developed by various physicists, notably Krœnig and Clausius, and later by Maxwell, Boltzmann and O.-E. Meyer. It became an important doctrine under the name of the *kinetic theory of gases*, and for some time became the ideal type for physical theory.

It is natural to link the theory of the formation of vapours with the kinetic theory of gases, as Clausius tried to do[12]. When a liquid is in contact with its vapour, a continual exchange of molecules occurs over the surface of contact. After a certain time, a state of dynamic equilibrium is reached, when as many of the atoms which the liquid allows to escape and penetrate into the vapour return from the vapour. The vapour is always saturated.

It was not long before the notion of dynamic equilibrium which Clausius introduced into the study of changes of physical state was entering into chemical mechanics.

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[11] Pierre Prévost, *Recherches physico-mécaniques sur la chaleur*. Genève, 1782.

[12] R. Clausuis, *Poggendorff's Annalen*, vol. C, p. 353, 1857.—*Théorie mécanique de la chaleur*, 1st. edition, vol. II, mémoire XIV.

A mixture of oxygen, hydrogen and water vapour subjected to a given pressure is raised to a given fixed, but quite high, temperature. After a certain time chemical equilibrium is established and no increase or decrease in the concentration of the water vapour in the gaseous mixture is observed. It is not that the oxygen and hydrogen have ceased to combine, or that the water vapour has ceased to decompose, but the number of molecules of water vapour which are formed at a given temperature is [163] exactly equal to the number of molecules of the same substance which break up at the same temperature. All chemical equilibrium is a dynamic equilibrium, a state where the permanent rates of two reactions, the one the inverse of the other, exactly compensate one another.

The idea had been mentioned as an aside by Malaguti[13]; Williamson applied it to phenomena of etherification and Clausius to electrolysis. During the period that Sainte-Claire Deville gave his lectures *sur la Dissociation* and *sur l'Affinité*, two professors from Christiania, Guldberg and Waage[14], inspired by the works of Pierre Prévost, took this hypothesis as the foundation of a chemical statics.

At the same time the hypotheses of Clausius regarding vaporisation inspired a theory of dissociation from Pfaündler in Germany. "I now come," wrote Pfaündler[15], "to the explication of the *dissociation of vapours* and, to this end, I frame the following hypothesis: within the vapour of a partially decomposed compound, while the temperature remains constant, *the number of molecules which break up is exactly equal to the number of molecules which are formed by their atoms coming together*. This explanation necessarily presupposes that *at a given instant, the molecules are not all animated by the same movement*. The same explanation of vaporisation given by Clausius supposes that the molecules situated at the surface of the liquid do not all move in the same way. But according to the mechanical theory of heat, this irregularity in the distribution of movement is extremely likely ... Consequently, if the temperature stays constant at a given value, the number of particles put at liberty goes on increasing until the moment when the number of molecules which are reformed in a given state will become equal to the number molecules which break up during the same time. From that moment, the *equilibrium* between [164] decomposition and recombination reigns as long as the temperature remains invariable."

Pfaündler was soon followed by Horstmann in Germany and by Lemoine and Joulin in France.

It is easy to see how this chemical statics might be constituted. Formulas are constructed representing the rate of each of the two inverse reactions considered to

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[13] Malaguti, *Annales de Chimie et de Physique*, 3rd. series, vol. LI, p. 328, 1857.

[14] Guldberg and Waage, *Les Mondes*, vol. V, p. 105 and p. 627, 1864.—*Études sur les affinités chimiques*, Christianja, 1867.

[15] Pfaündler, *Poffendorff's Annalen*, vol. CXXXI, p. 55, 1867.

comprise the main activity of the system, and putting these two rates equal to one another yields the equation which governs the equilibrium of the system.

In reality, this method suffers from a high degree of arbitrariness. Experiment is not able to give us knowledge of the rates of each of the two inverse reactions, but only the excess of one of the two rates over the other. That is to say, the rate of the resultant reaction is accessible to observation. In order to gain knowledge of the expression of the two rates which matter to us, it is necessary to have recourse to hypotheses. Often enough, the form of these hypotheses will vary considerably with the taste of the physicist. The theory will lose more in reliability and logical value than it will gain in flexibility in dealing with the facts.

However great this flexibility might be, it does not succeed in saving the theory of dynamic equilibria from contradiction with experience.

Take the analysis of a reaction which played a major role in the development of chemical mechanics, that which Pfaündler chose as his example, the decomposition of carbonate of lime into lime and carbonic gas.

Two reactions proceed simultaneously: the decomposition of carbonate of lime and the recombination of carbonic gas with lime. The rate of the first reaction depends on the temperature to which the carbonate of lime rises. But, evidently, it depends besides on the area of the free surface of the pieces of carbonate of lime and is proportional to this area, because the emission of carbonic gas occurs exclusively through this surface. The rate of the [165] second reaction depends on the temperature and the pressure of the carbonic gas, but it is also proportional to the area of the surface of the lime which abuts the carbonic gas—it is, in fact, over the extent of this surface that lime absorbs carbonic gas. If we now set the expressions for these two rates equal, the equation for the equilibrium of the system which is obtained embodies the proportion in which the surface of the fragments of carbonate of lime stands to the surface of the quicklime. The state of equilibrium which is established in the system depends of the value of this proportion. It is easily demonstrated that the dissociation pressure of the calcium carbonate at a given temperature varies in the same sense as this proportion: it increases if the free surface of the carbonate of lime increases, and diminishes if the free surface of the lime increases.

It is easy to submit these expectations to test by the facts. The experiment is very easy to conduct. It has been done by Debray, and the result very clearly provides a formal contradiction of the propositions that we have just stated. At a given temperature, the dissociation pressure of carbonate of lime is absolutely determined, and does not depend in any way on the extension of the surface of the lime or of the carbonate of lime.

The theory of dynamic chemical equilibrium is therefore discredited by the facts and this has been recognised since 1873 by Horstmann, who had at first been a warm adherent. "It has been established," he wrote of this period[16], "from contradiction with experiment, for it is not possible to explain in a satisfactory way the fact verified many times, that the mass of the solid substances has no influence on the degree of dissociation."

The theory of the atomists, which only ascribes shape and movement to material, or which like the Newtonian theory endows atoms with attractive and repulsive forces, has remained incapable of agreeing [166] with the phenomena of dissociation. The two doctrines between which physicists were divided during the eighteenth century, and which bore such an abundant harvest during the first half of the nineteenth century, has tried in vain to build a chemical mechanics.

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[16] Horstmann, *Leibig's Annalen der Chemie und Pharmacie*, vol. CLXX, p. 208, 1873.

CHAPTER 10

CHEMICAL MECHANICS BASED ON THERMODYNAMICS

Should [167] chemical mechanics therefore remain purely empirical? Should it be a simple collection of experimental laws? Should it relinquish any claim to general principles which link it to other parts of physics, as the various branches of a tree are connected together by the common trunk from which they grow? Not at all. There is a prime doctrine, which is the repository of the fundamental rules from which the various disciplines constituting physics must follow and, in particular, chemical mechanics. This doctrine, H. Sainte-Claire Deville pointed out, is Thermodynamics.

His perceptiveness was great, because at the moment Sainte-Claire Deville nominated it as holding the key to chemical mechanics, Thermodynamics, still in its infancy, presented a kind of chaos in which the most disparate hypotheses were supplemented with the most contradictory axioms[1].

Thermodynamics rests on two principles: the principle of equivalence between heat and [168] work, and Carnot's principle. The principle of equivalence, apparently closely connected with the hypothesis introduced into science by the mechanical theories of the Epicurean, Cartesian and Newtonian schools, that heat consists of a movement of the ultimate particles of bodies, was, during the era of which we are now speaking, the only principle universally known and applied. The second principle, based by Carnot on an experimental induction, modified by Clausius in such a way that it becomes compatible with the principle of equivalence, but retaining, after this modification, the form of a postulate which its remote consequences verify, was still obscure and neglected. Reserved for the initiated alone,

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[1] We are not able the analyse in detail here the evolution thermodynamics has undergone, an evolution which has only indirect relations to the subject now being dealt with. We permit ourselves to refer the reader to the following writings: P. Duhem, "Les Théories de la chaleur" *Revue des Deux-Mondes,* vol. CXXIX, p. 869, and vol. CXXX, pp. 380 and 851, 1895.— "L'Évolution des théories physiques, du XVIIe siècle jusqu'à nos jours" *Revue des Questions scientifiques,* 2e série, vol. V, 1896) [translated in this volume as "Theories of Heat" and "The Evolution of Physical Theory"].

it was not vulgarised; moreover, its form, freed from all suppositions about the constitution of material and the nature of heat, was not liked by the physicists who were intoxicated by mechanical hypotheses and demanded above all that Thermodynamics confirm and make them more precise.

Over the years, physicists tried hard to give Carnot's principle an interpretation which accords with the mechanical theory of heat. Their attempts were powerful and ingenious; but they remained in vain. Then a strange turnabout made an incalculable impact on the minds of those who enquired into the theories of physics which we can barely glimpse today. Weren't they wearied by the futility of their efforts in interpreting Carnot's principle mechanically? Didn't they despair of the sterility of the atomic hypotheses and, particularly, the kinetic theory of gases? Didn't they suddenly become conscious of the true nature and of the exact import of physical methods? Suddenly, it was their conception of Thermodynamics that was profoundly modified.

Not only did they cease to claim that Carnot's principle was deducible from mechanical principles and the hypothesis that heat is a movement; not only did they accept the principle [169] as a postulate whose more and less remote consequences came within the bounds of experimental control; they even turned little by little to break off the lines which attached the equivalence principle to ancient suppositions about atoms, molecular forces, the nature of heat, and to give the principle an exposition like that first given of Carnot's principle. Then, these new tendencies were gradually extended to various branches of physics. Mechanical hypotheses had for a long time been considered indispensable for a rational physical theory. They came to be considered like the remnants of outmoded methods, to be banished from various doctrines, and all the fundamental laws of physics were regarded as propositions subject to a single condition, the accordance of their corollaries with the truths of fact. Thus, at first Carnot's principle apparently involved strange characteristics which distinguish it from all other principles admitted up to then as physical theories; now, it has become the model that principles constituting sound theory should imitate.

While Thermodynamics, divorced from all associations with mechanical assumptions, was constructed in accordance with a logical form which would serve as an example for various branches of physics, it extended its field of applications. Previously, the theory of heat was regarded as a part of physics, for the same reason as the theories of electricity, magnetism and capillarity. In the course of the progress of thermodynamics, this view was modified. It was realised that the domain of its laws covered not only the theory of heat, but the most diverse theories too. In particular, the research of Helmholtz, W. Thomson, and R. Clausius made it clear for everyone that the new methods of science provided unforeseen resources for the study of electric phenomena. Gradually, it was understood [170] that Thermodynamics was not a branch of physics, but the trunk from which several subjects branched off. It was not a study of a particular order of phenomena, but the collection of general principles applicable to the study of all phenomena. These laws govern all the changes that it is possible to produce in the inorganic world.

The phenomena governed by Thermodynamics are very varied: condensation and dilation of fluids, elastic deformation of solids, electrification, induction, changing intensities of currents. But as for the primary such change, it is appropriate to quote the most simple and obvious of them, the change of distance in space, *locomotion.* The law of locomotion is now introduced as a corollary of Thermodynamics, and rational Mechanics is no more than a particular application of this vast science, comprising the most simple and best known of its consequences.

What an upheaval in the ideas of physicists! Thirty years ago, rational Mechanics still seemed the queen of science of which all other physical doctrines must be an expression. It was required that Thermodynamics reduce all its laws to mere theorems of Mechanics. Today, rational Mechanics is no more than the application to a particular problem of *locomotion* of this general Thermodynamics, of this *Energetics* whose principles encompass all the transformations of the inorganic world or, according to the peripatetic description, all *physical movements.*

Despite their immense variety, the physical movements of the peripatetics do not exhaust the capacity of Thermodynamics. The Stagirite philosopher did not rank among movements *generation* and *corruption*, the disappearance of a substance accompanied by a new substance, the destruction of elements followed by the formation of a mixt, the destruction of a mixt preceding the regeneration of [171] the elements, in a word, that which we today call the change of physical or chemical state. And yet, these changes of state do not escape the grips of Thermodynamics.

The founders of this science, Carnot and Clapeyron, followed by Clausius, Rankine and W. Thomson, applied it to the transformation from liquid to vapour. J. Thomson and W. Thomson used it to enrich the unexpected results of the study of fusion. G. Kirchhoff deduced important formulas relating to the phenomena of dissociation. Thermodynamics was thus prepared, by the analysis of several changes in physical state, to take hold of chemical reactions. It would yield a chemical Mechanics, just as Sainte-Claire Deville had wished.

The creation of this chemical Mechanics is the work of three men who, without knowing one another, worked simultaneously without the research of any one being able to influence that of the other: J. Moutier in France, Horstmann in Germany, and J. Willard Gibbs in America. Their discoveries, completed in Germany by Helmholtz, in Holland by J.-H. Van 't Hoff and Bakhuis Roozboom, in France by H. Le Châtelier, inaugurated a greatly extended science whose principal results are uncontested today.

We will not examine here questions about what the essential theorems of this science are, what service it daily renders practical chemistry, and many more. What is important for us is the manner in which it conceives the notion of a mixt.

We have said that nothing in this doctrine makes appeal to any hypothesis about the constitution of material, nothing in it presupposes the existence of atoms or molecules. The notion of a mixt can only figure there in the most simple and obvious way, that is to say, in the last analysis, in the peripatetic form.

How, for example, does this science treat the combination of carbonic gas with lime or the dissociation of calcium carbonate? It [172] allows that a certain mass of carbonic gas and a certain mass of lime may disappear, and that it produces a mass of calcium carbonate equal to the sum of the first two masses; and that a certain mass of calcium carbonate might cease to exist, provided that there appears a certain mass of lime and a certain mass of carbonic gas recreating by their sum the mass of carbonate destroyed. Finally, according to the teachings of chemical analysis, it recognises that the mass of carbonic gas and the mass of lime which disappeared or appeared in the two unidirectional reactions stand to one another as the numbers 44 and 55.9. Beyond this, it postulates nothing about the constitution of calcium carbonate, about the intimate nature of the phenomenon which transformed this substance to lime and carbonic gas or which regenerated this substance at the expense of the lime and carbonic gas. Of these three substances: lime, carbonic gas and calcium carbonate, nothing figures in its equations, other than the observable and measurable physical properties such as the mass of each of them, the volume that it occupies, the pressure that it supports, and the temperature to which it is taken.

In summary, in all that is supposed by chemical mechanics regarding the generation and destruction of chemical compounds, we find nothing that does not accord with the analysis of the notion of mixt given by Aristotle. Of course, the law of conservation of mass and the law of definite proportions are invoked there; but in complementing and making more precise the results of the Stagirite, these laws do not modify its character. According to Aristotle, and following contemporary thermodynamicists, the elements do not actually exist any more within the mixt; they exist only as a possibility.

A question arises immediately, precisely and inevitably: what distinction does the new chemical Mechanics establish between a physical mixture and a chemical compound?

Between a physical mixture and a chemical compound [173] it establishes no distinction, or to speak in a more precise way, the principles of thermodynamics, which are its foundations, do not allow the attribution of any sense to these terms. They provide nothing which indicates in its reasoning or in its equations whether a phenomenon is a chemical reaction or a simple change of physical state.

The only distinction that can be introduced in its deductions and the mathematical qualities which accompany them is the distinction between substances which have a fixed composition and bodies with a variable composition. Calcium carbonate is always formed from a mass of carbonic gas and a mass of lime which stand as the numbers 44 and 55.9. On the other hand, to form a mixture of air and water vapour, arbitrary proportions of the two gases may be taken. These are the characteristics which it can understand and which it must take into account.

But are the elements which form a body of indefinite composition simply mixed? Are they not partially combined and does the chemical compound resulting from their union not remain mixed with the excess of the remaining free elements? For the chemical Mechanics based solely on the principles of Thermodynamics these questions are empty of all sense.

A chemist mixes some hydrogen and some chlorine and, in imitation of Bunsen, he studies the gradual change undergone in the various properties of the mixture. He interprets his observations by saying that the hydrogen and the chlorine combine gradually to form hydrochloric acid. He speaks of the mass of the hydrochloric acid that the gaseous system encloses, at a given instant, of the masses of hydrogen and chlorine still free which, at the same instant, are mixed with the hydrochloric gas. The physicist who adheres to the principles of Thermodynamics does not understand this language at all. With Sainte-Claire Deville, he can only see in the phenomenon studied a change of state, as he sees a change of state in [174] the vaporisation of water or in the transformation of white phosphorous to red phosphorous. But in the latter two cases, each small part of the body which is transformed passes without intermediaries from a first state to another, completely different, state. In the first case, on the other hand, the modification is produced in a continuous fashion: the system does not pass from one state to another without traversing all the intermediate states.

In a rational science, to say that the principles of the science leave a certain expression devoid of all sense is to say that it is permissible to attribute to the expression a desired sense by an appropriate definition. So it is in the case that now concerns us.

When some chlorine and hydrogen are mixed, the properties of the mixture first closely resemble the properties of hydrogen, if only a little chlorine is taken, and chlorine, if only a little hydrogen is taken. Gradually, these properties are modified. If the masses of chlorine and hydrogen are taken in the ratio of 35.5 to 1, they tend to become identical with the properties of the gas chemists call hydrochloric acid. They approach them to a greater or lesser extent if the mixture is not of this composition. It is found convenient to express these facts by saying that the system contains some hydrogen, some chlorine and some hydrochloric acid, and that the proportion of hydrochloric acid, at first zero, is continually augmented. Provided that these words are taken as a conventional language and not as the expression of a true state of the material within the system, there is nothing to be disputed, and chemical Mechanics would have no scruples in using such language.

But once more, this language implies no translation into quantitative symbols which could figure in algebraic equations. I have before my eyes a mixture formed by taking 2 grammes of hydrogen and 71 grammes of chlorine, and I could express a proposition such as the following: at the present instant, [175] this mixture encloses 1 gramme of free hydrogen, 35.5 grammes of free chlorine and 36.5 grammes of hydrochloric acid. This proposition is neither true nor false. It has no sense. How could we give it one? Could we try to make this proposition correspond to an algebraic relation accessible to chemical Mechanics, in which this science could recognise truth or error? Could we fix this sense in a non-arbitrary fashion which would be legitimate—although without interest—and in a way which accords, in its applications, with that adopted by chemists, guided by atomic hypotheses?

The problem thus posed cannot be resolved in its complete generality. Only in certain particular cases is there a final or sketchy solution. Horstmann and Gibbs have given a completely satisfactory solution in the case where the substances mixed are gaseous and very near to the ideal state that physicists call the state of a perfect gas.

Let us take the mixture of which we spoke a moment ago. Let us also take 1 gramme of hydrogen, 35.5 grammes of chlorine and 36.5 grammes of hydrochloric acid, and enclose them separately from one another in receptacles of the same volume as that of the mixture. Finally, take all these receptacles to the same temperature. If the *internal potential*[2] of the mixture under consideration is equal to the sum of the *internal potentials* of the three isolated gases, the mixture is said to enclose 36.5 grammes of hydrochloric acid, 1 gramme of free hydrogen and 35.5 grammes of free chlorine.

This is the definition proposed by J. Willard Gibbs.

This definition fulfils all the prescribed conditions. It is translated by an algebraic equation [176] which expresses a relation between two physical quantities. This equation has its place in thermodynamic reasoning which can draw out its consequences, compare these consequences with facts of experience, ascertain the confirmations or falsifications that they engender, and consequently, recognise whether the mixture has or lacks the composition indicated. And, on the other hand, the consequences of this definition are consistent with the propositions that chemists are in the habit of expressing regarding mixtures of gases, although the idea that they are formed of such a mixture would for them be connected with some atomic hypotheses. This definition, for example, complies with the law of gas mixtures, and with the law of gas mixtures and vapours.

With this definition formulated, it is logical and legitimate to study how the composition of a mixture of gases, certain elements of which can either dissociate or combine, varies with different circumstances. This study caries the illustrious names of Horstmann and Gibbs.

Attempts have been made, in some other cases, to do what these great physicists have accomplished for mixtures of ideal gases. J.-H Van 't Hoff and Svante Arrhenius have exerted themselves in the attempt to establish an analogous

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[2] We will not take the time to define what must be understood by the *internal potential* of a system. To understand what is at issue here, is suffices that the reader knows that the internal potential of a system is a quantity that depends of the state of the system and which plays an essential role in the thermodynamic study of the system.

definition in the case where a mixture of several liquid substances encloses a great excess of the one of them. Perhaps this latter attempt has not been as completely satisfactory as the former. It would be inopportune to discuss that here. Whatever its degree of certitude and precision, it manifests no less the train of thought that directs all research within chemical Mechanics.

This train of thought, it seems to us, can be brought out and formulated in these terms:

All hypotheses about the intimate nature of material, about the structure of mixtures and chemical compounds, and particularly all atomic hypotheses, would be banned from the domain of science. It would not make any use of principles drawn from such hypotheses. If an expression only has as much sense as is admitted, explicitly or implicitly, [177] by these suppositions, it is ruthlessly rejected. Alternatively, before adopting it, it is given a new definition, completely uninhibited by the doctrines to which it has been resolved not to make any further appeal. The definitions and propositions of chemical Mechanics will concern, in the last analysis, only quantities representing measurable physical properties. Chemical Mechanics, thus constituted, will not pride itself on penetrating to the very heart of material and revealing the *quid proprium* of chemical reactions. Its aim, more modest, but more certain, is to classify and order the laws experience allows us to discover. The agreement of its corollaries with the facts will be its criterion of certitude.

It suffices for this new science to know the composition of a mixture, that is to say, the mass of the elements which must be destroyed in order to create the mixt and which the corruption of the mixt can regenerate. On the ruins of the notion of a mixt that the atomists have built, it constructs once more the simple and solid conception that Aristotle formulated.

CONCLUSION

We [179] have followed the evolution of the notion of mixt through the ages, from the first awakening of scientific thought with the Greek philosophers to the abstruse and rapid development that chemical doctrines have undergone during the century which has just ended. In the context of a thousand vicissitudes that follow the incessant discovery of new facts and the bitter struggle between different systems, we have seen the essential traits which characterise this evolution. And these traits appeared to us to resemble those which mark the history of the great theories of physics[3].

At the moment when the Greek genius undertook the rational study of nature, two methods are present, each claiming to be alone capable of leading the human mind to the understanding of material things: the mechanism of the atomists and the peripatetic physics. Ancient philosophy was divided between these methods. But in the middle ages, the schools proclaimed the excellence of the Aristotelian method.

Weary of scholastic physics, the thinkers of the renaissance and the seventeenth century vigorously put back the mechanism in which they saw the principle of all rational physical theory, and restored [180] most of the explications conceived by the Greek atomists. These hypotheses, borrowed from Epicurus and Lucretius, inspired them while they created all the parts of physics and chemistry. Under the influence of Newton, the physics of the seventeenth century became more complicated and transformed the atomic and Cartesian physics by introducing into its reasonings mutual attractions and repulsions between various parts of matter. But it remained essentially mechanistic. Mechanics directed the marvellous development of physical theories to the end of the eighteenth century and during the first half of the nineteenth with a supreme and incontestable authority.

Little by little, however, by the very effect of this development, mechanical hypotheses came up against obstacles on all sides which were more and more numerous and difficult to surmount. The atomic, Cartesian and Newtonian systems gradually lost favour with physicists and made way for methods analogous to those advocated by Aristotle. Present-day physics is tending to return to a peripatetic form.

This profound change was by no means accomplished under the influence of a preconceived philosophical idea. It was not the result of a desire to bring our new

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[3] Cf. P. Duhem, "L'évolution des théories physiques du XVIIe siècle jusqu'à nos jours" *Revues des Questions scientifiques*, 2e série, vol. V, 1896 [translated in this volume as "The Evolution of Physical Theories"].

science closer to the ancient Aristotelian doctrines. Men, like Sainte-Claire Deville, who have contributed the most to modifying the orientation of physico-chemical methods, cared little about Aristotle's views. The change was accomplished, so to say, by the force of things. Struck by the disagreement of their theories, based on mechanical hypotheses, with the facts which experience revealed, physicists and chemists set about minutely examining the foundations of these theories. They were obliged to be more precise, to define better the nature and import of the logical procedures which were employed in mathematical physics. And from their many efforts there emerged a science of a kind, new among us, reminiscent, in a striking and unforeseen manner, of a physics twenty-two centuries old.

This [181] transformation, accomplished without any contribution from peripatetic philosophy, was, however, produced at the very moment when a large number of thinkers were striving to instil ideas which are essentially those of Plato, Aristotle, and the great commentators Saint Augustine and Saint Thomas into the thought of our time. Even those who consider such a project illusory readily acknowledge that scholasticism merits neither the sarcasm nor the disdain which has not so long ago been lavished upon it.

Such an upheaval in the ideas which have dominated and guided physical theories is certainly—by its very nature, by the causes which have produced it and by the circumstances in which it was accomplished—one of the phenomena most worthy of the attention that intellectual history offers us.

It is not necessary, however, to exaggerate the peripatetic characteristics which contemporary science presents and claim that it is only the development and natural extension of Aristotle's physics. A quarter of a century of efforts without let-up, guided by the most powerful geniuses known to modern humanity, have not increased and enriched physical theories without modifying the essential trends, without leaving their imprint on that which is to all intents and purposes the core of these theories.

Let us try to indicate precisely to what extent the current method followed by physical sciences might be regarded as peripatetic and where, on the other hand, it begins to distinguish itself essentially from what could be conceived by philosophers of antiquity and the middle ages.

For Aristotle, all philosophical research was based on a very minute logical analysis of the concepts that perception has made to germinate in our understanding. Each notion is appropriately stripped down to the exact contribution of experience, that which essentially constitutes the notion, and the parasitic ornaments with which fantasy dresses it up are strictly rejected. What has this to do, for example, with philosophising on mixts? It will require, above [182] all, an exact analysis bringing out the distinction between elements, which cease to exist at the moment when the mixt is created, and the homogeneous mixt whose smallest part contains the elements potentially and can regenerate them by the appropriate corruption. In the view of the atomists, these necessary and sufficient conditions for the constitution of the notion of a mixt are substituted by hypotheses about the persistence and juxtaposition of atoms. These hypotheses, whose objects are not in any way perceptible by our legitimate means of knowing, should be relentlessly banished to the realm of pipe dreams.

Contemporary physics too puts an exact logical analysis of the notions furnished by experience at the foundations of all theory. It endeavours by such analysis not only to mark with precision the essential elements that compose each of these notions, but also to meticulously eliminate all parasitic elements that mechanical hypotheses have gradually introduced.

The analysis that contemporary physics takes as the point of departure for each theory proceeds according the same method as the peripatetic analysis. But it differs in the number of objects concerned and the detail of the facts that are presented to it. Aristotle was not able to examine anything other than that which could be known to vulgar observation with the aid of our natural means of perception. He was sometimes still dealing with incomplete and inexact observations. Since the Renaissance, the power, penetration and precision of our senses have been prodigiously increased by the use of instruments daily more perfect, and by experimental methods daily more meticulous. Experiments which continually grow in number and detail, introduce into science at each instant new ideas or complicate concepts already formed. The physicist's analysis is therefore applied to a material incomparably richer than that at the disposal of Aristotle, to a material whose riches grow indefinitely.

It [183] is not enough, for example, for whoever meditates on chemical theories to analyse the two connected notions of mixts and elements; lots of other notions are grafted onto these and require attention. It is necessary to penetrate the ideas of equivalent masses, chemical analogy, chemical substitution, valence, isomerism, etc., and to know the contents of these ideas in order to discuss their exact sense and true import. It is not enough to make appeal to the testimony of completely bare senses. A balance must be used, or a goniometer, a saccharimeter, and all the instruments which fill the laboratories of chemists and physicists.

This analysis is clearly profoundly different in form and extension from that which solicited the attention of Aristotle. Nevertheless, the logical dissection made by the Stagirite was very precise. Quite often, a modern physicist has had to devote much time and energy to unearth ideas clearly perceived by the ancient philosopher from a milieu of suppositions piled up by mechanical theories. We have thus seen chemistry recover, by a slow development, the peripatetic notion of mixt.

In addition, especially in the case when contemporary science is constrained to transform the results of the Aristotelian analysis, the changes that it brings are sometimes linked in such an exact way with ancient ideas that they seem to complement and enrich them rather than profoundly modifying them. Aristotle had seen that a mixt or a group of elements can never be born without at the same time a mixt or a group of elements being destroyed. *Corruptio unius generatio alterius*,[4] said the scholastics. Modern chemistry completes and makes the principle precise by showing us that the mass destroyed is always equal to the mass created.

It is possible, however, that the results to which Aristotle was led in applying a logical analysis to our various physical notions were completely overturned by the examination of these notions as it is carried out today, and the [184] mechanics of locomotion stood in its place. But even in that case, the imperishable fame of the Stagirite would remain undiminished, the fame of having taken such an analysis to the foundations of science, the fame of having created a method to which physics saw itself constrained to turn after having taken imagination for a very long time as its guide.

It is by this preliminary logical analysis, and only by it, that peripatetic physics and contemporary physics approach one another. Once this analysis terminates, these two physics separate and pursue different objectives along diverging paths.

In the contemporary sense of the word, peripatetic physics is a branch of metaphysics. If it distinguishes in each of our physical concepts elements which compose it, that is to penetrate more completely the nature of the object than this notion represents. Behind each of these elements brought into prominence it places a reality. When, for example, it has dissected the notion of mixt, it tries to conceive how material and the form of components give way to the material and the form of mixt, and the accidents and the substances of bodies[5] stand in this relation to one another.

Contemporary physics is not metaphysics. It does not propose to penetrate behind our perceptions and come to know the essence and intimate nature of the objects of these perceptions. Its aim is completely different[6]. It proposes to construct, by means of signs taken from the science of numbers and from geometry, a symbolic representation of what our senses, aided by instruments, make us know. Once constructed, this representation is prepared for reasoning in a very easy, quick and consequently more certain fashion than the purely experimental knowledge [185] that it replaces. This ploy enables physics to take on a scope and precision that it could not have attained without assuming the schematic form that is called theoretical physics or mathematical physics.

Henceforth, to each of the elements that logical analysis leads it to discover in one of the concepts with which it deals, it does not make any metaphysical reality

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[4] [corruption of the one is generation of the other]

[5] *les substances des ces corps.*

[6] We have developed this point in the following writings: "Quelques réflexions au sujet des théories physiques" *Revue des Questions scientifiques*, 2e série, t. I, 1892.—"Physique et Métaphysique" *Ibid.*, t. II, 1893.—"Quelques réflexions au sujet de la Physique expérimentale" *Ibid.*, t. III, 1894. [All three papers are translated in *Essays in the History and Philosophy of Science*, trans. and ed. by Roger Ariew and Peter Barker, Hackett, Indianapolis and Cambridge, 1996.]

correspond, only a geometric or algebraic character of the symbol that it substitutes for this concept.

For the concept of mixt, for example, it substitutes a chemical formula. The idea of the analogy between two mixts is expressed by a collection of equalities between the indices taken on by certain letters. The idea of derivation by substitution is represented by means of certain features. The dissymmetry of a geometric figure serves to indicate a body endowed with the ability to rotate.

It is clear that between this symbolic representation of what is given in experience and a metaphysical study of things that our sense perceive, it is no longer possible to establish a rapprochement. Theories of modern physics are radically heterogeneous with peripatetic physics. These two physics are only connected to one another by the logical analysis that is their common point of departure.

ESSAYS

ESSAY 1

THEORIES OF HEAT

I

The Precursors of Thermodynamics[*]

I

The thermometer, wrote the abbé Nollet, "came for the first time from the hands of a peasant from North Holland. In truth, this peasant, called Drebbel, was not one of those rough men who knew nothing but the work of the land; it seems that he was naturally very industrious, and had a certain familiarity with the physics of his day." Ingenious inventor no less than impudent charlatan, who made out to have found perpetual motion at the same time as having made great progress in the art of dying fabrics, Drebbel was able to gain the favours of James I. Rudolph II allowed him a fat pension and took him to his heart. Ferdinand II, himself occupied by thermometry, chose him as his son's tutor.

Drebbel's thermometer—an invention he might have taken from Porta and in which he was certainly preceded by Galileo—comprised a vertical glass tube terminating at its upper end in a bulb of the same material and with its lower end plunged into a beaker full of water or some coloured liquid. On heating the glass bulb, a portion of the air contained there must force back the water and escape. When the air was allowed to return [870] to the ambient temperature, the external pressure made the liquid rise in the tube. The liquid rose less high in proportion to the greater pressure acquired by the air contained in the glass bulb as it was warmed. The variations in the pressure of a mass of air whose volume changes little was thus useful in demonstrating the "increases of heat and cold."

This impractical apparatus was, however, commonly used in Germany until 1621. The members of the Academy *del Cimento*, inquisitive about any progress in

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[*] Originally published as Part I of "Les Théories de la Chaleur" with the subtitle "Les Précurseurs de la Thermodynamique," *Revue des deux mondes*, 129 (1895), 869-901. All three parts are reprinted as an appendix to the 1992 reprint of Duhem's *L'Évolution de la Mécanique*, Vrin, Paris. The pagination is that of the original.

physics, were quick to replace it by a more convenient instrument, one which still serves us today. A liquid which is enclosed in a transparent bulb, extended in a narrow tube, expands more than the bulb and rises in the tube when it is heated, and descends when it is cooled. The Florentine Academy let no discovery in physics pass without seeking some application of it in the art of healing. Hardly had Galileo recognised the constant period of oscillation of a pendulum than the pendulum was put to use to determine the frequency or slowness of the patient's pulse. The thermometer, rendered portable and easy to handle, became forthwith, in the hands of the Venetian physiologist Santorio Santori, a sensitive and precise indicator of the progress of fever. Santori's writings made the valuable instrument popular and it was soon to be found generally available in enameller's shops under the name of the *Florentine* or *Sanctorius* thermometer.

It is difficult to imagine the interest aroused by the indications of this apparatus "worthy of Archimedes." Everyone was curious to observe the ascent or descent of the coloured spirit of wine in the glass tube because, Nollet wrote, "the physicist, guided by the thermometer, worked with greater certitude and success; the good citizen is better informed about the variations which affect the blood of men and the products of the earth, and the individual who seeks to procure the conveniences of life is advised of what he must do to live throughout the whole year with a steady temperature." According to Amontons, Colbert planned to make a large number of thermometers and send them to different parts of the earth to make observations on the seasons and climates. He was forced to abandon his project because of the imperfections inherent in spirit of wine thermometers of this period. Different thermometers gave readings which were not comparable.

No fixed rule governed the etching of degrees on the stem of thermometers. Thus, different instruments did not express the same warmth nor the same coldness by the same number of [871] degrees. When they were placed in the same place, the one was higher, the other lower; the one showed 30° and the other only 20°. Some physicists thought of choosing a year with a very cold winter and a very warm summer, marking the lowest and highest points reached by the spirit of wine in the course of their excursions and divide the interval between the two points into a hundred equal parts. Such a thermometer allows, it is true, its owner to compare the heat of summer with the rigours of the winter from one year to the next. But in communicating his observations to another physicist, he only gives to him information deprived of sense unless he sends to him, along with the observations, the instrument with which they were made, or, at least, an instrument graduated at the same time in the same place.

An astronomer who is asked the length of the pendulum which beats once a second would not be taken seriously if he replied that the pendulum has the same length as his stick, while hiding his stick. What is expected from him is the number of feet, of inches and of lines[1] which measure the length requested. This information enables the questioner to construct a pendulum beating seconds. Similarly for the construction of thermometers, suppose there were a rule which enabled the obtaining, no matter where or when, of comparable instruments, instruments which reliably indicated the same number for the same intensity of heat. Such was the problem which engaged the efforts of physicists at the end of the seventeenth century and the beginning the eighteenth.

The problem was solved for the first time in 1702 by Amontons. The method he proposed, having been alternately abandoned and readopted, has today become, after all the ups and downs, the normal method to which all authors subscribe in order to determine absolute temperature.

Two all important observations provide the basis of Amontons' method.

Take two masses of air in two glass bulbs. Each of these masses is separated from the external air by a curved tube full of mercury constituting a manometer. Suppose that at a given temperature one of these two masses supports the pressure of one atmosphere and the other a pressure of two atmospheres. Suppose now the two masses of air are heated equably while more mercury is poured into the manometers in order to maintain the volume occupied by each invariable. While the pressure supported by the first mass increases by a certain amount, the pressure supported by the second mass increases by twice as much. The second pressure remains always double that [872] of the first. Thus, when two masses of air are heated equally while the volumes of the receptacles which contain them are held constant, the pressures supported by the two masses remain in the same ratio. This was Amontons' first observation.

The second, which can be made with an arbitrarily graduated thermometer, is as follows: The temperature of boiling water is invariable. Not only does the thermometer, when immersed in water, remain after boiling for several hours at the same level to which it was taken when the water was first brought to the boil; on every occasion when it is immersed in boiling water, it also shows the same reading. In order to be rigorous, Amontons was obliged to add this restriction: provided that the pressure of the atmosphere has the same value in all cases. The subsequent progress of physics was to show the necessity of this restriction, which Newton had already recognised.

When a bulb full of air is connected to a manometer and the pressure supported by the air carefully noted when the bulb is immersed in boiling water, and then the pressure which, in different circumstances, restores the air to the same volume is also noted, the relation between the latter pressure and the former could be regarded as expressing the relation between the temperature to which the air is taken in the latter circumstances and the fixed temperature of boiling water. This relation would

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[1] [A line is one twelfth of an inch.]

have the same value for any thermometer, so constructed, that might be used, thus ensuring a means of obtaining comparable instruments.

So, following in Drebbel's footsteps, Amontons proposed that a mass of air under variable pressure maintaining a constant volume be taken as a thermometer. The rule by which he attached, to each degree of warmth or cold, a certain temperature—that is to say, a certain number, the larger the more intense the warmth and the smaller the colder it becomes—is the same rule which Desormes and Clément, on the one hand, and Laplace on the other, were to reintroduce a century later. It is the rule which the works of Sadi Carnot, of Clausius, and of W. Thomson, were to suggest for the measurement of absolute temperature.

The profound reasons that lead us today to prefer above all others the definition of temperature proposed by Amontons could not be foreseen at the beginning of the eighteenth century. The large dimensions and the cumbersome shape of the thermometer that Amontons had envisaged and the necessity of taking into account the variations of atmospheric pressure in order to interpret its readings [873] prevented the majority of physicists from adopting this instrument. It was therefore necessary to construct spirit-of-wine thermometers which could be compared. This was done by Réaumure.

In 1730, Réaumure noticed that a thermometer placed in freezing water attains a certain degree and remains fixed although the water has not entirely solidified. In circumstances which will cause water to solidify, the same thermometer, immersed in the freezing liquid, returns to the same point. The temperature at which water freezes is therefore a temperature which is always the same, a fixed temperature. The progress of physics has led to certain corrections to this law. It has uncovered causes which make the freezing point of water vary. This has led physicists to no longer take as a fixed temperature the freezing point of water, but the point of fusion of ice, and to take the most meticulous precautions in the observation of this point. But neither the corrections, necessary as they are, nor the fact the Florentine academicians had, by chance, accepted the invariability of the point of fusion of ice, diminishes the importance of Réaumure's discovery.

Réaumure deduced from this discovery of a fixed temperature how comparable spirit-of-wine thermometers could be manufactured.

A glass bulb, elongated into a narrow tube and filled with spirit of wine, is immersed in freezing water. A line is etched at the place to which the liquid level reaches and marked *zero*. The volume occupied by the liquid under these conditions is determined. The tube is divided into sections whose interior capacity represents, at the temperature of freezing water, aliquot [i.e. an integral number of] parts of the this volume, say thousandths. These divisions are numbered from the line marked *zero*. If during the course of an experiment the spirit of wine is seen to become level with the division marked *five*, it is known that, between the temperature of freezing water and the temperature of the experiment, the spirit of wine contained in the glass has been subjected to an *apparent* expansion of five thousandths. If, in the manufacture of thermometers, care is taken always to employ spirit of wine endowed with the same properties—and Réaumure prescribed meticulous rules for the preparation of such a liquid—and if the changes which the variable nature of the glass entail for the law of expansion of the thermometric container are neglected, instruments are obtained which always indicate the same degree when they are heated the same amount, [874] and will assign the same number to the same degree of cold and the same degree of heat.

If two thermometers manufactured in accordance with the rules laid down by Réaumure are to be rigorously comparable, it is necessary that they be constructed from the same glass and filled with the same liquid. Should the glass of which both are constructed not have exactly the same composition and the same temper, or the alcohol with which they are filled not have exactly the same concentration, then the readings of the two instruments will not be in agreement. Should the spirit of wine of the one have a greater apparent dilation than the spirit of wine of the other, and they are placed in identical conditions, within bodies everywhere equally warm, the first indicates a degree more elevated than the second.

In order to reduce these differences, it is natural to require thermometers, of whatever material they are constructed, to give the same readings for *two* fixed temperatures. Two points are marked on the stem of the thermometer [indicating] where the level of the liquid reaches at the lowest of these two temperatures and where it reaches at the highest. The interval delimited by these two points of the stem is divided into a certain number of sections with the same interior volume, and the divisions are extended beyond the fixed points. In such thermometers, the liquid level is seen to reach the same line for the same degree of heat, despite the slight variations which might arise from the nature of the glass and the liquid.

It remains to choose the two fixed temperatures which determine the thermometric scale employed. Physicists were a long time in deciding. In 1688, Dalencé took as fixed temperatures, on the one hand, that of a mixture of water and ice, and on the other, that determined by the fusion of butter. In 1694, Renaldini recommended that the two fixed points of the thermometer be determined, on the one hand, by a mixture of water and ice, and on the other, by boiling water, but this procedure could not be applied to the spirit-of-wine thermometers which were the only ones used at that time. At the temperature of boiling water, the pressure of the alcohol vapour is so high as to shatter the thermometer reservoir. Renaldini's method was not practical until Musschenbroeck's mercury thermometer had become widespread. In 1720, Delisle chose the temperature of iced water and the rather invariable temperature of the cellars of the Paris observatory to graduate his thermometer.

Around 1714, a skilful craftsman from Danzig, Daniel-Gabriel Fahrenheit, [875] made alcohol thermometers for chemists which he replaced in 1720 by mercury thermometers. These thermometers gave readings which stood in very close agreement with one another. According to the chemist Woolf, Fahrenheit prided himself in being able to make a thermometer comparable to those he had already made, wherever he might be and without having before him any instrument previously forged by his hand. But special reasons prevented him divulging the procedure by which he achieved such concordance. This procedure, drawn up with the advice of the astronomer Roemer, was only the method of Dalencé. But Fahrenheit took as the lower reference point the temperature of a mixture of ice and ammonium muriate [i.e. chloride]—which was, he believed, the greatest cold that could be obtained—and, for the upper reference point, the temperature of the human body.

Finally, in 1742, the Swede Anders Celsius proposed to reinstate the method of Renaldini and divide the interval that a mercury thermometer covers between the temperature of melting ice and the temperature of boiling water into a hundred degrees. He marked the first temperature with the number 100 and the second with the number 0. Linné reversed this order and succeeded in giving the mercury thermometer the form under which we know it.

Manufactured with pure mercury and glass of consistent quality, all the *centigrade* thermometers give comparable readings. If another liquid is substituted for mercury, or the glass from which the bulb and stem of the thermometer is made is changed, then instruments are obtained which, enclosed in the same uniformly heated body, will not give exactly the same readings. They will indicate the same number of degrees when they are immersed in melting ice, however—they always indicate 0°—and when they are engulfed in vapour emitted from boiling water at atmospheric pressure—they always indicate 100°. Between these two temperatures, where any divergence must disappear, this difference would not, in general, be noticeable.[2] At least within these limits, all thermometers should be, to all intents and purposes, comparable.

Anders Celsius' idea is the starting point of modern thermometry. This idea has, without question, been developed, and the meticulously exact instruments constructed by skilled specialists today have come a long way from the centigrade thermometer used by the Uppsala physicist. But throughout this development it has remained, at least in all essential respects, the same.

II

Among [876] the various thermometers that physicists have conceived, from Galileo or Drebbel to Celsius or Linné, which of them is it that justifies its name? Which of them is it whose degrees measure the warmth of bodies?

For the first physicists who used the thermometer, there was no question of measuring heat. The physics of the School taught that heat is a *quality*, possessed

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[2] [More loosely translated, the thought must be "No discrepancy is therefore possible at these two temperatures, but even in between, the discrepancies are not in general noticeable."]

by all bodies with a greater or lesser intensity. Heat was not a *quantity*, and could not be measured by a number.

Bacon declared war on substantial forms and occult qualities. He wanted to drive them out of science. Heat was not for him a quality, but a movement. "The definition or true form of heat," he said, "that which belongs to the universe and not merely to the senses, can be put in a few words as follows: Heat is an expansive movement, compressed and existing in the particles. This expansion is first modified so that, while exerted in all directions, it nevertheless has an upwards tendency ..." The scholastics would not abandon the Aristotelian physics of antiquity for this new physics, for which they have been reproached.

Descartes sought, in accordance with his method, a quantitative element under the quality expressed by the words 'warm' and 'cold', and he regarded heat as a quantity susceptible of measurement.

According to the Cartesian philosophy, material is merely extension. Nothing more need by assumed than what is studied in geometry, various shapes and movements, and all the qualities entertained by the scholastics, in particular warmth and cold, should be reduced to shapes and movements. What, then, is heat? A very rapid and violent agitation of the various parts of a warm body, mainly of the smallest and most subtle, those which Descartes called the *third element.*

A body is struck by light, and the pressure of which this light consists is exerted on the various parts of the body. But it is exerted irregularly, sometimes compressing this point, sometimes another, sometimes agitating one extreme of a particle, sometimes the other end. The equilibrium of particles is thus disrupted, and they are agitated energetically.

The [877] agitation of the particles struck by the light gradually spreads to those which have not been illuminated. Heat is propagated. The calorific movement does not stop at the same moment that the cause which engendered it ceases. Only gradually do the particles of the *third element* return to equilibrium; only gradually is the heat dissipated.

The material particles to which the heat has communicated an unusual[3] movement can no longer be contained in as tight a space as when they were either at rest or animated by a less violent movement, because they have irregular shapes and so occupy less space when rest allows them to be intertwined than when continuous agitation separates and scrambles them in unordered fashion. Thus, heat expands nearly all bodies, some more, some less, according to the shape and arrangement of the particles which compose them.

In a liquid body, the smallest parts shake up one another in different ways. The parts of a flame, perpetually agitated, can, by communicating their movement, render most bodies liquid. When fire melts metals, it does not act with any other power than when it burns wood. But because the parts of metals are all very much

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[3] *inusité.*

alike, the flame cannot shake up the one and not the other, and thus it makes the entire body entirely liquid. On the other hand, the parts of wood are so unalike that it can separate the smallest ones and render them fluid, that is to say, make them "fly away in smoke," without affecting the largest parts to the same degree.

When agitated by fire, the various parts of a body will exert variable pressure on the ether which surrounds them, and this pressure, instantaneously transmitted to the most distant regions of the ether, will be nothing but the light emitted by incandescent bodies.

The movement which dilates bodies, which melts them, which reduces them to smoke, and which generates light, also explains for us why a flame warms us. Everything which shakes up the small parts of our hands in different ways can excite in us the sensation of warmth, "because, merely by striking the hands, they are warmed, and any other body can also be warmed, without being taken before a fire, provided only that it is agitated and shaken in such a way that several of its small parts are shaken and can move like those of our hands."

Now, one of the fundamental points of the Cartesian doctrine [878] has it that there is a number corresponding to an assembly of bodies in movement, a number which measures the intensity of the agitation which animates the system of bodies, the *amount of movement* which it possesses. This number is doubled when either the size of one the moving bodies, or when the speed with which these bodies are carried, is doubled. In a word, the number is obtained by multiplying each mobile mass by the speed which animates it and adding together all these products.

In a warm body there are particles animated by a small but very rapid movement. A given body, carrying a determinate degree of heat, contains a certain amount of this movement. This amount of calorific movement in a warm body is the *amount of heat* which it encloses.

The larger the agitated particles are, or the more rapid is the movement which animates them, the more heat the warm body will possess. The movement of parts of the air, which make it extremely fluid, does not give it the power of burning, because "between the parts of air, if there are some very large ones, such as the atoms which are seen there, they move very slowly. And if there are some which move very fast, they are correspondingly small." On the other hand, among the parts of a flame, "there is a greater number with the size of the biggest of those of air, which move with much greater speed." Only then is the amount of movement large enough for burning, as appears "from the fact that the flame which arises from brandy or other very subtle bodies, hardly burns at all, and that, on the contrary that which arises from hard and heavy bodies is raging hot."

Thus, Descartes put the purely qualitative notions of warmth and cold as physicists had considered them until then into correspondence with a quantitative notion, a quantity, the amount of heat, thereby incorporating the study of heat into his *universal arithmetic*, as he called it, which was to encompass the entire field of physical sciences.

This conception of the amount of heat which Descartes created reigned for a whole century without undergoing any modification to speak of. It was subjected, it is true, to the counter-coup of the revolution which was directed towards dynamics. Leibniz was to show that the rule put forward by Descartes to estimate the intensity of the agitation animating an ensemble of bodies was unsuitable, and had to be replaced by another. Instead of multiplying the mass of each body by its speed, it was necessary to multiply by the square of the speed, and the role attributed by the Cartesian philosophy to the amount of movement was reserved [879] for the *vis viva*.[4] The amount of heat present in a body was defined as the *vis viva* of the internal movement agitating the small parts of the body. But, except for this point, the Cartesian ideas about the nature of heat remained unchanged. Even Newton, while knocking down Descartes' and Huygens' theories of optics, expressed himself like Descartes when it came to heat. "Light," he said, "acts on bodies by heating them, that is to say, by exciting vibratory movement within them which constitutes heat. On the other hand, heated beyond a certain point, all solids become luminous, and this emission of light is produced by the vibratory movements which agitate the various parts."

When a cubic foot of gold, a cubic foot of lead, a cubic foot of water and a cubic foot of air are equally warm, they contain the same amount of heat. The amount of heat in a body at a determinate temperature depends only on its volume and is proportional to this volume. This was a law generally acknowledged at the beginning of the eighteenth century. Pierre de Musschenbroeck and the abbé Nollet state this law in their treatises on physics and describe experiments which they consider appropriate for its demonstration.

Is it possible to measure the amount of heat contained in a unit volume of any body at a given temperature? Does the thermometer provide any such indication? Of all the various thermometers that physicists have conceived, is there any which rises by exactly one degree each time the amount of heat contained in a cubic foot of material is increased by some given amount, each time that the substances which compose it undergo the same gain in heat? This, and only this, would indicate a number of degrees proportional to the increase undergone by the *vis viva* of the calorific movement within a body with which it comes into contact, when the body passes from the fusion point of ice to the point of warmth or cold to which it is taken. Nothing else would be a true *thermometer*.

The problem solicited the attention of physicists who, at the beginning of the eighteenth century, were seeking to perfect the thermometer, and all recognised that they could not resolve it. Thermometers with a high degree of comparability facilitated the study of any body and allowed it to be said with certainty: "This is as warm, warmer or less warm, than that." They indicated nothing more. To take a

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[4] *la force vivre* [Although often translated as "kinetic energy," the term "vis viva" is used throughout as a translation of this phrase.]

body from 0° to 100°, it is necessary to provide a greater amount of heat than to take it from 0° to 20°, but [880] there is nothing to show that it requires five times more. Musschenbroeck said that when the substances which go to make up a thermometer "come to be dilated by a certain amount of fire, we are ignorant of whether double this amount of fire would dilate them two times as much ... Consequently, the thermometer can only enable us to see whether the mercury is rarefied more or less by means of more or less fire. It does not allow us to see any more, and we should never conclude more." Réaumure was no less precise in the affirmation of this truth: "Each of the equally spaced degrees in two thermometers, and perhaps in the same one, will certainly indicate an equal degree of dilation of spirit of wine, but not an equal degree of heat. It is not certain that heat increased by equal degrees always produces equal increases of volume in spirit of wine ... Two thermometers in which spirit of wine is unequally raised indicate only that the one has received a certain number of degrees of heat more than the other, but not in what relation these different degrees stand to one another."

The determination of the amount of heat required to take a cubic foot of material from one degree of the thermometer to another is, however, the most essential thing that must be known if the study of heat is, with Descartes, to be reduced to universal arithmetic. "Mr. de Réaumure," it says in the *Histoire de l'Académie* for the year 1730, "does not believe it possible to arrive at this knowledge exactly, since it is blocked by the many obscurities which always remain in our understanding."

III

The solution which Réaumure despaired of finding was, however, rather easy to discover. Black and Crawford provided it some forty years later.

To raise the temperature of a pound of water from the point of fusion of ice to the point on the centigrade thermometer marked 1°, it is necessary to increase the heat enclosed in this pound of water by a definite amount. This invariable quantity can serve as a standard for the measurement of amounts of heat, as the unit of heat. To take two, three or four pounds of water from the temperature of 0° to the temperature of 1°, two, three or four units of heat are required. On the other hand, when one, two or three pounds of water are cooled from 1° to 0°, they lose an amount of heat equal to one, two or three units.

Now [881] take 10 ounces of mercury heated to 100[°] in the steam from boiling water and immerse it in 33 ounces of water which melting ice has brought to 0°. The mercury will be cooled and the water warmed. After a short time the collection of the two bodies will have reached a common temperature of 1°. The 10 ounces of mercury have lost a certain amount of heat, precisely that which would be required to reheat it from 1° to 100°. What has become of this heat? It has been given up to the 33 ounces of water and raised them from 0° to 1°. The observation which we have just made allows us to estimate the amount of heat. It teaches us that to raise a pound of mercury from 1° to 100°, 33 units of heat are required. In the same way, we can estimate the amount of heat necessary to take a pound of mercury from 1° to 50°, and by subtraction, we know how much heat a pound of mercury gains when it is heated from 50° to 100°.

This method of mixtures is very general. It makes possible the measurement and estimation of the gain in heat undergone by any body when taken from one temperature to another. Its first effect was to demolish the law propounded by Nollet, Musschenbroeck and the majority of physicists at the beginning of the eighteenth century. Equal volumes of different substances do not absorb the same amount of heat when heated equally. A little less heat is required to heat two cubic feet of mercury 1° than to raise a cubic foot of water by the same amount. Each substance, at each temperature, possess a *specific heat*. This is the amount of heat required to raise the temperature in question of unit weight of the substance to another one degree higher in the scale of temperature, and to determine it one must turn to experiment. Determination of specific heats became one of the principal subjects of study for physicists at the end of the eighteenth century.

It is no longer necessary to know whether every increase in the same number of degrees of mercury in the thermometer corresponds to an equal increase in heat in the body in which it is immersed. The question no longer had any sense unless the nature of the body is specified. Rather, this question which had so preoccupied physicists, took on a different form after the discoveries of Black and Crawford. It was transformed as follows: Does a given thermometer, for example a mercury thermometer, experience the same gain of heat every time that it rises by one degree in whatever region of the thermometric scale in which this rise occurs? The method of mixtures provides for a resolution of the [882] question. De Luc showed that practically the same amount of heat is always required to make a mercury thermometer rise one degree anywhere within the scale.

Black was to draw one further very important discovery from the method of mixtures in 1762.

Take a pound of ice when it begins to melt and whose temperature is thus 0°, and tip it into eighty pounds of water at 1°. The ice will melt and the water cools. After a certain time, the ice will have entirely disappeared and eighty-one pounds of water remain. A thermometer immersed in this water indicates exactly 0°.

We know that the eighty pounds of water taken at a temperature of 1° and cooled from 1° to 0° have given up eighty units of heat. What has become of this heat? The pound of ice that we took has been transformed into a pound of water, but its temperature has not changed. It was 0° before the operation, and it is 0° after. Thus, a pound of ice absorbs a considerable amount of heat in melting, an amount measurable by the number 80, and that without the temperature varying. Conversely, a pound of water at 0° is converted to a pound of ice also at 0° with the release of eighty units of heat.

Black's observation explains better an old experiment which the Florentine academicians performed without interpreting it. They filled a vase with ice very finely crushed and, having inserted a thermometer, allowed it to come to the temperature of the bath. Then, immersing the vase full of ice in boiling water, they noticed that the heat made the ice melt while the temperature remained stationary. The heat of the boiling water was absorbed by the ice which passed into the liquid state without the thermometer feeling any effect.

Black was able to observe that other solid substances, like ice, absorbed a certain amount of heat on melting without showing any change in temperature. Furthermore, the vaporisation of water, and of other liquids, is also accompanied by a large absorption of heat although the vapour is not warmer than the liquid.

Black's observation provided a new way of estimating amounts of heat. Each time a body makes one pound of ice melt at 0° in the course of cooling or undergoing any other change, it is said to have given up eighty units of heat. Wilcke in 1772 and [883] Lavoisier and Laplace in 1783 deduced from this principle a new method of calorimetry which was, for a long time, preferred to the method of mixtures.

Black's experiments showed that heat communicated to a body can behave in two very different ways. If the body undergoes no change of state, its temperature rises and it makes a thermometer in contact with the body rise. But if the body undergoes a change of state—if from solid it becomes liquid, or if from liquid it is transformed into vapour—it stores the heat without making it warmer, without making the thermometer immersed within it rise. This heat becomes *latent*. If the body undergoes an inverse change of state—if the liquid solidifies, or if the vapour condenses—it gives up heat without any fall in temperature. It heats up bodies in its environment without cooling. The heat that it has stored in the latent state becomes *liberated*.

These phenomena are so familiar today that we easily misunderstand the importance of the revolution in the ideas of physicists that their discovery produced. Some quite simple reflections suffice, however, to make clear the enormity of this revolution.

The *amount of heat* was introduced by the Cartesians as a quantity which could express in numbers our sensations of warmth and cold. The amount of heat contained in a body was more or less large according as we feel the body to be more or less warm. A cubic foot of iron, a cubic foot of water, and a cubic foot of air each enclosed as much heat as one another when they were equally warm.

In creating calorimetry, Black and Crawford showed that bodies of different nature raised from the same temperature to the same temperature absorb unequal amounts of heat. Consequently, the two expressions *two bodies are equally warm* and *two bodies contain, per unit of volume, the same amount of heat*, could no longer be taken synonymously as they had been until then.

Was it at least allowable to think that when a body of a given nature was heated, it was provided with a certain amount of heat, and that it is cooled by taking away this same amount of heat. The discovery of latent heat rendered this view no longer tenable. It broke entirely with the sense that the word 'heat' has in everyday language and the sense it acquires in the language of physicists. A body can gain [884] heat without becoming warmer, and it can lose heat without becoming colder.

Bodies have the property of affecting our senses in a way which can be more or less intense, of appearing to us more or less warm. This property is no longer represented by physicists as a quantity; they no longer measure it. All that they can do is to describe the various intensities of this quality in a scale of numbers which increase at the same time as bodies are heated. Each thermometer provides a similar scale. The amount of heat, on the other hand, is a quantity measured by the various methods of calorimetry. But this quantity, without direct relation with the property of a body of being more or less warm, measures something that the physicist supposes is in the body, not by virtue of his sense perception but by virtue of his theoretical ideas.

The theoretical ideas of physicists regarding the amount of heat were themselves transformed by Black's discoveries.

IV

The various parts of a warm body are, according to the Cartesians, animated by a very small, very rapid movement. The amount of heat enclosed in the body is the measure of this internal agitation, representing the amount of movement, according to Descartes, and the *vis viva*, according to Leibniz and Huygens. Great though the success of this theory was, it never managed to eradicate certain basic theoretical postures that it was intended to supplant. Just as the scholastics continued to regard heat as a quality, chemists—sons of alchemists—persisted in attributing to all bodies a fluid substance, namely *fire*.

Newton agreed with Descartes' ideas on heat. But light, for him, rather than being the effect of movement, was the impression produced on our eyes by a special substance, constituted of very slender corpuscles which luminous bodies throw out at extremely high speed. Is the heat which frequently accompanies light the effect either of this same substance or of an analogous substance? Many of Newton's disciples thought so and abandoned the Cartesian doctrine.

The discovery of the principal manifestations of electricity brought another triumph for this doctrine. Electrical phenomena [885] seemed to be so successfully explained by the properties of a very subtle fluid capable of penetrating all bodies, of circulating rapidly in conductors, and slowly in insulators, that the existence of electrical fluid was soon accepted even by those who were most averse to the introduction of such substances into physical theories. And with electricity accepted, the existence of fire could not take long. Perhaps the two fluids were even identical.

So, at any rate, the abbé Nollet taught and his works were published under the title *The spectacle of fire or a course in experimental electricity.*

Several physicists were already so convinced of the substantial existence of fire that they disputed amongst themselves over the properties of such a body. Is fire heavy? Many thought so because, when it is accumulated in an intensely heated metal, the fire transforms it to an earth much heavier than the metal. Jean Rey, it is true, had in 1630 explained this increase in weight by the fixation of atmospheric air in the heated metal, and Boerhave supported this view with delicate experiments. But, on the other hand, in 1670 Boyle gave what seemed to be a decisive test of the heaviness of fire. In a tube, hermetically sealed so that nothing could enter except heat, he calcined lead and found that after calcination the lead had increased in weight. Moreover, Stahl soon developed his chemical system which excluded Jean Rey's explanation. S'Gravesande, Lémery and Musschenbroeck also found no difficulty in regarding fire as a heavy body. Homberg went so far as to think of fire as very condensed, not unlike sulphur.

Even philosophers, still hesitating between the supposition that heat consists of a movement and the hypothesis that fire is a fluid substance, overcame all their doubts with the discovery of latent heat absorbed during the fusion of ice. How could the Cartesian hypothesis be reconciled with Black's observations? External bodies give up to a pound of ice all the *vis viva* measuring twenty-four units of heat. The *vis viva* of the movement that vibrates the particles composing this ice must increase by this amount. This movement should be much more lively in the water produced than in the ice from which it came. Why, then, if the sensation of heat is but an effect produced on our organs by this lively agitation of material particles, does the water not seem warmer than the ice from which it is formed?

This objection seemed insurmountable to Black and the majority of his contemporaries. It was the high point of the reaction against [886] Descartes' ideas, a reaction actively pursued in metaphysics and dynamics by Leibniz, and in celestial mechanics and optics by Newton. The storm swept away the reduction of material substance[5] to extension together with the conservation of the amount of movement, the explanation of heaviness by vortices as well as the undulatory theory of light. The Cartesian hypothesis about the nature of heat also disappeared in this storm. It was accepted that heat is a fluid.

This fluid was distinguished from all other known substances by being deprived of weight. When penetrating a body, heat does not make it heavier, and on leaving it, it does not make it lighter. If a calcined metal increases its weight, that is not because it stores heat, but because the oxygen of the air is combined with the heated metal. This was definitively established by Lavoisier in 1772.

Although without weight, caloric fluid does at any rate possess all the other essential properties of bodies. Placed in the presence of another body, it can

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[5] *substance.*

penetrate the other substance in every direction and mix with it in the manner of a menstruum rather than entering into combination with it. It can also combine as an acid combines with an alkali.

When a certain amount of heat penetrates a body, a part of this heat remains in the free state, dispersing itself in the spaces left between the material molecules like a gas spreads into the pores of a porous substance. It is this pressure which pushes the molecules of ponderable substance apart in such a way as to dilate the substance. It is the greater or smaller value of this pressure that the rising and falling of the mercury in a thermometer denotes, showing the higher or lower degree of temperature. It is this pressure which acts on our organs and produces the sensation of heat. This pressure exerts effects on bodies like those produced by the pressure of a gas. According to Montgolfier, as Prévost tells us, when the powder is ignited in the soul of a canon, the large amount of heat which is suddenly produced combines its pressure with the pressure of the gas released to violently force out the cannonball from the gun.

Another part of the heat which penetrates a body is combined with the molecules which compose the body. This part loses its pressure on combination, just as oxygen loses its pressure when united with a metal, and being deprived of pressure, it [887] remains without effect on a thermometer and on our senses. This is latent heat.

This combination of fluid caloric with the molecules of ponderable matter is compared, in all respects, by physicists with chemical combination. When the revolution which Lavoisier brought about made it necessary to create a rational chemical nomenclature, the committee charged with the task of fixing this nomenclature did not forget the material to which the effects of heat are due, and their name *caloric* was universally adopted. All works dealing with the new science treated caloric just as they treated oxygen and muriatic acid. Lavoisier's *Elementary Treatise on Chemistry* begins with a chapter *on the combinations of caloric and the formation of elastic aeriform fluids*. Such phrases as the following are to be read in Berthollet's *Chemical Statics*: "Just as it requires different amounts of acids to produce the same degree of saturation with different bases, so are different amounts of caloric required to produce the same degree of saturation in different bodies, or, what comes to the same, to raise a given temperature to another determinate temperature." "When caloric produces the liquefaction of solid bodies, it acts as a solvent and, from that point of view, it can assimilate them."

Soon chemists wanted to penetrate further into the constitution of this substance, and the divergences between them on this subject were striking. Lavoisier regarded caloric as a simple substance and in 1781 protested with vehemence against Scheele who, considering heat as a combination of vital air and phlogiston, would "take away from fire and light the quality of an element which has been attributed to them by philosophers both ancient and modern." De Luc, on the other hand, following Trembley and Le Sage, regarded fire as a substance composed of light and another element which Prévost called the *base of fire*. The same De Luc thought that "electricity is decomposed by too much density and manifests its most immediate ingredients: light, fire and a substance with a phosphoric odour." But these divergences did not shake the belief in a caloric fluid and, in 1803, Berthollet could conclude an exposition of the reasons militating in favour of this belief with the following phrase which was not disowned by the most illustrious and prudent physicists of this time: "Should anyone not be willing to regard this conformity between the properties of caloric and those of a substance which enters a combination as a rigorous proof of its substantial existence, he [888] cannot refuse to agree that the hypothesis of its existence has no drawback, but does have the advantage of introducing into the explanations of phenomena only general and uniform principles."

V

The air that the open lips gently exhale has the warm temperature it has taken up in the lungs; when, on the other hand, it is greatly compressed, and escapes from the mouth in a powerful breath, the air is cold. The two contrary effects—is it necessary to say?—have been noticed ever since antiquity. The passer-by, guest of the satyr, makes the most of them:

> The one cools my soup,
> The other warms my fingers.

The satyr is content to throw out of his lair this strange being

> whose mouth
> breaths warm and cold

More curious than the satyr, physicists at the beginning of the nineteenth century wished to calculate the cooling felt by a mass of air when it expands, thereby creating the branch of science we today call thermodynamics.

The observation which served as the point of departure for these researches is due to Cullen. When a vacuum is created in a container with the aide of a pneumatic pump, the rarefying of the air cools it. Cullen, and Nollet after him, attributed this phenomenon to the humidity of the apparatus in which it appears and regarded it as the cold produced by the evaporation of water. Lambert, in his *Pyrometry*, was the first to consider it as a proper effect of the expansion of air. De Saussure, in his *Hygrometry*, accepted Lambert's view and the support of experimental predictions. He showed that when depressurising air, dried by potassium so that a hygrometer indicated the highest degree of dryness, with a pneumatic pump, the decrease in temperature noticed by Cullen is still obtained. "But these physicists," wrote Desormes and Clément, "skilful as they were, hardly suspected, in all probability, the significance of Cullen's little observation. It was left to Dalton to draw attention to this phenomenon with some remarks of great subtlety."

Dalton [889] studied not only the cold produced when air is rarefied in a container, but also the heat which it releases when allowed to enter a reservoir which is empty or filled with air at a low pressure. He thought, on the strength of the speed of assent of the thermometer, that he produced momentarily in this experiment a temperature well over what the instrument was capable of indicating. He assured himself that the heating of the mass of air attained at least 28°. This observation, together with others Dalton published in 1802, led him to maintain that the calorific phenomena produced by the compression and depressurising of gases would be the subject of a very important department of the science of heat.

Laplace lived in Arcueil, his residence bordered on that where Berthollet had established his laboratory. A garden without fences connected them. Laplace and Berthollet put together the fruits of their thoughts. *Chemical Statics*, like *Celestial Mechanics*, bore traces at many points of this fruitful collaboration which was later to result in the *Mémoires de la Société d'Arcueil.* Laplace who had from 1783, together with Lavoisier, written the immortal *Memoir on Heat*, never lost interest in the research which aroused the interests of physicists in the heating of gases by compression. Finally, he included a short note in Berthollet's *Chemical Statics* whose two pages contained one of the most important conceptions in the theory of heat. At first these ideas went unnoticed. Desormes and Clément did not cite this note from *Chemical Statics* in their great work published in 1812. Physicists were all startled when [it transpired that] Laplace had developed these ideas completely in *Celestial Mechanics*.

At this time there was a young chemist working in the laboratory at Arcueil, Gay-Lussac, "whose talents," Berthollet said, "are a great help to me in particular." In order to test a hypothesis of Laplace's, Gay-Lussac had already shown that all gases expand equally under an equal rise in temperature, and this discovery illustrated it, although Dalton had acquired priority in a work then little known by French physicists. Gay-Lussac had, in Berthollet's laboratory, under the eyes of Laplace who, no doubt, inspired his work, conducted an experiment which laid one of the foundations of the theory of heat.

Two balls of 12 litres, the one full of air and the other empty, each enclosing a very sensitive thermometer, were brought into communication. The [890] air escaped from the one ball and entered the other, so that it expanded in the first and was compressed in the second. In the first, the temperature fell, and it rose in the second. The contrary effects were already known, but—and this is the essentially new result of Gay-Lussac's experiment—the fall in the thermometer in the first ball is exactly equal to the rise in the second. The decompression of the gas in the first ball absorbs a certain amount of heat, while the compression of the gas in the second releases precisely the same amount, so that the entire experiment is accomplished without the gas releasing or receiving the least amount of heat from bodies in the environment.

Gay-Lussac published this observation in 1807, in the *Mémoires de la Société d'Arcueil*. He added a remark suggested by Laplace: a gas which increases its volume is cooled if not provided with heat. To maintain an invariable temperature when it is expanded it must be provided with a certain amount of heat. A given mass of gas therefore contains, at a given temperature, more caloric as the volume it occupies is increased. Let us take, then, two masses of a gas at 0°—of air, for example—occupying equal volumes. Evidently, these two gases contain equal amounts of caloric. Take these two masses of air to the temperature of 100°, but exert on one of them, during the heating, a gradually increasing pressure so as to prevent any increase in volume. The other is allowed to expand freely under an invariable pressure. At 100° the second occupies a much greater volume than the first. It therefore contains a much larger amount of caloric. Thus, in order to raise the temperature of the two masses of air by the same number of degrees, it is necessary to provide unequal amounts of heat. The second requires more heat than the first. In other words, the specific heat of air heated *under constant pressure* is greater than the specific heat of air heated *at constant volume*. Few propositions among those stated in physical theories and been as fruitful in consequences as this.

VI

The determination of the specific heat of gases appeared, in consequence of the research just mentioned, as [891] one of the most important problems that could be put to experimental physics, and this question was also announced as a competition by the Institute. In September, 1812, two manufacturers, Desormes and Clément, submitted a memoir to the judges of the competition. Not content to make known a certain number of specific heats of gaseous substances, they developed, by reason and experiment, the ideas of Lambert and Dalton concerning the thermal phenomena which accompany the changes of volumes of gases. Because of the novelty and peculiarity of the ideas they proposed on the subject of temperature, their work attracted "the disfavour of the commissioners of the Institute," who awarded the prize to the memoir of Delaroche and Bérard which only contained experimental determinations of specific heats. These determinations were not, however, more exact than those which Desormes and Clément had achieved. It was only in 1819 that Desormes and Clément published the piece that they submitted to the Institute in 1812, in the *Journal de physique, de chimie et d'histoire naturelle*. This memoir, entitled *Experimental determination of the absolute zero of heat and of the specific caloric of gases*, deserves our attention.

The calorimetric method conceived by Black permits the measurement of the amount of caloric gained or lost by a body when in undergoes a transformation of a well-determined nature: heating or cooling a certain number of degrees, fusion or freezing, vaporisation or condensation. But what is the amount of heat contained in a given body in a given state? How much caloric is there, for example, in a kilogram of water at the temperature of melting ice? That is a question which the ordinary methods of calorimetry provide no way of solving.

Dalton was the first to tackle this question, followed by Desormes and Clément. They proposed to determine the absolute value of the mass of caloric contained by a given body at each temperature, and consequently, to determine at which temperature the body would no longer encapsulate any amount of caloric. Having reached this state, the body would not be able to cool further; it would have reached the *absolute zero* of temperature. If we suppose all bodies brought to this point where they contain no more caloric, Desormes and Clément say, "A very different image of nature would remain for us from that we have before us. Not only would life no longer exist in this dreary universe we are trying to describe, [892] but all kinds of movement on the earth would cease. There would no longer be an atmosphere, no longer any flowers, no longer any seas, only immobility and death everywhere."

"To determine the distance from this very singular state in which our minds could strip bodies of all sensible heat, to that which we habitually live, and express this distance in ordinary degrees of the thermometer, or rather to fix the absolute zero of temperature—that is one of the most interesting problems that our curiosity could wish."

Which body was it whose absolute heat content Desormes and Clément proposed to determine? The circumstance that all bodies have the property of dissimulating, in the latent state, greater or lesser amounts of caloric makes it very difficult to measure the total amount of heat they conceal. In order not to have to reckon with latent caloric, Desormes and Clément were going to appeal to vacuum [where] material molecules no longer exist, and it need not be feared that a part of the caloric remains combined with them.

It remained to determine, at each temperature, the caloric in a space empty of air. But before this determination can be contemplated, it is necessary to fix the thermometer which will report the temperature because the number that is called temperature has no sense if the scale on which it is read has not been defined. It is still a space empty of all ponderable material which will serve to define the temperature. Such a space contains no caloric fluid. It contains all the more as it becomes warmer. Let us agree to take a number proportional to the pressure acquired by the caloric fluid in a space empty of air as a measure of the temperature, and chose the coefficient of proportionality in such a way that it passes over one hundred units when it moves from the point of fusion of ice to the boiling point of water. We have then obtained what Desormes and Clément call the *absolute temperature*.

But this thermometer is purely abstract. What real apparatus do we know which could give, exactly or approximately, the readings of this ideal instrument? Desormes and Clément assume that the number of degrees through which a centigrade thermometer, whether it be of air or mercury, rises or descends between the temperature of melting ice and the temperature of boiling water is practically the same as the number of degrees the absolute temperature rises or falls.

The caloric fluid is a compressible and elastic fluid, comparable [893] on all points to a gas. The law first discovered by Boyle and Townley, then by Mariotte, could be applied to it. The density of such a fluid is proportional to its pressure, or in other words, the amount of caloric enclosed within an empty space of given volume is proportional to the absolute temperature. If, therefore, we determine the amount of caloric contained in an empty space of given volume at two points of the thermometric scale separated by a determinate number of degrees—for example, at the fusion point of ice and the boiling point of water—then a simple calculation will tell us which numbers correspond to these two points on the absolute scale and what amount of caloric the empty space considered contains for each degree of this scale.

But how is the amount of caloric enclosed within an empty space at the fusion point of ice, for example, to be determined? Suppose a determinate amount of air is allowed to enter this empty space; it will be warmed. Following Leslie and de Saussure, and Dalton, Desormes and Clément attributed the warming of the air to the absorption of caloric enclosed within the empty space. This experiment therefore provides us with the means of evaluating this caloric by a true method of mixtures.

To apply this method, it is necessary to know the specific heat of air, which was determined by the experiments of Desormes and Clément and those conducted at the same time by Delaroche and Bérard. It is also necessary to know the temperature acquired by the air introduced into the container, and this reading is very difficult to obtain. Radiation and conduction quickly dissipate the gain in heat. A mercury thermometer, whose mass is considerable, is too slow in coming to an equilibrium temperature with the air, and cannot indicate with any precision the initial heating. Desormes and Clément had the ingenious idea of requiring the introduced air itself to indicate the temperature to which it is taken; the reading of the pressure attained immediately after its introduction into the bulb provides this indication.

But the experiment that we have just described is still only an ideal experiment. In reality, the bulb which Desormes and Clément, following Dalton, allowed the air to enter is not an empty bulb. It is a bulb already enclosing some air at a pressure less than that of the atmosphere. Little matter; the measure of the amount of heat released during the rapid compression of any mass of air from the amount of heat absorbed in the sudden expansion of an aeriform fluid allows the evaluation [894] of what caloric there is in a given volume of space empty of all ponderable material at a given temperature.

Consider the experiment conducted by Gay-Lussac in 1807. What do we see at the beginning of the experiment? One volume full of air, and an empty volume, each enclosing a determinate amount of caloric. What do we see at the end? All the space is filled by a mass of air which was contained in the full bulb, and its temperature is that which it had in this bulb. The system has passed from one state to the other without absorbing or releasing any caloric. Therefore, if, as Gay-Lussac remarked, the rarefied air encloses, at the same temperature, more caloric than the condensed air contained, then the gain in caloric that he had seen is precisely equal to the amount of caloric contained in the empty space that it was going to occupy: "caloric seems to belong to space." A gas which is rapidly decompressed cools because, in order to return to its original temperature, it must be provided with the mass of caloric which is contained in an empty space equal to its increase in volume. A rapidly compressed gas is warmed because, in order to prevent its temperature varying, it would be necessary to remove an amount of heat precisely equal to that contained in an empty space equal to the contraction which it has undergone: "It is the reduction in volume, the disappearance of space, which abounds in caloric." The experimental study of thermal phenomena which accompany the rapid decompression or condensation of a gaseous mass would therefore make known the mass of caloric which fills a given empty space at the temperature of the experiment. Repeated within an enclosure surrounded by melting ice, and in an enclosure surrounded by the vapour of boiling water—enclosures whose temperatures, by definition, differ by one hundred degrees absolute—it would give us knowledge of the absolute zero of temperature.

Desormes and Clément thus found that the absolute zero of temperature was, on the ideal thermometer, 267.50° lower than the fusion point of ice. In other words, ice melts at the absolute temperature expressed by the number 267.50° and water boils, under atmospheric pressure, at the absolute temperature expressed by the number 367.50°.

Desormes and Clément sought to confirm this essential result by other methods. We cite only the most important.

Each time that the centigrade temperature falls one degree in the range between the boiling point of water and the fusion point of ice, a mass of air or an aeriform fluid subjected to a constant pressure contracts by the same fraction of the volume that [895] it would occupy in melting ice. This fraction has been determined by Gay-Lussac to be 1/266.66.[6] If gases preserve some invariable properties while they are cooled, it would suffice to reduce the temperature some 266.66° below the temperature of melting ice to reduce their volume to nothing. This point therefore marks the extreme limit of cooling that it is possible to impose upon a gas, the absolute zero of temperature. The absolute temperature of melting ice, equal to 267.50° according to the first method, would be 266.66° according to the second. "We recognise," Desormes and Clément declared, "that so singular a concordance is for us a powerful reason to believe in the precision of our conclusion."

The importance of the nouvelle ideas introduced into the theory of heat by Desormes and Clément cannot be better appreciated than to subscribe to the judgement that they imparted on their own work in 1819:

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[6] After Regnault's investigations, it was approximately equal to 1/273.

"The solution to the problem to which we drew the attention of physicists is, perhaps, as important for the understanding of the phenomena of heat as was the response of Galileo to the pompous men of Florence for [understanding] the theory of atmospheric phenomena."

VII

It is difficult to determine the extent to which the conceptions of Desormes and of Clément could have influenced the development of Laplace's ideas. On the one hand, the note that Laplace inserted in 1803 in Berthollet's *Chemical Statics* shows him to be, from that time, a master of the principle on which his theory of heat rests. On the other hand, the complete development of this theory, as it is unfolded in volume V of *Celestial Mechanics*, published in 1823, offers analogies with the views of Desormes and Clément too numerous and profound for it to be possible to disregard their influence, all the more so since Laplace cites the research of these two experimentalists and makes use of the numerical results they obtained.

Laplace distinguishes in all bodies, first, the molecules of material, second, the latent caloric combined with the molecules of material, and third, free caloric. The molecules of material attract one another, like the stars in the sky, but follow a different law. The molecules of material also attract particles of free caloric and [896] are attracted by such particles. Finally, the particles of free caloric repel one another. As for the molecules which compose latent caloric, Laplace attributes to them neither attraction nor repulsion.

By virtue of the attraction which they exert of the particles of free caloric, the ponderable molecules condense the greater part of the caloric which forms a kind of atmosphere around each of them. Other ponderable molecules and their atmospheres of caloric exert an action on the atmosphere of each molecule which detaches fragments from it. These torn fragments wander in the intermolecular space until another molecule attracts them and absorbs them into its atmosphere. When the state of a body becomes invariable, the atmosphere of each molecule allows, in unit time, a mass of caloric to escape equal to that it gains hold of during the same time.

All the attractive and repulsive forces at play in the interior of a body are only felt at inappreciable distances. Beyond a very small radius of activity, they become negligible. But, although this radius of activity is always extremely small, its size varies with the category of actions that are considered. The repulsion of caloric for caloric is felt much further than the attraction of one ponderable molecule on another ponderable molecule or on a fragment of free caloric.

In the interior of gases and very rarefied vapours, the ponderable molecules are very distant from one another. The attraction which these molecules exert on one another can thus be neglected, as well as the attraction exerted by each of them on the calorific atmospheres which surround their neighbours. In the interior of a similar body, only two kinds of actions come into play in any appreciable way, the attractive action that each ponderable molecule exerts on the free caloric condensed around it, and the repulsive action that the various parts of the free caloric exert on one another.

These hypotheses, together with some simple assumptions about molecular radiation, constitute the basis of the theory developed by Laplace.

From this theory it followed, first of all, that at constant temperature the density of a gas is proportional to the pressure that it supports. This is the law discovered experimentally by Boyle, and then rediscovered by Mariotte. Besides the note inserted in *Chemical Statics*, we see that this same law has guided Laplace in the choice of hypotheses.

It [897] also follows from this theory that at a given temperature, the amount of free caloric contained in a mass of gas is proportional to the volume occupied by this mass of gas. This proposition, which Laplace had established by 1803, Desormes and Clément had also deduced from their principles. But Laplace rejected their principles. For Desormes and Clément, "caloric seems to belong to space." The caloric contained in a gas is of a precisely equal amount to that which fills a space of the same volume at the same temperature. The experiment conducted by Gay-Lussac in 1807 seems to provide a satisfactory demonstration of this view. According to Laplace, on the other hand, the caloric fluid spread throughout a space empty of all ponderable material is "very rare." It is "an insensible part of the heat contained in the body, as is recognised from the experiments that have been conducted to condense this heat." How, if Laplace's ideas on this point are accepted, is it possible to explain the experiment of Gay-Lussac, which seems to agree so naturally with the hypotheses of Desormes and Clément? The air which doubles in volume during this experiment should, at the end, enclose twice the amount of caloric that it enclosed at the start according to Laplace's theory. The experiment shows that no amount of heat is taken from the environment. If, then, the excess of caloric which is acquired in expanding is not to be found beforehand in the empty space that it fills, from where can this excess have been taken? The author of *Celestial Mechanics*, who does not cite Gay-Lussac's experiment although it was performed before his eyes, remained silent on this subject.

Although the caloric fluid that fills a space empty of all ponderable material is extremely rare, its density is, however, not zero. The density is as great as space is warm. It is natural the chose this density—or a number to which is proportional—to register the *absolute temperature.*

Now Laplace's theory demonstrates that the pressure acquired in each circumstance by a mass of air maintained at constant volume is proportional to the absolute temperature to which it is taken in this circumstance. The relation of absolute temperature between containers is equal to the relation between the acquired pressures in these two containers by the air thermometer at constant volume. The absolute temperature is determined by Laplace according to the rule proposed in 1702 by Amontons: "The air thermometer thus becomes the true thermometer which should serve as a model for others, at least within the limits of pressure and density [898] where this fluid obeys the general laws of elastic fluids very closely." If it is agreed that one hundred degrees on the absolute scale correspond to the interval of temperature which separates the fusion point of ice and the boiling point of water, the absolute temperature of melting ice would be 266.66°. The definition of absolute temperature which Laplace adopted is identical with that proposed by Desormes and Clément.

As for the determination that physicists had given to the amount of heat contained in empty space, we have seen that Laplace rejected the principle. Did this mean that the experiments conducted by Desormes and Clément aimed at obtaining this determination had become useless? Not at all. The results the these experiments still had a clear sense and provide the theory of heat with precise information. They provide knowledge of the amount of caloric that is released by a certain mass of air when it is rapidly compressed. This caloric is that which must be taken away from this mass of air if it is to be subjected to the same diminution in volume, while maintaining its temperature invariable throughout. Knowing this amount, we know, by the same fact, how the heat contained in a gas varies when made to vary its volume without varying its temperature. We can then calculate the excess of specific heat of a gas heated at constant pressure over the specific heat of the gas heated at constant volume. The experimental determinations of Delaroche and Bérard, and of Desormes and Clément, provided Laplace with the first of these two specific heats. Desormes and Clément, when studying the thermal effects of rapid compression of gases, and Gay-Lussac and Welter, pursuing analogous research on expansion, provided him with the means of calculating the second. He found that the relation between the specific heat at constant pressure and the specific heat at constant volume was, for atmospheric air, equal to 1.375. Later, very precise experiments raised the value of this relation to approximately 1.40.

VIII

The numerical determination of this relation was, for Laplace, of great importance. It allowed him to achieve a solution of a question which had confounded the efforts of the greatest geometers since Newton, namely the calculation of the speed with which sound is propagated in air and other gases.

Newton had indicated a simple rule for calculating this speed: [899] that the pressure of the gas be divided by its density. This yields a number equal to the square of the speed with which sound is propagated in a pipe filled with the gas. This rule does not agree at all with the experimental determinations of the speed of sound: it provided a smaller value than was given by experiment, the gap between them being approximately a sixth of the observed value. Experimental error was not sufficient to account for the considerable discrepancy, and Newton's formula was certainly inexact. Where does this inexactitude come from?

Newton had arrived at the rule just stated by an obscure argument. Several geometers thought that a more exact calculation would provide a different rule, but Lagrange, and Euler after him, showed that this view must be rejected. A correct integration of the equations which govern the small movements of a mass of air led them to rediscover, in the case where these movements are propagated by plane or spherical waves, the expression for the speed of sound proposed by Newton. Newton's error was not, therefore, a fault of algebra. It must lie in the hypotheses which the author of the *Principia* had adopted.

Newton assumed that the density at each point of a mass of air traversed by sound is proportional to the pressure at that point. Lagrange remarked that this hypothesis could be modified in order to make the discrepancy between the calculated and the observed speed of sound disappear; it suffices to suppose that the pressure is not in fact proportional to the density, but to a certain power of the density, the exponent of which was approximately 1/3. But what plausible reason, other than the desire that theory should accord with experiment, could be invoked to justify this change of hypothesis? Hadn't the experiments conducted by Boyle, Mariotte and several other physicists shown that there is a constant relation between the density of a gas and the pressure which it supports?

Laplace discovered the reason why the law of Boyle and Mariotte should not be applied to the parts of a gaseous mass which has been made to vibrate. The legitimate application of this law requires that the temperature of a gas remains invariable at each point, but this condition is not fulfilled while the sonorous movement is propagated in a mass of air. Each gaseous particle is alternately condensed and dilated, and condensation releases heat while dilation absorbs it. These alternatives succeed one another very rapidly and [900] are reproduced for each particle a great number of times per second. A gaseous particle does not, therefore, have the time to give up the heat released by compression to the surrounding fluid, nor to take up the heat absorbed by dilation. The result is an incessant variation of temperature, rising as the density is increased, and falling as the density diminishes. Boyle's and Mariotte's law relating the pressure and density of a gas at constant temperature is not the law which should be applied to this particle. The relation of dependency of the density on the pressure in this case is that which expresses the complete absence of any heat exchange between the particle and the material of the environment. Laplace indicated which relation this was; it takes the form Lagrange predicted if the two specific heats of the gas are supposed constant. It establishes a constant relation between the pressure and a certain power of the density, the exponent of this power being none other than the ratio of the specific heat of the gas at constant pressure to the specific heat of the gas at constant volume. The various experiments that had been conducted led Laplace to attribute this ratio the value of 1.375. It exceeds the value Lagrange proposed by only a small amount.

Since 1803, Laplace wrote in connection with the heat produced by the compression of a gas, "The heat thus released has a noticeable effect on the speed of sound. It produces the excess in speed compared with that given by the usual theory, as I have ascertained by calculation." In 1807, Poisson developed this remark of Laplace's in a beautiful memoir entitled *Theory of sound.* Finally, he published the rule which should be substituted for Newton's to calculate the speed of sound in 1816, which he stated as follows:

"The speed of sound is equal to the product of the speed given by the Newtonian formula and the square root of the ratio of specific heat of air at constant pressure and the specific heat at constant volume."

It was vital that a comparison be made between this new rule and experimental results, for which purpose they were determined again in very precise fashion, taking account of the pressure, temperature and hygrometric state of the atmosphere in which sound was propagated; "for if precise observations had given birth to a theory, the perfection of theory prompts, in turn, the precision of observations." In response to Laplace's request, the Bureau des Longitudes made a fresh determination of the value of the speed of sound, while Gay-Lussac and Welter, on the one hand, and Desormes and Clément on the other, undertook once more the careful determination [901] of the ratio of specific heats. The speed of sound as calculated from Laplace's formula was equal to 337.715 meters per second, and the observed speed was 340.889 meters per second. The errors inevitably arising in such a complete assemblage of experiments was easily sufficient to explain the discrepancy of 3.174 meters between these two values.

This rather perfect numerical agreement, resolving a problem which had long embarrassed physicists, provided a precise confirmation of Laplace's theory. Moreover, this theory took its place within the harmonious collection which formed the various branches of mathematical physics at the beginning of the century. It returned the study of heat to the analysis of attractive and repulsive forces like those accounting not only for the movement of the stars, but also the effects of optics, electricity, magnetism elasticity and capillarity. The number and extent of the laws embracing this vast synthesis—the clarity of the hypotheses on which they were based, the perfection and elegance of the analytic methods which served in their development, the splendour and precision of the confirmations with which experiment supported their boldest predictions and their most detailed formulas—excited the enthusiasm of geometers and philosophers. Never had the human mind believed it had come closer to divining the entire system of nature, of discovering the equations which determine the trajectory of the smallest atom as well as the orbit of the largest star. No one, when reading the lines with which he concluded the exposition of his theory of heat, could accuse Laplace of exaggerating the importance of the results he had obtained:

"The phenomena of the expansion of heat and the vibrations of gases are reduced to the attractive and repulsive forces which are only effective at imperceptible distances. In my theory of capillary action, I reduced the effects of capillarity to such forces. All terrestrial phenomena depend on this kind of force, just as celestial phenomena depend of universal gravitation. The consideration of such forces seems to me to have now become the principal object of mathematical Philosophy."

II

The Creators of Thermodynamics*

I

When Laplace, a young man of twenty-eight years, enlivened by his personal meditations on the theory of heat, proposed to physicists the investigation of molecular attraction—the ultimate explanation of terrestrial phenomena by Newtonian attraction is the ultimate cause of celestial movements—he was revealing one the greatest discoveries to which natural philosophy had ever given birth. The science whose first principles he proposed would destroy the caloric hypothesis and supplant it with the doctrine of molecular attraction. It would, so to say, pour physics into a new mould, and finally force it to become aware of the true import of its methodology and of the exact sense of its laws.

In 1824 Sadi Carnot published his *Reflections on the motive power of heat.*

Sadi Carnot declares somewhere in this brochure that he assumes his reader is "familiar with the latest progress in modern physics relating to gaseous substances and heat." He certainly had a detailed knowledge of this progress, to which the number of references to the writings of Laplace, Poisson, Desormes and Clément, Gay-Lussac and Welter bear [381] ample witness. However, although the researches of these great geometers and physicists were a great help to him in developing the consequences of his discovery, it must be said that the first idea of this discovery had not been suggested by any of his precursors. His own reflections were to germinate within his own mind.

At this time, the more widespread use of heat engines gave rise to numerous attempts to modify these contraptions in order to make them deliver more work while using less combustion. One proposal was to substitute water by a liquid, ether, for example, whose vaporisation absorbed less heat. Another proposal was to make use of the expansive force of gases instead of employing the pressure of the vapour emitted by a liquid. Guided as they were by confused and incomplete ideas about the theory of steam engines, these attempts often made for bitter disappointments and ruinous set-backs for their inventors. The absence of any proper theory which could enlighten the engineer who wished to perfect thermic motors, of

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* Originally published as Part II of "Les Théories de la Chaleur" with the subtitle "Les Créateurs de la Thermodynamique," *Revue des deux mondes*, 130 (1895), 380-415.

any rule capable of confining the ambitions of the inventor within reasonable limits, made a deep impression on Carnot. What cause had up to then prevented the blooming of a theory? Why is the engineer abandoned to the most inaccurate conceptions and the crudest empiricism? It is because "the phenomenon of the production of movement by heat has not been considered from a sufficiently general point of view. It has only been considered in engines whose nature and mode of action do not permit it to take on all the extension of which it is capable. The phenomenon is found to be truncated in some way and incomplete in such engines, and it becomes difficult to recognise its principles and study its laws."

In order to gain a clear view of the configuration of a massif of mountains, it is necessary to climb to the highest, from where the eye surveys all the peaks in the chain. Similarly in physics, the surest way of sorting out a complicated problem nearly always consists in contemplating it in all its fullness and generality. "To envisage the principle of the production of movement by heat in all its generality, it is necessary to conceive it independently of any mechanism, of any particular agent. It is necessary to establish from reasoning applicable not only to steam engines, but to all heat engines imaginable, whatever the nature of the substance implemented could be, and in whatever manner it can be acted upon."

How could this very general heat engine that Sadi Carnot would study be constituted?

Suppose [382] a mixture of water and water vapour is taken to a temperature of 120° and under a pressure of two atmospheres, which is the pressure of the saturated vapour at this temperature. Imagine that under this same pressure of two atmospheres and, consequently, at the fixed temperature of 120°, all the water which was liquid passes into the vapour state. The system which undergoes this transformation absorbs heat provided by a certain *source*, a certain *furnace*.

Suppose now that the steam thus generated is placed in a cylinder rendered impermeable to heat, and that it is expanded by pushing back a piston which forms one end of the cylinder. This expansion, produced under conditions which prevent the steam taking up heat from the surroundings, will reduce the temperature. Suppose the pressure of the steam is allowed to decrease until the temperature of the system reaches 100°. The pressure of the steam is now equal to one atmosphere.

Then suppose that under this constant pressure of one atmosphere and, consequently, at the constant temperature of 100°, a part of the steam is condensed to the liquid state. During this condensation heat is given up to external bodies, which act as a source of cold, as a *cooler*.

Finally, suppose the system is reintroduced into a cylinder impermeable to heat and, by compression, the temperature of the mixture of water and steam is elevated in such a way as to bring it back to exactly the state in which it was found at the beginning of this series of modifications.

The sequence of operations just carried out on the water and the water vapour can be accomplished with another liquid in contact with its vapour, or with a non-liquifiable gas, or with any other substance. The details of the modifications undergone by the system change, but they have all retained the same essential characteristics, which are as follows:

In the first place, the sequence of transformations brings the system back to exactly the same state that it presented before undergoing the first of them. This sequence of transformations is closed, so to say, on itself; it constitutes what is called a *cycle.*

In the second place, this closed sequence of transformations, this cycle, comprises two modifications each brought about at an invariable temperature—they are called *isothermal* changes—and two other modifications each of which is brought about in a container which is impermeable to heat—called the *adiabatic* changes.

Of the two isothermal changes, that which is conducted at the [383] higher temperature is accompanied by the absorption of a certain amount of caloric given to the system by a hot source, a furnace. The one produced at the lower temperature is accompanied by the release of a certain amount of caloric, given up by the system to a cold source, to a cooler. Naturally, the system takes just as much heat from the furnace as it gives up to the cooler because, on returning to its initial state after running through the cycle, it should enclose the same mass of caloric that it contained before embarking on the cycle. Moreover, for each of the two adiabatic changes, the system is completely isolated from external bodies and unable to gain or lose heat.

This, according to Carnot, is the sequence of operations which are reproduced indefinitely in an ideally perfect heat engine which is realised more or less crudely by the engines employed in industry. This sequence of operations is now called the *Carnot Cycle.*

The production of work by a heat engine is seen to be intimately connected with the transport of a certain amount of caloric from a furnace to a cooler whose cause is the restoration of equilibrium in the caloric. Just as water can only turn a mill or a turbine on condition that it descends from a higher level to a lower, so heat can only generate motive power provided that it passes from a hot body to a cold body.

It is possible to reverse a Carnot cycle, for example the particular cycle which we have described in detail. It is possible to vaporise water under the pressure of one atmosphere and at the fixed temperature of 100°, to compress the vapour produced in a cylinder impermeable to heat until it has attained the pressure of two atmospheres and a temperature of 120°, then under this pressure to condense a part to the liquid state and finally to let the system expand in a cylinder impermeable to heat until it regains its original state. The system would then absorb a certain amount of heat while it was maintained at the temperature of 100°, heat which it would restore while it was at the temperature of 120°. It would transport caloric from a cold body to a hot body. But although this transportation would be accompanied by the production of motive power, that could only be obtained by *forcing* the system to describe the reverse cycle by dispensing motive power. It is just the same as not being able to raise water which has fallen from a lower position to a higher position without dispensing a certain amount of work.

A [384] certain Carnot cycle, described between temperatures of 120° and 100°, has the effect of transporting a certain amount of caloric taken from a body whose temperature was 120° to another body whose temperature is 100°. At the same time, it provides a certain amount of work. If the same cycle is reversed, a new cycle is obtained which would raise up from the temperature of 100° to the temperature of 120° exactly the same amount of heat that the first cycle made descend from 120° to 100°. In addition, the new cycle consumes exactly as much motive power as the first cycle produces.

With these preliminaries established, we come to the major proposition stated by Sadi Carnot:

Consider all the cycles that can be described between two given temperatures, for example between the temperature of 120° and the temperature of 100°. Whatever the nature of the substances used in these cycles, and whatever variety of force to which it is subjected or machinery that it puts into action, a given amount of caloric transported from the furnace to the cooler will give rise to a certain amount of motive power. There is no advantage in substituting one of these cycles for another; they are all equally *efficient.*

How did Carnot demonstrate this proposition which seems so paradoxical at first sight?

Imagine two cycles described between 120° and 100°, the first more efficient than the second. While these two cycles transport the same amount of heat from the furnace to the cooler, the first produces more work than the second. Suppose the engine described in the first cycle be put to work and a part of the work it produces drives in reverse the engine constructed in accordance with the description of the second cycle. There remains a certain amount of disposable work, the excess of work generated by the first cycle over and above the work which would be produced in the second cycle if it were followed in the direct sense, but which it consumes when it is traversed in the inverse sense. Then, the second engine would take a certain amount of caloric from the cooler to the furnace precisely equal to that transported by the first from the furnace to the cooler. After these two simultaneous operations the furnace and the cooler would both be found in their initial states exactly. It would therefore be possible to reproduce this same sequence of operations indefinitely, generating the same amount of work at each revolution. "This would not only be a perpetual motion, but the creation of an indefinite motive force without the consumption of caloric or any other agent. [385] Such a creation is entirely contrary to received ideas up to the present, to the laws of mechanics and of sound physics; it is inadmissible."

According to Sadi Carnot, as we have seen, an engine functioning in accordance with the ideal cycle that he imagined is the best heat engine that can be constructed. It is therefore possible to state the following proposition:

"The maximum motive power that can be developed by a determinate amount of heat is independent of the means by which it does so and of the substances employed to produce this motive power. This maximum is uniquely fixed, in the last analysis, by the temperatures between which the transport of caloric is conducted."

II

This proposition was rich in consequences. The engineer seeking to perfect a heat engine working between two given limits of temperature no longer needs to pay any attention to the nature of the substances which compose the engine. Replacing one substance by another does not affect the size of the utilisable effect that can be obtained. What he must change is the transformations to which these substances are subjected. They should be modified so that together they approach the Carnot cycle as closely as possible. Substituting ether for water in a steam engine does not change the value of the maximum efficiency that can be expected of this engine. What he must study, if he wants to obtain an efficiency close to the maximum, is the cycle described by the vapour at the heat source, in the cylinder and in the condenser. But let us leave aside the industrial significance of Sadi Carnot's principle, and concentrate on the consequences which arise regarding the theory of heat.

"According to the ideas established so far," Carnot says, "the motive power of heat can be nicely compared with that of a waterfall. Both have a maximum that cannot be exceeded, whatever might, on the one hand, be used by the engine to receive the action of the water, or whatever substance, on the other hand, might be used to receive the action of heat. The motive power of a waterfall depends on its height and on the amount of liquid. The motive power of heat also depends on the amount of caloric employed, as well as on what could be called, in effect, the *height of its fall*, that is, the difference in temperature between the bodies which [386] perform the exchange of caloric. In the case of the waterfall, the motive power is rigorously proportional to the difference in levels between the upper and lower reservoir. With the fall in caloric, the motive power certainly increases with the temperature difference between the warm and cold bodies, but we do not know whether it is proportional to this difference; we do not know, for example, whether the fall of caloric from 100° to 50° produces more or less motive power than the fall of this same caloric from 50° to 0°."

To solve the problem posed by Sadi Carnot in the passage just quoted, it evidently suffices to determine the work that can be generated by a unit of caloric *falling* from an arbitrary temperature to a temperature fixed once and for all, for example 0°. For, if we know the motive power developed by a unit of heat falling from 100° to 0°, and the motive power developed by a unit of heat falling from 50° to 0°, then we see without difficulty the motive power generated in falling from 100° to 50°: it would be the difference between the first two. We would also know the motive power developed by two or three units of heat falling from 100° to 50°; it would be two or three times the power produced by a unit of heat when undergoing the same fall.

The problem is reduced to that of determining the motive power developed by a unit of heat falling from a given temperature to the temperature of melting ice. This power is independent of the material in which it is developed. It may therefore be supposed, for the purposes of calculation, to be produced by means of a body whose properties are well known, for example of a gas. It was thus that Carnot was able to evaluate it. To succeed, he made a hypothesis still not justified by the experiments known at this time. He supposed that a gas heated at constant volume had a specific heat independent of the temperature indicated by an air thermometer. He could, as J. Bertrand has remarked, have done without this hypothesis, which accorded badly with his own principles.

The power thus calculated is not at all proportional to the temperature of the hot source. It depends on this temperature in a very complicated way. The motive power developed by a unit of caloric is not proportional to the height of the fall undergone by this caloric. In falling a given number of degrees, a given amount of heat produces less work as the fall is removed to more elevated regions of the thermometer.

In [387] order to pinpoint the temperature, Sadi Carnot and his commentator Clapeyron took the degrees of the air thermometer that Desormes and Clément, and Laplace, had proposed as a normal thermometer, which they thought capable of indicating, by its variations, the variations of absolute temperature. Sadi Carnot's discovery led W. Thomson to conceive of a definition and mode of determination of absolute temperature very different from the definition and mode of determination adopted by Desormes and Clément and by Laplace.

Let us suppose that the specific heat of air maintained at constant volume does not depend of the temperature read on the thermometer conceived by Amontons. The thermometer enjoys a remarkable property: each time it rises one degree, the air which it encloses absorbs the same amount of heat regardless of which part of the temperature scale it is produced in. This characteristic has seemed extremely important to all physicists who, since Réaumur, have been engaged in thermometry. W. Thomson, on the other hand, considered its significance slight. On his view, the essential characteristic that should be possessed by an absolute scale of temperature is that the degree should be defined by a property which is independent of the substance employed. Now the proposition discovered by Carnot allowed such a definition of degrees absolute to be found. If we say that the temperatures of two bodies differ by one degree absolute when a unit of caloric, *falling* from warmer to colder, produces an amount of work equal to unity, we will have the thermometric scale realising the condition required by W. Thomson.

Using this thermometric scale, the expression is immediately obtained for the amount of work that can be produced by a unit of heat in passing from a body taken at a certain temperature to another body taken at the fusion point of ice. This work is, by definition, equal to the number of degrees absolute separating the temperature of the heat source from the temperature of melting ice. A calculation, inverse to that which served to link the work at the temperature of the heat source read on the air thermometer will serve to establish the relation existing between the temperature read on the air thermometer and the new absolute temperature. There will be no equality, nor proportionality, between these two temperatures. The ideas of W. Thomson lead, therefore, to a rejection of all that Desormes, Clément and Laplace had thought about absolute temperature.

The modification introduced to the principles established by Carnot's predecessors by W. Thomson regarding the theory of [388] heat bore mainly on the form of these principles. But those who have thought carefully about these principles had already glimpsed the time when their foundation would be overthrown. Laplace's theories were difficult to reconcile with the celebrated experimental results obtained by Gay-Lussac in 1807. Carnot's ideas suggested that pressure influenced the relation between the two specific heats of gases, while the experiments of Gay-Lussac and of Welter seemed to show that the relation is independent of pressure. Prudent minds readily subscribed to Sadi Carnot's opinion. "The fundamental principles on which the theory of heat rests will need to be very carefully examined. Several experimental facts appear more or less inexplicable in the present state of the theory."

The revision of the principles of the theory of heat was made necessary by a revival of Cartesian ideas. Sadi Carnot undertook it, Robert Mayer inaugurated it and Clausius brought it to a successful conclusion.

III

The eighteenth century rejected one after the other all of the hypotheses on which the Cartesians had built physics. The theory of universal attraction had got the better of the doctrine of vortexes, and the optics of emission replaced wave optics. Yet if there is any branch of physics where the defeat of Descartes' ideas was not absolute, where the triumph of the new doctrines was not entirely assured, this is surely the theory of heat.

Newton, who was the veritable initiator of the physics of the eighteenth century, had retained ideas similar in every way to those of Descartes in application to heat. "Does not light," he said, "warm bodies by agitating them and exciting a vibratory movement of their various parts which constitutes heat? Is not the emission of light produced by the vibratory movements of hot bodies?" It required a century of investigations in physics, the explanation of electric and magnetic phenomena by the actions of imponderable fluids and the discovery of the absorption of latent heat accompanying fusion and vaporisation in order for the majority of physicists to abandon the view of heat as very small movements of material particles and agree to attribute it to a special substance. Still, their confidence in the existence of caloric was never as complete as their faith in the reality of luminous [389] corpuscles, and [even] the most convinced allowed more than one indication of doubt to slip into their writings.

Certain well established and easily stated facts—the heating of a piece of iron that is hammered, or of a body that is rubbed—seemed easier to reconcile with the Cartesian theory than with the caloric hypothesis. If the heating of a body is due to the penetration of a fluid into the body, how can the action of hammering or the action of rubbing increase the amount of caloric that it contains? If, on the other hand, heat is a very rapid agitation of the elements of a body, is it not natural that concussion and shaking brought to the exterior can increase the *vis viva* of this movement?

Descartes had already invoked the heat produced by percussion as a test of his thesis. Robert Boyle, always hesitating between the supposition which made heat a substance and that which made it a movement, took a similar argument to favour the second hypothesis. He was led to remark that when a nail is driven into a piece of wood, it is necessary to strike the nail on the head many times before the temperature of the head is sensibly warmed. The *vis viva* of the hammer traverses the nail and breaks the wood, leaving only a small fraction of this *vis viva* stored in the iron. But from the moment when the nail, driven completely into the mass of the wood, cannot advance further, a few strikes suffice to communicate to it a considerable heat. "The impulsion given by the strike of the hammer being incapable of driving the nail further or breaking it, it must be expended in the production of that internal movement which is heat."

Lavoisier and Laplace, in their *Mémoire sur la chaleur* which they read to the Institute on 18 June, 1783, presented the two theories of heat between which the opinions of physicists were divided. They recapped first the doctrine of caloric, then the hypothesis that heat is a movement. "We will not decide between the preceding two hypotheses," they said; "several phenomena seem to favour the latter, such as, for example, the heat produced by the friction of two solid bodies; but there are others which are more easily explained with the former."

If the advocates of the Cartesian theory can raise the production of heat by percussion and friction in objection against the supporters of the substantial existence of caloric, they can in turn be opposed by the absorption of latent heat which accompanies fusion and vaporisation. How can the [390] principles of Descartes explain that ice, on melting, absorbs a large amount of heat without changing temperature? This heat supplied to ice by the surrounding bodies is a diminution in the *vis viva* of movement agitating them. This *vis viva* cannot be lost; it must therefore be recovered in the water resulting from fusion, which must be warmer than the ice from which it originates—a result contradicted by experiment. But this difficulty, embarrassing for the pure Cartesian mechanism which composes bodies with parts agitated without acting on one another, disappears if it is supposed, with Newton, that the parts exert on one another attractive and repulsive actions. Any change of the state of aggregation of the parts would be accompanied by positive or negative work of the their mutual actions. If this work is positive, it will entail an increase in the *vis viva* of the molecular movement, and if it is negative, it will determine a decrease in the *vis viva*. In the latter case, a part of the heat liberated would be absorbed by the latent state; in the former, a certain amount of latent heat will again become free. The existence of latent heat, a decisive argument against the pure Cartesian doctrine, will no longer be of value in opposition to the hypothesis that heat and cold are effects produced on our organs by a certain movement, provided that this hypothesis is allied with Newton's dynamic ideas. Lavoisier and Laplace were first to recognise this: "If heat is a fluid, it is possible that, in combination with several substances, it combines with them or that it withdraws from them; but there is nothing to show *a priori* that free heat is the same before and after combination; there is nothing to show this as yet in the hypothesis where heat is only a *vis viva* of the molecules of a body, because the molecules of substances which combine and act on one another in virtue of their reciprocal affinities are subjected to the action of attractive forces which can change the amount of *vis viva* and thus that of heat."

Laplace, so prudent and reserved in 1873, was to become the most steadfast champion of the caloric theory. But although his works, together with those of Gay-Lussac, Desormes and Clément, and Poisson, enriched this theory with marvellous discoveries and assured for it the assent of most physicists, isolated thinkers continued to attribute heat to a rapid movement of material molecules and to raise against the new doctrine more and more pressing objections.

Rumford, who was the director of a foundry for cannons in Munich, had noticed the considerable heat released during the drilling of [391] a canon. He repeated the observation in scientific fashion, and on 25 January, 1798, he communicated the result to the Royal Society of London. With the aid of a mill driven by a horse, he arranged a blunt drill to turn in a cylinder of bronze of 13 English pounds. In the space of two hours, by a pressure Rumford estimated as a hundred hundredweights, the drill had reduced 4,115 grains of bronze to powder. The amount of heat released during this operation had raised 26.38 pounds of water from freezing point to the boiling-point temperature. To the account of this experiment, which shows nicely the generation of heat by means of friction, Rumford added the following reflections: "In reasoning on this subject, we should not forget the most remarkable circumstance that the source of heat generated by friction in these experiments seems to be inexhaustible. It is hardly necessary to remark that a thing that an isolated body or a system of bodies could continue to produce indefinitely, without limit, can definitely not be a material substance. It seems to me extremely difficult, not to say impossible, to form an idea of a thing being able to be excited or communicated in these experiments, unless this thing should be movement."

The following year Humphry Davy repeated a similar experiment and expressed himself on the subject in similar terms.

The argument of Rumford and Davy was precise and forceful: those who held onto the substantial existence of caloric were worried. In his *Statique chimique*, Berthollet tried to refute it: copper filings are perhaps not identical with the copper from which they come; while detaching themselves under the pressure of the drill, they might have undergone a change of state; their density, their specific heat might have varied, and the transformation could have produced the release, in the form of free heat, of a part of the caloric that had been stored in the copper in a latent state. But Rumford had foreseen this loophole and closed it in advance by showing that the filings formed during the experiment had the same density and the same specific heat as the block of metal from which they had been torn. It remained therefore beyond doubt that it was possible to create heat by movement and that if an inexhaustible source of movement was available, heat could be generated indefinitely.

The production of heat by percussion or by friction had long been the only objection against the caloric theory. But at the very moment when this theory acquired [392] its full development, progress in optics created new difficulties.

The discoveries of Young and Fresnel relegated to oblivion the system of emission which had long triumphed and brought back into favour the forsaken theory of waves. Light was no longer the effect produced on our retina by the small projectiles thrown into space with very high speed; it consisted of very rapid movements of the ether. This hypothesis, backed by precise and striking experiments, was soon accepted by the overwhelming majority of physicists. Now, if light is a movement, then how could heat, which radiates with light, and which generates light in intensely heated bodies, be anything other than a movement? When light is absorbed by a black body and warms it, shouldn't it be accepted that the luminous movement is transformed inside the absorbing body to a calorific movement, and, as Fresnel wrote in 1822, "isn't the amount of *vis viva* which disappears as light reproduced as heat?" Fire and light have affinities which no physicist has ever dared contest. How could the return of the theory of light to the Cartesian doctrines not carry along the theory of heat in a similar evolution?

IV

"When a hypothesis is no longer sufficient for the explanation of phenomena, it should be abandoned."

"This is the case with the hypothesis according to which caloric is considered to be material, like a subtle fluid."

Sadi Carnot expresses himself thus in a note found among his papers after his death.

From the point of view of logic, the principle stated by Carnot is indisputable. A theory of physics which is formally contradicted by a well-established fact is a theory it would be absurd to defend. The history of science is woven of accounts of the violence done to this principle. The human mind has such a need to group the facts of experience in a theory that it always refuses to abandon a system contradicted by observation; it resorts to multiple ruses, subterfuges and semblances of explanation to turn or dissimulate the objection, attracted more to the protecting of a theory that is known to be false than abandoning it and being left free to the chaos of empiricism. It is only decided to reject the controverted hypothesis when another, more general and comprehensive, has succeeded in grouping in a single synthesis the [393] facts which could already be explained and the facts which have hitherto remained inexplicable. The refutation of a false idea serves no purpose if the idea which is to replace it is not stated at the same time.

The theory of heat offers some remarkable examples of this historical law.

In 1807, under Laplace's eye, Gay-Lussac made the air from a full reservoir flow into an empty reservoir, establishing the absence of any release or absorption of heat during the change. Desormes and Clément had proclaimed a supposition about the caloric contained in empty space which Laplace rejected, and Laplace knew that they had taken it very naturally from the observation of Gay-Lussac. The results of this observation are evidently irreconcilable with the theory of heat developed in the *Mécanique céleste*; nevertheless, the author of *Mécanique céleste* was content to pass over Gay-Lussac's experiment in silence.

Laplace, Berthollet, Desormes and Clément, all advocates of the caloric theory, knew that friction released heat. All admitted more or less clearly that this constant, undeniable fact contradicted their hypotheses. They continued, however, to reason as if these hypotheses were true. The supposition that heat is the sensible manifestation of a certain material substance would only be abandoned when a new theory treating heat as the effect produced on our organs by a particular kind of movement had accounted not only for the phenomena explained by the advocates of caloric, but also those which their adversaries raised in objection against them.

Let us follow the efforts by which the idea that heat consists of very small and rapid movements of material molecules was developed into a theory, *the mechanical theory of heat.*

One of the important propositions of mechanics, the law of *vis viva*, is stated thus: When a material system is in movement under the action of certain forces, the work effected by theses forces during a certain lapse of time is always equal to the increase undergone by the *vis viva* of the system during this same time. Thus, to all positive work produced by the forces acting there corresponds, for the system, a precisely equal gain in *vis viva*; and to all negative work accompanying the encounter with the acting forces, there corresponds an equal part of the *vis viva.*

If the amount of sensible heat contained in a body is nothing but the *vis viva* of certain movements of the molecules [394] of the body, it is no longer surprising that the work done by the forces which act on a system and consumed by the system engenders a certain amount of heat in it. It is no longer surprising that the work done by the system against the acting forces entails a loss of heat by the system. The production of heat by friction or percussion and the production of work at the expense of heat in heat engines, is thus easily explained.

But there is more.

The amount of *vis viva* acquired in the form of heat by a body which consumes work should be exactly equal to the work done. The amount of *vis viva* of calorific movement lost by a body which produces work should be exactly equal to the work generated. Therefore there should be a constant proportionality between the amount of work consumed and the amount of heat produced in the first case, and between the magnitude of work generated and the amount of heat destroyed in the second case. The coefficient of proportionality measures how many units of work it is necessary to expend in order to produce one unit of heat, and how many units of work can be produced by destroying one unit of heat. In other words, it indicates how many units of the *vis viva* of calorific movement which agitates the molecules of a body increases when the amount of sensible heat contained in a body is increased by one unit. It tells us the *mechanical equivalent* of a unit of heat.

Following a publication from 1839 by Seguin, his uncle, the illustrious J.-M. Montgolfier, had been the first to notice "a kind of relation between the amount of heat dispensed and the amount of force produced." In steam engines, the vapour is merely caloric's intermediary for producing the force, and "there should be a direct relation between the movement and the caloric, independent of the intermediary of vapour or of all other agents which might be substituted for it." It might be supposed that Seguin interpreted, in the sense of the ideas which began to emerge in 1839, a proposition to which Montgolfier attached completely different conceptions. Montgolfier, Pierre Prévost tells us, attributed to the expansive force of fluid caloric the same mechanical effects that it was customary to attribute to vapour pressures or heated gases.

The first to clearly define the mechanical equivalent of heat, the first to have indicated the proper experimental way of determining its value, and the first to have given an approximate estimation of this value is assuredly Sadi Carnot.

As [395] early as 1824, in publishing his *Réflexions sur la puissance motrice du feu*, Sadi Carnot asserted that "the main foundations on which the theory of heat is based stand in need of very close examination." He undertook this examination, but his premature death in 1832 was a loss to science which prevented him from publishing his results. The notes found among his manuscripts show traces of the discoveries to which his fruitful meditations had led.

According to Carnot, the old theory of caloric should be rejected because it is contradicted by the facts. It is incompatible with "the development of heat by percussion and the friction of bodies." On the other hand, at the time when Carnot was writing, nearly all physicists, convinced by the discoveries of Young and Fresnel, regarded "light as the result of a vibratory movement of fluid ether. Light produces heat or, at least, accompanies radiant heat and fades with the same speed. Radiant heat is therefore a vibratory movement. It would be ridiculous to suppose that it is an emission from bodies, while the light which accompanies it would be merely a movement. Could a movement (that of radiant heat) produce a body (caloric)? Undoubtedly not; it can only produce movement. Heat is therefore the result of a movement. Thus, it can, quite simply, be produced by the motive power and itself produce this power."

"Wherever there is destruction of motive power, there is, at the same time, the production of heat in amounts precisely proportional to the amount of motive power destroyed. Reciprocally, wherever there is a destruction of heat, there is production of motive power."

There is an absolutely constant relation between the magnitude of work achieved and the amount of heat produced which is the mechanical equivalent of one unit of heat. Can the proper procedures for experimentally determining the value of this number be imagined? Certainly, and here is the programme for some the these "experiments to conduct on heat and motive power":

"Repeat Rumford's experiment on the drilling of a metal in water, but measure the motive power consumed and the heat produced;

"Strike a piece of lead in several ways, and measure the motive power consumed and the heat produced;

"Agitate water vigorously in a small barrel ..., measure the motive power consumed and the heat produced."

But [396] while waiting for physicists to carry out these experiments with the desired care, does the physical data permit a preliminary estimation of the mechanical equivalent of heat? "Following some ideas that I have formed on the theory of heat," says Sadi Carnot, "the production of a unit of motive power necessitates the destruction of 2.70 units of heat, each unit of motive or dynamic power representing the weight of a cubic metre of water raised by a height of one metre." In other words, to raise the temperature of one kilogramme of water by 1°—to produce one calorie—it is necessary dispose of an amount of work equal to 370 kilogramme metres.

What were the ideas which furnished Carnot with the first approximate evaluation of the mechanical equivalent of heat? The notes which he left are mute on this subject. But it may be supposed that they are not essentially different from those which, in 1842, furnished Robert Mayer with a nearly identical evaluation.

V

Sadi Carnot's notes on the equivalence of heat and work were not published until 1878. Robert Mayer was therefore led by his own reflections on similar conditions without having been influenced by the ideas of the French physicist, and physicists justifiably associate the principle of the equivalence of heat and work with the name of the doctor from Heilbronn.

Like Sadi Carnot, Mayer accepted that the expenditure of a certain amount of work generates a proportional amount of heat. He discovered the means of calculating the amount of work which produces one calorie in the study of thermic phenomena accompanying the changing volumes of gas.

Take a litre of air at a given temperature, for example the temperature of melting ice, under a given pressure, for example the pressure of one atmosphere. We propose to make this mass of gas occupy twice the volume, the temperature remaining that of melting ice and the pressure taking the value of a half-atmosphere assigned to it by Mariotte's law. We can obtain the result by expanding the gas slowly, in such a way that the temperature remains invariable and the pressure that it supports being, at each instant, that which maintains it at equilibrium. [397] We can also obtain the result by putting the receptacle containing the air in contact with another receptacle, also of one litre capacity, but entirely empty. The air rushes into the second receptacle, and it suffices for us to wait for the temperature, momentarily disturbed, to return through the entire mass to the fusion point of ice.

According to the experiment conducted by Gay-Lussac in 1807, this second operation entails neither the absorption nor the release of heat. Now, what difference is there in these two operations? In the second, external bodies neither produce nor take work from the gas, because it is expanded into the interior of a vase whose rigid walls undergo no displacement. In the first case, the gas performs easily calculated work in order to overcome the external pressure. This work is equivalent, according to Robert Mayer, to the amount of heat that is absorbed in the first operation and which would not be absorbed during the second. If, therefore, this amount of heat which generates known work can be determined, the mechanical equivalent of heat can easily be evaluated.

Now, the data possessed by physicists in 1842 allowed the calculating of this amount of heat.

Let us take again this mass of air occupying a volume of one litre at the temperature of melting ice and the pressure of one atmosphere. Let us first double the volume while maintaining its temperature constant: it absorbs the amount of heat that we wish to determine. Then, while maintaining its volume invariable, let us heat it to a temperature of 273°: it absorbs an amount of heat equal to 273 times the product of its weight with the specific heat of air at constant volume.

Instead of submitting our mass of air to the two successive transformations, let us simply heat it from 0° to 273° under the constant pressure of one atmosphere. It occupies a volume of two litres at 273° and absorbs, in this new change, an amount of heat equal to 273 times the product of its weight with the specific heat of air at constant pressure.

We have transformed our mass of air from the same initial state, in which it occupied a volume of one litre at the temperature of melting ice, to the same final state, in which it occupies a volume of two litres at the temperature of 273° in two different ways. The amount of heat absorbed in the realisation of the first process should be equal to the amount of heat absorbed in the realisation of the second. We can therefore evaluate the [398] amount of heat whose magnitude is important to us. It is equal to 273 times the product of the weight of gas with the excess of the specific heat at constant pressure over the specific heat at constant volume.

Such is the very simple reasoning by which Mayer related the value of the mechanical equivalent of heat to the difference which exists between the two specific heats of a gas. The calculation, which could be carried out with the data available at the time, showed him that to produce one calorie it is necessary to dispose of 367 kilogramme-metres. This is very nearly the result obtained by Sadi Carnot.

Mayer's reasoning has not only the advantage of providing an approximate value for the mechanical equivalent of heat. It also throws much light on the theory of gases. If a gas which is expanded under constant pressure absorbs more heat than a gas expanded at constant volume, that is because in order to overcome the external pressure, it produces work in the first case which is not produced in the second. If, in Gay-Lussac's experiment which Laplace could not explain, a gas is expanded without either releasing or absorbing any amount of heat, it is because no work accompanies this expansion. The laws of expansion of a gas which Laplace and Poisson proposed within the [confines of the] caloric hypothesis are easily recovered, together with all their consequences, in the new doctrine. So the discoveries which had given the most credit to the substantial existence of caloric could also be invoked to support the mechanical theory of heat.

Robert Mayer's writings were hardly to influence the development of science more than did the unpublished notes of Sadi Carnot. They were published, but they were not read. For the idea of the equivalence of heat and work to be spread among physicists, it was necessary that Joule in England and Colding in Denmark rediscovered it, each without any foreign influence. It was necessary that the many experimental determinations, realising for the most part, without their authors knowing it, the programme outlined by Sadi Carnot, should come to fix the very approximate value of the mechanical equivalent of heat in the neighbourhood of the number 425. It was above all necessary that Helmholtz launched his paper *on the conservation of force*, an astounding manifesto which announced to science the advent of new doctrines. It is only much later that the priority of the doctor from Heilbronn was recognised, and much later still that it has been possible to do justice to the instinctive foresight of our compatriot.

VI

In [399] 1850, the ideas on which the doctrine of the equivalence of heat and work rested were established. It seems the time had come to give this doctrine a dogmatic statement. This is what Clausius, in the first part of a memoir, quite rightly regarded as the backbone of thermodynamics.

The molecules of bodies are animated by very small, rapid movements. The *vis viva* of these movements represents the amount of *free* heat, the *sensible* heat within a body. This *vis viva* is the greater the more elevated the temperature.

On the other hand, attractive and repulsive actions are in general exerted between these molecules which only become appreciable for very close neighbours. Consequently, all variation in volume or temperature, all change of physical or chemical state by a body following upon a change in the disposition of these molecules of the body, is positive or negative work of these actions.

This is not, in the majority of cases, the only work produced when a body undergoes a modification. Perhaps the body undergoes the action of certain external forces, of gravity, or of the pressure of the atmosphere. When the body is transformed, these forces also effect positive or negative work.

Thus, while a body is undergoing a certain change, it absorbs or releases a certain amount of heat which is equivalent with the increase or decrease in the *vis viva* of the molecular movement. But, in addition, it releases or absorbs an amount of heat equivalent to the positive or negative work effected by both the internal and the external forces which attract the various parts. If the former effect represents, in the new doctrine, the absorption or release of *free* heat as understood in the old doctrine, the latter effect represents, in the mechanical theory of heat, what the theory of caloric regarded as a release or absorption of *latent* heat. In the mechanical theory, latent heat "is not merely, as its names suggests, hidden from our perception; it does not exist at all. It is consumed as work during the change of state." The hypothesis regarding the nature of latent heat which Lavoisier and Laplace had suggested in 1783 was henceforth adopted.

We [400] have just seen that three parts should be distinguished within the heat absorbed by a body: the heat which serves to increase the *vis viva* of the molecules, the heat which is consumed in doing internal work, and the heat consumed in doing external work. It might be possible to calculate the latter part when the external forces to which the body is submitted during its transformation are known—such forces can, in general, be measured. On the other hand, in most cases the former two parts cannot be calculated because of our ignorance regarding the way the molecules of the body are moved and the laws with which they attract one another.

It therefore seems that it is never possible to calculate, in any complete fashion, the mechanical effect to which a certain absorption of heat is equivalent. Consequently, it seems that attempts to try to determine by experiment the value of the mechanical equivalent of heat would be illusory. There is none!

Let us take a body and submit it to a cycle of transformations which bring it back to its initial state. After going through the cycle, the *vis viva* of the movement agitating the molecules will assume its original value; it will undergo neither increase nor diminution. The molecules will take up their former dispositions. Now the attractive or repulsive forces exerted between the molecules are of such a nature that they effect as much positive work as they do negative work in a change where the point of application of each of them describes a trajectory which closes on itself and brings it back to the point of departure—a hypothesis admitted by all the geometers who have treated the actions of molecules. Thus, in the quantity of heat absorbed by a body undergoing a cyclic transformation, the former two parts will be absent; only the latter remains. When a body undergoes a succession of changes which bring it back to the state from which it was taken, the amount of heat it absorbs is exactly equivalent with the work that it produces in overcoming the external forces.

It is therefore possible to evaluate the mechanical equivalent of heat by determining, on the one hand, the amount of heat absorbed by a system of bodies which describe a closed cycle of transformations, and on the other, by calculating the effective work during the course of the cycle. The method employed by R. Mayer is an application of this principle. Among physicists who, after R. Mayer, have measured the magnitude of this constant, there are those who [401] have neglected to make the body on which transformations operate traverse a complete cycle; these methods are not legitimate.

We have just brought to light an essential characteristic which distinguishes the internal forces acting between the molecules of a body and the external forces associated with various parts of the body. If, after any modification, a body returns to its initial state, it is certain that the total effective work of these molecular actions during the course of these modifications is reduced to zero. This is not necessarily the case with the effective work of external forces, which may by positive, zero or negative.

This proposition is itself contained within a very general truth: when the initial and final state of a body is given, the work produced by the molecular attractions during the course of the change undergone by the body is determined without ambiguity; a body can pass from the same initial state to the same final state by an infinity of different processes, and whichever process is employed, the work done by the internal actions remains the same.

Things are entirely different with external forces. Without changing the initial or final state of a system, however the process serving to take the body from one to the other of these states is varied, the corresponding change in the work done by the external forces will in general have a different value.

We have already given a striking example of this truth. We have taken a mass of air which occupies a volume of one litre at the temperature of melting ice, and by two distinct processes, we have brought it to occupy, at the same temperature, a volume of two litres. In one of these processes, we expanded this mass of air at constant temperature under a pressure continually equal to that which maintained equilibrium. The external pressure then does a certain amount of negative work. In the other process, we connected the receptacle in which the gas was originally enclosed with another, empty, vessel of the same capacity. The gas rushed into the vacuum; the temperature was lowered a certain number of degrees in the first receptacle and increased by an equal number of degrees in the second. We allowed the temperature to return to its former value throughout the entire mass. Throughout this process the gas was moved into the interior of a rigid envelope, as a result of which the external pressure did no work. Thus, in conducting the gas from the same initial state to the same final state by two different processes, we made the external forces do [402] different [amounts of] work, negative in the first case and zero in the second.

These remarks lead to an important result.

Suppose a body is transformed from a given initial state to a given final state by various processes. Whatever the process employed, the increase undergone by the *vis viva* of the molecular movements remains at the same value; the work done by the internal actions remains at the same value; but the work done by the external forces will not be the same in all cases; it will vary with the process employed for the transformation of the body. Therefore, each process capable of taking the body from the given initial state to the given final state requires the absorption of a different amount of heat.

Thus, in the example we have just cited, the gas absorbs a certain amount of heat while expanding during the first process, but while expanding during the second process, it neither gains nor loses heat.

This necessary consequence of the new doctrine reverses the most universal principle admitted by the old theories of heat.

For Descartes, the various parts of a heated body were in a state of extreme agitation. The amount of heat contained in a body was the amount of movement of this agitation. When the body passed from one state to another, it absorbed an amount of heat equal to the excess of the amount of movement encapsulated in the final state over the amount of movement encapsulated in the initial state. To calculate this excess, it sufficed to know these two extreme states. It was not necessary to know by which route the body had passed from one to the other. The two termini of a transformation alone determine the amount of heat absorbed during the transformation. In particular, when these two termini coincide, when the body has traversed a cycle which brings it back to its initial state, the heat gained by the body would have the same value as if no modification has been produced, namely the value zero. While traversing the cycle, the body released as much heat as it absorbed.

Following the discoveries of Leibniz, the Cartesian theory was modified. The amount of heat was no longer the amount of movement of internal agitation of the body, but the *vis viva*. But what was said about the amount of movement could be represented by the *vis viva*. The heat absorbed by a body which passed from one state to another continued to depend uniquely on the [403] two states, and to be independent of the process which carried the body from the one of these states to the other. In particular, it remained necessarily zero in the case where the final state coincided with the initial state.

The caloric hypothesis supervened, for which the quantity of heat contained in a body is the mass of caloric fluid that it encloses. The amount of heat absorbed by a body which undergoes a change is the increase in the mass of the fluid during the change. To know this increase, it suffices to know how much caloric the body encloses at the start of the transformation, and how much it contains at the end. What happens during the interval is of little importance. If the change undergone by a body closes in a cycle, the body contains as much caloric in its final state as in its initial state; the gains of heat are exactly compensated by the losses.

The existence of latent caloric was a triumph for the caloric hypothesis. This existence which Lavoisier and Laplace had shown could, however, be reconciled with a mechanical theory of heat formed by the synthesis of the mechanism of Descartes and the dynamism of Newton. In this synthesis, the free heat is the *vis viva* of the molecular movement. The latent heat released in a change of state is the work accomplished by the attractive or repulsive forces which act between the molecules during this change of state. Like the decrease in *vis viva*, this work depends only on the two extreme termini of the change of state. The value of the quantity of heat released depends only on the initial state and the final state, and not at all on the intermediate states that the body traverses.

If, therefore, physicists were divided regarding the nature of heat, they were unanimous in recognising that the heat absorbed by a body during a transformation depends only on the state from which the body departed and that to which it arrived. They were unanimous in proclaiming that during the traversing of a closed cycle a body releases as much heat as it absorbs. In 1783, Lavoisier and Laplace considered writing on heat admitting only the principles common to all theories that could be formed on the nature of heat. They did not hesitate to take as the foundation of their deductions the following axiom: "All variations of heat, whether real or apparent, which a system undergoes in a change of state are reproduced in the reverse order when the system passes back to its original state." Berthollet made use of this axiom in the study of various problems [404] related to solutions; Desormes and Clément, Laplace, Poison, Sadi Carnot and Clapeyron employed it constantly in their reasonings and in their calculations. In 1840 Hess placed it at the base of thermochemistry. Mayer himself applied it, without stating it, in the memoir where he put forward the first law of thermodynamics.

This principle, regarded by all as the firmest base of the theory of heat, was undermined by the law of the equivalence of heat and work. It was this principle that Clausius declared inadmissible. When a body passes from one state to another, the amount of heat that it absorbs depends on the work done during the change by the external forces, and hence, varies with the change. To inform us on the subject of this amount of heat, it does not suffice to say to us that this is the body at the start and this is what it is at the end; it is necessary to recount for us the history of the body from the start of the change until the end. It is no longer possible to speak simply of a body, taken in a given state, containing a determinate amount of heat; for, if it is brought back to this state after having undergone a series of changes, it will in general have absorbed more heat than it has released, or released more heat than it has absorbed. It is still possible to speak of the amount of heat absorbed or released by a body while it is undergoing a determinate transformation. But it is not any longer possible to speak of the *amount of heat enclosed in a body* taken in a given state; henceforth, these words are devoid of sense.

VII

Sadi Carnot writes in his *Réflexions sur la puissance motrice du feu:*

"We implicitly suppose in our demonstration that when a body undergoes any changes, and after a certain number of transformations, it is brought back identically to its original state, that is to say, to this state considered relative to the density, the temperature, and the mode of aggregation; we suppose, I say, that the body is found to contain the same amount of heat that it contained from the start, or alternatively, that the amounts of heat absorbed or released in its various transformations are exactly compensated. This fact has never been brought into question; it was first admitted without reflection and then verified in many cases by experiments with the calorimeter. [405] To deny it would overturn all the theory of heat for which it serves as the base."

The law of Robert Mayer denies this principle; the entire theory of heat is overturned and should be erected anew.

In many respects this restoration is easy. Employment of the confounded principle is avoided in the determination of the mechanical equivalent of heat, and the properties of gases and vapours are recovered without the aid of this principle as they had been established before in the caloric hypothesis. All these alterations are made, so to speak, of themselves. But it seems to be less easy to reconcile the new doctrine with the discoveries to which Carnot had been led by a principle incompatible with this doctrine.

In 1849, W. Thomson found himself confronted by two contradictory principles of the theory of heat: on the one hand, the principle of the equivalence of heat and work, to which the experimental research of Colding and above all Joule, and the recent paper of Helmholtz, lent a higher and higher probability, and on the other hand, the principle that the heat absorbed by a body during a change of state depends only on the initial and final state—principles on which the admirable series of deductions of Carnot's rested. He hesitated between the two principles, and, going beyond experimental refutation, he concluded by opting in favour of the axiom that Carnot took from the tradition: "If we abandon this principle," he said, "we run up against innumerable other difficulties that cannot be surmounted without new experimental research and without erecting the theory of heat completely on a new base." It is uncommon that a physicist resolves to abandon a hypothesis incompatible with the facts, that he consents to reject a theory contradicted by experiment, before having discovered a more comprehensive hypothesis and developed a theory more in conformity with nature!

Too vigorous to tolerate any constraint, the British imagination says goodbye to the rules of logic: The German rigour of Clausius's mind was more precisely adopted to the laws of the experimental method. Full of admiration for Carnot's work, but convinced that nothing remained of this work than that which accorded with the principle of equivalence of heat and work, which had become truths of observation, he tackled head-on the difficulties which had made Thomson recoil and, in the second part of his *Mémoire sur la force motrice de la chaleur*, he gave an exposition of the theory which the English believed impossible to build without new experimental research.

According [406] to the principles accepted by Sadi Carnot, a body which describes a cycle absorbs exactly as much heat as it releases. In particular, an engine which functions by following a Carnot cycle gives up to the cooler an amount of heat precisely equal to that which it gained from the heat source. This proposition is incompatible with Mayer's law. If the engine provides a certain work, the amount of heat taken from the heat source exceeds the amount of heat given up to the cooler, and the excess of the former over the latter is equivalent with the work produced by the engine. The inverse occurs if the engine absorbs work. The proposition Carnot used in his deductions should therefore be rejected. But, although this proposition plays an essential role in the results Carnot stated, its rejection does not necessarily mean the rejection of these results. From false premises it is possible to deduce true conclusions. According to Clausius, it is possible to retain what is essential in Carnot's theory.

What is essential in this theory is the demarcation established between characteristics of the two kinds of Carnot cycle, namely *direct* and *inverse* cycles. A body which describes a direct cycle absorbs heat while it is carried to a higher temperature and releases heat while it is maintained at a lower temperature. On the other hand, a body which describes an inverse cycle releases heat at the higher temperature and absorbs it at the lower temperature. Whether the amount of heat absorbed is equal to the amount of heat released, as was believed in Carnot's time, or whether it differs, as we teach the law of Mayer, is of little importance. Every system which describes a cycle of the first kind transports heat from a hot body to a cold body. Every system which describes a cycle of the second category transports heat from a cold body to a hot body. Now the former systems—those which transport heat from a hot body to a cold body—are the only ones which can make the external forces do negative work, and which can function in opposition to these forces; which can, in a word, be regarded as the appropriate engines for *producing* motive power. On the other hand, systems which transport heat from a cold body to a hot body can only produce this effect by means of positive work from the external forces; they *consume* power. They are not *motive* engines, but *refrigerator* machines; *a system which describes a Carnot cycle cannot transport heat from a cold body to a hot body unless this transport is accompanied by positive work from the external forces.* This is the proposition which Clausius [407] regarded as the most profound intuition of Sadi Carnot's, and is the proposition that he demanded be retained as a sort of axiom of the theory of heat, an axiom just as important for this theory as the law of Mayer.

When an engine functions by following the Carnot cycle, each unit of work produced requires a certain amount of heat from the furnace. The amount of this heat depends on the temperature limits between which the cycle is described, but not at all on the nature of the engine which produces the work. The preceding axiom easily furnishes us with a demonstration of this theorem.

Let us imagine that two different engines each describe Carnot cycles between the same limits of temperature. Let us suppose that in order to produce one unit of work, the first takes less heat from the furnace than does the second. Let us run the engines simultaneously, but while the first proceeds so as to produce a unit of work, the second proceeds in the inverse sense, in such a way that instead of producing a unit of work too, it consumes this work. Thus, this engine gives up to the warm body an amount of heat which it would have taken up if it had proceeded in the direct sense. Taken together these two engines might be regarded as a single system describing a Carnot cycle; during the course of the cycle the system neither produces nor consumes motive power because the first engine produces a unit of work while the second consumes this same amount of work. Secondly, the hot body provides heat for the first engine but it receives more of it from the second engine. It has, in a word, therefore absorbed a certain amount of heat, and because the completion of the cycle by the two engines entails neither the production nor the consumption of motive power, Mayer's law requires that the cold body has provided two engines taken together with an amount of heat exactly equal to that which the hot body has received. Consequently, the two coupled engines succeeded, in the course of describing a Carnot cycle, in transporting a certain amount of heat from a cold body to a hot body while the total work done by the external forces is reduced to zero. This consequence would be in contradiction with Clausius' axiom.

The axiom Clausius gives us therefore saves Sadi Carnot's fundamental law from any contradiction with the principle of the equivalence of heat and work. When an engine operates following a Carnot cycle, the ratio of the work [408] produced by this engine to the amount of heat provided by the furnace depends neither on the nature of the substances entering into the constitution of the engine nor on the arrangement of its components; the ratio depends only on the two extreme temperatures between which the cycle is described.

No experiment directly verifies Clausius' axiom. If this axiom can be rendered probable, it is only in virtue of the agreement the experimenter reaches by the comparison of observed facts with distant consequences of the theory of which this axiom serves as base. These characteristics are common to all physical theories; whoever analyses the mechanism of science closely attributes them even to the suppositions habitually regarded as the copies[7] of observation. But although a superficial mind might easily fail to appreciate these distant consequences, in this axiom these copies are strikingly apparent even to the less attentive. At first, this law seemed to be one which, of all the principles of physics, was endowed with a strange and exceptional nature, and it gave rise to discussions. Some, with Zeuner, saw there a self-evident truth, as with the axioms of geometry. Clausius responded to them rightly that it is possible, without absurdity, to deny the exactitude of his postulate, and that this exactitude can only be established by experimental confirmations. Others, with Rankine or with Hirn, thought they found, both in the phenomena of radiant heat and in complex modifications, facts which conflict with Clausius' law. But he discussed these objections with minute rigour and uncovered the confusions which had led his rivals into error. Consolidated by these various trials, the principle that a Carnot cycle cannot transfer heat from a cold body to a hot body unless external forces produce positive work was finally admitted without contradiction and, along with it, the consequences which are deduced from it.

VIII

When an engine describes a Carnot cycle, the relation between the work produced by the engine and the amount of heat it takes from the furnace is independent of the nature and arrangement of the bodies which compose the engine; it depends only on the two extreme temperatures between which the engine functions. Moreover, the work produced by the engine is equivalent to the excess of the amount of heat taken from the furnace over the [409] amount of heat delivered up to the cooler. Consequently, an elementary calculation allows the replacement of the foregoing proposition with the following: When a heat engine describes a Carnot cycle, the amount of heat taken from the furnace stands to the amount of heat given up to the cooler in a relation which does not depend on the nature of the engine. This ratio depends only on the two extreme temperatures between which the cycle traced by the engine is comprised.

How does this ratio depend on the temperature of the furnace and the temperature of the cooler? This problem, where the temperature of the furnace and the temperature of the cooler vary at the same time, is reduced without difficulty to

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[7] *décalques*.

another, simpler, problem: How does the ratio between the amount of heat taken from the furnace and the amount of heat given up to the cooler vary when the temperature of the furnace is supposed variable and a cooler is chosen with the fixed temperature equal to the point of fusion of melting ice?

Let us suppose that whatever the temperature of the furnace might be, we know how to solve this latter problem. How do we resolve the former problem? How, for example, will we calculate the ratio of the heat taken to the heat returned in an engine where the temperature of the furnace is the boiling point of water, and the temperature of the cooler the boiling point of alcohol? We will calculate the value of this ratio, on the one hand, for an engine functioning between the boiling point of water and the point of fusion of ice, and on the other hand, for an engine functioning between the boiling point of alcohol and the fusion point of ice, and we will divide the first of these values by the second.

Let us therefore imagine an engine which describes a Carnot cycle between any higher temperature and a lower temperature equal to the point of fusion of ice. The relation between the amount of heat taken from the furnace and the amount of heat given up to the cooler depends solely on the temperature of the furnace. How does it depend on it? In order to be able to reply to such a question, it is necessary to put each temperature into correspondence with a number; it is necessary to make a choice of thermometer.

Let us take a gas, and suppose that the gas obeys Mariotte's law at all temperatures and under all pressures. Suppose that this gas neither absorbs nor releases heat when given access to an empty container. We will say that this gas is a *perfect gas*. (There are no perfect gases in nature; there are only gases: air, hydrogen, nitrogen, oxygen and carbon dioxide [410] in the conditions of temperature and pressure where they are ordinarily observed, differing little from the ideal gas state that we call perfect.) Imagine that we enclosed a perfect gas in a receptacle put in communication with a manometer, and that at each temperature we measured the pressure which maintained the gas under the given volume. This pressure will increase with temperature. We agree to regard the increase in temperature as proportional to the increase in pressure. Let us fix the coefficient of proportionality in such a way that the difference between the boiling point of water and the fusion point of ice is marked by the number 100. We will have defined the perfect gas centigrade thermometer, a thermometer which cannot be constructed, which cannot be realised in a concrete way, and which only exists by way of an abstraction in the understanding of the physicist, but which is very closely approached in ordinary conditions by air and hydrogen thermometers. It is the temperature read on the perfect gas centigrade thermometer that Clausius introduced into his formulas.

The problem which now occupies us is thus resolved by a very simple formula. The ratio between the amount of heat that an engine takes from the furnace, and the amount of heat it gives up to the cooler whose temperature is the fusion point of ice, has the number 273 as its denominator—the inverse coefficient of dilation of a perfect gas—and as numerator the same number, 273, increased by the temperature of the furnace.

Consequently, an engine functioning by following a Carnot cycle takes from the furnace and gives up to the cooler, whatever the temperatures of these two bodies, those amounts of heat which stand to one another as the temperatures of the furnace and that of the cooler, provided the number of degrees corresponding to each of these temperatures is increased by 273. In other words, these amounts of heat stand to one another as the *absolute temperatures* of the furnace and the cooler if the words "absolute temperature" are given the sense that Desormes and Clément had attributed to them—the sense which Laplace had adopted.

Returning, in a way, to the series of deductions of Clausius, W. Thomson has proposed to recapture, in somewhat modified form, the idea that he had put forward at the time when the caloric hypothesis seemed to be the necessary foundation of Carnot's law and to require of the latter the definition of absolute temperature.

Let us take an engine which describes a Carnot cycle and whose cooler is formed of a mass of melting ice. The ratio [411] of the amount of heat taken from the furnace to the amount of heat given up to the cooler is independent, as we know, of the nature and arrangement of the bodies which comprise the engine; it depends only on the temperature of the furnace. It is the greater the colder the furnace. Let us agree to regard this ratio as the relation between the absolute temperature of the furnace and the absolute temperature of melting ice. This convention will fix, except for a factor, the absolute temperature of any body. If we want the interval between the fusion point of ice and the boiling point of water to correspond to a hundred degrees centigrade, the proportionality factor would be fixed and the definition of absolute temperature allows for no ambiguity. Moreover, this definition would be given without the intervention in any way of the properties of a real thermometric body, such as air or mercury, or of an ideal substance, such as a perfect gas. Besides, it is possible to compare the absolute temperature with indications given by a thermometer of mercury, of air and of a perfect gas. It will be found that the absolute temperature is always 273 degrees greater than the centigrade temperature read on a perfect gas thermometer. In other words, the ratio of the absolute temperatures of two enclosures would be equal to the ratio of the pressures which maintained the volume of a mass of perfect gas placed in each of these two containers invariable.

Thus, in reconciling Carnot's law with Robert Mayer's law, Clausius led W. Thomson to revive the determination of absolute temperature proposed by Desormes and Clément and adopted by Laplace, a determination which Thomson had formerly suggested be abandoned. The first thermometric scale proposed in 1702 by Amontons became the normal scale to which thermodynamics henceforth related all temperatures.

IX

This is not the last word on Clausius' work.

When a system describes a Carnot cycle, the amount of heat taken from the furnace stands to the amount of heat given up to the cooler as the absolute temperature of the furnace is to the absolute temperature of the cooler. Therefore, if the amount of heat taken from the furnace is divided by the absolute temperature of the furnace and the amount of heat given up to the cooler is divided by the absolute [412] temperature of the cooler, the two quotients obtained are numerically equal to one another.

What Clausius called *the value of the transformation*—or more briefly, *the transformation*—undergone by the system is obtained by dividing the amount of heat released by a system during a certain change by the absolute temperature to which the system is taken during this change. All changes of state which release heat correspond to a positive transformation. All changes which absorb heat correspond to a negative transformation.

Let us take a system which completes a Carnot cycle; among the changes it undergoes, there are only two which have a value of transformation. These are the heating undergone on contacting the furnace and the cooling undergone on contacting the cooler. The other two modifications of the system neither absorb nor release heat, and their value of transformation is zero. A negative transformation corresponds to the action of the furnace, and a positive transformation to the action of the cooler, and these two transformations are of the same magnitude. Their sum is zero; the negative transformation exactly *compensates* the positive transformation.

This property of Carnot cycles can be extended to any series of changes whatever in nature which take the system in a certain state and bring it back to that state, in a word, to all cycles. Let us take each change whose succession constitutes a cycle, calculate the value of the transformation corresponding to it, and then add all these values together. We always obtain a sum equal to zero; the negative transformations always compensate exactly for the positive transformations.

We said that this beautiful proposition was general, that it appertains to all cycles. It is necessary, however, to add a restriction, and it is not one of Clausius' lesser claims to fame for making this restriction precise.

In order to establish the essential law to which all imaginable engines which describe a cycle are subject, Sadi Carnot supposed, without ever changing the nature of the bodies which compose the engine, nor the bodies which encompass and act on it, that it is possible to trace the engine through the same cycle in the opposite sense, that it is possible to make it consume work equal to that which it had previously developed, and that it is possible to replace any release of heat by an equivalent absorption and all absorption by an exactly compensatory release of heat. The propositions [413] demonstrated by Clausius are subordinated under the same hypothesis, namely that the body to which they are applied describe a *reversible* cycle.

But the cycles really produced in the physical world are not reversible.

Here is a gas contained in the body of a pump closed by a piston, and this piston is loaded with a weight. If the weight is sufficiently heavy, the piston will be driven in and the gas will be compressed. The external forces, represented here by the weight loaded onto the valve, do positive work, and a certain amount of heat will be released. If, on the other hand, the weight loaded onto the piston is very small, the piston will be pushed back and the gas will expand. The work of the external forces will be negative and the system will absorb heat. Matters can be arranged so as to obtain the first group of phenomena or the second. But trying to place weights on the valve which, without any change in this weight, can equally well be lowered as risen, and the gas can equally well be compressed as expanded, and heat might be absorbed or released at will, would evidently be a chimerical task. A given system, in given conditions, is necessarily transformed in a given direction, and not indifferently in one direction or the inverse. The change that it undergoes is not reversible. Taken literally, the words *reversible change* are a nonsense.

These words are, however, capable of taking on a precise significance, but via a detour which we must follow.

Loading the piston with a suitable weight which closes the body of the pump in which there is a gas, you can depress the piston. Putting a little less weight on the piston still depresses it. In order that the piston begins to be depressed, it suffices that the load surpasses a certain amount so small that the weight would hold the gas exactly at equilibrium. Similarly, in order that the piston be raised, if suffices that it carries a load which is a little smaller than that which holds it exactly motionless. You can therefore take two loads differing from one another as little as you please and yet chosen in such a way that the one compels the piston to sink and the other allows it to be raised. A given system, also surrounded by given body, undergoes a change the direction of which is always perfectly determined. But it is possible to choose the external conditions in which the system is placed in such a way that an infinitely small variation in these conditions [414] suffices to reverse the direction of the change of state produced. For this, it suffices that the bodies enclosing the system differ infinitely little from those which would be maintained at equilibrium.

This said, what could be meant by the words: such a proposition is only true for a reversible change? Their sense is as follows: the proposition in question is never, properly speaking, true. No change exists to which it can be applied with complete rigour. But the error perpetrated in applying this proposition to a certain change of state can be more or less great. It is smaller as, in order to reverse the direction of the change of state, a lesser variation is required in the external conditions in which the system undergoing the change is placed. The proposition in question is as little removed from the truth as the forces to which the system is submitted are, at each instant, closer to those which would maintain it at equilibrium.

We have said that when a system traverses a cycle, the negative transformations that it undergoes compensate exactly the positive transformations. We have added that the exactitude of the theorem supposes the reversibility of the cycle traversed by the system. What does that mean? The theorem in question is not applicable to any cycle actually described because no actually traversed cycle is reversible. For no real cycle is it allowed for us to affirm the rigorous equality between the sum of the positive transformations and the sum of the negative transformations. But we can safely state that the more the forces which modify the system studied are, at each instant, closer to those which arrest all change of the system and maintain it at equilibrium, the less these two sums of the transformations will differ from one another. The consequences which we will deduce from Clausius' theorem, the properties of the system which this theorem will lead us to discover, will never be rigorously exact while the system is in the process of change. But the more the causes which determine the change tend to disappear, the more these consequences will border on the truth, and the more the properties will approach those experiment reveals. For a system at equilibrium, these consequences are exactly applicable, and the properties will apply in full.

Thus, in introducing into their arguments this notion of reversibility, whose strange and paradoxical character had not attracted the attention of Carnot and had not been clearly perceived by Clausius, [415] Thermodynamics began to possess an indirect—at least in appearance—but logical way of discovering the properties possessed by material systems at equilibrium. The fruitful method, employed by Clausius and W. Thomson, by James Thomson, by Kirchhoff, by Moutier, by Tait, and by a host of physicists it would take too long to cite, has given an abundant harvest of new laws, often remarkable for their unusual and unexpected character, always minutely verified by experiment. The method has transformed the theory of the various changes of physical state, of the various changes of chemical nature, of fusion, of vaporisation, of dissolution and of dissociation.

Let us now take a system which describes a cycle which is real, and consequently, irreversible. We do not know, yet, whether the positive transformations produced during the course of traversing the cycle are compensated by the negative transformations or not. Clausius has affirmed, rather than demonstrated, that, in this case, the two categories of transformations are never compensated exactly, and that the sum of the positive transformations always exceeds the sum of the negative transformations. In other words, the sum of all the transformations produced during the course of a *real* cycle would *always* be a positive amount. A fundamental proposition whose exactitude and fruitfulness is affirmed more each day in the most diverse fields of physics, thanks to the discoveries of Horstmann,[8] of Gibbs and of Helmholtz; a proposition that compelled audacious minds, inspired by W. Thomson, to exceed the boundaries of physics and enter into the domain of metaphysics. But we cannot follow the consequences of this law. It would carry us too far from the fundamental notions of thermodynamics. It would oblige us to discuss the applications, in all branches of physics, of a doctrine whose description we would like to confine to general principles.

Born from the hypothesis that heat is a movement, modern thermodynamics came to free itself from this supposition, and even to round on it and definitely reject it. It remains for us to retrace the stages of this latter evolution.

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[8] [Duhem writes "Hortsmann," but is presumably referring to the same August Friedrich Horstmann (1842–1929) that he refers to elsewhere (see index), despite consistently using the same spelling in Pt. III, §IV of this paper.]

III

*Heat and Movement**

I

"Heat is the result of movement," we read in the posthumous notes of Sadi Carnot. "Thus it is quite clear that it can be produced by the consumption of motive power and that it can produce this power ... But it would be difficult to say why, in the development of motive power by heat, a cold body is necessary; why, in consuming the heat of a warm body, no movement can be produced."

Carnot's theory, as its author had developed it, was manifestly in contradiction with the hypothesis that heat is a movement. It contradicted the law of the equivalence of heat and work which itself follows logically from this hypothesis. In changing the basis of this theory, in making it rest on the axiom that every Carnot cycle which passes heat from a cold body to a hot body requires work provided by exterior forces, Clausius made this evident contradiction disappear. Carnot's theory as Clausius developed it no longer ran counter to Mayer's law. It was no longer explicitly incompatible with the mechanical theory of heat. Does it follow that it was compatible with it? One of the theories rests on the hypothesis that the amount of heat released by a [852] body which changes state is equivalent, partly to the loss of kinetic energy possessed by the molecules of this body, partly to the work effected by the external or internal forces applied to these molecules. The other [theory] rests on the hypothesis that a Carnot cycle cannot make heat flow back from a cold body to a hot body. Isn't there an implicit incompatibility, a contradiction whose logical significance is not diminished by not being so striking? That is a question which a physicist can and should put.

To respond to this question, to demonstrate that the second principle of thermodynamics is in agreement with the supposition that heat is a movement, there is only one method: take, as the point of departure, the hypothesis of the mechanical nature of heat; if need be, make it more precise, specify this hypothesis by several supplementary suppositions evidently compatible with it; then, from these premises, deduce by rigorous reasoning the demonstration of Clausius' axiom or of an equivalent proposition.

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* Originally published as Part III of "Les Théories de la Chaleur" with the subtitle "Chaleur et Mouvement," *Revue des deux mondes*, 130 (1895), 851-868.

This is the path followed by Boltzmann, Clausius and more recently by Helmholtz. They have assimilated a body to a system of material points animated by a very small and rapid movement. They supposed this movement to be such that the average state of the system is practically the same at every instant. They admitted that the average active force of this movement was proportional to the absolute temperature of the body, and they sought to deduce the laws that Clausius linked with Carnot's ideas from theorems of dynamics.

Have their efforts led them to success? Despite the resources of analysis brought into play by those who have undertaken these investigations, it must be said that they have dashed the hopes that were aroused. Without entering into technical details which would be out of place in this study, let us recognise that they have succeeded in linking the laws of dynamics with the properties of reversible transformations, although not without laying themselves open to certain criticisms and some objections. But let us recognise that they have not yet been able to give any account of properties of irreversible changes—that is to say, of all real changes. Is this lack of success merely temporary? Does the future hold for us a full and satisfactory reduction of the laws stated by Sadi Carnot and Clausius to the principles of dynamics? Or on the contrary, are the principles of dynamics forever and essentially incapable of explaining the second principle of thermodynamics? Although this [853] would seem at first sight to be rash, it is the view to which several physicists who have made this problem the object of their meditations are inclining towards. I content myself by citing the name of H. Poincaré: "The mechanism is incompatible with Clausius' theorem"—so concludes the illustrious geometer.

II

Loss of belief did not have to wait for the difficulties attending the hypotheses regarding the mechanical nature of heat to be pointed out. The unfertility of a theory, the kinetic theory of gases, that had at first excited great hopes had for a long time aroused the suspicions of physicists regarding these hypotheses.

Heat is a movement of the smallest parts of bodies. This movement is extremely rapid, but the trajectories described by each particle always remain confined within a very small space. Such are the assertions which serve as the basis of the mechanical theory of heat. These assertions are certainly informative about the nature of heat, but the doctrine they furnish is very general, with few details. Inquiring minds have made some effort to satisfy their curiosity. They would penetrate the most intimate particulars of the movement which constitutes heat, learn the form of the trajectory described by each particle and determine the law of the forces that these various particles exert on one another.

Certainly, molecules should not be subject to the same forces, nor describe the same trajectories, in a solid body, as in a liquid or in a gas, and in an easily liquifiable vapour as in a permanent gas. If there is one category of bodies which offers a chance of discovering the laws of calorific movement, it is surely the family of gases which are difficult to liquify, the perfect gases. All the mechanical and thermic properties of these bodies are known; they are governed by equations of remarkable simplicity and uniformity. This simplicity had already attracted the attention of physicists who followed the caloric hypothesis. It was to perfect gases that Laplace applied his supposition in order to pursue it to its ultimate consequences. And it is therefore by the purely mechanical explanation of the properties of perfect gases that it was appropriate to begin the analysis of the movement that we call heat.

Besides, everything does not have to be created in this explanation; the principles which must serve as points of departure were already to be found from the time the mechanical theory of heat was revived. [854] The invention of these principles is linked, by an uninterrupted tradition, to the very origins of modern physics.

Torricelli and Pascal established that air can exert a pressure; Boyle, relying on their view, undertook experiments whose results provided his disciple Richard Townley with the law of compressibility of air: *The elastic force of air is inversely proportional to the volume of the air occupied.* In 1676 Mariotte established this law by some new observations. Bacon had already said of the expandability of bodies in general, and of air in particular: "Since there is here a thing (and I do not know whether there is any other comparable thing) clearly fundamental and universal, we should prepare ourselves to broach it; because in so far as we have not seized it, philosophy would be entirely incoherent and disintegrated." The discoveries of Boyle, of Townley, and of Mariotte were not of such a nature as to diminish the importance that Bacon attributed to the problem.

The Cartesians sought to solve it in conformity with their principles.

Descartes developed for himself a conception of the expandability and compressibility of bodies in terms of an idea which derived logically from the way in which he represented the essence of material. The essence of material is nothing other than extension in length, breath and depth; the same body therefore always occupies the same volume. If a body seems to us to occupy a variable volume, sometimes greater, sometimes smaller, that is because in reality, in the space which increases or decreases, there are two bodies. The separate parts of the one, of fixed amount, approach and recede from one another; this is the one we see, the body to which we attribute the rarefaction and condensation. The other, which we do not see, is found in variable amount in the interstices left free by the parts of the former, more abundant when the former seems dilated, less abundant when the it seems compressed. The material of the sponge occupies an invariable volume, but it seems to become distended when water fills its pores, and to contract when water runs away.

This is the fundamental idea on which all the theories put forward by the Cartesians on the subject of the air's elasticity rest.

For some, the molecules that compose the air are perforated with pores and grooves twisted into spirals; a subtle fluid runs like a torrent in these pores, and the pressure it exerts on their surfaces tends to straighten them out. For others, amongst whom Robert Boyle should be named, the molecules of air are springs, elastic strips rolled into a helix which strive to be distended. Newton found these explanations inadequate: [855] "Representing the molecules of air," he said, "as elastic and branching strips, like the branches of a water willow folded upon themselves and intertwined, the expandability of the air will be difficult to explain; it can only be done by attributing a repulsive force to the molecules which obliges them to recede from one another." But Newton's explanation, which was to be adopted by the school of Lavoisier and Laplace, was not of the kind to satisfy the Cartesians.

In 1702 Amontons established that an equal increase of heat increases the pressure of the air in proportion to its increase in weight. Naturally, the *Histoire de l'Académie* explains this discovery by way of the generally accepted principles: "The reason for it is that the action of the heat consists in an infinity of small, very agitated particles which penetrate bodies. When they enter into a mass of air, they open up [the bodies] and develop spiral strings, not only because of the new bodies which are lodged in their interstices, but mainly because they are bodies which move with great violence. From this comes the increase in the volume of the air. When it is confined in such a manner that it cannot expand, the particles of heat which tend to open these whorls, but do not open them at all, thereby increase their force of elasticity, which would cease if they were freely opened."

Parent was struck by Amontons' discovery: "This phenomenon," says the *Histoire de l'Académie* for 1708, "led him to an idea that might seem rash: that the air is not elastic at all. That air has an elasticity was, apparently, a very strange paradox at the time of the discovery, and today it would be no less a paradox that it does not have it." It is therefore necessary to imagine, according to Parent, that the parts of air are neither folded strips which open, or whorls which are rolled up, nor anything analogous. They are simple, small, inert molecules which float in an ethereal material infinitely more subtle and always violently agitated. The more abundant the material ether, the more rapidly it moves and the more the molecules of air tend to recede from one another; thereof the apparent elasticity of the air. The molecules of air do not have this elasticity by themselves; if they press the walls of the vessels which enclose them, if they drive back the mercury of a manometer, it is not by a force which is really their own; it is simply in consequence of the movement the agitation of the material ether communicates to them.

Parent had merely developed an idea that Malebranche had expressed in 1674 in his *Recherche de la vérité* and applied it to gaseous bodies.

What [856] is the cause holding the various parts of a hard body so closely united, of a steel rod, for example? The question had been posed to Descartes: "I see," replied the philosopher, "no other adhesive or cement than rest." The inadequacy of the explanation was obvious. Malebranche attributed the cohesion which united the various parts of a hard body to the *gravitation of the ether*, that is to say, in accordance with Cartesian principles, to the vortices of subtle matter. Equally, the movements of the ether explain the elasticity of elastic bodies. "Elastic bodies must right themselves by the exertions of some movement. In fact, if reasoning about bodies and their properties is to be based only on the clear ideas that one might have, no other force or other action than what arises from the movement of matter will ever be attributed to it... It is therefore necessary to say that the movement that constitutes the force of elastic bodies is that of the subtle or invisible matter which engulfs them and which penetrates the pores."

III

If Parent was preceded by Malebranche in the explanation of elasticity, then Malebranche, in his turn, was anticipated by Leibniz.

In his *Theoria motus concreti*, published in Mayence in 1671, Leibniz had no hesitation in affirming that "all bodies are elastic; if, after they have been compressed, they are left to themselves, the gyratory movement of the ether brings them back to their original state." All the effects of the air are explained by the conjunction of two causes: the *gravity* of air and the tendency it has to spread and to dilate. Leibniz gave this tendency the name of *elater* [i.e.expanding], but this force of expansion, this elater, is not caused by the air itself; it is explained by the vortex movements of the ethereal substance, and by its collisions with the air molecules. Leibniz would have been surprised that a physicist of Boyle's ability had thought it possible to explain the elasticity of air by assimilating its molecules to woolly curls or spirals which regain their shape when they have been compressed: "It is not by its own force that a bent spring relaxes," but by an effect of the ethereal gravitation.

Throughout the eighteenth century, the majority of physicists followed Newton's view. Action at a distance explains the capacity of gases to expand, along with other celestial and terrestrial phenomena; it was the basis of the theory of aeriform fluids which was to become fully developed in the Laplace's *Mécanique céleste*. [857] Later, it was to provide Poisson and Navier with the general laws of elasticity for solid bodies. Meanwhile, a small group of philosophers faithful to the essential principles of Descartes' doctrine developed the theory of the expansive force of gases which Parent had sketched. This school, which flourished in Switzerland, isolated from the Newtonian environment of Europe, could rightly be called the Bernoulli school.

The friendship which united Leibniz with the heads of the Bernoulli family probably explains the anti-Newtonian tendencies of the great family of geometers, a tendency which was still alive when Daniel and Johann Bernoulli II continued to maintain in 1746 that, as they wrote, "Everything in the world happens by way of matter and movement. This principle of Descartes' is rather striking, and it seems at first sight to be so clear that it is surprising that it has been questioned, I will not say by which of the ancient philosophers, but by our greatest modern philosophers, such as Newton, and a large number of others who have been drawn by his authority and who have all introduced the principle of the mutual attraction of matter, existing and innate in matter itself and uniquely produced by the immediate will and efficacy of God. Does this principle accord with our reason?"

Since 1683 James Bernoulli, in imitation of Leibniz, sought the explanation of the elasticity of all bodies in the swirling movements of subtle material. For him, as for Malebranche, the *gravitation* of the ether caused the cohesion of hard bodies. The pressure of the air is not solely the effect of its weight, but also of its "passive resistance." This passive resistance, analogous to Leibniz's elater, is itself produced by the gravitation of the ethereal matter.

His brother, Johann Bernoulli I, developed and made this idea more precise. In 1724 the *Académie des sciences* had announced a prize on the subject of the determination of the laws of the transfer of movement between perfectly hard bodies. Johann Bernoulli interpreted this word *hard* in the sense of *elastic*, and used the occasion to elaborate a hypothesis analogous to that of Malebranche, Leibniz and James Bernoulli on the subject of elasticity. The interpretation that he had given to the question was not approved by the Académie and his paper was rejected. But he was happier when in 1726 the competition concerned the laws of collision for *elastic* bodies.

"All physicists," said Johann Bernoulli, "admit a subtle matter which, because of its movement, was the cause of the elasticity of bodies." What he tried to discover were the [858] details of the mechanism by which the agitation of the ether produces the elastic force of various kinds of matter and, in particular, of gases.

Johann Bernoulli considered a container full of gas to contain a very subtle ether which penetrated the pores of all bodies with ease, and in particular those which constitute the walls of the container, traversing the container in all directions with extreme rapidity. In these torrents of subtle matter swim "numerous corpuscles too large to escape through the pores of the container." Being of various shapes and sizes, they "allow intervals between them so spacious that all these corpuscles, assembled in a heap, would not, perhaps, occupy more than a hundred thousandth part of the container." These small masses, carried by the violent current of the subtle matter, move haphazardly and collide with one another; "but the corpuscles, thus agitated in every direction, and hampering one another by opposed rectilinear movements, will each soon find themselves determined to move so as to be the least obstacle to the movement of the other corpuscles, that is to say to change its rectilinear movement to a circular movement about a centre." A large number of spherical surfaces, each of which will appear to be covered by a multitude of small mobiles and swirl around its own particular centre, will thus be formed in the container. The centrifugal force arising from these gyratory movements will explain the effects that are attributed to the elasticity of the air. "Let us just now consider the dispositions that all the spherical surfaces will take in the container, and the force that they exert on one another and against the interior walls of the container, and we will understand that all the surfaces, both large and small, of all degrees, will be dispersed in the extension of the container in just the way that Descartes conceived that the universe was full of vortices of all shapes and sizes."

These considerations constituted rather an outline of a theory than a theory; they took a more precise form in the Xth. section of *Hydrodynamique*, published in 1738, by the eldest brother of Johann Bernoulli I, Daniel.

Daniel Bernoulli represented the particles composing a gas as animated by an extremely rapid movement; they strike against the walls that they encounter, and the effect produced by each of them on the wall they collide with is measured by the kinetic energy that it possesses at the moment of collision. These innumerable collisions, repeated during very short intervals, produce the appearance of a uniform and constant pressure. The magnitude of this pressure is proportional to the number of molecules which strike the [859] wall in a given time and to the average value of square of the speed with which the particles move.

Let us leave the temperature invariable and reduce the volume of the gas. The mean square of the speed animating the molecules does not vary, but the number of particles striking a given surface in a given time will be increased. It will increase precisely in proportion to the reduction in the volume of the gas. The pressure of the gas will therefore be inversely proportional to its volume, conforming with the observations of Boyle, Townley and Mariotte.

Let us, on the other hand, maintain the gas at constant volume, but increase the temperature. The number of molecules which strike a wall in unit time will not change, but these molecules will, on average, be animated by a greater speed. The pressure of the gas will therefore increase, and the increase it undergoes will be proportional to its initial value. Thus is Amontons' experiment explained.

"It is clear," Daniel Bernoulli wrote in 1746, "that this idea about air corresponds perfectly with all of its properties. It explains in what its elasticity consists, its property of undergoing great condensations and dilations, why its elasticity is pretty much inversely proportional to its volume, why this elasticity is increased by heat, and finally why this elasticity is proportional to the square of the speed with which the parts are moved. I can even demonstrate, concerning certain experiments that have been carried out, what the absolute speed should be in the movement of agitation for a given degree of heat, what the size of the particles is in relation to their average interval, into what volume the air can be condensed by an infinite force, what is the speed of sound, what the absolute sound of a scupper pipe at a given height should be, etc. And all these results have a striking character of truth which marvellously confirms the idea that I have just presented of elastic fluids such as air."

This passage was rich in promises. Daniel Bernoulli has not held all of them. Experimental knowledge of his time would not easily have allowed him to embark on the investigations that he indicates regarding the size of gaseous molecules and the magnitude of their intervals. As for his discoveries in acoustics, they number among his more beautiful claims to fame, but his hypotheses on the nature of gaseous substances are not part of this.

In his *Hydrodynamique* Daniel Bernoulli considered gaseous molecules in motion without worrying about the cause of this motion. Had he abandoned the hypothesis that this motion [860] itself arises from the agitation of a more subtle material? Certainly not. In 1746, the *Académie des sciences* judged a competition whose subject, proposed in 1744, was the nature and properties of magnets. Three memoirs were given prizes: the first was Du Tour's, the second Léonard Euler's and the third was given to a collaboration between Daniel Bernoulli and his brother Johann Bernoulli II. These three pieces proposed to explain the properties of magnets according to Cartesian principles by means of subtle matter. The Bernoulli brothers considered this subtle magnetic matter to be a simple elastic fluid, resembling air, which gave them occasion to expostulate their ideas about fluidity and the elasticity of fluids. They regarded air as a mass of small bodies moving in every direction and colliding continually. "This confused motion," they added, "must undoubtedly be sustained by a very subtle fluid which passes through air." Thus, in 1746 Daniel and Johann Bernoulli II stuck to the essential hypothesis about the cause of *elasticity* which their uncle James Bernoulli had enunciated in 1683 and their father Johann Bernoulli I had developed in 1726. This family of geometers could justly apply the words of Cicero, which the *New mechanical and physical principles tending to explain the nature and properties of magnetism* carried as a motto: *In sententiâ permaneto, enimvero nisi alia vicerit melior.*[9]

Daniel Bernoulli's teaching at the University of Basle gave rise to a pleiad of physicists in Switzerland. At the a time when the majority of minds were to be seen looking to the attractions and repulsions exerted at a distance between material molecules for all the laws of terrestrial and celestial mechanics, these physicists held to the principles of the Cartesian cosmology and made all their theories rest on movement and collision. Amongst them we find Lesage, who accounted for universal attraction by the impact of *ultramondain corpuscles* on material molecules, and who, at a time when the existence of caloric fluid was undisputed, explained the expansibility of this fluid by the agitation of a very subtle material which circulated in its pores. [We also find] Trembley, who became indignant on seeing Lavoisier treat expansible fluids without concerning himself with the essence of *expansibility*, [as well as] De Luc, who adopted and developed the hypotheses of his friend Lesage concerning caloric, attributed the elasticity of gases and vapours to the movement of fire which penetrated them, and explained the movement of molecules of fire by the movement of more subtle particles, the luminous corpuscles, "so that light is the primary cause of the expansibility of all terrestrial

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[9] [You should stick to your view unless confronted by another which is better in respect of truth.]

fluids, whether coercible and ponderable, or incoercible and imponderable, that it [861] forms by uniting more or less intimately with other substances." It is, finally, Pierre Prévost, Lesage's friend, disciple and executor of his will, who expounded the theory of radiant heat in accordance with the ideas of Lesage and De Luc.

IV

We have now arrived at the beginning of the nineteenth century. In England, Newtonian ideas began to lose ground and Cartesian ideas were beginning to gain the upper hand again. Humphry Davy constituted gases of vortices of matter and ether and sketched a theory in many ways analogous to that of Johann Bernoulli I. This theory was to be developed by Rankine at the time of the renaissance of the mechanical theory of heat, a renaissance to which he was to make an important contribution. For their part, Waterston and John Herapath adopted an idea like that Daniel Bernoulli had expounded in his *Hydrodynamics*; they formed a gas from molecules which collided during a rapid movement whose cause they did not seek. This hypothesis was taken up again by Joule, at the time when Krœnig was developing it in Germany.

For Joule and for Krœnig the molecules of a gas move in a straight line with an extremely rapid motion, since they are in general situated at considerable distances from one another, and consequently exert only insignificant actions on one another. The movement of each molecule remains rectilinear and uniform until the molecule comes to be at a very small distance from a similar one. A collision then results, and the molecules move off in another direction. When the gas molecules encounter a solid wall, they assail it with a veritable bombardment, and their innumerable collisions, repeated at very short intervals, produce the effect of a continuous pressure. This pressure is proportional to the number of hits received by unit surface area of the wall during unit time, that is to say, to the density of the gas—this is Mariotte's law. It is also proportional to the average kinetic energy of the molecular motion, that is to say to the absolute temperature—this is Gay-Lussac's law.

Clausius constructed a complete mathematical edifice on these premises that Boltzmann, O. E. Meyer and Maxwell were to alternately develop and modify. Soon the new theory gave the most detailed and unforeseen information about the nature and motions of gas molecules: the average length of path covered by a molecule between two [862] collisions, the number, mass and dimensions of molecules—none of these details, the subtlety of which seemed for ever to steal them from our gaze, remain hidden from him [Clausius]. Surprised by these results, the minds of physicists felt once more the headiness that the hypothesis of molecular attraction and its marvellous consequences intoxicated the contemporaries of Laplace and Poisson; It seemed as though the definitive form and the eternal kind of physical theory had been found. It seemed that the dream of Laplace was near to being realised, and that human thought would become sufficiently penetrating to follow the trajectory of the least atom in the midst of a body with the same precision as the orbit of a planet in the sky.

Then, gradually, the contradictions and difficulties which had not at first been seen but which arose one by one as so many objections to the kinetic theory of gases, cooled the enthusiasm that it had created.

The first authors of the kinetic theory had assimilated the molecules of air and of other gases to the simple material points that a great speed carries along a straight line. But in this hypothesis, the ratio of the specific heat at constant pressure to the specific heat at constant volume takes a much greater value than experiment assigns to it. In order to reduce the value of this ratio, Clausius was obliged to complicate the theory. The molecules are no longer simple dimensionless material points, but small bodies whose size, however small it might be, cannot be neglected. While the centre of gravity of each molecule moves in a straight line, the molecule revolves around its centre of gravity and vibratory movements impart a periodic variation to its shape.

But then a new difficulty emerged: in order to account for the various laws of which experiment has given us knowledge, Clausius was obliged to assume that the kinetic energy of the rotatory and vibratory motion stands to kinetic energy of translational motion in a ratio which remains the same under all pressures and at all temperatures. To begin with, no way of rationally explaining this strange law was envisaged. Nevertheless, by introducing some new hypotheses into the kinetic theory, Maxwell succeeded in accounting for the constancy of the ratio of the two kinds of kinetic energy. But are the new hypotheses entirely acceptable? On this point W. Thomson contradicts Maxwell, and, placed between the irreconcilable views of these two powerful minds, physicists hesitate to declare an opinion.

Not content to frustrate physicists by the uncertainty [863] of the hypotheses on which it rested, the kinetic theory of gases soon discouraged them by its unfruitfulness. It is true that, when applied to certain dissociation phenomena, it led Naumann to the discovery of an important law; but the realisation was not long in coming that this law could be deduced from the thermodynamic properties of perfect gases alone, without any hypothesis about the nature of the motions animating their molecules. In this same domain of chemical mechanics, certain fundamental and incontestable facts provided irrefutable arguments against the ideas of Bernoulli and of Clausius by Horstmann,[10] who had at first been a warm supporter. "One arrives," he wrote in 1873, "at contradictions with experiment because the fact, many times verified, that the mass of solid bodies has no influence of the degree of dissociation cannot be satisfactorily explained." Thus, physicists gradually lost faith in this theory which they had first lovingly embraced.

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[10] [Duhem writes "Hortsmann".]

V

With endeavours to reduce the propositions of Sadi-Carnot and of Clausius to the principles of dynamics frustrated and attempts at explaining kinetically the properties of gaseous bodies curtailed, were more failures needed to inspire an extreme distrust on the part of physicists regarding investigations seeking to discover the nature of motion constituting heat? If the failure of mechanical hypotheses was not to carry the entire edifice of thermodynamics with its fall, it was necessary at all costs that it should be be based as little as possible on them. It was necessary to ask for a minimum of information, and to borrow no more principles than were strictly necessary, from the supposition that heat is a form of motion. Clausius, always so logical and prudent, had in any case set an example and outlined the path to follow. His ideas on the nature of calorific motion in gaseous bodies preceded, we know by his own acknowledgement, the time when he conceived his celebrated memoir *on the motive force of heat.* While editing this memoir, however, he was wary of making any allusion to hypotheses by which the properties of gases were, according to him, explained. He avoided letting the doubtful or adventitious character of these hypotheses be to any degree imparted to the two principles that he provided as the base of thermodynamics. Later, when he brought together in a collection the various memoirs that he had published on the theory of heat, he was careful [864] to group all the works of pure thermodynamics in a first part, in order that their independence from his investigations into the kinetic theory of gases, published in another part, would be exhibited. The exposition of thermodynamics, which constitutes the first part of his works, drew only once on the hypothesis of calorific motion: he took it as a premise for deductions which led to the principle of equivalence of heat and work.

Were these precautions taken by Clausius and, following his example, by the majority of authors who have written on thermodynamics, sufficient to quiet all their qualms and put all objections to rest? Certainly, of the hypotheses on the nature of heat, only those which referred to more general, less detailed, matters were taken. But wasn't that still too much? It was admitted, in accordance with them, that the molecules of a body are agitated by movements of very small amplitude, but of very great speed. It was admitted that the amount of heat released by a body which is transformed is equivalent, on the one hand, to the reduction of kinetic energy of molecular motion, and, on the other, to the work performed by both the internal and the external forces. It was admitted that the work performed by the internal forces throughout a change depends only on the state of the body at the beginning and the state of the body at the end of the change. These suppositions certainly attract the mind by their clarity, their simplicity and their generality. But could they be regarded as absolute certainties? Could they no longer be made the object of doubt? Did they not seem incapable, after all, of accounting for Clausius' law, taken in the its complete and general form, in the form in which it applies to irreversible phenomena? This incapacity is perhaps still only a presumption, only a particular opinion of certain physicists inclined to scepticism. Others, more confident, might hope one day to triumph over this obstacle. But aren't they bound to recognise that their hope is not a certainty, that they might be lured; that perhaps, someday, the impossibility of reducing the principle of Sadi-Carnot and of Clausius to the fundamental hypotheses of dynamics will be rigorously demonstrated; what would remain of the theory of heat following such a discovery? Well, what it was after Rumford's experiment made clear to everyone the impossibility of the substantial existence of caloric, and what optics was after Young's investigations had established the falsity of the emission hypothesis: a theory to be reworked.

Is it not the clear duty of the physicist [865] henceforth to take up the foundations of thermodynamics and to avoid, by judicious precautions, the problems that would be created if this doctrine were, even for a moment, to put science under suspicion? Besides, this revision is easy. It requires only a very slight modification in the exposition of the theory of heat. The logical order followed by Clausius and his successors invoked the suspicion that heat is a movement. But what use did he make of it? He required it only to serve as a premise for the demonstration of this theorem: when a body completes a cycle of changes, the amount of heat that it releases stands in an invariable relation to the work done by external actions exerted on the body. Well, instead of making this proposition a *theorem* and demonstrating this theorem from a conjecture on the nature of heat, why not consider it as a *principle*, as a *physical hypothesis* demonstrated by the totality of its experimental consequences, as *a kind of axiom* analogous to that which Clausius made use of to rescue Carnot's theory from the same fate that befell belief in a calorific substance? The two parts of thermodynamics would then be developed by logically similar procedures, both independent of the supposition that heat is a movement, and therefore indifferent to the future that science reserves for this supposition.

Such is the prudent method which, without hiding his predilection for purely mechanical explanations, G. Kirchhoff inaugurated in the teaching of the theory of heat. G. Lippmann, a student of Kirchhoff's, brought this method to France and became its convinced champion. It is generally adopted today in the teaching of our faculties and schools, in our manuals and our treatises.

VI

When a body describes a closed cycle, the amount of heat that it releases stands in an invariable relation to the work done by the external forces.

A body which describes a Carnot cycle cannot take heat from a cold source and give it up to a warm source unless the external forces do a certain positive work.

These are the two fundamental hypotheses on which modern thermodynamics rests.

The statement of these two hypotheses involves the same notion, the notion of the amount of heat released by a body [866] undergoing a change. What meaning is attributed to the words: *amount of heat?*

For the Cartesians, the amount of heat released by a body undergoing change is the reduction in the amount of motion animating the small parts of the body.

For those who, while holding to what is essential in Descartes' idea, correct it by taking into account Leibniz' discoveries, the amount of heat released by a body is what is lost of the molecular kinetic energy accompanying the change undergone by the body.

For upholders of the materiality of caloric, the amount of heat released by a body is the reduction in the mass of caloric it contains, whether it be in the free or the latent state.

For the physicists who seek to reconcile Black's discovery with the idea that heat is a motion by calling on the aide of molecular actions, the amount of heat released by a body is, in part, the reduction of kinetic energy of the motion of various parts of the body, and in part the work done by the actions of molecules.

For the adherents of the mechanical theory of heat, the amount of heat released comprises, in part, the reduction of the kinetic energy of molecular motion, and in part the work done by all forces, as much external as internal, exerted on the body.

Varied though the thoughts of these physicists are, they are, nevertheless, all agreed on one point: for all physicists, the amount of heat is an abstraction whose definition is the result of the theoretical system they adopt. What they argue about is [the nature of] this abstraction that they introduce into their deductions and calculations in terms of its definition. In each application, no doubt, they substitute for this abstraction a concrete number provided by the readings of a calorimeter. But it is in analysing the abstract notion of the amount of heat that they justify the employment of a calorimeter and the fixing of the rules according to which the measurements of this instrument should be combined, corrected and interpreted in order to provide an approximate estimation of the amount of heat.

Today, physicists introduce the amount of heat into their theories by an inverse process. The amount of heat is no longer an abstract notion for them, defined by the theory and approximately measured in each particular case by a calorimeter which the same theory explains and whose employment it justifies. What they introduce in their arguments and in their formulas under the name of amount of heat is nothing [867] other than the very measure provided by the calorimeter; it is not defined otherwise. According to the majority of physicists, the amount of heat released in a change is, by definition, an amount proportional to the weight of water that each change takes from the temperature 0° to the temperature 1°, or again an amount proportional to the weight of ice that this change induces to pass into the liquid state.

Now is this adequate? Is what is called the amount of heat released during a change simply an amount proportional to the weight of ice that can be melted during this change? Isn't it necessary to add to this definition some complement such as the following: "supposing that all the heat released by the change is employed in melting the ice"? Now, how could it be known whether all the heat released by the change has been employed in melting the ice if some alternative notion of the amount of heat is not available? What could this complement mean if the amount of heat released was, by definition, proportional to the weight of ice melted? Is the amount of heat simply what the calorimeter measures? How, if this is true, will it be explained that physicists, instead of simply taking as the value of an amount of heat the crude result of a calorimetric determination, subject this result to various complicated corrections to the value on which their views might be in agreement? Is it not because in reality they reason about a certain abstract, ideal, amount of heat, the concept of which exists more or less clearly, more or less consciously, in their minds, because the properties that they attribute more or less confusedly to this ideal amount of heat justifies the use of a calorimeter as an instrument for measuring amounts of heat *approximately*, and because in reasoning about this ideal amount of heat they recognise the possibility of increasing, by means of corrections, the precision of this measure? Are the so-called modern definitions of the amount of heat anything other than concrete examples in which an abstraction is found to be involved? But isn't a minute analysis required to separate this idea from examples in which it is involved and to give a clear definition? If the physicists who imagine themselves only to introduce a concrete idea into their reasoning have, in reality, an abstract concept in mind of the amount of heat to which they necessarily, but unconsciously, think of, even when they only believe themselves to be speaking of the magnitude measured by the calorimeter, what could this confused, indecisive, latent notion be, [868] if not a residue of theories believed to have been abandoned entirely, remnants of the hypothesis of fluid caloric or of mechanical suppositions? Will hypotheses really have been driven out of science in so far as the concept of the amount of heat has not been given a clear and general definition which makes no implicit and unnoticed appeal to suppositions which are doubtful or rejected today?

The continual shifting of ideas that physicists have professed regarding heat, like the vicissitudes of the theories of optics, are striking examples of the evolution that all theories of physics have undergone from the seventeenth century to the present. The abstract ideas which are the foundations of these theories were constructed by Descartes entirely from concepts taken from geometry and kinetics, with its figures and motions. Newton substituted the dynamic for the geometric element: the weights of material, motion, attractions and repulsions—there you have all his physics; yet his school put rest where the Cartesians had put agitation whenever it could. During its youth, the nineteenth century created, by a durable and fruitful synthesis of these two doctrines, a mathematical physics all of whose elements are taken from geometry, kinematics and dynamics. Bodies of various shapes, more or less complicated motions, various attractions and repulsions—these are the materials with which it constructed the theories of optics, of heat, of elasticity, of capillarity, indeed, of electricity and magnetism. But on its decline, wearied by the vicissitudes which the definitions of abstract ideas employed in physics have undergone, it tried to dispense with these ideas and to introduce into its reasonings only concrete concepts which are directly measurable. In actual fact, underlying such reasoning abstractions remain hidden and bear the confused trace of rejected theories. In order to completely reject these hypotheses and construct a physics which would be free of them, it is necessary to take a fresh look at the definition of the abstract ideas that this physics cannot do without. What principles should guide us in this revision of the concepts on which the various theories of physics rest? An attentive study of the laws which have governed the evolution of these theories for nearly three centuries would perhaps allow us to catch a glimpse of the rules that must be followed in order to achieve the reform.

ESSAY 2

THE EVOLUTION OF PHYSICAL THEORIES FROM THE SEVENTEENTH CENTURY TO OUR DAY*

I

The theories of modern physics are born of a reaction against scholastic philosophy. It would be impossible to understand the generation of these theories, to disentangle the law of their evolution, by abstracting from philosophical doctrines that they claimed to supplant.

The School thrived on the thought of Aristotle—thought explained, developed and sometimes altered, in innumerable commentaries. It could be said that Aristotle has condensed the spirit and the method of his philosophy almost at the beginning of his work, in that part of the Organon where he proposes to classify all the ideas of men in a small number of essentially distinct and irreducible *categories*.

All the ideas that represent *substances* to us are arranged in a primary category; all those which represent to us *accidents* are arranged in the other categories. Among the accidents that a substance might present, some belong to the category of *quantity*, others to the category of *quality*.

Here are some sacks of corn. Each of them contains a certain number of grains; this number is a quantity. There are times of different duration: hours, days, years, [464] centuries; these durations are quantities. There are paths of various lengths; these lengths are quantities. There are fields differing in shape and aspect; each of these fields has an area and this area is a quantity.

Why is the same name of quantity given to these so different attributes of number, duration, length and area? What are the common features of the dissimilar notions?

Two sacks of corn might contain the same number of grains, or the one might contain more than the other; two times might be of the same duration or of unequal

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durations; of two different paths, the one might be as long, shorter or longer than the other; two fields might have the same area or different areas. Here we have grasped a first common feature of all attributes for which the name quantity is appropriate; all are susceptible of equality and inequality.

But this is not the only distinctive trait which serves to define the category of quantity.

Take various measures of corn which contain different numbers of grains and put them all into the same sack. This sack now contains a certain number of grains, a number which exceeds that of each of these measures. Whatever the order in which you mix all these measures of corn, this number remains the same; it is the *sum* of the numbers of grains of corn contained in each measure.

Take various times, equal or unequal; their succession will form a new time, of greater duration than each of them, but whose duration does not depend on the order in which the various temporal parts succeed one another.

Take several different paths and place them end to end; their succession will be a new path, longer than each of the first ones. However the way in which they are placed end to end is changed, [465] the shape of the path obtained might well change but the length of the path remains invariable.

Take some surfaces of various shapes and juxtapose them; their union forms a new surface, greater than each of the former surfaces. Their mode of juxtaposition influences the shape of the resulting surface, but not the area of this surface.

Thus, if an attribute belongs to the category of quantity, it is possible to group the objects exhibiting this attribute in such a way that the resulting complex object presents the same attribute, but to a higher degree, and this degree will be independent of the order which governed the grouping. This feature is expressed in these terms: quantities of the same kind are susceptible of *addition*.

It is because quantities possess all the features that we have just analysed that they can be represented by means of a particular kind of quantity, by means of numbers. A well known operation, the measure, effects this substitution of numbers for quantities, an exact substitution which allows the unification in a single science, *Arithmetic*, not only the study of numbers, but also the general study of all quantities.

These features of equality, inequality and addition define precisely the category of quantity. Outside this rigorously delimited domain extends the unlimited category of quality. "Quality," says Aristotle, "is one of those words which are taken in many senses." The shape of a geometric figure which makes it a circle or a triangle is a quality; the sensible properties of bodies—warmth and cold, light and dark, red and blue—are qualities; being of good health is a quality; being virtuous is a quality; being a grammarian, a geometer or a musician are all qualities.

"Some qualities are not susceptible of more or [466] less. A circle is not more or less circular, and a triangle not more or less triangular. But the majority of qualities are susceptible of more or less; they are capable of *intensity*; a white thing can become more white."

What is the difference between the intensity of a quality and the magnitude of a quantity?

The large number of grains enclosed in a sack of corn can always be obtained by combining the heaps of corn each containing a smaller quantity of grains. A century is a succession of years; a year, a succession of days, of hours, of minutes. A long road covers several leagues in joining end to end the short segments which a walker passes with each step. A very extensive field can be decomposed into patches of lesser area. Any quantity whatsoever can always be obtained by the addition of quantities of the same kind and smaller magnitude.

Nothing of the sort is to be found in the category of quality. Juxtapose several equally red bodies, and the collection of them is the same red, not a more intense red. Bring together two equally warm bodies, and the collection of them is as warm as each of them, not warmer. However many balls of snow you amass, said Diderot, you will not succeed in warming a furnace. In general, a quality taken with a determinate intensity cannot be formed by the addition of things of the same quality but with a lesser intensity. The very word addition loses all meaning in the category of quality and there is nothing on which the measure can build.

Alone among the sciences, arithmetic leaves out any consideration of quality and contemplates only the laws of quantity. Even geometry recognises some qualities among the objects of its investigations, for the shape of various figures is a quality. As for physics, it is essentially the study of sensible qualities of bodies. Not [467] that the consideration of quantity has no place in this science, for "physical bodies exhibit volumes, surfaces, lines and points—things which occupy the mathematician," so that certain parts of physics, astronomy for example, are at the same time mathematical sciences. But whereas the geometer studies magnitudes and shapes in abstract fashion, by separating them from natural bodies where they are found accompanied by qualities, the physicist cannot keep these qualities outside his speculations. According to the naive comparison employed by St. Thomas Aquinas, following Aristotle, the one studies the curvature of a nose without being concerned about the nose of which it is the profile, the other occupies himself with the nose in the flesh where this curvature is to be found.

The geometer knows of only one kind of change, the change of shape and position in space—*local movement*. The physicist conceives and analyses a *movement* infinitely more general which embraces, in its various forms, all kinds of change in the substance and qualities of bodies: movement, the local movement by which shape and position change; but also movement, the act by which a quality becomes more or less intense, by which a body becomes more or less warm, a source of light more or less bright; movement, the operation by which qualities are transformed from one to the other, by which a solid becomes fluid, and liquid changes to vapour; movement, the appearance and disappearance of a quality, the electrification of a piece of amber that is rubbed, the extinction of a flame that is blown; and movement, the combination which unites the simple elements to form mixts, the decomposition which resolves mixts into their elements. Such is the infinite variety of movements which offer themselves for the contemplation of the physicist, but which escape the reasoning of the mathematician because the attributes which change in these movements are qualities and not quantities.

II

What [468] an incoherent, shabby, crumbling edifice scholasticism in its decline has built on so simple, so broad and so solid a base. The rest is well known; instead of studying nature, secrets were sought in the strange and narrow commentaries where the thought of Aristotle was over-elaborated and deformed. Instead of searching for the laws connecting the various physical phenomena to one another, it sufficed to attribute each of them to a new quality of bodies, to a specific virtue, to a substantial form, by which it was thought the ultimate cause is revealed. The lightness of movement, the horror of vacuum, sympathies and antipathies of all kinds were to form a chaos of bizarre denominations and puerile or ridiculous explanations; such was physics at the end of the sixteenth century.

This science had come to the point of provoking a feeling close to disgust on the part of those few minds concerned with rigour and enamoured of clarity. In their horror of the pedantic nonsense that they heard delivered every day under the authority of Aristotle they came to confuse the great works of the Stagirite and the masters of the Schools such as St. Thomas Aquinas with the ridiculous and futile verbiage of their later heirs.

"Aristotle," wrote Bacon, "has corrupted natural philosophy with his dialectic. He has wanted to construct the world with his categories .... The first idea has given us the primary elementary qualities; the second, occult properties and specific virtues. Both hark back to an order of vain speculations in which the mind finds rest, in the belief that it assesses things on the basis of a single trait, and is diverted from substantial knowledge." And against Aristotle's *Organon* Bacon set the *Novum organum.*

What a strange work this book is, which claims to give us the logic of science! [469] Bacon drew the following conclusion to his attack against the qualities and powers entertained by scholastic philosophy: "But, neglecting these distinctions, if it is observed, for example, that there is in bodies a principle of mutual attraction, in such a way that they do not allow that the continuity of nature be broken and torn apart and vacuum produced, ... or if it is said that there is in bodies a tendency to aggregate in masses of the same nature, dense bodies tending towards the globe of the earth, light and rare bodies towards the celestial orb, these and similar distinctions would be the true physical kinds of movements. The others, on the contrary, are purely logical and scholastic."

The new physics retained, therefore, from the scholastic heritage the horror of vacuum, sympathies and antipathies, lightness and gravity; from alchemy it borrowed its aim, which is "to give silver the colour of gold, or a more considerable weight, ... or transparency to some non-diaphanous stone, or toughness to glass, or vegetation to some non-vegetative bodies."

In order to obtain these marvellous results, it was necessary to "illuminate the texture and true constitution of these bodies, on which all the properties and all occult and, as one says, specific virtues of things depend."

What method should be followed in order to attain this profound and intimate knowledge of nature? For each investigation, a table of positive facts, a table of negative facts, a table of degrees or comparisons and a table of exclusions and rejections is set up. Twenty seven kinds of privileged facts are distinguished designating bizarre allegorical denominations: facts of migrations, indicative, borderline and hostile facts, facts of the cross, of the lamp, of divorce, of the course of water, of the rod ...

Does Bacon give us an example which would allow us to appreciate and to grasp the essence of the functioning of [470] this marvellous instrument? He uses his method to gather a "first vintage concerning the form of heat" and here is the juice of this harvest: "Heat is an expansive, fighting movement which operates in the molecules of bodies." Concerning the nature of the expansion, he had to add the following: "a movement from the centre to the circumference, combined with a movement upwards." Concerning the second feature of movement, he had to add that "the action is not sluggish, but occurs with a certain rapidity and even violence."

The eighteenth century, and ours after, have wanted to see in the *Novum organum* what Bacon had wished to put there: the programme for the physics of modern times. In fact, this book exerted no influence at all on the development of experimental science. At the time Bacon wrote it, the new physics saw its true founder in Galileo.

III

Galileo led physicists to the study of nature more by his example than by his precepts. He showed how an experiment should be conducted, and how the results should be interpreted in order to obtain the law linking physical phenomena from the same group. Broadly speaking, the experimental method got off the ground when the first man sought to give an account of the things around him. But more than anyone else, Galileo contributed, by the rational use of instruments and the employment of geometrical language and deductions, to giving it the precise, systematic and scientific form which characterises modern physics.

Galileo preferred not to introduce into physics the specific qualities and virtues considered by the scholastics. In his *Dialogues*, one of the interlocutors recalls the explanation [471] of the ebb and flow [of the tides] proposed by Kepler: the moon is endowed with a virtue of attraction on the waters of the sea. "With these two words, sympathy and antipathy," wrote Galileo through the mouth of the interlocutor Sagredo, "our physicists seem to account for a large number of accidents and phenomena that we see accomplished in nature every day. But this kind of philosophising has, in my view, a great likeness with the way one of my friends paints. He would write on the canvas with chalk: here, I would like to have a fountain with Diane and her nymphs, and some greyhounds; there, a hunter with the head of a stag; in the distance, open countryside, a copse, and a hill. Then he would let the artist paint all these things and go away convinced that he has painted the metamorphosis of Actaeon, having contributed nothing more than the title."

Despite his severity towards the sympathy that Kepler attributes to the moon and the waters of the sea, Galileo seems not to have banished all occult qualities from his physics. He still spoke of the gravity of bodies. But one day Newton was to identify the specific virtue that Galileo retained in his reasoning with the one he joked about.

IV

The aim and characteristic feature of Cartesian physics was to drive away qualities entirely from the study of material things.

Among the sciences, arithmetic alone is free of all notions borrowed from the category of quality; and it alone conformed to the ideal that Descartes proposed as the whole science of nature.

As for geometry, the mind comes up against the qualitative element because that science remains "so compelled by the consideration [472] of figures that it cannot exercise the understanding without greatly tiring the imagination." "The meticulousness with which the ancients used the terms of arithmetic in geometry, which could only proceed from their not seeing their relationship sufficiently clearly, caused much obscurity and embarrassment in the way in which they were explained." This obscurity and embarrassment would disappear if the qualitative notion of form and shape were banished from geometry and only the quantitative notion of distance and the equations relating the mutual distances from another of the points studied is retained. Although their objects would be different, the various branches of mathematics considered amongst its objects "nothing but the various relations or proportions to be found there," in which case it suffices to treat these proportions in general by the methods of algebra without worrying about the objects in which they are found or the figures in which they are realised. In this way, "all that falls under the consideration of geometers is reduced to the same kind of problem, to search for the value of the roots of several equations." The whole of mathematics is reduced to the science of numbers, where only quantities are treated; the qualities have no place.

The qualities banished from geometry must now be banished from physics. To accomplish this, it suffices to reduce physics to mathematics, which has become the science of quantity alone. This is what Descartes strove to accomplish: "I acknowledge no principles of physics," he said, "which are not also acknowledged in mathematics."

What, first of all, is matter? "Its nature does not consist of hardness, nor of heaviness, warmth or other qualities of this kind," but only of "extension in length, size and depth." It is nothing else but that matter, "divisible, mobile and endowed with shape, which geometers call quantity and which they take as the object of their demonstrations." Matter is [473] therefore quantity. The amount of some particular matter is the volume that it occupies. A vessel encloses just as much matter, whether it be filled with mercury or with air. "Those who claim to distinguish material substance from extension or from quantity either put no idea whatsoever under the name of substance, or have a confused idea of an immaterial substance."

What is motion? Again, a quantity. Multiply the quantity of matter that includes each of the bodies in a system by the speed of these bodies, add together each of these products and you will have the quantity of motion of the system. As long as the system does not collide with any foreign body which gives or takes from it motion, it retains an invariable quantity of motion.

Thus, a single, homogeneous matter, about which we know nothing except that it is extended, is distributed throughout all the universe. This matter is divisible into parts of various shape and parts which can move in relation to one another. These are the only true properties of that which bodies are made of; and from these properties should be derived all the apparent qualities which affect our senses. The aim of Cartesian physics is to explain how this reduction is carried out.

What is gravity? The effect produced on bodies by the vortices of subtle matter. What is a hot body? A body "composed of small parts which move about separately in a very fast and violent motion." What is light? A pressure exercised on the ether by the motion of bodies excited and instantaneously transmitted over the greatest distances. All these qualities of bodies, without exception, are to be explained by a theory in which only the geometric extension, the various figures that can be drawn there and the various motions of which these shapes are susceptible is considered. "The universe is a machine [474] in which there is nothing to be considered except the shapes and motions of its parts." Thus, the whole of the science of material nature is reduced to a kind of universal arithmetic from which the category of quality is irrevocably banished.

V

It would be difficult, in our age, to imagine the extraordinary enthusiasm with which Descartes' physics was received. Physics, which had up to that time been the domain of obscure entities and occult virtues, of the strangest, and equally sterile, sympathies and antipathies, became as clear and ordered as geometry. The admirable discoveries contained in *Optics* and *Meteorology* were, moreover, the certain guarantee of the new method.

The popularity of this physics, which took the universe apart as easily as a clockmaker separates the wheels of a clock, which explains the mechanism of nature as clearly as that of a mill, spread beyond the circle of scientists, and Molière's doctor was sure to raise a laugh from the pit by invoking the *virtus domitiva* of opium.

The foundational principle of Cartesian physics—that everything in the material world is explained by extension and movement—soon found only the occasional adversary among scientists worthy of the name. Nevertheless, although the principle remained uncontested, discussions of the applications Descartes had made of it were not long in coming.

Descartes had declared the speed of light to be infinite, adding that his physics would be overturned from top to bottom if this proposition was controverted. Roemer demonstrated that this speed was finite, although very large, and made its value known. Huygens too felt bound to write in his *Treatise on Light:* "It has always [475] seemed to me, and to many others with me, that Mr. Des Cartes himself, who had the aim of dealing with physics intelligibly and who had surely succeeded as well as anyone before him, has said nothing which is not full of difficulties, or even inconceivable, on what light and its properties are."

This same Huygens wrote in his *Discourse on the cause of heaviness*: "Mr. Descartes has recognised more clearly than those before him that nothing more would ever be understood in physics than what can be reduced to principles that do not exceed the scope of our mind, such as those which depend on bodies, considered without qualities, and their movements. But since the greatest difficulty consists in showing how so many diverse things are effected by these principles alone, it is this that he has not succeeded in in the several specific subjects that he set out to examine, amongst which, in my view, is heaviness."

Sometimes this same Huygens was bolder, and went as far as to put in doubt the essential principles of Cartesian physics. "As for vacuum," he said, "I find no difficulty in admitting it, and I even believe it necessary for the movement of small particles relative to one another, not being of the opinion of Mr. Descartes, who would have it that extension alone is the essence of bodies, but also adding perfect hardness which renders them impenetrable and incapable of being broken or crushed."

The popularity of the Cartesian reform jeopardised it by arousing a host of mediocre and ignorant disciples of Descartes who were quick to invent the most complicated and bizarre mechanisms to account for phenomena that they have not even condescended to study. The vortices of subtle matter and fluted corpuscles are not given any explanation. Descartes had paved the way himself in his proud haste to comprehend all the effects of nature in his system.

Pascal [476] encountered these Cartesians, who were hardly less ridiculously devoted to the word of the Master than the last decadent scholastic doctors, in the person of Father Noël, the author of *Plein du Vuide* and the physicist who defined light as "a luminous movement of transparent bodies which are moved luminarily by lucid bodies." The author of *Pensées* also wrote: "It should be said on the whole: that happens by shape and movement, because that is true. But to say which [shape and movement is involved], and to build that machine is ridiculous, because it is useless, and uncertain, and arduous.[1] And even if it were true, we would not think that all the philosophy worth an hour of effort."

VI

Pascal did not go so far as to cast doubt on the very principle of the Cartesian reform, or to reject the reduction of the whole of physics to the study of shape and motion, or to propose a return to the qualities of the Schools. Leibniz was so daring.

Leibniz had met people who believed "the precepts and views of Mr. Des Cartes nearly as strongly as the word of God," and who substituted commentaries on *Principles of Philosophy* and *Treatise on the World* for the study of nature just as the scholastics commented on *Physics*. No doubt the bad temper caused by the narrowness of such minds explains the keenness with which he undermined the foundations of the Cartesian philosophy—a keenness of which one of his contemporaries could write, with some appearance of justice: "It has seemed for long time that Mr. Leibniz has wanted to establish his reputation on the ruins of that of Mr. Descartes." But Leibniz had other, more profound and purely scientific, reasons for taking issue with Descartes.

In [477] reducing matter to geometric extension alone, Descartes reduced to the same fact motion and the only movement known to geometers, the change of position of one figure in relation to another figure, to *relative* motion. He defined it as: "The transport of one part of matter, or of a body, from the neighbourhood of that with which it is in immediate contact, and which we consider as being at rest, to the neighbourhood of some others."

When two bodies distance themselves or approach one another, we can say that a movement is produced in the system of these two bodies. But it is possible to attribute this movement exclusively to one of the two bodies, or just as well exclusively to the other, or yet again to distribute it between the two. All attribution of movement to a body presupposes that rest is attributed to some other body, taken as a reference object. But these attributions are arbitrary, and can be reversed freely; there is no absolute motion.

This is one of the necessary consequences of Descartes' system. To those who accused him of merely seeking, in his affirmation that all motion is relative, a roundabout way of avoiding being condemned like Galileo, the great geometer disdainfully responded that they did not understand anything of his philosophy.

The principle that all movement is relative—that absolute motion is a nonsense—was to dominate mechanics completely for all who accepted the reduction of matter to extension alone. It certainly dominated Cartesian mechanics; the

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[1] [Also quoted making this point in Duhem's "Une nouvelle théorie du monde organique", *Revue des questions scientifiques*, 33 (1893), 99-133; p. 116.]

fundamental law on which it rested, the conservation of the quantity of motion, was in accord with this principle.

Unfortunately, the conservation of the quantity of motion is not an admissible law, and Cartesian mechanics is false. As a matter of necessity, it must be abandoned if the rules of the dynamics first outlined by [478] Galileo, and completed by Huygens and Leibniz, are to be followed. And this new dynamics, accepted without dispute more or less as soon as it was discovered, could not satisfy the hypothesis which reduced all movement to the change of mutual position of bodies. The concept of relative motion was not sufficient, and required of necessity that the idea of absolute motion have a sense, corresponding to something real. If the relative position of two bodies has changed, it is no longer a matter of indifference whether the movement which produces this change is attributed to the one or the other. If the distance from the sun to the earth is increased or decreased, it is not a matter of indifference whether it is an effect of the movement of the earth or an effect of the movement of the sun.

"All this shows," Leibniz declared, "that there is in nature something other than that which is purely geometric, that is, extension and its modifications of whatever kind. And after careful consideration, it becomes clear that it is necessary to add some superior or metaphysical notion, namely that of substance, action and force." ... "Although I am persuaded that everything occurs mechanically in the material world, I cannot but believe that the principles of mechanics, that is to say, the first laws of motion, have a more sublime origin than those of pure mathematics can furnish." ... "Accordingly, I find that in nature it is necessary to employ, in addition to the notion of extension, that of the force which makes matter capable of acting and resisting." ... "This notion of *force* is highly intelligible, although it falls within the province of metaphysics."

If there are other things in material substance than extension in length, breadth and depth, and geometric shape, it must be that this something is a virtue, a form, belonging, in other words, to the category of quality. "I am aware that I advance a great paradox when I claim to reinstate in some way [479] the old philosophy and to recall *postliminio*[2] the substantial forms that have been banished." ... "I have long been persuaded of the futility of these beings, which I have been unwillingly obliged to take up with vigour having conducted investigations myself which led me to recognise that our modern thinkers have not quite done justice to St. Thomas and other great men of that time, and that there is much more that is sound in the views of the scholastic philosophers and theologians than might be imagined, provided it is used appropriately and in its proper place."

He would not in the least have approved the ridiculous way in which the decadent scholastics treated physics. "I still agree that the consideration of these forms is of no use in detailed physics and in particular, should not be employed in the

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[2] [As though by the right, according to Roman law, of a banished person to resume civil liberties on return from exile.]

explanation of phenomena. And that is where our scholastics were lacking, and the doctors of the time followed their example, thinking that they could give an account of the properties of bodies by mentioning forms and qualities, without troubling themselves to examine their mode of operation, as if one could be content with saying that a clock has the horological quality resulting from its form, without considering in what this consists."

The modern physicist, on the other hand, is wary of making direct appeal to qualities and substantial forms in order to explain the phenomena that he studies. For him, all that is qualitative in a body is united and condensed in a single notion, that of the force that this body exerts and is subjected to. By means of this force, together with shape and motion, he should account for the phenomena that the material world presents to us. He should therefore explain them mechanically, but his mechanics includes an element, force, which "is something different from size, shape and motion," which cannot be entirely reduced to the category of quantity.

VIII

This [482] way of treating physics, so different from practices imparted to minds by Descartes, seemed astonishing to those, still numerous in our day, who followed the views of this philosopher. Was not Newtonian physics a poorly disguised return to occult qualities, to sympathies and antipathies of the schools? Does the attribution of an attractive or repulsive action whose nature remains unknown explain a phenomenon?

I cannot accept, Huygens declares, the mutual attraction and repulsion that Newton attributes to the small parts of bodies, "because I think I can clearly see that the cause of such an attraction is not explicable by any principle of mechanics, nor the rules of motion ... It would be a different matter if it was supposed that heaviness were an inherent quality of bodily matter. But that is something I believe Mr. Newton does not agree to, because such a hypothesis would quickly distance us from mathematical or mechanical principles."

"*Everything in the world happens through matter and motion*," wrote Daniel and Johann Bernoulli II in 1746. "This principle of Descartes is something so striking, and it seems so clear from the first, that it is surprising that it has been contested by I will not say which of the old philosophers, but by our greatest modern philosophers such as Newton and a large number of others who have followed his authority, all of whom have introduced the principle of the mutual attraction of matter, existing and innate in matter itself, and produced solely by the immediate volition and efficacy of God. Can our reason accept this principle?" Daniel and Johann Bernoulli modestly added, it is true: "It would be wrong, however, to deny all that human understanding [483] has difficulty in comprehending, and whose reality allows itself to be felt only by its effects."

One of the most scrupulous and logical of Descartes' disciples, Gamaches, appeared yet more severe towards Newton: "Feeling that physics would always impede him," he said, "he banished it from his philosophy. And afraid of being forced to sometimes call on its help, he was careful to set up the intimate causes of each particular phenomenon in primordial laws. All difficulties were ironed out in this way. His work turned on just those tractable subjects on which he could bring his calculations to bear. A phenomenon analysed geometrically becomes for him a phenomenon explained. Thus, this illustrious rival of Mr. Descartes soon had the singular satisfaction of being thought a great philosopher by virtue of being a great geometer."

These attacks were not allowed to go without reply.

Of those who accused him of confounding the mathematical exposition of a phenomenon with the explanation of that phenomenon and thus harking back to the deplorable errors of the scholastic physicists, Newton had already replied in his *Optics*: "To explain each property of things by endowing them with a specific occult quality by which would be generated and produced the effects manifested to us, in not to explain at all. But drawing from phenomena two or three general principles of motion, then explaining all the properties and actions of bodies by means of these clear principles, is truly a great progress in philosophy, even though the causes of these principles have not been discovered. This is why I do not hesitate in proposing the principles of motion, while leaving aside the investigation of causes."

But had the Cartesians not just reproached Newton for returning to occult qualities, and of treating gravitation as an occult cause? What, then, is an occult cause? Is it something whose existence is clearly revealed by observation, although its nature remains obscure? [484] Is it not rather what is conceived without adequate evidence of the underlying circumstances? Which physicists most frequently appeal to such occult causes? The Newtonians, or the upholders of the Cartesian School who, instead of delivering an experimental study of nature, invent vortices of subtle matter everywhere, beyond the grasp of the senses, traversing every body and always endowing the requisite property in order to give an account of the most perplexing phenomena? "Their speculations are nothing but a tissue of hypotheses, despite the care they take to reason only in accordance with the laws of mechanics. It might be a beautiful fable that they tell, but it is only a fable." So Roger Cotes put it when he presented the second edition of Newton's *Principles* to the world of science.

IX

The fruitfulness of Newtonian physics assured it of success.

Whereas the principle of universal gravitation, subjected to mathematical analysis by all the great geometers of the 18th century, furnished the minutely precise formula of the slightest irregularities in celestial motions, and the geodesic measures—one of the most beautiful claims to fame of the Paris Academy of Science—proved Newton's theory to be right about the shape of the earth, the theory Huygens derived from the Cartesian vortices was refuted.

Soon the new methods brought success for terrestrial physics as striking as in celestial mechanics.

Newton had suggested the hypothesis that the reflection and refraction of light is due to the actions exerted by bodies at short distance on light corpuscles. [485] This hypothesis enabled Laplace to recover not only the simple laws of reflection and refraction, but also the laws of double refraction of Island spar which Huygens had linked up with ideas close to those of Descartes. action at a distance

Laplace based a theory of heat on an analogous hypothesis, giving an account of all the thermal effects accompanying the expansion and contraction of gases, and explaining the veritable mechanism of the propagation of sound in air.

Newton asked himself whether the rising of liquids in capillary tubes was not due to actions exerted at very small distances between the particles of the tube and the liquid. Clairaut, Jurin, Sègner and Young all tried to subject this hypothesis to calculation, clearing the way for Laplace who took it as the basis of a detailed theory which was minutely verified by experiment.

Newton had tried to explain chemical phenomena by the attractions of affinity exerted between different substances. An at the beginning of this century, Berthollet, in his *Essay on Chemical Statics*—a work whose depth and insight continue to astonish today—endeavoured to show that "the powers that produce chemical phenomena are all derived from the mutual attraction of the molecules of bodies, to which the name of affinity is given to distinguish it from astronomical attraction."

Is the cohesion of solids not also the effect of molecular actions which the various parts of bodies exert on one another? Newton merely posed the question; Boscovich insisted on it, and so it was that Poisson, Navier and Cauchy erected a complete theory of elasticity of solid bodies on the hypothesis of molecular attraction—one of the most beautiful theories of mathematical physics.

Newton had drawn attention to the analogy between electric and magnetic actions [486] and gravitation; Tobie Mayer and Coulomb showed that the laws of these various actions is expressed by the same formula and Poisson founded the mathematical theories of electricity and magnetism on this discovery, emulating celestial mechanics as much by its beauty and fecundity as by its difficulties.

Finally, hardly had Ørsted and Ampère discovered the phenomena of electromagnetism and electrodynamics than its explanation was reduced to mutual actions bound by the fundamental rules of Newtonian physics.

In the thirty-first and final question of *Optics* Newton had outlined a bold programme in which all the phenomena of terrestrial physics would be explained by mutual attractions and repulsions exerted at a distance. And how reality has exceeded the most daring predictions of this programme! Poisson also announced the advent of the "*Physical Mechanics*, whose single principle would be to reduce everything to molecular actions which transmit the action of the given forces from one point to another and which are intermediaries in their equilibrium." Laplace too wrote "All terrestrial phenomena depend on this kind of force, just as celestial phenomena depend on universal gravitation. The consideration of these forces, it now seems to me, should be the principal object of mathematical philosophy."

But what are these forces which are exerted at great distances between celestial bodies, or at small distances between molecules of matter? Are they the essential and immediate properties of matter, irreducible to any mechanism, or, on the other hand, the effects of a yet unknown mechanism? Like Newton, who contented himself with having established by induction the existence of universal attraction and who declined [487] to put forward any hypothesis on the origin of this force, and like Leibniz, who recommended the physicist to reduce the explanation of all phenomena to matter, movement and force, leaving to the metaphysician the burden of pressing as far as possible the analysis of these three elements, the most illustrious Newtonians resisted analysing the notions of attraction and repulsion at a distance which they introduced into their theories. "I therefore think," wrote Boscovich, "that any two material points are equally determined to approach one another for certain values of their distance, and to move apart from one another for other values of this distance, and this determination I call force, attractive in the first case, and repulsive in the second. By the name force, I do not understand the expression of a mode of action, but simply its determination, whatever it may result from." Laplace said the same on the subject of universal gravitation: "Is this principle of a primordial nature? Is it just a general effect of an unknown cause? Here our ignorance of the intimate properties of matter brings us to a standstill and deprives us of any hope of responding to these questions satisfactorily."

X

The beginning of the nineteenth century marks the zenith of Newtonian physics.

At the very moment when this doctrine reached its full development, the progress of the study of nature would come to contradict it at more than one point and soon certain main branches of physics pushed on in a different direction from that in which the eighteenth century had directed them.

Optics was first; rejecting the hypothesis of emission, it was constructed by Young and Fresnel on a new plan, taking up again the wave hypothesis that the [488] Cartesian Huygens had proposed. Then the science of heat, abandoning the theory of caloric, became, thanks to Laplace, one of the most fruitful applications of the doctrine of molecular actions in attributing the effects of heat to small and rapid movements of the ultimate parts of bodies. These developments, whose history we have retraced,[3] led minds down a path little different from that Descartes had followed.

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[3] See *Revue des Deux Mondes* for 1 May 1894, 15 June, 15 July and 15 august 1895. ["Theories of Heat", translated in this volume.]

So powerful and durable had the ideas of Newton been, however, that although they profoundly modifyed certain parts of theoretical physics, physicists remained faithful to the fundamental principles on which the doctrine of attraction rested.

Young and Fresnel proposed an optics which was the natural development of the Cartesian optics of Huygens. But when it came to explaining the elastic properties of the ether whose waves propagated the luminous vibrations, Fresnel supposed it to be formed of material points which attract one another at small distance, and Cauchy brought to the service of this hypothesis the prodigious power of his analysis.

Sadi Carnot, Robert Mayer, Joule, Colding and Helmholtz admitted, like Descartes, that heat consists essentially of a movement of the ultimate particles of bodes. But Clausius could only give a systematic form to their ideas by making appeal in his reasoning to the work effected by molecular actions.

The renaissance of the mechanical theory of heat brought back into vogue the purely kinetic explanation of the properties of gases that the Cartesian school of the Bernoullis had preserved and developed in Switzerland while Newtonian physics triumphed in all the academies of [489] Europe. But even this explanation could not avoid the introduction of molecular actions, and Maxwell was obliged to invoke them in order to avoid discrepancy between theory and experiment.

Thus, among those who contributed most to the development of the mechanical theory of heat we find a good number of convinced Newtonians. Some of them, such as Athanase Dupré and Hirn, following the example of several philosophers of the eighteenth century, had no misgivings about regarding the mutual attractions and repulsions of molecules as the primary, irreducible and essential properties of molecules.

However, although in abandoning luminous corpuscles and caloric fluid, optics and the theory of heat were not entirely rid of forces acting at a distance, this partial return to Cartesian physics carried in its wake a reaction against the hypothesis of attractions and repulsions. Again, a large number of philosophers and physicists conceived the wish to reduce all phenomena in the inorganic world to matter and motion, without employing any quality, any primordial force or any affinity. Again, the pure mechanics tended to reject dynamism. Attempts at explaining, without any action at a distance, universal gravitation, the properties of luminous ether, and electric and magnetic phenomena followed one another without interruption for many years. These attempts were often ingenious; but they were sterile. They laboriously explained the known laws without revealing anything new. Moreover, none of them seemed to reunite the approbation of a great school of physics until the day when the admirable discoveries made by Helmholtz in the domain of hydrodynamics were to give mechanical doctrines an energetic impulse.

Cauchy [490] has shown that it is possible to represent very simply the modification undergone by a very small part of a body during an infinitely short time which tends to deform it in whatever way. Such a modification always results from three simpler modifications: first, the particular material undergoes a deformation which expands it unequally in three conveniently chosen rectangular directions; second, it turns through a small angle about a certain straight line through its centre of gravity called its *instantaneous axis of rotation;* third, it is transported, without changing shape or orientation, a short distance along a determined direction. One or two of these three types of modification—expansion, rotation and translation—might be absent; for example, such and such a particle of the mass in question might not undergo rotation. When the infinitely small movement of a particle includes an instantaneous rotation, it is called *vortex motion.*

The vortex motions of fluids arise from peculiar properties.

Let us consider a fluid, gas or liquid, which we suppose completely lacks viscosity, and let us imagine that this fluid is brought into motion. If, at any instant of the motion, a particle of this fluid lacks turbulent motion, then it will be without it for the entire duration of the movement. If, on the other hand, it is endowed with rotation, then at no instant will this rotation cease or change its sense.

There is more. Take a particle endowed with an instantaneous rotation and extend the axis about which it turns outside its mass. This axis will encounter a new particle contiguous with the first and turning in the same sense about an axis slightly different from the first. It is therefore possible to determine step by step a row of similar particles. [491] One could speak of a pearl necklace, all aligned on the same thread of silk about which they turn. Among these pearls, some, the biggest, turn slowest; smaller ones have a more rapid rotation. But all turn in the same sense. Presently, the ideal thread of silk connecting the turbulent pearls moves right through the mass of the fluid, only to stop at the surface bounding the fluid. Then we have a *vortex tube.* Soon it will close on itself in a flexible necklace, in which case we have a *ring vortex.*

When a fluid without viscosity contains a tube vortex or a ring vortex, the mass of the fluid which at a given instant composes this tube or this ring is also that which will compose it indefinitely. The silk thread connecting the turbulent pearls to one another is but an ideal string; it is also unbreakable. It can be deformed and displaced; the tube or ring can bend, undulate and travel through the mass of the fluid in every direction. But the thread cannot be cut; each of the pearls composing the tube or ring is invincibly tied to its partners.

Scatter these strange ring vortexes in the body of a fluid lacking vortex motions. You will see them approach or recede from one another as if induced by forces acting at a distance—fictitious forces which are only the apparent effect of the pressures engendered by the vortexes in the intervening fluid. The formulas governing these forces are close mathematical analogues of the electrodynamic laws established by Ampère.

These astonishing propositions are not hypotheses; they are *theorems* which rigorous deductions extracted from the principles of hydrodynamics. It was left to the prudent logical mind of Helmholtz to establish these certain propositions.

The bold imagination of W. Thomson was to make a new physics spring from these theorems.

Let [492] space be filled with a fluid ether lacking viscosity, and let innumerable ring vortexes formed from the same fluid float in the remaining ether not possessing any vortex motion. Each of these ring vortexes will be a material system of invariable mass, indivisible and eternal; in a word, an *atom*. The dimensions, the shapes, the speeds of rotation of the various ring vortexes can offer an infinite variety; it would therefore be possible to have infinitely many kinds of atoms, and chemists should no longer be surprised if experiment reveals for them each day a new simple substance. These vortexes approach or recede from one another as if actions were exerted at a distance on one another. These actions would be fictitious forces, the effects of the pressure that the ring vortexes generate in the ambient ether. Thus was constituted a world formed from a single material, without qualities, only capable of shape and motion—the world as the Cartesians claimed it to be.

"But," said Huygens, "the greatest difficulty consists in showing how so many different things are brought about by these principles alone." So too are W. Thomson, Tait, Maxwell and Lodge obliged to deduce the theory of light, the fundamental laws of chemical action, and the explanation of electrical and magnetic phenomena from the *gyrostatic* hypothesis. It is above all the British physicists who have contributed to the development of the doctrine of vortexes. Their intelligence, better suited to imagine the functioning of complicated mechanisms than to understand qualities accessible only by abstraction, makes them the natural apostles of the new Cartesianism.

Have they succeeded in transforming it into a complete theory, logically connecting the various branches of physics which have so far invoked the hypothesis of actions at a distance? It must be recognised [493] that their efforts are far from having attained this ideal. The applications that they are able to make of the theory of vortexes are presented in the form of isolated sketches, without any connection between them. Each of these sketches presents analogies with one part of physics—in the form of a *mechanical model*, in the words dear to the English physicists—rather than constituting a true theory classifying together experimental laws in rigorous logical and perfectly ordered succession.

As with the original Cartesianism, this new Cartesianism lures with the simplicity and generality of its first hypotheses. But as with it[s predecessor], it is not long before the mind becomes discouraged by the complexity, the bizarreness, the arbitrary and far from natural ways, by the improbable combinations which it employs in "constructing the world machine." An invincible sentiment warns us that matter cannot be constituted as W. Thomson and Maxwell imagine, and we are tempted to agree with Pascal: "This is all ridiculous; for it is all useless, uncertain and laborious." The doctrine of vortexes has met with little support among the physicists on the Continent. Helmholtz, whose works lay at its foundation, has never agreed to adopt to.

Does Newtonian dynamics, the system of action at a distance which was more successful than the Cartesian system, suffice for all the needs of modern physics? Without speaking of difficulties encountered in elasticity and optics which, if not insurmountable, are at least insurmounted, dynamics as well as the pure Cartesian mechanics remains powerless to account for one of the laws dominating modern science—the law carrying the names of Carnot and Clausius. The two doctrines which for two hundred years have wrangled over the field of physics, have not been able to adapt the new ideas introduced by thermodynamics.

XI

H. Poincaré [494] is one of the geometers who has contributed most to bringing this truth to light. The dynamics of Leibniz, of Newton and of Boscovich, like the pure mechanics of the Cartesians, is incompatible with thermodynamics. Certain thinkers are appalled by a conclusion which leads "to the reversal of the great reform from which modern physics emerged and the more or less concealed restoration of old occult qualities"—to which H. Poincaré eagerly responds: "I have never had a thought of reinstating occult qualities ..."

Other, more audacious physicists went so far as to draw that conclusion in the face of which the illustrious geometer seems to have slipped away. "Yes," they said with Rankine, "the pure Cartesian mechanism, which attributes shape and movement to matter, but denies all other qualities, is remarkably sterile; yes, the dynamic system formulated philosophically by Leibniz and practically realised by Newton, the system which would condense into a single element, force, all the qualities of matter, is not as flexible in conforming to the essential laws of present-day physics. We must therefore admit that matter might possess various qualities which are not reducible to shape and movement, qualities whose existence the physicist might establish and whose effects he might study, but which it cannot explain, qualities which should be ultimate elements of his theories which will remain for him *occult*, but which will none the less be very certainly and very exactly known. When a body seems warm to us, it is not that it contains a particular fluid or that its molecules are excited by a certain small movement. It is that it possesses a certain quality, a certain degree of intensity—a quality whose intimate nature remains unknown to us, but whose existence [495] and modifications are revealed with minute precision by the experimental method. It is this quality that we call *warmth*. Light is not a vibratory state of the ether; it is a quality. Magnetisation is a quality; electrification is another.

It is not at all necessary to attribute to each new phenomenon, in imitation of certain scholastics, a new irreducible quality—a new essential property of matter. Confronted by a hitherto unknown phenomenon, the physicist asks himself first whether it is a new effect of an already discovered property. He will employ all the resources of the experimental method to encompass the fact that has just come to light within the framework of what is already established. But when attempts judiciously conducted, fully and ingeniously varied, have not been able to yield this reduction, he no longer hesitates to see in the phenomena under study the manifestation of a new primary quality.

When chemists call a substance *simple*, it is not that a philosophical analysis has led them to recognise that the material of this substance does not result from the union of other substances. They call a substance simple because neither heat nor electric current nor sparks nor the various reactions have so far been able to decompose it. So this designation is entirely provisional and a substance that is simple today may be a compound tomorrow. In the same way, what physicists call a *primary* quality is a quality the experimental method has not so far been able to reduce to another. But this reduction, presently impossible, may, in a more or less distant future, be the effect of a bold theory or a successful experiment. Today, light and electricity designate two distinct qualities; one day, perhaps, they will be regarded more as two different manifestations of one and the same quality.

In reinstating warmth, light, electricity and magnetism [496] in the category of quality, do physicists want to abstain from the language of mathematics, so precise and so concise, which has brought to the arguments of physics so much order and clarity, and has been such a powerful aide in the admirable developments of this science? Not at all. Certainly, warmth, light, electricity and magnetism, excluded from the category of quantity, will no longer be *magnitudes*, will no longer be *measurable*. Numbers will none the less furnish appropriate symbols for representing the various states of each of these and numerical scales offer convenient marks for designating the degree of their intensity. The physicist will note this intensity like an examiner, with the numbers by which a candidate is graded, without claiming to measure it. To qualities expressed by the words being warm, being luminous, being magnetic and being electric, correspond symbolic numbers which are called temperature, luminous intensity, magnetic intensity and amperage. Warmth, light, electricity and magnetism, which are qualities, escape the grips of algebra; but temperature, luminous intensity, magnetic intensity and amperage, which are numbers, will be governed by this science. The laws of physics which bear on qualities will be faithfully expressed by algebraic formulas, and the pure quantity, the *whole number*, will be the ultimate element of the language which will serve to describe the world of qualities.

The mathematical theories thus constituted no longer claim, like the Cartesian theories, to explain the laws discovered by the experimental method by going back from cause to cause as far as the simple and irreducible metaphysical elements of material things. The quality, provisionally regarded as a primary quality to which these theories reduce a group of properties, is not analysed by them. These theories are content to designate it by a name, to note its intensity by a number which increases and decreases at the same time as this intensity is [497] magnified or attenuated. They leave to metaphysics the onus of going beyond. They do not pride themselves in knowing what light is, what warmth is, or what electricity is, but only what effects are attributable to light, what to warmth and what to electricity.

The very word explanation takes on a new sense for them. "Do you want to account for a complex phenomenon? Set it out geometrically; you will have done everything." So Gamaches ironically summarised Newton's method; and it is so that what a modern physicist understands by explaining a phenomenon can be faithfully defined. Note its place in the logically ordered and mathematically expressed classification called *theoretical physics*: that is the goal of his efforts.

Physics developed in accordance with the ideas of Descartes or of Newton, was dominated by a most exalted science, mechanics, whose laws were the supreme rules of its theories. If the explanation of physical phenomena is not reduced, in the last analysis, to the notions of matter, movement and force, mechanics is no longer the supreme guardian of the general principles of physics. Must we therefore renounce constituting a very lofty and general science which furnishes the mould into which the theories of each branch of physics must run? No. But it is necessary that this science, larger than the old mechanics, ceases to be devoted solely to the study of local movement in order to embrace the general laws of all transformations of material things, the laws of *physical movement* understood in the broad sense of Aristotle. It is necessary that it treat not only changes of position in space, but also of all movement of alteration, of generation and corruption. Now, this science is not waiting to be created; the principal lines are already drawn. They have been traced by the physicists of this century who, in the course of seeking to reduce warmth to movement, have succeeded in condensing the most diverse branches [498] of physics into a single science which they have called *Thermodynamics* and which Rankine, the first to assert its new role, called *Energetics*. The formulas of thermodynamics embody the laws of local movement, of movement which makes heavy bodies fall and the heavenly bodies accomplish their revolutions, and of the movement which agitates solids, liquids and gases, and gives rise to hurricanes in the sky, to the ocean waves as well as the chords of an organ or a harp. But it also encompasses the laws of all physical movement—movement by which qualities appear and disappear, increase or diminish in intensity, by which a body is heated or cooled, magnetised or demagnetised; movement by which a whole group of qualities gives way to a different group of qualities, by which a solid body becomes fluid, by which a liquid is transformed into vapour; movement by which simple bodies unite to form mixts, by which mixts are resolved into their elements, by which bodies are dissolved in one another, by which chemical compounds are brought about and dissociated.

This science, whose construction appears to be the great work of physicists of the nineteenth century, just as the construction of dynamics was the great work of the physicists of the eighteenth century, is truly the *Physics* whose broad outlines Aristotle had sketched. But it is the physics of Aristotle developed and made precise by the efforts of experimenters and geometers, efforts continued without respite for nearly three centuries.—It is the physics of Aristotle, but it is also the physics of Descartes, since it is to Descartes that it owes the general use of numbers, not only for measuring magnitudes of all the quantities that it considers, but also the grades of intensity of all the qualities that it employs—a usage which truly realises the universal mathematics that the great philosopher of the seventeenth century dreamt of.—It [499] is also the physics of Kepler, Galileo, Pascal and Newton. For Kepler, Galileo and Pascal gave it the method which allows it to transform the indications of instruments into laws expressed by algebraic formulas. And Newton taught it the art of bringing together and ordering the laws and theories.—It is also the physics of Euler, Lagrange, Laplace, Poisson, Green and Gauss, because the great geometers have created the mathematical forms which permit it to state its principles and deduce consequences from them.—It is, finally, the physics of Robert Mayer, Sadi Carnot, Joule, Thomson, Clausius and Helmholtz, because it owes to them the new ideas which broadened the old mechanics.

Impatient to leave the field in which the physics of the Schools had held it enclosed, the human mind took three centuries and thousands of scientists to beat a path towards the true science of the material world. The direction of this path has frequently changed, and today we note with astonishment that it has closed on itself and we are brought back to the point of departure. Nevertheless, during this immense labour there is not a traveller whose work has been lost, even if this work has not always been used as the author intended; it often plays a different role in today's science than the role he attributed to it. It has taken up the place assigned in advance by He who leads all this activity.

ESSAY 3

THERMOCHEMISTRY: IN CONNECTION WITH A RECENT BOOK OF MARCELIN BERTHELOT*

I

In 1879 Mr. Marcelin Berthelot published an extensive work entitled *Essai de Mécanique chimique, fondée sur la Thermochimie* [*Essay on Chemical Mechanics Based on Thermochemistry*]. This work was the summary and synthesis of nearly twenty years' research by the indefatigable experimenter and his students in the area of calorimetric chemistry. While pursuing his researches Mr. Berthelot was taken, as he puts it, "to the limits of his own thought," and he never seems to have been obliged, throughout these years, to have modified the general plan of the edifice which he has so laboriously raised.

Today, less than twenty years after the publication of *Essai de Mécanique chimique, fondée sur la Thermochimie,* Mr. Berthelot offers to the scientific public a yet more extensive work.[1] Despite the change of title, the two enormous volumes of *Thermochimie* [*Thermochemistry*] seem to be a second edition of the *Essai de Mécanique chimique,* and yet what a difference there is between the first of these works of the author and the second!

In [362] the *Essai de Mécanique chimique*, all the experimental observations, all the experimental results are arranged around the principles of Thermochemistry, and in particular, around the famous law of maximum work. Affirming this law, explaining the contradictions it encounters with experiment, verifying these consequences, emphasising its superiority over older rules of chemical mechanics such as the laws of Berthollet, for example; this is the continual preoccupation of the author in this work.

In *Thermochimie*, not only does the law of maximum work no longer take pride of place; it is no longer the principal idea which dominates and orders all the facts.

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* Originally published as "Thermochimie, à propos d'un livre récent de M. Marcelin Berthelot," *Revue des Questions Scientifiques*, 42 (1897), 361-92.

[1] M. Berthelot, *Thermochimie. Données et lois numériques. – Tome* I: *Les lois numériques. Tome* II: *Les données expérimentales*. – 2 forts volumes in-8°; Paris, Gauthier-Villars et fils, 1897.

With the exception of the first chapter, the principle is entirely passed over in silence. It seems that Mr. Berthelot is applying himself to the extrication of all theoretical ideas and, in particular, of that which he has hitherto held closest to his heart, from the innumerable experimental observations accumulated by himself and his students. What he presents for us is not an enlarged and transformed version of the edifice which was his first work. He has revised this edifice from top to bottom. He has merely retained the materials, which he has repruned, and made more numerous, but he has not put them together. It seems that the fragility of the first construction has aroused in him an insurmountable distrust of all new attempts at shaping the observations of thermochemistry.

Why this distrust? What cause underlies this development in Mr. Berthelot's mind? An account of the circumstances which have led him to write the first chapter of his work, and a careful study of the first chapter, will allow us to guess at the reply it would be appropriate to give to these questions.

II

The [363] older Physics always classed chemical combination among the sources of heat, and decomposition among the sources of cold. On discovering that certain decompositions could release heat and, consequently, that the inverse combinations must absorb heat, Favre upset thermochemical ideas profoundly. After this discovery, it was no longer permissible to hold that all exothermic reactions are combinations and all endothermic reactions are decompositions. Should a contrast between these kinds of reaction be sought, it is necessary to look in another direction for the opposition which can be appropriately establish between them.

It was then, in 1854, that a Danish chemist, Mr. Julius Thomsen, in some admirably clear and precise memoirs, proposed the thermochemical system. In this system, exothermic reactions are still opposed to endothermic reactions, but not as in the older chemistry. The former are, according to Mr. Thomsen, the only ones which can be produced directly; the latter can only be produced indirectly. An endothermic reaction is only possible when accompanied by another reaction releasing more heat than the endothermic reaction absorbs. This is the law that Mr. Berthelot later called the *principle of maximum work.*

The thermochemical system of Mr. Thomsen was already constituted in its entirety when Mr. Berthelot began research in calorimetric chemistry in 1865. Moreover, his first publications made hardly any allusion to the principle of maximum work. No more than a few incidental phrases relating to this principle are to be found. The principle is made precise in the writings published by [364] Mr. Berthelot in 1869. But only in 1873 was it stated as a fundamental law of thermochemistry—twenty years after Mr. Thomsen had formulated it.

Treating with disdain the claim to priority put forth by Mr. Thomsen, Mr. Berthelot has since then employed all the resources of his inventive mind and his indefatigable activity to explain, to avoid, and to turn the innumerable contradictions that the principle of maximum work receives from experiment. It would be impossible to say what ingenuity and labour has been spent in this sterile task. The *Essai de Mécanique chimique* is, for the most part, a summary of these attempts in which the knowledgeable scientist apparently uses pettifogging chicanery in reference to Nature.

Next to the laboratory of the Collège de France where Mr. Berthelot pursued his research in thermochemistry, another laboratory, that of the École Normale Supérieure, inaugurated another chemical mechanics. H. Sainte-Claire Deville, a marvellously sagacious mind, who penetrated as well, perhaps better, than Claude Bernard the mechanism of experimental science, had sown the notion of *dissociation*. He saw it around him, growing and bearing fruit. H. Debray, Messrs. Troost and Hautefeuille, Isambert, Mr. Gernez and Mr. Ditte, all students of Deville, accumulated experimental results which manifested, at higher temperatures, a continual contradiction between the principle of maximum work and nature. They dissociated exothermic compounds: water, carbon monoxide, sulphuric acid, carbonic acid and hydrochloric acid; they formed directly compounds which were considered to be formed indirectly: the oxide of silver, oxygenated water, ozone, hydroselenic acid and hydrotelluric acid.

This School of chemists restricted itself, at first, to discovering, by the most ingenious methods, the facts of experience. But it soon came to pass that these facts, over whose discovery [365] no preconceived theoretical ideas presided, came to fall under the laws of Thermodynamics all by themselves. One theoretician, an assiduous visitor at Deville's laboratory, J. Moutier, inaugurated chemical mechanics based on thermodynamics. In 1876, J. Moutier announced a major proposition, establishing a hitherto unsuspected opposition between exothermic and endothermic reactions which characterised the new thermochemistry: Of two reactions, the one the inverse of the other, the exothermic one is the one which occurs at the lowest temperature, and that occurring at the highest temperature is endothermic.[2]

Under the powerful influence of Mr. Marcelin Berthelot, the new chemical mechanics, created from the union of the notion of dissociation and thermodynamical theories, disappeared from the country which saw its birth. The laboratory of the École Supérieure gradually abandoned the study of dissociation. The research of Sainte-Claire Deville and his students, which provided, as it were, the key to the mechanism of chemical reactions, was no longer seen in the chemical treatises except as a curiosity happily dealt with in a couple of lines. J. Moutier died without being recognised, and perhaps his name would never have been mentioned by those who write on chemical statics if the student he trained and to whom he took care to communicate the very root of his thought did not take every opportunity to promulgate his master's claims to fame.

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[2] [These points are explained more clearly in section III of "The Work of J. H. van 't Hoff."]

III

Driven from France, the new thermochemistry flourished abroad. Four powerful minds, Horstmann, Gibbs, Helmholtz and van 't Hoff have been the main contributors to its development.

Unknown [366] to one another, and nearly contemporaries, the work of Horstmann and the work of Gibbs complemented, as it were, one another: the former less ample, but more concrete, richer in consequences immediately comparable with experiment; the second more abstract, more algebraic, but bearing, at the same time, the stamp of a majestic grandeur with a sense of the mark of genius.

Briefly, chemical mechanics owes to Horstmann and to Gibbs two essential steps forward.

The first is the complete theory of dissociation in the body of a system enclosing a mixture of perfect gases. As Mr. Horstmann has shown, the formulas found are in accordance with the results obtained by Mr. Naumann's studies of the dissociation of ammonium carbonate. They are also in accord, as Mr. J. Willard-Gibbs has shown, with the variable vapour densities determined by Cahours, by Bineau, by Wurtz, by Mr. Naumann, and by Messrs. Troost and Hautefeuille. They have also received many other confirmations.

The second step is of a more abstract character, but at the same time, one of more general significance.

In the last analysis, all the efforts of chemical statics might be regarded as an attempt to discover the function which should play the role, in this science, that statics attributes to the *potential of internal forces* of the system under study.

In the old chemical mechanics, which Berthollet based on the hypothesis of the actions molecules exert at short distance, the function sought is the potential of these molecular actions.

For thermochemistry, the role of this function is reserved for the *internal energy*, U, the consideration of which Clausius introduced into thermodynamics.

For the new chemical mechanics, whose laws Gibbs has developed, the *internal thermodynamic potential* is a more complex function. Built up from the [367] internal energy U, the *entropy* S and the absolute temperature, T, it is given by the expression $F = U - TS$. The importance of this function in thermodynamics had already been indicated by F. Massieu. Gibbs and Maxwell called it the *available energy*; Helmholtz called it the *free energy*.

Without adding anything essentially new to the great discoveries of Massieu, of Horstmann, and of Gibbs, H. von Helmholtz, in recasting the ideas of these physicists in his own melting pot, in branding them with the seal of his genius, in welding them with the boldest views of electrodynamics, made a major contribution to bringing the new doctrine to the attention of physicists.

Finally van 't Hoff, less of a mathematician and more of chemist than his renowned competitors, produced from Thermodynamics one the laws best able to illuminate chemical mechanics, *the law of displacement of equilibrium by temperature*: when the temperature of a chemical system at equilibrium is raised, its composition is changed; if the temperature is perfectly constant, the reaction thus produced would absorb heat. In a large number of cases, this law restores, by a different route, consequences like those which were forthcoming from the law of J. Moutier. But this, forgotten in France, was unknown abroad.

It is superfluous to depict here the influence that these various works exert on the research of physicists and chemists, both in Europe and America. Entire schools in Amsterdam, Leyden, Göttingen, Leipzig and Ithaca have made it their business to perfect chemical mechanics, both from the theoretical and experimental point of view. Special reviews have been created for the publication of the results of this incessant labour. And the influence of the new discipline was soon to be felt in the domain of the philosophy of nature: the impact of this new doctrine [368] has made the mechanical systems, triumphant since Descartes, reel at their foundations.

IV

At the time when this great scientific movement took form, when Helmholtz completed the publication of his research *Sur la thermodynamique des phénomènes chimiques* [*On the Thermodynamics of chemical Phenomena*], when van 't Hoff gave to the public his *Études de Dynamique Chimique* [*Studies in Chemical Dynamics*], we made every effort to make the principles of the new doctrine known in France, and to discuss and complete them. Of the reception which met these attempts we will only say one thing: nothing was missing which might discourage a beginner. It has since become clear to us that the thermochemical doctrine has enjoyed an indisputable authority in France, that no suggestion for chemical mechanics was even considered unless the principles of this doctrine inspired it, and that the first task of whoever would make a success of the new theory must be to clear the ground by burying the principle of maximum work lock, stock and barrel. Contributing to this task was the principle object of the small book that we published in 1893 under the title of *Introduction à la Mécanique chimique*.[3]

After a detailed history of chemical mechanics which retraced the genesis of the principle of maximum work and established the incontestable priority of Mr. Thomsen, we broached the discussion of the various ways by which Mr. Berthelot has sought to defend this principle against the repeated attacks from experiment.

We showed, first, that Mr. Berthelot was obliged to distinguish between *physical changes of state*, for which [369] the principle is manifestly false, and *chemical changes of state*, for which it would be true. Nearly all the great minds that have meditated on the principles of chemistry, from Berthollet to H. Sainte-Claire Deville, have recognised that it is impossible to trace this distinction with

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[3] P. Duhem, *Introduction à la Mécanique chimique*, Gand (Ad. Hoste, éditeur) and Paris (Georges Carré, éditeur). – 1893.

precision. But his indecision has itself furnished Mr. Berthelot with a convenient subterfuge, by allowing him to classify as *physical* all those phenomena which contradict his theory.

We then showed Mr. Berthelot attributing to the extraneous energy[4] of the electric spark a host of combinations where the decompositions are produced in the sense contrary to the principle of maximum work. Now, by the laudable invention of an apparatus of hot and cold tubes, H. Sainte-claire Deville has taught us to see in the action of a series of electrical sparks only a convenient way of catching in the act, as it were, reactions which are produced by themselves at a very high temperature.

Finally, we showed Mr. Berthelot to be at odds with the phenomena of dissociation manifested by exothermic compounds at high temperatures, and managing to construe the facts compatibly with the principle of maximum work only by admitting that an absorption of heat at constant temperature might be considered as an intervention of *extraneous energy*. "This subterfuge found," we said, "thermochemistry has nothing more to fear from phenomena of dissociation; on the contrary, it will call them to its aid in order to explain all the reactions capable of embarrassing it.

"Just one remark on the subject of this subterfuge:

"If providing heat to a system is an operation which brings an extraneous energy into action, the third principle of thermochemistry must be changed from "All reactions accomplished without the aid of extraneous energy release heat" [370] to "All reactions which do not absorb heat release it."

"To escape the conflict with experiment, the third principle of thermochemistry has taken various forms; but in order not to be strangled by the close reasoning of H. Sainte-Claire Deville, it has been constrained to disappear in a ridiculous tautology."

V

This attack could not go without challenge. Prepared by a number of allusions in the *Traité pratique de calorimétrie chimique*, published in 1893, Berthelot's response appeared in the form of a very extended note in the *Comptes Rendus de l'Académie des Sciences* (session of 25 June, 1894). With some of the points developed, this note forms the first chapter of *Thermochimie*.

In responding to us, Mr. Berthelot does not name us at all. The views that we have defended are attributed to "people who indulge in calculations of mathematical physics." Why? We will not waste time pursuing this. Personal matters are not of interest; only disputes over ideas. That the ideas against which Mr. Berthelot step by step defends himself in this first chapter are those whose cause we had taken up is

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[4] *l'énergie étrangère.*

sufficiently manifest that we would be authorised to sound the charge which should shatter the last effort of thermochemistry.

We will not return to the historical question. The reader of our *Introduction à la Mécanique chimique* has available all the documents of the case. He knows that, ten years before Mr. Berthelot had just suspected the principle of maximum work, Mr. Julius Thomsen had clearly stated it and had put it forward as one of the fundamental laws of thermochemistry. We will content ourselves with attacking [371] and destroying one by one the redoubts raised by Mr. Berthelot in defence of this principle.

This attack will, moreover, be easy.

Mr. Berthelot has not found any new reason nor any new argument for saving the principle of maximum work which we have not already refuted in our *Introduction à la Mécanique chimique*. He has at best revived old arguments and given them a more precise and definitive form; but by the same count, he makes them easier to grasp and to knock down.

Mr. Berthelot enumerates these ways of salvaging the principle of maximum work himself.[5] They consist in "separating the quantities of heat of purely chemical origin from quantities of heat extraneous to chemical action properly speaking, such as:

"Those which correspond to external mechanical work and, in particular, in the change of condensation of gases;

"Those which correspond to purely physical changes of state, such as fusion and volatilisation;

"Those which are brought into play by the additional, physico-chemical, intervention of water and solvents, intermediaries passed over in silence in the ordinary accounts of reactions;

"Finally, the quantities of heat absorbed in reversible chemical decompositions, that is to say, in dissociations, where the external calorific energies are brought together with internal energies of essentially chemical origin."

Such are the battlements of thermochemistry; in each, the breach is gaping wide.

VI

We [372] will first of all show, by means of an example, what use Mr. Berthelot makes of the distinction between heat due to chemical action and heat due to physical transformations.

In an electric arc, solid carbon taken in the presence of hydrogen combines with it to give a gas, acetylene. No one disputes that this direct transformation is accompanied by a considerable absorption of heat. There we have a fact. For the pure experimenter who respectfully accepts, without mutilating, without contorting, what nature teaches, this fact formally contradicts the principle of maximum work.

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[5] *Thermochimie*, vol. I, p. 8.

How does Mr. Berthelot restore agreement between experiment and theory? "Around 4000°," he says,[6] "the temperature of its effective synthesis, the heating of solid carbon, considered in isolation, transforms this element into a gas whose existence is confirmed by various tests. The act of heating therefore increases considerably the energy of this element; then the gas resulting from the combination [*sic.*][7] of carbon is combined with hydrogen with a release of heat that can be estimated approximately. For each atom of carbon and hydrogen entering into combination, it would be greater than +34 cal. and even +42 cal."

Thus, where the unprejudiced mind would only see an endothermic transformation—a transformation from solid carbon and gaseous hydrogen to gaseous acetylene, Mr. Berthelot distinguishes two transformations. The one, the volatilisation of carbon, is endothermic, but no cognisance need be taken of it as far as the principle of maximum work is concerned because it is a physical transformation. The other, the combination [373] of gaseous carbon and hydrogen should satisfy the principle of maximum work because it is chemical, and it does in fact satisfy it; it is exothermic. Mr. Berthelot says so, at any rate.

This distinction between physical and chemical transformations cannot be avoided by the champions of the principle of maximum work. It is very clear, in fact, that this principle cannot be presented as a law applicable to all changes of state. It is very clear that the most well known changes of physical state—fusion and vaporisation—are in fact produced with the absorption of heat. Thus, from the instant he stated the principle, Mr. Julius Thomsen had restricted the import to "purely chemical actions."

Now, that is one of the essential faults of thermochemistry. Berthollet had already understood that it was impossible to draw a line of demarcation between changes of physical state and changes of chemical state. Between the action by which a mixture of hydrogen and chlorine are transformed into hydrochloric acid, and the action by which ice is transformed into water or water into vapour, there is a whole range of kinds of transformations, and the passage from the one to the other is too extremely smooth for it to be said where chemical changes stop and where physical changes begin. Since the work of Sainte-Claire Deville, this truth has been apparent to all, and it will be the immortal claim to fame of the chemist of the École Normale Supérieure to have affirmed that no chemical mechanics was viable unless it embraced in the same system of laws both changes of physical state and chemical reactions.

Far from impeding Mr. Berthelot, the absence of any line of demarcation between physical changes and chemical changes puts him at ease and allows him to place a single kind of transformation in the one category or in the other according to his needs. Allotropic, isomeric and polymeric transformations [374] each become for

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[6] *Thermochimie*, vol. I, p. 14.

[7] "le gaz résultant de la combinaison du carbone se combine à l'hydrogène." ["the gas resulting from the volatisation of carbon ..." would perhaps be more appropriate.]

him a Jack-of-all-trades that at a given signal passes from physics to chemistry or conversely.

What about a salient example?

"The sulphide of carbon[8] is endothermic at ordinary temperatures, when it is considered to be formed from solid sulphur and polymerised. But sulphur, taken in isolation, uses some of the energy under the influence of the heating and passes from the solid state to the gaseous state, first tricondensed, then monocondensed. It is the latter state that it possesses at the actual temperature of the synthesis of sulphur and carbon, that is 800°. The known facts and analogies[9] indicate that this additional energy would then take a value sufficient to render exothermic the combination of sulphur and carbon."

Thus, in order to bring the principle of maximum work into agreement with the direct formation of the sulphide of carbon starting from the elements, we must count among physical modifications, which escape the principle in question, the transformation of the vapour of tricondensed sulphur S_6 to gaseous monocondensed sulphur S_2. The most common logic requires that all analogous polymeric changes should be classed among physical changes of state; but would you expect Mr. Berthelot to bow to common logic?

The idea of a certain polymeric change soon [375] springs to mind when considering the condensation of sulphur vapour, namely the transformation of oxygen into ozone. The parallel between the two changes is pressed to such a point by some chemists as to call tricondensed sulphur S_6 the *ozone of sulphur*. Now, two pages[10] prior to treating the transformation of sulphur S_6 to sulphur S_2 as a physical change, Mr. Berthelot treats the transformation of ozone to oxygen as a chemical change and places it besides the decompositions of hypochlorous acid and hydrogen peroxide.

The chemical equation which connects the two vapours of sulphur, polymers of one another,

$$3S_2 = S_6,$$

has precisely the same form as the equation

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[8] *Thermochimie*, vol. I, p. 14.

[9] The facility with which Mr. Berthelot uses a heat of transformation in his arguments which is absolutely unknown to us is remarkable; in fact, he tells us as much himself (*Thermochimie*, vol. II, p. 61):

> *Tricondensed gaseous sulphur* changes to *normal gaseous sulphur:* the heat brought into play is unknown, but it ought to be considerable, by analogy with other polymerised bodies.

Let us add that, apart from sulphur, only two examples of polymerisation of simple gaseous bodies is known: the transformation of iodine I to I_2, which releases an *unknown* amount of heat, and the transformation of oxygen to ozone, which *absorbs* heat. What a well-founded analogy!

[10] *Thermochimie*, vol. I, p. 13.

$$3C_2H_2 = C_6H_6$$

which expresses the transformation of acetylene (C_2H_2) to benzene (C_6H_6). If Mr. Berthelot had any concern for self-consistency, this latter equation should, like the former, represent for him a physical change and not a chemical combination. Yet we read:[11]

"The reciprocal combination of hydrocarbons constitutes one of the cleanest and most fruitful methods of synthesis ... This combination includes, as a particular case, polymerisation, that is to say the reunion of two or more molecules of an unsaturated hydrocarbon in a single molecule.

"Free acetylene combines directly with itself, in such a way as to give rise to diacetylene $(C_2H_2)_2$, to triacetylene $(C_2H_2)_3$ or benzene, to tetracetylene [376] or styrene $(C_2H_2)_4$, to pentacetylene or naphthalene hydride $(C_2H_2)_5$, to hexacetylene or tetrahydride or acenaphtheline $(C_2H_2)_6$, etc. ..."

VII

The blurred region where the boundary of physics and chemistry is lost includes not only allotropic, isomeric and polymeric changes; it also includes the immense domain of phenomena of dissolution and mutual mixture. Berthollet had already shown that the phenomenon of dissolution could be assimilated to that of combination, and had insisted on the impossibility of attributing the effects to physical cohesion rather than to chemical affinity. Oh! how convenient the uncertainty and how well it serves the interests of the defenders of thermochemistry. At each instant, the phenomena of dissolution and of mixture, the actions between dissolved bodies, give rise to absorptions of heat, and it will therefore be easy to account for the exceptions to the principle of maximum work in terms of the physical part of the action of water and solvents, an action which, in order not to be committed, will be called[12] "*physico-chemical action*"! In *Thermochemie* Mr. Berthelot confines himself to mentioning this subterfuge; but in his *Essai de Mécanique chimique* he makes continual use of it to reduce reactions in which dissolved substances take part to the rule of maximum work. "With such arguments," one of the physicists who have best studied this part of the work of Mr. Berthelot said to me one day, "it is possible to prove whatever you like."

VIII

In [377] discovering the phenomena of dissociation, H. Sainte-Claire Deville has dealt the system of thermochemistry a blow from which it has tried in vain to recover. Deville had actually shown that the most strongly exothermic substances—

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[11] *Thermochimie*, vol. I, p. 486.

[12] *Thermochimie*, vol. I, p. 8.

water, carbonic acid, sulphurous acid, carbon monoxide, hydrochloric acid—could be partially decomposed into their elements provided that the temperature is sufficiently high. In our *Introduction à la Mécanique chimique* we have shown that thermochemistry struggles in vain against this objection, which constrains it to count all sources of heat as extraneous energies, that is to say, to transform the principle of maximum work into this ridiculous tautology:

All reactions which do not release heat absorb it.

Mr. Berthelot responds to this argument in these terms:[13]

"Briefly, phenomena attributable to internal energies of systems, which play the principal role—all the cases in which there is no dissociated compound—should be distinguished from [those attributable to] external energies of calorific order which intervene in indisputable fashion and at constant temperature, producing the heat absorbed in dissociations. Apart from this latter state, it seems that calorific energies need not be made to play any chemical role in a system, I repeat, *maintained at constant temperature*: it is perhaps that point which has been misunderstood."

Excuse me, Mr. Berthelot, I have understood you perfectly. I have understood that you have counted calorific energy as extraneous energy only with great reluctance; that it was an issue which [378] you have used as a last resort to escape the grip of the facts discovered by H. Sainte-Claire Deville; that you would like to close this issue forthwith because you are too shrewd not to have seen that the principle of maximum work entirely disappeared on that account. But what I have equally well understood is that logic has not been given its due. According to you, to explain dissociation phenomena the words *extraneous energy* can be understood in the sense of *absorption of heat*. If these words can take this sense *in this particular case*, then they cannot be prevented at your pleasure from taking this sense *in general*, and I am then in the right in replacing the phase:

All reactions accomplished without the intervention of extraneous energy release heat,

By this other one:

All reactions accomplished without the absorption of heat release heat.

Besides, you too, you have also understood me. You have understood that the principle of maximum work would never be reconcilable with the phenomena of dissociation, the theory of which has, on the other hand, been a continual occasion of triumph for thermodynamics. And you acknowledge this when you write:[14]

"It is above all in the case of dissociation, the preceding calculations and considerations expressively excluded, that entropy plays an essential role and introduces predictions which escape in part from the primitive statement of the principle of maximum work. There is there, in fact, a fundamental aspect of the question, developed since my first investigations in Chemical Mechanics by the

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[13] *Thermochimie*, vol. I, p. 8.

[14] *Thermochimie*, vol. I, p. 27.

work of Messrs. Gibbs and Helmholtz on non-available energy, which has resulted in a whole discipline of new and essential notions."

IX

Just [379] as at higher temperatures exothermic compounds are resolved into their elements, so endothermic compounds are formed directly at the expense of their elements. As soon as H. Sainte-Claire Deville had experimentally discovered the first part of this major law, the exactitude of the second part became probable. Nevertheless, it took a certain time to demonstrate it.

A series of sparks can induce the formation of a great number of endothermic compounds at the expense of their elements. From the beginning of his investigations Mr. Berthelot counted electric sparks as extraneous energy and explained the syntheses in question by the intervention of this extraneous energy. H. Sainte-Claire Deville has broached the idea that a series of sparks has no other effect than to take a small mass of gas to an extremely high temperature, after which it quickly cools and is diffused into the ambient mass. According to this idea, the reactions produced by a series of electric sparks should be regarded as spontaneous reactions at high temperature. H. Sainte-Claire Deville has verified this brilliant idea by reproducing some of the decompositions that can be determined by a series of electric sparks with an apparatus of hot and cold tubes. Later, with the same apparatus, Messrs. Troost and Hautefeuille produced the direct synthesis of certain endothermic compounds—silver oxide, ozone, hydrogen peroxide—some of which can also be created under the action of a series of sparks. It was thus well established that endothermic reactions observed in a gas mixture in which a series of sparks could be made to pass are all, in fact, reactions which are produced by [380] themselves at high temperatures. Consequently, these reactions, be they dissociations or combinations, are all flagrant exceptions to the rule of maximum work.

Mr. Berthelot takes little account of these numerous and well-established exceptions, contenting himself with rejecting them *en bloc* and refusing to take issue:[15] "We will not discuss here the effects produced in a system different points of which are at different temperatures, restricting ourselves to observing that in such effects there is nothing resembling permanent equilibrium sustained at constant temperature."

But this refusal to discuss the matter, however radical it might be, cannot rid thermochemistry of all the examples of direct synthesis of endothermic compounds. Among these syntheses there are those which are observed in uniformly heated spaces. How does Mr. Berthelot explain that? By resorting to a very simple subterfuge which he had already suggested in a memoir published in 1877, in *Annales de l'École Supérieure*. These compounds, endothermic at ordinary

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[15] *Thermochimie*, vol. I, p. 15.

temperatures, are in reality exothermic if the temperature at which they come into being and the conditions in which they are formed are taken into account. Between ordinary temperatures and the temperatures at which they can be generated, their heat of formation has had to change sign. "Things[16] can happen, particularly as a result of isomeric changes undergone at this temperature by elements and by their compounds."

Taking the examples of the synthesis of acetylene and carbon sulphide, we have shown how Mr. Berthelot brings into account changes of physical state and isomeric or polymeric changes, [381] and by such considerations he sought to make probable a change of sign of the heat of combination. "It is not hypotheses which are at issue," Mr. Berthelot[17] adds. What is at issue? He does not say, contenting himself with the following affirmation:[18] "In fact, for the compounds which have just been mentioned, and in so far as they remain endothermic, no one has ever established that there would exist at any temperature a definite pressure of dissociation between the compound and its elements"—an affirmation which he repeats later:[19] "In summary, the known facts do not allow envisaging endothermic compounds in general, *and in so far as they preserve this character*, as susceptible to reversible equilibria."

To this decisive affirmation, I will limit myself to raising just one counterexample which has been minutely studied, first by Mr. Ditte, and then by Mr. H. Pélabon, the example of hydroselenic acid.

Between 300° and 500°, in a system enclosing liquid selenium and hydrogen, a certain quantity of gaseous hydroselenic acid is formed. The limit attained in these conditions of temperature is the same as that which would be achieved either starting from selenium and free hydrogen, or from a system enclosing an excess of hydroselenic acid. In the given system, maintained at a given volume, the proportion of hydroselenic acid existing at the moment of equilibrium increases with temperature, provided this temperature does not exceed 500°. A theorem of thermodynamics, which Mr. Berthelot is willing to say[20] is "irreproachable, perhaps, from the point of view of an absolute mathematical calculus," therefore teaches us that hydroselenic acid [382] is endothermic in the conditions described. Its endothermic character persists, moreover, at ordinary temperatures, as has been directly verified by experiments, first of Mr. P. Hautefeuille, then of Mr. Fabre, conducted in the very laboratory of Mr. Berthelot. It seems to me that the most rigorous logician cannot ask for a more convincing example.

Alas, I well know that Mr. Berthelot has a more subtle mind than the most rigorous logician. My objection does not embarrass him for a moment. He will affirm—on what evidence, I do not know—that liquid selenium is absolutely

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[16] *Thermochimie*, vol. I, p. 14.
[17] *Thermochimie*, vol. I, p. 14.
[18] *Thermochimie*, vol. I, p. 13.
[19] *Thermochimie*, vol. I, p. 15.
[20] *Thermochimie*, vol. I, p. 14.

incapable of combining with hydrogen, and that it is first reduced to vapour, a modification which can, without detriment of the principle of maximum work, absorb as much heat as pleases him since it is purely physical. Once vaporised, selenium combines with hydrogen, but with the release of heat, once more saving the principle of maximum work.

I confess that I do not understand why Mr. Berthelot makes such a difficulty of admitting that an endothermic compound can be formed directly from its elements, provided that the temperature is given a sufficiently high value. He has never considered denying the dissociation which exothermic compounds, such as water or carbon monoxide, undergo at high temperatures. He has never dreamt of claiming that, in the conditions where this dissociation is produced, it has ceased to absorb heat in order to release it. Having tried to explain this dissociation by taking the sources of heat to be extraneous energy, today he prefers to exclude it from the domain of thermochemistry and abandon it to thermodynamics. Why not consider the formation of endothermic compounds at high temperature in the same way? The methods which have served to establish this formation are identical [383] to those which have served to establish the dissociation of exothermic substances. The first category of phenomena contradict the principle of maximum work for precisely the same reason, and for none other, as the second. Like the second, it ceases to be embarrassing if it is agreed to regard an absorption of heat as an intervention of extraneous energy. Like the second, it might be excluded from the domain of thermochemistry and delivered to thermodynamics which, moreover, has already taken hold of it and subjected it to a minute analysis whose conclusions experiment daily verifies. Why, therefore, does Mr. Berthelot greet these two reciprocal categories of phenomena so differently?

Would Mr. Berthelot be drawn by a violent reaction into re-establishing an opposition between decomposition and combination analogous to that admitted in the old chemistry, according to which direct decomposition can absorb heat whereas direct combination should always release it? Has he failed to recognise the principle, undisputed in the school of Mr. Julius Thomsen as in the school of Sainte-Claire Deville: The rules of chemical mechanics should make the distinction between exothermic and endothermic reactions, but it is of little significance whether a reaction is a combination, a decomposition or a double decomposition?

Well, having excluded from the suzerainty of thermochemistry first purely physical changes of state, then allotropic, isomeric and polymeric changes, then the phenomena of dissolution, and finally the phenomena of dissociation of exothermic substances and abandoned them to the prerogative of thermodynamics, would Mr. Berthelot fear thermochemistry being deprived, in turn, of the phenomena of the synthesis of endothermic substances, gradually making the principle of maximum work a kind of king without a kingdom?

But [384] no, Mr. Berthelot has no such fears. Let thermochemistry disappear entirely and make way for thermodynamics; let all chemists, deserters from the thermochemical camp, cease in their arguments to attribute to the internal energy the role played in statics by the potential of the internal forces; let them, in imitation of Gibbs and Helmholtz, confer this role on the thermodynamic internal potential. What does it matter? "The principle of maximum work[21] does not thereby suffer a blow: what is at issue is the quantity of heat Q or the quantity $(Q - T(S_a - S_b))$, and it will always be the consideration of the initial state and the final state which will determine the possibility of a direct reaction at the temperature at which it is accomplished."

The first chapter of *Thermochemistry* is concluded with this strange phrase. Should it be seen as a recognition of defeat, an act of submission to triumphant thermodynamics? Should it be seen as a last trick of the looser, a last report of unlikely victory intended to conceal the sorrows of the rout?

X

The rout is complete. After the first chapter, in the course of which Mr. Marcelin Berthelot has used up his last reserves in favour on the principle of maximum work, this principle disappears almost entirely from the account of thermochemistry. It barely reappears in some allusions in the course of the fifteen hundred pages where no more than the immediate results of experiment and purely empirical relations figure.

It will not be expected of us that we enter into the detailed discussion of this formidable arsenal of numerical results. [385] Instead, we will examine just one question: do they supply all the experimental documents which thermodynamics needs to transform the various terms of the formulas of chemical mechanics into numbers? We can reply to this question: no.

The work that Mr. Berthelot has just written summarises an era of experimental thermochemistry. Thermochemistry had, of necessity, to come through this era first; but it is not necessary that it remains there. It is high time that it abandon its old methods, purely empirical for the most part, and follow the more systematic paths traced for it by thermodynamics.

A comparison will capture our thought.

When a mountainous country is opened for the first time by explorers, they hasten to draw a summary map, marking roughly the position and height of the principal summits. Each new exploration corrects the old information and supplies new information.

But although useful for guiding the first pioneers, this summary map is not adequate for the administration of a civilised country. When it comes to building roads, railways, and canals, engineers demand detailed and precise topographical surveys, which supply them with the dimensions of the least elevation of the ground, which shows them the least bending of each contour line. An army of topographers invade the region, and each squad patiently, minutely, sketches the

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[21] *Thermochimie*, vol. I, p. 27.

relief of the small part of the ground which has been confided to it, drawing one of the squares whose union comprises the detailed map of the country.

The results of experimental thermochemistry in question resemble the summary map sketched by the first explorers of a range of mountains. The main summits are marked there, with an approximate position. [386] We know more or less exactly the quantity of heat brought into play by the main physical and chemical changes brought about in more or less well determined conditions. But we cannot follow the undulations of the chain between the summits. What we lack is what geographers call the plan of the ground.

The amount of heat brought into play by a reaction or a given transformation varies with all the circumstances surrounding the reaction or the transformation: temperature, pressure, the greater or lesser state of dissolution of the reacting substances. For all the important reactions of chemistry, thermodynamics needs to know the expression for the heat of reaction as a function of all these variables. It is not a single experiment which is demanded of the thermochemist who studies a reaction; it is a detailed, and frequently very extensive, monograph.

Nothing will better convey the importance of what has so far been done in experimental thermochemistry, and of what still remains to be done, than the comparison between the summary map of a portion of thermochemical land, such as has been sketched by Mr. Berthelot and his students, and the detailed map of the same portion, such as has been drawn by an observer experienced in the most precise procedures of calorimetry and concerned to satisfy the requirements of thermodynamics.

I read in the *Thermochemistry* of Mr. Berthelot:

Sodium acetate

$C_2H_3NaO_2 = 82.$

. . . .

Solution: $C_2H_3NaO_2$ + water, at 7.5° . . + 4.1 cal.
Hydrate: $C_2H_3NaO_2.3H_2O$ + water, . . – 4.8 cal.

Nobody will challenge the usefulness of these results; but are [387] they sufficient? Do they supply thermodynamics with all that it needs to be able to justly regard as known the calorimetric properties of solutions of sodium acetate?

The heat of dissolution of a salt is not constant. The amount of heat released or absorbed when a gram of the salt is dissolved in a certain mass of water depends of this mass of water. In other words, the heat of dissolution is a function of the concentration of the solution produced. It is necessary to determine this function by a series of calorimetric operations, stopping only when experimentation becomes impossible because the solution is nearly saturated.

The addition of water to a solution also induces a thermic phenomenon which leads to the notion of the heat of dilution. The initial concentration and the final concentration of the solution both influence the heat of dilution. The law which governs this influence should be determined and, as the phenomenon of saturation no longer limits the possibility of dilution, this law should be pursued to extreme concentrations of the strongest supersaturated solutions.

When a salt can exist in the anhydrous state and in the state of a hydrate, the determination of the heat of solution under the two states allows the determination of the heat of hydration of the anhydrous salt.

The heat of solution of the salt, anhydrous or hydrated, the heat of dilution of solutions and the heat of hydration of the anhydrous salt depend on the temperature at which the transformation is effected. The law of this dependency is difficult to determine by direct experiment, but a simple calculation yields it when the specific heat of the anhydrous salt, the specific heat of hydrated salt and, for all values of the concentration, the specific heat of the solution are known. The experimenter [388] should determine these specific heats while pursuing the study of solution to concentrations which are as great as possible.

It is only when this collection of experimental reports has been united that it is possible to declare the calorimetric study of a salt and its solutions complete.

The complete calorimetric study of sodium acetate[22] has been recently carried out by Mr. E. Monnet, in work which has been presented in a thesis for the doctorate of the Faculty of Sciences at Bordeaux. This work, which is a model of experimental precision, settles the technique that should be followed by thermochemists concerned with the study of a saline solution in accordance with the exigencies of the new chemical mechanics.

On the work of Mr. Berthelot we would willingly write these words: *How experimental thermochemistry has been treated so far;* on the memoir of Mr. E. Monnet: *How it should be treated in the future.*

From this comparison, one conclusion emerges: an immense labour is required to bring experimental thermochemistry to the state required by the new chemical mechanics. Two experiments on the dissolution of sodium acetate suffice, strictly, to supply the results which we found in the work of Mr. Berthelot. Some thousands of determinations, two or three years of strenuous work, are necessary to bring the monograph of a saline solution to a successful conclusion according to the method of Mr. E. Monnet.

This immense labour frightens certain thermochemists; as Mr. Berthelot himself indicates,[23] "how great is the number of physical and chemical results necessary to make [389] possible the execution of the exact calculation of entropy." It even seems that this mass of experimental investigation required by the new chemical mechanics is, for many, the true reason which induces them to reject this doctrine whose foundations they dare to question without more ample examination. Foolish!

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[22] E. Monnet, "Sur l'étude calorimétrique complète d'un sel" *Mémoires de la Société des Sciences Physiques et Naturelles de Bordeaux*, 5th, series, Vol. III, 1897.

[23] *Thermochimie*, vol. I, p. 20.

They may prefer to allow error to indulge their apathy than to contribute by ruthless effort to the triumph of the truth. They will not prevent the truth from triumphing, but they oblige it to triumph against them.

XI

In presenting to the public[24] "the last work that he will be called upon to publish," Mr. Berthelot seems to be gripped by a sentiment of bitter melancholy. "At the end[25] of a very long scientific career sustained for half a century by continual work and attested by incessant publications," he casts a glance over his life. He sees this life full of honours. Not content with having been called to the highest scientific positions, with having been accorded the most powerful influence on the organisation of his various teachings, his country has confided in him important political functions. Decorated with all the orders of Europe, member of all the Academies, he has become something of an official representative of Modern Science. If the majesty of this Divinity has been offended by some impious person it is he who excommunicates the sacrilegious person; it is he who receives the oaths of allegiance; it is he who presides at the sacred banquets where the sacrificial victims are slaughtered. Nevertheless, in the midst of his triumph, Mr. Berthelot is pursued [390] by an uneasy sadness that he has recently described[26] in poignant terms. Among the motives for this sadness, besides those which make life bitter for whoever has seen life, Mr. Berthelot gives us a glimpse of one[27] which seems to us well worth meditating over: "The radical impossibility of attaining an absolute goal." Reaching the end of his career, Mr. Berthelot notes that the goals that he has laboriously striven to attain were chimeras, that the ideas to which he was passionately attached were erroneous, that the time and effort devoted to defending these ideas has been employed in combating the truth.

At the beginning of his life in science, Mr. Berthelot was devoted to organic chemistry. The syntheses he achieved nearly forty years ago drew the unanimous admiration of the intellectual world for the young demonstrator from Balard, and this admiration was well-merited. The author of the synthesis of acetylene, formic acid and alcohol seemed to be called upon to support with a vigorous impulse the movement, so powerful and yet so logical, which carried chemistry to the conquest of the world of substances produced by living beings. Nothing of the kind happened. Leaving to his brilliant rival Wurtz the glory of being the apostle of chemical atomism in France, Mr. Berthelot, driven by his evil genius, declared himself the adversary of the new doctrines and notations. He used his great authority to stop them at the doors of our Faculties, of our Primary Schools and of our Grammar

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[24] *Thermochimie*, preface, p. xvii.

[25] *Thermochimie*, preface, p. xvii.

[26] M. Berthelot, "Introduction à la correspondance de E. Renan et de M. Berthelot" (1847-1892) *Revue de Paris*, 15 July, 1897.

[27] *Loc. cit.*, p. 230.

Schools. He became isolated in an organic chemistry of his own, closed to the fruitful influence of the discoveries of other schools, condemned to an obstinate sterility.[28] Today, the organic chemistry of Dumas, of Laurent, and Gehrhardt, of Wurtz and of Kékulé reigns undisputed, developing its formulas in all the treatises and memoirs, encumbering [391] laboratories, dispensaries and factories with its new products. Mr. Berthelot sees himself constrained, in his later publications, to adopt some of its ideas and language. But his discoveries have hardly had any part in the genesis of these ideas and in the formation of this language.

In synthesising a host of products from raw material Mr. Berthelot seems to have been driven by an idea which goes beyond chemistry and encroaches on the domain of philosophy. He wanted to fill the gulf separating raw material from living material and pressed for the day, often glimpsed in his dreams, when a living substance, if not a living being, would emerge from the chemist's retort. But the substances he produced were not of living matter; they were residues of death. The gulf separating chemical substance[29] from living bodies is dug and has become an abyss. Mr. Berthelot has seen Claude Bernard gradually abandon his initial belief in a reduction of life solely to the laws of physics and chemistry. He has seen the admiration of philosophers as well as the recognition of the common crowd turn towards the lucid mind and upright man whose work was based on the radical impossibility of making life emerge from a chemical preparation.—I am speaking of Louis Pasteur.

From organic chemistry, Mr. Berthelot went on to thermochemistry. The time when he embraced with ardour a science such as that of Favre and of Thomsen is also the time when new discoveries began to contradict this doctrine, when H. Sainte-Claire Deville inaugurated the study of dissociation, when thermodynamics tried to apply its laws to chemistry. The marvellous suppleness which he "is able[30] to transpose his mind almost instantaneously from one order of notions to another," his prodigious talent as an experimenter and his indefatigable activity seemed to predestine Mr. Berthelot to the construction of this new chemical mechanics, [392] which required both a theoretician and an observer, and which required one to be at the same time a mathematician, a physicist and a chemist. His evil genius drove him to cling to the condemned doctrine, and to defend it against attacks from the new ideas. To this sterile and thankless task he directed all his ingenuity, all his time and all his labour, as well as all the time and labour of his numerous and active collaborators he had the rare good fortune to meet. Today it is all too obvious not to acknowledge that thermodynamics has created, without him and in spite of him, the chemical statics to which he had dreamed of associating his name.

While he contemplates the ruins of the ideas for which he has combated, Mr. Berthelot lends an ear to the murmurs issuing from the body of French physicists

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[28] *farouche stérilité.*

[29] *la substance chimique.*

[30] *Revue de Paris, loc. cit.*, p. 228.

and chemists, still prevented from raising their voice by a remnant of superstitious belief.[31] And with "the loathing of treachery, deception and desertion"[32], these murmurs will bring him a kind of comment anticipated by these words:

"Tell me where these teachers and these doctors that you have known when they were yet living and who flourished in their science are now. Others presently occupy their place, and I do not know whether they even think of them. During their life, they seemed to be something, but now no one speaks of them."[33]

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[31] [I have adjusted what I take to be an anacoluthon in Duhem's text.]

[32] *Revue de Paris, loc. cit.*, p. 230.

[33] [Thomas à Kempis] *De Imitatione Christi*, book I, chap. 3, verse 5.

ESSAY 4

THE PHASE LAW, IN CONNECTION WITH A RECENT BOOK OF WILDER D. BANCROFT* [1]

I

When following the march of natural philosophy during the second half of our century; when looking among the never-ending discoveries, sometimes more dazzling than important, to disentangle the laws according to which our conception of the external world evolves, a part of this history of science soon presents itself as worthy of very particular attention. I wish to speak about the history of the relation between thermodynamics and kinetic theories.

Like two twin sisters, the two disciplines were borne at the same moment of the same germ. It was not at first possible to distinguish them. It was not possible to separate the first conception of the principle of the conservation of energy, the first notion of the mechanical equivalent of heat, the affirmation that heat is a particular mode of movement and the attempts that were made to discover the proper nature of the "movement that we call heat."

Between these sister doctrines, the apple of discord is [55] the principle of Sadi Carnot. Rather than renounce the theory of heat based on the Carnot's law, W. Thomson proposed abandoning the idea of the equivalence between heat and work. R. Clausius, it is true, soon showed that it is not at all necessary the resort to such an extreme position. [He showed] that it is possible, without relinquishing the conquests of Sadi Carnot, to modify the principles on which they rested in such a way as to dispel any contradiction between these principles and the law of equivalence, and that by combining the law of equivalence with Carnot's law, it is possible to create a logical and fruitful science, that of thermodynamics.

But if there is no longer any flagrant contradiction between the two laws on which thermodynamics is based, there remains a glaring disparity. The one, the principle of the conservation of energy, issues from the philosophical hypothesis

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* Originally published as "La Loi des Phases, à propos d'un livre récent de M. Wilder D. Bancroft," *Revue des questions scientifiques*, 44 (1898), 54-82.

[1] Wilder D. Bancroft, *The Phase Rule*, 8^0 pp. viii + 255, Ithica, New York, 1897.

that heat is a particular mode of movement, and that all changes established in bodies are reducible to local movement. The other, the principle of Carnot and Clausius, is a kind of postulate, arising from induction from the most vulgar observations and therefore subject, in its remote consequences, to the authority of experimental methods.

Clausius was acutely aware of this disparity. He sought to attenuate it in his memoirs dedicated to thermodynamics by reducing the role of kinetic hypotheses as much as possible. He borrowed from them no more than was necessary to establish the law of the conservation of energy, and speedily abandoned them. When he assembled his researches he was at pains to separate into different volumes those which, by the diffidence with which they borrowed from kinetic hypotheses, seemed to him to offer the greatest chances of certitude, from those which, being bolder, if not more rash, endeavoured to penetrate more profoundly the nature of the movement we call heat.

But while seeking to conceal the disparity between the origin [56] of the two principles of thermodynamics, Clausius only succeeded in bringing the importance of the disparity more quickly to the attention of critical minds and pressing them to re-establish the symmetry between the two pillars of the theory of heat.

In order to succeed, two options were indicated: either change the primary significance of the principle of the conservation of energy and make of it the exact logical counterpart of the postulate of Carnot and Clausius, or deduce from the kinetic hypotheses both the law of the conservation of energy and the law of increase in entropy.

The acknowledged leader for the first option was G. Kirchhoff. In his exposition of the theory of heat, the principle of the conservation of energy and Carnot's principle are presented as two postulates arising by induction and verified by the totality of their experimental consequences. Thermodynamics is then developed according to a new kind of theory in physics: saved from all philosophical hypotheses about the structure of bodies, about the nature of the phenomena seated within them. Concerned only to link the measurable features of the various changes—masses, quantities of heat, temperatures, pressures—by its formulas, it inspires confidence in its certitude by its temperate claims and the modesty of its affirmations.

With the second approach are associated the attempts, more powerful than successful, of Boltzmann, Clausius and Helmholtz. The profound meditations of these physicists on the principles of mechanics could not, in fact, derive from these principles the great law obtained by Clausius in extending Carnot's axiom, that any modification of an isolated system results in an increase in the entropy of the system.

War was declared between the two approaches, a war more and more disastrous for the kinematic doctrines. They seemed, only fifteen years ago, to be of a kind all physical theory should conform to. Today, [57] it seems quite close to rejoining the physics of molecular attraction, which flourished so during Laplace's time, in the archives of bygone science. It is one of the episodes of this war, in which the two doctrines joined in battle and chemical statics emerged victorious, that we wish to relate today. A decisive defeat for kinetic hypotheses, this battle was the occasion of one of the more beautiful triumphs of thermodynamic theory.

II

Kinetic physics was not slow in formulating a chemical statics. In this very respect it was far in advance of thermodynamic theories, which penetrate the domain of chemical mechanics only with much prudence, circumspection and with due deliberation.

In the body of a gaseous mass which seems to us to be at rest, kinetic physics sees a perpetual agitation. Atoms move in a straight line with a terrifying speed, collide and rebound, bearing down on and violently bombarding the solid walls. If the gas is a compound gas, the molecules, undergoing these agitations and blows, do not remain invariably composed of the same atoms; at each instant, the molecules split and fall apart; their scattered atoms run freely back and forth until the moment when they encounter other free atoms with which they aggregate together anew. "We are thus led," writes Williamson,[2] "to admit that in an aggregate of molecules of each compound, there is a perpetual exchange of its constituent elements. Let us suppose, for example, that a vessel containing hydrochloric acid is filled with a large number of molecules [58] of composition ClH. The considerations which we have exposited lead us to admit that each hydrogen atom does not remain at rest in its position relative to the chlorine atom with which it was at first combined, but that it perpetually changes place with other atoms of hydrogen."

These continual exchanges of atoms between molecules, these incessant combinations and decompositions, occur not only within the bulk of the compound gases. Liquid compounds equally should display such behaviour. This, at any rate, is what Clausius[3] admits in order to explain how electric current is propagated through an electrolyte.

How is it possible to establish chemical equilibrium in a system which is the seat of such continual changes? There can be no question of equilibrium properly understood as the complete absence of change, but only of an apparent equilibrium, of a stationary state of the system, where no change reveals itself to the observer because change in a determinate sense, produced during a given time, is exactly compensated by a modification in the inverse sense and of the same size, produced during the same time. Chemical equilibrium is thus a veritable *mobile equilibrium*, to use the idea and the word introduced in the theory of radiant heat by Pierre

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[2] Williamson, *Annalen der Chemie und Pharmacie*, Vol. LXXVII, p. 37; 1851.

[3] R. Clausius, *Poggendorff's Annalen*, vol. CI, p. 338; 1857.

Prévost,[4] the last representative of this school of Swiss physicists who, together with the Bernoullis, Deluc and Lesage, jealously guarded the kinetic traditions from the time when Cartesianism flourished to the advent of the mechanical theory of heat.

This assimilation of the state of equilibrium established in the changes of physical and chemical state to a mobile equilibrium is encountered for the first time in a memoir published [59] in 1857 by Clausius[5] under the title "On the nature of the movement to which we give the name heat." He applied it to the equilibrium established between a liquid and its saturated vapour and expressed himself on the subject in terms such as the following:

"A phenomenon which seems to me to be of particular interest is that of *vaporisation*, and I have sought to account for it in the following manner:

"We have said above that in a liquid a molecule remains, during its movement, in the spheres of attraction of the neighbouring molecules and that it leaves them only to be placed in another analogous position in relation to other neighbouring molecules. But this is only relative to the mean value of the movements; and since these are all irregular, it must be admitted that the speeds of a determinate molecule deviate between limits extending considerably on both sides of the mean.

"If we first consider the surface of a liquid, I admit that, in the various movements occurring in every sense, it is possible that a molecule, by a favourable combination of translational, rotational and oscillatory movements, should deviate with such vigour from the neighbouring molecules that before losing all its speed by their force of attraction, it has already left their sphere of action and continues to move in the space situated above the liquid.

"Suppose that this space is limited and at first empty. It is gradually filled with molecules as they are carried along. They behave in the space just as a gas, making impacts with the wall during their movement. Now, one of these walls is constituted of the liquid itself, and this does not, in general, reflect a molecule when it collides with it, but retains and assimilates [60] it by the attraction that the other molecules immediately exert on it when it comes near them. Equilibrium is therefore established when it sheds a number of molecules into the space above such that, during unit time, there are on average as many molecules colliding with the surface of the liquid and which are retained by it, as there are of others which are emitted from it. This state of equilibrium is therefore not a state of rest in which vaporisation has stopped, but a state in which there is a continual vaporisation and an equally strong condensation compensating it."

Having put forward his principles, Clausius shows how they explain the dependence that exists between the vapour pressure and the temperature, the law of mixing for gases and vapours, the effect of pressure on boiling-point temperature, and various other facts.

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[4] Pierre Prévost, *Recherches physico-mécaniques sur la chaleur*, Genève, 1782.

[5] R. Clausius, *Poggendorff's Annalen*, vol. C, p. 353; 1857.

Around the same time, the research of Berthelot and Péan de Saint-Gilles on the phenomena of etherification and the discovery of the phenomenon of dissociation by Henri Sainte-Claire Deville soon attracted attention to the notion of chemical equilibrium. Deville had very clearly illuminated the analogy which exists between a state of chemical equilibrium and the state of equilibrium established in a change of physical state such as that of vaporisation, which should alleviate the temptation to extend the hypothesis of mobile equilibrium formulated by Clausius for the second state to the first state.

Reading the passage cited above where Clausius gives, in accordance with the principles of the kinetic doctrine, the explanation of equilibrium between a liquid and the saturated vapour of the liquid suggested to Pfaündler[6] the principles of a theory of dissociation within a gaseous system. "I now come," he says, "to the explanation of the *dissociation* of *vapours*, and to this end [61] I frame the following hypothesis: within the vapour of a partially decomposed compound, provided the temperature remains invariable, *the number of molecules which split is exactly equal to the number of molecules that are formed by the recombination of their atoms*.

"This explanation necessarily supposes that *at a given instant, the molecules are not all animated by the same movement;* similarly, the explanation of vaporisation given by Clausius supposes that the molecules situated at the surface of the liquid do not all move in the same way. But according to the mechanical theory of heat, this irregularity in the distribution of molecules is extremely probable.

"... Consequently, if the temperature remains constant at a given value, the number of free particles will increase until such time as the number of molecules reforming in a given time becomes equal to the number of molecules which split during the same time. From this moment, *equilibrium* between decomposition and combination reigns as long as the temperature remains invariable."

About the same time Pfaündler was writing these lines, Guldberg and Waage[7] published an essay on chemical mechanics where chemical equilibrium is treated as the effect of two inverse and equivalent modifications, and soon the idea first expressed by Clausius was extended, so that one should no longer speak of *chemical equilibrium*, but only of *two inverse reactions limiting one another*.[8]

III

How [62] did this notion of mobile equilibrium come to allow the establishment of a chemical statics? In a very simple way, it seems: the system under study is the site

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[6] Pfaündler, *Poggendorff's Annalen*, Bd. CXXXI, p. 55; 1867.

[7] Guldberg and Waage, *Études sur les affinités chimiques*, Christianja, 1867.

[8] It seems that Malaguti *Annales de Chimie et de Physique*, 3rd. series, volume LI, p. 328, 1857 was the first to consider a chemical equilibrium as the effect of two inverse, equally fast, reactions. The idea expressed by Malaguti received little comment. It has not influenced the development of kinetic doctrines in chemistry.

of two continual, inverse changes. Take the formula representing the speed of the first reaction and the formula which represents the speed of the second reaction, put them equal and you obtain the condition for each of these two reactions, at each instant, being exactly compensated by the inverse reaction and for the system to be at equilibrium.

But in order to put this method into practice, it is necessary to know the law governing the speed of each of these two inverse changes. What will teach us this law? Experience? That is not possible: neither of the changes which occupy us can be studied independently of the inverse change. Under all conditions, the two changes are simultaneous, and their resultant effect alone is accessible to our methods of observation.

Consider, for example, a receptacle enclosing hydrogen, chlorine and hydrochloric acid. At each instant, hydrogen atoms and chlorine atoms enter into combination to form hydrochloric acid; but also at each instant, molecules of hydrochloric acid are split to give free chlorine and free hydrogen. If, from one minute to the next, we determine the increasing proportion of hydrochloric acid in the gas mixture, we will not know the speed of the first reaction; we will only determine the excess of the speed of the first reaction over the speed of the second. The expression for each of the two speeds remains unknown to us.

It [63] is therefore only by way of hypotheses that the speed of each of the two inverse reactions occurring in a chemical system can be determined—that, for example, the speed of combination of hydrogen and chlorine and the speed of destruction of hydrochloric acid can be determined, speeds whose difference alone is observable.

The most logical method evidently consists in requiring that the formulas which govern the two inverse reactions be added to the assembly of suppositions and arguments on which Krœnig and above all Clausius have built the kinetic theory of gases. This is the method that Julin[9] has sketched, and which has been followed by Naumann[10] and Horstmann[11], who has pushed the method so far as to be able to numerically calculate the variable vapour densities of dissociating gaseous compounds such as amylene hydrobromide, phosphorus perchloride and nitrogen peroxide. The numbers resulting from the theory agree satisfactorily with the numbers obtained by experiment.

This method is not, however, the one usually followed. Bedevilled by analytic problems, wavering in the face of incertitudes about certain suppositions regarding molecular collisions, it has, besides, the grave defect of being applicable only to systems formed of reasonably perfect gases. It is thus to hypotheses which are more immediate, more general, more arbitrary but flexible and easy to model on the facts

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[9] L. Joulin, *Annales de Chimie et de Physique*, 4th. series, v. XXX, p. 248; 1875.

[10] Naumann, *Annalen der Chemie und Pharmacie*, V. Suppl. Bd. CCCXLI.

[11] Horstmann, *Breathe der Deutschen Gesellschaft*, 1st. year, p. 210; 1868.

of experiment, that chemists have had recourse, in particular Guldberg and Waage[12] and G. Lemoine.[13] [64] These hypotheses, and more or less successful and fruitful formulas which have been deduced from them, will not delay us here. For the point which should now deserve our attention does not depend on them.

To understand this point, we will address a classic dissociation phenomenon, the first phenomenon to which Pfaündler extended the conception of mobile equilibrium introduced by Clausius in the kinetic theory of vaporisation, the dissociation of calcium carbonate. First, we reproduce what Pfaündler says:[14]

"As an example of these phenomena of dissociation to which the hypothesis is immediately extended, I will choose the decomposition of calcium carbonate.

"Heated in an enclosed space from a certain temperature, calcium carbonate undergoes a dissociation. A certain number of its molecules whose internal movement exceeds a certain maximum are decomposed. The molecules of carbonic acid released move straight into the space, and their density will be augmented until such time as the molecules absorbed in unit time become exactly as numerous as the molecules emitted in the same time. Suppose that the temperature is lowered. The number of molecules returning soon exceeds the number of molecules emitted, and the substance *absorbs* carbonic acid. Imagine that the carbonic gas is swept up by a current of air or of some other indifferent gas. The emission of carbonic acid molecules is not diminished at all, because the cause of the emission has not disappeared, but the return of the molecules is suppressed because these molecules have been expelled. The calcium carbonate is then seen to [65] *release* carbonic gas into the current of air at the *same* temperature at which it was seen, in the absence of the current of air, to be absorbed by the lime."

Let us follow this explanation closely and draw some immediate consequences.

Where is the place where carbonic gas is released? At the free surface of the pieces of Island spar. The speed of release depends, no doubt, on the state of agitation of the molecules of calcium carbonate and hence on the temperature and to some small extent on the pressure. But certainly at equal temperature and pressure, the mass of carbonic gas released in a given time will be proportional to the surface at which this release takes place, at the free surface of carbonate of lime.

Where is the place where carbonic gas is absorbed? At the surface of contact of the active lime and the gaseous atmosphere. The speed of absorption depends on the frequency of collisions between a carbonic molecule and a lime molecule, and the speed of the colliding molecules therefore depends on the pressure and the temperature. But certainly, at equal temperature and equal pressure, the mass of carbonic gas which combines with lime in a given time is proportional to the surface of contact of the lime and the carbonic gas.

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[12] Guldberg and Waage, *Les Mondes*, volume V, p. 105 and p. 627; 1864. – *Études sur les affinités chimiques*, Christianja, 1867. – *Journal für praktische Chemie*, volume XIX, p. 69; 1879.

[13] G. Lemoine, *Comptes Rendus*, 29 October, 1871. – *Annales de Chimie et de Physique*, 4th. series, volume XXVII, p. 289; 1872.– *Études sur les équilibres chimique*, Paris, 1881.

[14] L. Pfaündler, *loc. cit.*

Let us use the language of algebra to fix the results that we have obtained. Let P designate the pressure, T the temperature, S the free surface of carbonate of lime, and S′ the surface of contact of lime and carbonic acid. We can represent the speed of emission of carbonic gas by a formula such as

$$v = S\,f(P, T)$$

and the speed of absorption of the same gas by a formula such as

$$v' = S'\,f'(P, T),$$

$f(P, T)$ [66] and $f'(P, T)$ being two suitably chosen functions of temperature and pressure. To express that the system is at equilibrium, we should write that the speed v of release of carbonic acid is equal to the speed of absorption v' of the same gas, giving us the following equation of equilibrium:

$$f(P, T) = (S'/S)\,f'(P, T).$$

If we resolve this equation in terms of the pressure P, it is clear that we obtain a value for this pressure which depends on the temperature and the ratio S′/S, in which case the law of dissociation of carbonate of lime appears to us in the following form: In a system enclosing calcium carbonate, lime and carbonic gas, equilibrium is established when the pressure of the gas attains a value depending not only on the temperature, *but also on the ratio of the surface of contact between lime and carbonic gas and the free surface of calcium carbonate.*

Now, is this the law that experiment reveals? Not at all. The classic experiment of H. Debray showed that the law of dissociation of carbonate of lime, similar in all respects to the law of vaporisation, was the following: Equilibrium is established when the pressure of carbonic gas attains a value which depends *on the temperature alone.*

This discrepancy has not escaped the proponents of kinetic doctrines, who have sought to avoid it. G. Lemoine[15] presents a theory for the dissociation of carbonate of lime entirely similar to that we have just developed, except for one point: he supposes the two surfaces S and S′ to be equal to one another, which makes the ratio S′/S disappear, becoming equal to 1. To explain this equality of the two surfaces, [67] Lemoine says "The partial combination of carbonic acid already released occurs exclusively at the surface of the pieces of limestone. These pieces are covered over all their extension by a kind of coat, more or less thick, of caustic lime; but it is only on the latter superficial layer that the action of carbonic acid tends to occur."

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[15] G. Lemoine, *Annales de Chimie et de Physique*, 4th series, volume XXVII, p. 308; 1872.

Let us accept this explanation is valid when all the active lime enclosed within the system results from the superficial decomposition of fragments of Island spar. It is in any case easy to imagine an experiment where it no longer holds. This is the experiment:

Equilibrium is established in a system enclosing calcium carbonate, lime and carbonic gas. The temperature has the value T and the pressure of carbonic gas has the value P. Without any further change in the system, we introduce into it an appreciable mass of active lime. Nothing has been changed which influences the release of carbonic acid. The gas is released with exactly the same speed before the introduction of the active lime and after its introduction. The temperature and pressure have not varied, but the carbonic gas has been presented with a new surface on which the recombination with lime can occur. The speed of absorption of carbonic acid has been increased in the same ratio that the surface of contact between lime and carbonic gas has grown. The speed of emission and the speed of absorption of carbonic gas which were equal before the introduction of the active lime can no longer be equal after the introduction; the second speed has become greater than the first and the system is no longer at equilibrium. It is the scene of an absorption of carbonic acid. If the temperature is maintained, after the introduction of the active lime, at its previous value, the pressure of carbonic gas will have a value when equilibrium is attained which is less than that attained in the first equilibrium. *When calcium carbonate is dissociated in the presence* [68] *of an excess of active lime, the pressure of carbonic gas at a given temperature should be less according as the lime offers a greater surface for the absorption of carbonic gas.*

The experiment is feasible. It has been carried out by H. Debray. The result is absolutely precise: *Within the greatest limits, the pressure of dissociation is absolutely independent of the excess of active lime enclosed within the system; it depends exclusively on the temperature.*

Chemical statics based on kinetic hypotheses is thus condemned.

The experiment which condemns it is a very simple one, whose interpretation leaves no room for ambiguity. Easy to execute, it has been repeated many times by different observers on a range of substances apart from carbonate of lime. Further, the proposition whose falsity is demonstrated by this experiment is not the result of a complicated deduction in the course of which some false supposition, but foreign to the proper principles of the theory, might have slipped in. This proposition is an obvious, immediate consequence necessitated by the kinetic notion of chemical equilibrium. It can be said that the contradiction that we have just brought to light indisputably condemns the kinetic doctrines.

It is this that one of the first proponents of these doctrines, Horstmann,[16] recognised in 1873: "Contradictions," he said, "are reached with experiment because the fact, many times verified, that the mass of solid substance has no influence on the degree of dissociation cannot be satisfactorily explained." Changing his ideas

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[16] Horstmann, *Liebig's Annalen der Chemie und Pharmacie*, Bd. CLXX, p. 208; 1875.

from top to bottom, Horstmann became one of the founders of chemical statics based on thermodynamics.

IV

We [69] cannot say what this novel doctrine is here[17] without exceeding the limits of this article. We wish only to show that the chemical statics of heterogeneous systems, the stumbling block which has broken the kinetic hypotheses, has furnished thermodynamics with one of its most beautiful triumphs.

We are indebted to the American physicist J. Willard Gibbs for the chemical statics of heterogeneous systems based on thermodynamics. He has set out the essential laws in an essay[18] which remains one of the most powerful works of the nineteenth century.

A chemical system is always composed of a certain number of simple substances. But it sometimes happens that by the very designation given to the system, the masses of these various elements cannot be taken arbitrarily, and there exist certain relations between them. Thus, a system containing carbonate of lime, lime and carbonic gas is constituted of calcium, carbon and oxygen, and the masses of these three simple substances cannot be taken arbitrarily. By saying that these simple substances were grouped in the system in such a way as to form calcium carbonate, lime and carbonic gas exclusively, I have imposed on their three masses a certain condition. I may arbitrarily chose two of these [70] three masses—the mass of calcium and the mass of carbon, for example—but the third mass—that of oxygen—is then determined without ambiguity.

It is always possible to group the simple substances forming a system into a certain number of compounds or the remains of compounds in such a way that the mass of each of these groups can be chosen arbitrarily without contradicting the designation of the system. Thus, the system we have taken as an example cannot be constituted of arbitrary masses of calcium, carbon and oxygen. But it can be formed of an arbitrary mass of lime and an arbitrary mass of carbonic acid. Lime and carbonic acid are the *independent components* of this system.

In many cases it is possible to chose the independent components of a system in several different ways. Consider, for example, a system formed from hydrated crystals of sodium acetate and a solution of the salt in water. It is possible to take water and hydrated sodium acetate as independent components of this system. It is also possible to take water and anhydrous sodium acetate as independent components. But this indeterminacy which might offer a choice of independent components of a chemical system does not reflect on the number of independent

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[17] We have given an elementary account in our *Introduction à la Mécanique chimique,* Gand, Ad. Hoste and Paris, G. Carré, 1893.

[18] J. Willard Gibbs, "On the equilibrium of heterogeneous substances," *Transactions of the Academy of Sciences and Arts of Connecticut,* Vol. III, 1873-1876).

components. For a chemical system of a given nature, the number is absolutely determined; thus, in the system that we have taken as an example, the independent components can be chosen in two different ways, but whichever choice is adopted, their number remains equal to 2.

It is, in general, a very simple operation to determine the number of components of a chemical system when the formulas of the substances which comprise it are known. Henceforth, we will designate the *number of independent components* which constitute the system under consideration by the letter c.

The [71] heterogeneous systems which the chemist studies are decomposed into a certain number of homogeneous masses. A system constituted of water and water vapour is decomposed into a homogeneous mass of liquid water and a homogeneous mass of water vapour.

Several of the homogeneous masses which compose a heterogeneous system might have the same nature, the same physical and chemical properties. In a crystallising dish, where a saturated solution of sodium chloride is allowed to deposit the salt that it contains, the crystals of sea salt adhere to various points of the glass wall. Although separated from one another, the crystals have the same composition and the same properties. If they were welded to one another, they would form a homogeneous solid. These various masses which, although separated from one another, have the same composition and the same properties, belong to the same *phase*. In the crystallising dish which we have just mentioned, the crystals of sea salt constitute a phase. The saline solution constitutes another phase, and the system is divided into two phases.

It is, in general, very easy to enumerate the distinct phases encountered in a given system.

A homogeneous mixture contains a single phase.

A system comprising liquid water and water vapour is divided into two phases, the liquid and the vapour. A system containing crystals of sea salt and a solution of the salt is also divided into two phases, the solid salt and the solution.

A system constituted of calcium carbonate, lime and carbonic acid is divided into three phases: the solid carbonate of lime, the solid lime and the carbonic gas.

We will designate the *number of phases* into which a system is divided by φ.

The number c of independent components of the system and the number φ of phases into which the system is divided characterise the system from the point of view of chemical [72] statics. In yet more precise fashion, *the form of the law of equilibrium of a chemical system depends exclusively on the number*

$$\mathrm{V} = c + 2 - \varphi$$

which is called the VARIANCE *of the system.*

V

We now enumerate the forms that the law of equilibrium takes according to the value of this *variance*.

First, if *the variance of a system is negative*, the system cannot be at equilibrium at any temperature or under any pressure. Thus, at no temperature or pressure is it possible to observe the state of equilibrium of a system which contains at the same time sulphur vapour, liquid sulphur, orthorhombic sulphur and monoclinic sulphur. Such a system encloses a single component divided into four phases and the variance would be equal to -1.

When the variance of the system is equal to 0, the system is said to be *invariant*. There is only one temperature and one pressure at which the system can be at equilibrium, and the composition of each of the phases composing the system at equilibrium is, moreover, completely determined.

Consider, for example, a system containing water in each of its three states of ice, liquid and vapour. This system is composed of a single independent component ($c = 1$) divided into three phases ($\varphi = 3$) and it is invariant. It can therefore only be at equilibrium at one determinate temperature and one determinate pressure. Very careful investigations have shown that this temperature has roughly the value +0.0076°C, and that this pressure [73] is the pressure of saturated water vapour corresponding to this temperature, approximately 4.60 mm.

A system whose variance is equal to unity is said to be a *univariant* system. When observing a univariant system at equilibrium, either the temperature or the pressure can be given arbitrarily. At a given temperature, the pressure at which the system is at equilibrium has a determinate value; this is the *transformation pressure* at the temperature considered. The composition of each phase within the system at equilibrium is equally determinate. Under a given pressure, the temperature at which the system is at equilibrium has a determinate value; this is the *point of transformation* under the pressure considered. The composition of each phase at the moment of equilibrium is equally determinate.

The simplest type of univariant system is provided by a liquid topped by its vapour. A single component ($c = 1$) is divided into two phases ($\varphi = 2$). At a given temperature, equilibrium is established for a determinate value of the pressure, which is the *pressure of the saturated vapour* at the temperature in question. Under a given pressure, equilibrium occurs at a determinate value of the temperature, which is the boiling point under the pressure in question.

A system enclosing a single substance in both solid and liquid states is also a univariant system. Under a given pressure, equilibrium corresponds to a determinate temperature, which is the point of fusion under the pressure in question, and the fusion point depends only on this pressure.

A system enclosing a gas such as cyanogen and a solid polymer of this gas, such as paracyanogen, is again a univariant system. Here too, the establishment of equilibrium at a given temperature requires that the gas has attained a determinate pressure, a function of temperature [74] only, which is the transformation pressure relative to this temperature.

A system containing carbonate of lime, lime and carbonic gas is formed of two independent components and divided into three phases. At a given temperature, the system is in equilibrium at a determinate value of the pressure of the carbonic gas, a value which is called the *dissociation pressure* of carbonate of lime at the temperature of the experiment.

Examples of univariant systems can be multiplied.

A salt, anhydrous or hydrated, occurs in the presence of an aqueous solution of the salt topped by an atmosphere of water vapour. Two independent components ($c = 2$), the salt and the water, are divided into three phases ($\varphi = 3$), the solid salt, the solution and the vapour. The system is univariant. A state of equilibrium of the system can be observed at any temperature. Once the temperature is given, the vapour pressure and the concentration of the solution within the system at equilibrium have determinate values.

Some chlorine is dissolved in water. The solution encloses crystals of the hydrate of chlorine and is topped by a gaseous atmosphere which is a mixture of chlorine and water vapour. Two independent components ($c = 2$), water and chlorine, are divided into three phases ($\varphi = 3$), the solution, the crystalline hydrate of chlorine and the gas mixture. The system is therefore univariant. A state of equilibrium corresponds to each temperature, and in this state the pressure of the gas mixture is determinate, as is the composition of the gas mixture and the composition of the liquid mixture.

A mixture of liquid ether and water separates into two layers. The one, richer in ether, is accordingly lighter and floats while the other, richer in water, occupies the base of the vessel. A mixed vapour stands over the liquid. Two independent components ($c = 2$), ether and water, [75] are divided into three phases ($\varphi = 3$), the two layers of liquid and the mixed vapour. The variance of the system has the value 1. Such a system can be observed at equilibrium at any temperature, and it suffices to know the temperature in order to know the pressure of the mixed vapour at the moment of equilibrium as well as the composition of the gaseous layer and the two liquid layers.

These examples, which could be multiplied, give some indication of the infinite variety of univariant systems. Despite their diversity, the value of the variance which they have in common imposes on all of them the same form of the law of equilibrium. A transformation pressure, which is a function of the temperature alone, is found in all of them, as well as the propositions deduced from thermodynamics about the existence of this pressure—the celebrated equation of Clapeyron and Clausius, for example.

The role that univariant systems have played in the history of chemical mechanics is well known. It is because they addressed univariant systems that H. Debray, Isambert and Troost and Hautefeuille have found, in the course of studying chemical decompositions and allotropic modifications, a *dissociation pressure* and a *transformation pressure* analogous to the *saturated vapour pressure.* And it is in bringing out the analogy between dissociation pressure and transformation pressure with saturated vapour pressure that they have brought the great thoughts of Henri Sainte-Claire Deville into the most stubborn minds: There is no chemical mechanics distinct from physical mechanics; all changes of physical state or chemical constitution are governed by the same laws.

VI

The [76] importance of univariant systems should not detract from the equally important *bivariant* systems.

It goes without saying that what is at issue is systems whose variance is equal to 2. These are therefore systems divided into a number of phases φ equal to the number c of independent components which constitute them.

A bivariant system can be observed at equilibrium at all temperatures and under all pressures. When the temperature and the pressure are given, the composition of each phase of the system at equilibrium is determinate. This composition is independent of the masses of the independent components which constitute the system.

A very simple example of a bivariant system is provided by a solid salt taken in the presence of an aqueous solution of the salt. Two independent components, the salt and water, are divided into two phases, the solid salt and the solution. Such a system can be observed at equilibrium at all temperatures and pressures. The solution is them *saturated* with the salt, and the concentration of the saturated solution depends on the temperature to which the system is carried and the pressure it supports. But it is absolutely independent of the mass of the water and the mass of the salt that the system encloses.

Is another example of a bivariant system desired? An increasingly large mass of water is poured into a determinate mass of ether. The first portions of the water are totally mixed with the ether, but after a certain moment, the mixture separates into two layers, an upper layer richer in ether and a lower layer richer in water. We are thus dealing with a system constituted of two independent components, ether and water, which is divided into two phases, the two superimposed liquid layers. [77] Such a system is bivariant. If the temperature and pressure are maintained constant, the composition of each of the two layers remains invariable. As we add water to the mixture, we will see the mass of the upper layer diminish and the mass of the lower layer increase. But neither the concentration of the upper layer nor the concentration of the lower layer will undergo the least variation while the two layers remain in contact with one another or, in other words, while the system remains bivariant.

A host of important problems for chemical statics are associated with the study of bivariant systems. The theory of the solubility of gases is the theory of a bivariant system, for two independent components, the gas and the solvent, are divided into two phases, a liquid solution and a gaseous atmosphere which may be mixed or simple according as the solvent is volatile or not. The theory of the vaporisation of a mixture of volatile liquids is the theory of a bivariant system because two fluids, playing the role of independent components, are divided into two phases, the liquid mixture and the mixed vapour.

Systems whose variance is greater that 2 are said to be *plurivariant* systems. A plurivariant system can be observed at equilibrium at all temperatures and pressures, but knowledge of temperature and pressure is not sufficient to determine the composition of the different phases into which the system is divided. This composition depends on the magnitude of the masses of the various independent components which constitute the system.

Take, for example, two immiscible liquids in which a third substance is dissolved. Three independent components are divided into two phases, and the variance of the system is equal to 3. To know the concentration of the two solutions which remain at equilibrium in contact [78] with one another, it does not suffice to know the temperature and the pressure; is also necessary to know the relative values of the masses of the two solvents and of the dissolved substance.

VII

The several examples that we have enumerated show how simply and immediately the phase rule can be applied. A rule with such extremely important and very general predictions cannot fail to be of great use to chemists, whether they be engaged in the classification of known facts, or in guiding research among complex phenomena. The history of recent discoveries in the domain of chemical statics shows overabundantly, in fact, the extreme utility of this rule, which has served as a thread in the study of particularly complex chemical equilibria by H. W. Bakhuis Roozboom. Guided by the phase rule, Bakhuis Roozboom and his students have succeeded in disentangling certain systems that the experimenter, deprived of any theoretical help, has regarded as a veritable chaos. This beautiful work, accomplished in the laboratories at Leyden and Amsterdam, has contributed considerably in drawing the attention of chemists to the algebraic theorems demonstrated by J. Willard Gibbs.

Among the applications of the phase rule made by Bakhuis Roozboom, we cite just one particularly striking case, dealing with the properties of isomorphic substances.

Take two salts which are incapable of reacting together chemically, for example ammonium chloride and ammonium nitrate. Place them in the presence of a quantity of water insufficient to entirely dissolve the one or the other of the two [79] salts. Three independent components—water, ammonium chloride and ammonium nitrate—constitute the system. Moreover, the system is divided into three phases: the two crystalline salts and the aqueous solution of the two salts. We are therefore dealing with a bivariant system which can be put at equilibrium under any pressure and temperature. When equilibrium is established under a given pressure and a given temperature, the solution, saturated by each of the two salts, should have a perfectly determinate composition, independent of the masses of ammonium chloride, ammonium nitrate and the water which have been taken.

This is, in fact, what the old experiments of Rüdorff have already revealed, not only regarding the pair of salts we have mentioned, but also regarding a certain number of couples of salts which are not capable of reacting together chemically.

But Rüdorff's experiment has, at the same time, revealed a certain number of saline couples which are not subject to the rule stated above.

Take, for example, potassium sulphate and ammonium sulphate instead of ammonium chloride and ammonium nitrate. Again, put these in the presence of a mass of water incapable of dissolving them completely. Under a given pressure and a given temperature the system once more attains a state of equilibrium, but the composition of the solution within the system at equilibrium is no longer determined by knowledge of the pressure supported by the system and the temperature to which it is taken. It depends on the relative values of the masses of the salts and the water which have been brought together. If, without changing the temperature or the pressure, a certain mass of one or other of the two salts is added to the system, the solution is seen to change in composition, enriched in relation to the salt added, and impoverished in relation to the other salt.

These [80] characteristics are not consistent with a bivariant system; only a plurivariant system could display them. The calculation which has led us to regard the system of ammonium chloride, ammonium nitrate and water as bivariant must therefore become false somewhere when we try to extend it to the system of potassium sulphate, ammonium sulphate and water. Now, the error evidently cannot lie in the number of independent components, which is assuredly 3; it can only lie in the number of phases. The number of phases into which the system is divided cannot be equal to 3; it cannot exceed 2.

Whence comes this reduction in the number of phases?

Potassium sulphate and ammonium sulphate are two isomorphous salts. When left for a long time in contact with an aqueous solution, the masses of the two salts, the crystals of the one and the crystals of the other, cease to be distinct, and finally there are only mixed crystals, containing both potassium sulphate and ammonium sulphate. The experiments of Rüdorff, together with the theorems of J. Willard Gibbs, show us that the mixed crystals should be considered not as two phases, but as one. The crystals are therefore not, as a number of authors have supposed, simple mechanical mixtures—a juxtaposition or a tangle of crystalline flakes of potassium sulphate with crystalline flakes of ammonium sulphate. The two components are physically mixed in as intimate a manner as within the aqueous solution, and they constitute, in the expression created by van 't Hoff in connection with other matters, a *solid solution*.

This assimilation of a solid solution of mixed crystals by two isomorphous salts leads to a complete theory of the phenomena which are produced when two isomorphous salts are brought together with water. [81] This theory has received precise confirmation by Bakhuis Roozboom and his students. Moreover, the phase rule shows us that some mixed crystals constitute a veritable solid solution and count as a unique phase, dissolving in water in accordance with a completely different law than do crystals formed of juxtaposed flakes of two different salts, crystals which represent two phases. The study of these phenomena of dissolution is therefore capable of furnishing the crystallographer with a precise criterion for distinguishing the two sorts of crystal.

VIII

The example we have just cited well illustrates the utility of the phase rule. This rule is gradually attracting the attention of chemists and suggesting to them means of tackling the most complex questions of chemical mechanics. We have already spoken of the beautiful and fruitful research pursued in the Dutch universities under the direction of Bakhuis Roozboom. In Göttingen, Berlin and Leipzig much work is guided by Gibbs' theorems; in the United States, in the young and active University of Ithica where, under the impulse of Bancroft and Trevor, studies in physical chemistry are developed with ardour and the phase rule is the supreme master, ordering teaching and research. In the *Journal of Physical Chemistry*, emanating from this university, chemical work from the whole world comes to be classified according to the degree of variance of the systems studied.

The book of Bancroft's on *the phase rule,* published by the university of Cornell at Ithica, is the occasion of the writing of this article. We cannot analyse this book [82] without abusing the hospitality of *Revue des Questions scientifiques*; we will just say one word. It shows victoriously that the ideas of J. Willard Gibbs, even deprived of the formulas, are eminently suitable for organising and illuminating the already abundant riches of qualitative chemical mechanics.

ESSAY 5

A NEW SCIENCE: PHYSICAL CHEMISTRY*

I

"You will probably," some readers will say to me, "be speaking about *two old* sciences, chemistry *and* physics—two sciences whose official programmes are coupled to one another, as history and geography are coupled together, in virtue of a kind of prosody and because such combinations of words please the ear; two sciences which parsimonious budgets confide to one and the same school teacher or to the same baccalaureate examiner; but two sciences whose disparity becomes all the more striking the more they are brought together.

Treatises on chemistry always begin by happily enumerating the characteristics which distinguish the two disciplines, and should it not enumerate them, the reader will have no difficulty in discovering them.

What does he find in physics? Defined and measurable magnitudes, general laws relating the various magnitudes and having the form of mathematical theorems, consequences deduced from these laws by the methods of geometry and algebra, and they too cast in this precise and rigorous form; for submitting these consequences to the test of experience, meticulously designed and complicated apparatus whose smallest part is submitted to multiple tests; methods of measurement encompassed by reasonable precautions; as the results of these measurements, numbers [206] corrected and combined as a result of laborious calculations.

What does he find in chemistry? Enumerations of substances, descriptions of qualities, consistencies, colours, flashes, smells and flavours in a language frequently foreign, sometimes expressive, but always little concerned with geometric precision; symbols less algebraic than alchemical; an arsenal of retorts, bulbs, flasks, furnaces and crucibles for generating or destroying bodies and modifying qualities, [instruments] whose simplicity does not exclude a somewhat baroque and hermetic character; methods?—no, but rather ingenious procedures, and let us speak plainly, recipes.

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* Originally published as "Une Science Nouvelle: La Chimie Physique," *Revue Philomathique de Bordeaux et Sud-Ouest*, (1899), 205-19, 260-80.

Do you want to prepare phosphorous acid? Open Wurtz's *Dictionary* and read: "A current of chlorine is passed over a bed of phosphorus, immersed in water and always maintained in excess; then the solution is evaporated to remove the hydrochloric acid formed; the evaporation should be continued until the solution begins to discharge phosphureted hydrogen. The phosphoric acid obtained by this procedure forms a syrupy liquid which becomes a crystalline mass when the concentration is sufficient."

Do you want to make current jam? "Put the juice on the heat," the *Cuisinière bourgeoise* tells you, "with half a pound of sugar to a litre of juice; skim and let boil for about half an hour; pour a spoonful of it onto a plate: if it congeals, it is ready; put it into jars and let it become a jelly."

Do the two treatises not proceed by the same method? Instead of enumerating the all too visible characteristics which distinguish chemistry and physics, would it not be a delicate task—one made to test a subtle logician—to make precise the exact boundary between chemistry and cooking?

Thus, on the one side we have a *rational* science which seeks to formulate the laws of the material world in mathematical propositions, to condense these laws into a small number of very general principles from which everything can be derived by way of [207] logical deduction. This is physics. On the other side, we have a *descriptive* science, whose classifications relieve the memory and satisfy the imagination, but a science contemptuous of deductive reasoning and proud of the instinctive and fruitful intuition which leads each day to the synthesis of some new substance. Such is chemistry.

Is it possible to fuse two such heterogeneous disciplines into a single science and to speak of a physical chemistry?

II

This profound difference between the method of physics and the method of chemistry is by no means new. As old as the methods themselves, it has given rise to lively debates between physicists and chemists from the seventeenth century, and, as happens all too often between adepts at the rival disciplines, the sarcasm of chemists towards physicists was met by disdain for chemists on the part of physicists.

Enamoured of the order and clarity with which geometers perform their demonstrations, physicists, following the example of Descartes, were unwilling to acknowledge any principle not equally acknowledged in mathematics. Whatever recalled the qualities and substantial forms of the peripatetic school wrought horror in the minds of those for whom all is but shape and movement. Nourished by "the analysis of the ancients and the algebra of the moderns," and accustomed to expressing clear ideas in the style of the *Discourse on Method*, they responded with a veritable loathing of crude empiricism and the cabalistic gibberish of "chymists."

The chemists, for their part, welcomed with irony or pity the attempts of physicists to derive the world from extension and movement. Treating as chimeras the mechanisms which their rivals begot, they claimed to resolve bodies into their principles not by logic [208] and algebra, but by fire, aqua fortis, spirit of vitriol, mensurations, and the gentle and violent processes of the "Spagyric."[1] "The spagyric science is far more noble," wrote Beccher, the Stahl's teacher, "taking as principles truths of *fact* and of experiment, it penetrates the causes of the solid reasons of combinations and compounds: it endlessly discovers new products of nature. You will not find a word about this so penetrating, so subtle and so curious study in the books of philosophers. They are content with ideas, abstractions and chimeras; they cling to words, happily ignoring how ignorant they are!"

In the *History of the Royal Academy of Sciences for the Year 1669*, Fontenelle recounts for us the catalogue, more intriguing than impartial, of disputes which arose at that time between the empiricism of chemists and the mechanical rationalism of physicists. "Monsieur du Clos,"[2] he says, "continued this year with the examination that he had begun of the Essays on chemistry of Mr. Boyle ... Mr. du Clos, as great a chemist as Boyle, but perhaps with a more chemical turn of mind, did not find it necessary, nor even possible, to reduce this science to principles as clear as shape and movement, and he had no difficulty in accommodating a certain specious obscurity which had become well established. For example, if some Brazil wood is boiled in some alkaline sulphated salt, an intense crimson colour is produced, which is lost and suddenly degenerates into a yellowish one by mixing with aqua fortis, spirit of saltpetre or several other mineral liquors. Mr. du Clos attributes this beautiful red to the excitement of the sulphated salts, and Mr. Boyle to the new texture of the particles which form the surface of the liquid."

"Chemistry resolves substances into certain crude principles and tangibles, salts, sulphurs, etc. by visible operations. ... But physics, by delicate speculations, acts on the principles as chemistry does on substances; it resolves them into other principles yet more simple, into small bodies infinitely varied in shape and movement: that is the principal [209] difference between physics and chemistry ... The essence of Chemistry is more confused, more limited; it resembles more the mixts where the principles are more confused the one with the other. The essence of Physics is more distinct, simpler, clearer, seeking to return to first origins. The other does not go to the bottom."

Chemists were not pleased by such frivolous talk, which was not allowed to go unanswered. The course in chemistry that Rouelle, famous for his science and his eccentricities, gave in the Jardin du Roi frequently degenerated into violent diatribes against the physicists. Fontenelle's piece was more than eighty years old when one of Rouelle's favourite pupils, Venel,[3] was unable to restrain himself from replying sharply: "Chemists would hardly be tempted by any of the prerogatives on which

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[1] [Duhem explains in *Le mixte et la combinaison chimique* (p. 39, fn. 2) that this is a term which had long been used as a synonym for "chemistry."]

[2] [The passage quoted in the remainder of this and the following paragraph is also quoted in *Le mixte et la combinaison chimique* (pp. 37-8).]

[3] Article *Chymie* in Diderot and d'Alembert's encyclopaedia.

the pre-eminence accorded here to physics is established, for example the *delicate speculations* by which it resolves the chemical principles into small bodies moving and shaped in infinitely many ways, because they are curious neither of the infinity nor of the fictions of physics. But they will not admit to being wrong in having this confused and limited mind, less precise and less simple than that of physics. They will agree still less that physics would not go so far as chemistry. They delude themselves, on the other hand, that chemistry penetrates to the interior of certain bodies of which physics only knows the surface and external shape, *quam et boves et asini discernunt*,[4] as Beccher with scant courtesy put it in his *Physique souterraine*."

There cannot be any question, for chemists of Rouelle's and Venel's opinion, of reducing chemical phenomena to shape and motion, of accounting for reactions by mechanical arguments, and of building a *physical chemistry*. "We even dare," said Venel, "to defy anyone to present us with an explanation of a chemical phenomenon based on the known laws of mechanics which we could not demonstrate to be false and gratuitous."

III

The [210] moment when Venel threw down this challenge is also the time when ideas, which were one day to lead to a first essay on chemical mechanics, began to penetrate into the domain of chemistry and make their way.

At the end of his *Optics* Newton disclosed to his reader in the form of questions the insights which his genius had not brought to perfect clarity. One of these questions, the last, sketches a doctrine whose achievement and perfecting was for a hundred and fifty years the principal object of theoretical physics. The fall of heavy bodies to the earth, the eternal journey of the planets around the sun, the eccentric march of the comets, the revolution of the satellites around the stars with which they have become accompanied, and the ebb and flow of the ocean, were seen, at the command of Newton's genius, to be ordered under a majestic *theory*: each of these imposing facts became a logical and necessary consequence of a single law, the law of universal gravitation. They were all condensed into this single proposition: two particles of matter are attracted by a force proportional to the product of their masses and inversely proportional to the square of the distance separating them.

Is this the only force acting on the various parts of matter? Do they not exert on one another attractive or repulsive actions so weak, that when the parts that they attract are separated by a notable distance, they fade, so to speak, and leave all power to the universal attraction, but so strong, when the parts approach contact, that the universal attraction now produces no more than negligible effects? Do these attractive or repulsive forces not explain the hardness of solids, the rising of liquids in very narrow spaces, the rounded shape of globules of mercury, the expansive force

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[4] [which both oxen and asses discern.]

of gases and the bending of light rays which pass [211] from one medium to another? Can they not explain chemical reactions equally well? Are their various intensities not accounted for by the order in which metals displace one another in the body of various menstrua? It is in these terms that Newton, having laid down *celestial mechanics* at the end of the seventeenth century, outlined, at the beginning of the eighteenth century, the plan for a *physical and chemical mechanics*.

Welcomed only by some faithful disciples of Newton's, the hypothesis of molecular actions remained for a long time humble and practically ignored. To attract the attention of scientists to it, an ardent dispute between Clairaut and Buffon concerning the nature of these actions had to burst onto the scene of the *Académie des sciences*. Buffon triumphed pompously over Clairaut, but it was Clairaut who had the better argument. The ideas which Clairaut had maintained and that Buffon thought he had refuted were taken up and made more precise by Father Boscovich in a powerful doctrine in which Newton's mechanics were synthesised with Leibniz' metaphysics. They reached their full bloom in the work of Laplace.

What, in the first place, is both striking and surprising in Laplace's work is the breadth and power of the developments his genius gave to the doctrine of universal attraction. The eternal claim to fame of the geometer is having written the *Traité de mécanique céleste* and the *Exposition du système du monde*. If, however, a catastrophe destroyed the writings of the astronomer and algebraist down to the last line, allowing only the memoirs of the physicist to survive, Laplace would still have every right to be regarded as one of the most powerful minds to have tried to understand nature.

The whole of Laplace's physics rests on the hypothesis of molecular forces. It is to these forces he turns for the cause of simple and double refraction of light rays, and it is with the help of these forces that he constructed his theory of *capillary action*, a masterpiece which would have sufficed to make the author famous. With these forces he explained the heating and cooling accompanying the compression and expansion of a gas, and prepared the way for Sadi Carnot and for Robert Mayer.

With [212] such examples supporting the precept, Laplace proclaimed that molecular actions accounted, in the least detail, for all terrestrial phenomena as universal attraction accounted for all terrestrial motions. He announced the advent of *physical mechanics*, sister to *celestial mechanics*.

A pleiad of physical geometers, ready to welcome his teaching and follow up his work, gathered around Laplace. There has, perhaps, never been a time when science has seen such a reunion of geniuses inspired by the same aspiration and drawn by the same impulse towards a common goal. While Fourier brought geometry to the service of the laws of propagation of heat—the only ones which did not depend on mechanics—Poisson, Navier and Cauchy constructed the theory of elasticity of bodies by applying to molecular forces the methods which Laplace had taught them how to use. While Poisson derived the equations governing the vibrations of sonorous bodies of various kinds, Cauchy linked them to Fresnel's discoveries in optics. Coulomb's experiments verified that electrical and magnetic attractions and repulsions fell under laws similar in every way to the law of universal attraction. On this basis Poisson, aided by the instruments forged by Laplace, constructed the mathematical theory of static electricity and of magnetism. Soon, Ampère added to it the mathematical theory of electromagnetic phenomena and, having exploited the precious mine opened by these two geniuses with an extraordinary ardour, the nineteenth century prepared to bequeath to the twentieth century the seam that they had discovered and which their keen activity was not able to exhaust.

A superb confidence enlivened these men who, from the little question Newton posed, brought forth, with the help of mathematical analysis, the biggest, most ordered and, at the same time, the most minute and precise, system of natural philosophy that the human intellect had ever known. In the pride of triumph, in the fame to which the method led them, they struck up a chorus of enthusiasm and, among the numerous variations of this chorus, a theme [213] developed:[5] *Ac gloriatur geometria quod tam paucis principiis aliunde petitis tam multa præstet.*[6]

IV

The response to Newton's question given by the eighteenth century would not have been entirely satisfactory if alongside physical mechanics a *chemical mechanics*—born of the same idea—had not germinated and grown.

Confronting pure chemists, descendants and inheritors of the alchemists, disciples of Beccher and of Stahl, and confronting Rouelle's school, another school grew which, faithful to the traditions of Boyle and Lémery, claimed to introduce into chemistry the clear language and exact reasoning which had served the geometers and was the pride of physicists. At the head of this school was to be found Macquer, whose *Dictionnaire de Chimie* was a model of sober and precise style, and Guyton de Morveau, whose investigations led to the birth of the new chemical nomenclature. This school of chemistry was very popular with those scientists who thought, along with the abbot of Condillac, that a science is a well-constructed language and wrote like d'Alembert and Lagrange, and who had no time for Beccher's barbarisms or Stahl's style—a strange mixture of German and Latin. "I dare say," wrote Buffon, "that Mr. Macquer and Mr. de Morveau are the first of our chemists to have begun to speak French. This science was thus born when one began so to speak it."

Now, the masters of this new school professed that chemistry should be treated by the method employed in physics, and that chemical reactions are reducible, in the last analysis, to mechanical effects which find their explanation in the forces of affinity acting, according to Newton, between the proximate parts of bodies. "The doctrine [214] of attractions is the true key to the most occult phenomena of

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[5] NEWTON. *Philosophiæ naturalis principia mathematica. Præfatio ad lectorem.*

[6] [Geometry should pride itself in doing so much with so few principles taken from elsewhere.]

chemistry" said Macquer. Guyton de Morveau made this thought his own and sought, by calculations and experiment, to develop Buffon's views regarding the nature of this affinity. Bergmann was of the same opinion.

The use of these mechanical considerations in a science whose experimental data were always vague and uncertain was not always successful. The *tables of affinities* conceived by Geoffroy and improved by Machy, by Gellert and by Bergmann were not in accord with the facts at all. The chemists of the empiricist school, the students of Rouelle, revelled in these contradictions which they heaped upon their rivals, "the chemical theoreticians, the systemisers, the reasoners, the makers of tables." They declared with Monnet that "the system of affinities is a beautiful chimera, more appropriate for the amusement of our scholastic chemists than the advancement of this science." "These authors of chemistry," Monnet also said, "should fear posterity. If they were ever to go down in history, all that will remain of them are the facts. Our descendants will scoff at everything else; for chemistry is only a collection of facts, for the most part without connection between them and independent of one another."

Despite these burning contradictions, the victory was to pass to the method that Macquer called "our modern physical chemistry"; its was assured by Lavoisier.

Lavoisier was endowed with extreme prudence and a very acute critical sense which made his works models of experimental method. Moreover, he did not venture to seek the mechanical explanation of the phenomena that he analysed with so much sureness and wisdom in the system of affinities. None the less, he considered that "the part of chemistry most likely to become an exact science one day is that which treats of chemical affinities and elective attractions." He declared that "the science of affinities is to ordinary chemistry what transcendental geometry is to elementary geometry." Moreover, he clearly belonged to the school of chemical physicists in view of his continual concern for clarity and logical rigour, and because, with the [215] instruments of the physicist—the balance, the thermometer, the calorimeter—until then strangers to the chemist's laboratory, he introduced into chemical experimentation a precision with which it had not been much concerned. He also belonged to this school because the last adherents of the phlogiston doctrine, the most indomitable critics of the new theory of combustion, were precisely the empiricists, the inveterate opponents of the doctrine of affinities. Finally, he belonged to it because his first adherents and collaborators were precisely those who developed and perfected the system of molecular attraction, Guyton de Morveau, Fourcroy, Berthollet, Monge, and above all, Laplace. "The custom of living together, of our communicating our ideas, our observations, our way of looking," wrote Lavoisier on the subject of these physicists, "has established amongst us a kind of like-mindedness in which it is often difficult even for ourselves to distinguish who originally contributed what."

V

The moment when the new chemistry, born of Lavoisier's experiments, imposed his ideas and language on everything, is also the time when the system of attractive and repulsive molecular forces found a new legislator in Laplace, who subjected it to rigorous mathematical methods. A fruitful alliance was established between Lavoisier's chemistry and Laplace's physics. The reconciliation of these two doctrines was the work of Berthollet. It was in Arcueil, in a laboratory that a garden joined, without fencing, to Laplace's house, that Berthollet pursued his investigations into affinities. Berthollet wrote his *Essai de statique chimique* under the influence of Laplace, and Laplace in his turn borrowed considerably from Berthollet's work when composing the *Exposition du système du monde.*

"The [216] forces which produce chemical phenomena," wrote Berthollet, "are all derived from the mutual attraction of molecules of the substances to which the name 'affinity' is given in order to distinguish it from astronomical attraction." But whereas the effects of astronomical attraction are so simple as to be rigorously subjected to the calculus, "the effects of chemical attraction or of affinity are, on the contrary, so altered by the particular and usually indeterminate conditions that it is not possible to deduce them from one general principle ... It is, therefore, observation alone that must serve to establish the chemical properties of substances."

We should not turn to the system of molecular actions for the precise and detailed law of each chemical reaction, but only for certain guiding ideas which group and order the facts already discovered and suggest new experiments.

There are among the guiding ideas brought to light by Berthollet some which are still guiding principles of physical chemistry today, and which can be placed in the first rank.

The science of chemical reactions should consider mechanics as a model and standard. The rules which direct whether a system of given constitution, under determined conditions, provides the opportunity for a certain reaction or for the inverse reaction, should be formulated in imitation the rules indicating whether, in a given mechanical system, such-and-such a body is moved from high to low or from low to high. "The more general the principles attained in chemical theory, the more analogous they are to those of mechanics; but it is only by means of observation that they will attain such a degree, as it has already been possible to show."

In particular, the state in which a system will not undergo further reaction will be comparable to the state of a mechanical system which is no longer enlivened by movement. *Chemical equilibrium* should be connected with *mechanical equilibrium*: just as *mechanical statics* makes precise the conditions of mechanical equilibrium, so *chemical statics* makes precise the conditions of chemical equilibrium.

The [217] mechanical analysis of the conditions of equilibrium of a group of bodies cannot omit any of the forces which act upon them, whatever their origin might be. The chemist should do likewise. Chemical affinity does not only act on the various parts of the substances under study. Physical affinity or *cohesion* combines with chemical affinity or works against it, and the repulsive force of heat adds its effects to these other two kinds of force. The chemist cannot understand why a reaction proceeds or stops if he fails to take all of these actions into account. "From this it follows that there usually exists a relation between physical and chemical properties, that it is often necessary to have recourse to the one and to the other for the explanation of a phenomenon in which they are combined, and that it is appropriate to establish an intimate relation between the various sciences constituting physics in order that they may shed light on one another."

The attractions exerted between material particles of the same nature constituting *cohesion* and the attractions exerted between different particles constituting *affinity* come into play at the same time in all chemical reactions. "These two forces produce, according to their relations, different results which should be distinguished, but which should not be attributed, as do some physicists, to two affinities one of which they regard as chemical and the other as derived from the laws of physics." Laws of the same nature govern chemical reactions, such as oxidation and the neutralisation of acids and bases, and purely physical changes such as fusion, vaporisation and dissolution. The science which unites these laws is the general theory of *changes of state*, whether these changes of state be attributed to changes of physical aggregation or to changes of chemical constitution.

By taking into account at the same time forces of cohesion and affinity, as well as the actions exerted by caloric, it is possible to explain the various peculiarities observed in the phenomena of double decomposition, to account for equilibria established when all reacting substances remain dissolved, [218] and the complete decompositions which proceed when one of the resulting compounds is either insoluble or volatile and is eliminated. The precise statement of the rules governing these displacements is one of the triumphs of the doctrine of affinities and one of the reasons Berthollet can claim the admiration of chemists.

VI

The quantity of potash that can neutralise a given quantity of sulphuric acid is determinate. In the same way, the quantity of saltpetre or sea salt that a given quantity of water can dissolve is determinate. For Berthollet as for all his predecessors, for Stahl as well as for Macquer, these two phenomena were of the same order and should be explained by the same sort of reasoning. According to the system of molecular attraction the combination of sulphuric acid with potash, like the dissolution of saltpetre or sea salt in water, stops when all the forces of affinity and cohesion brought into play in the system reach equilibrium.

If some circumstance were to change—if, for example, the temperature were to rise or fall—the various forces would be modified and, consequently, the state of equilibrium into which they had led the system would no longer be the same as it was before the change. The quantity of saltpetre that can be dissolved in a given quantity of water increases markedly when the temperature is raised. Similarly, the quantity of acid that can neutralise a given mass of alkali should vary when the circumstances of the neutralisation change.

Perhaps it might happen in certain cases that a given mass of alkali always seems to neutralise the same quantity of acid, just as the quantity of sea salt dissolved by a given mass of water depends only slightly on the temperature. But these are special cases, due to propitious circumstances, and one should be wary of taking them as [219] distinctive of a general law. The proportions in which the elements come together in a combination are not fixed; they usually depend on the conditions in which the combination is brought about.

To this proposition, ardently and skilfully upheld by Berthollet, Proust opposed the contrary proposition: The weights of elements which associate to form a chemical combination stand in a rigorously fixed proportion, remaining the same whatever the conditions in which the combination has been formed. The existence of rigorously defined proportions between the constituents of a compound substance is a characteristic feature of a pure chemical compound. Where this feature is absent, chemical combination does not really obtain, but is masked by the effects of mixture or dissolution.

After a debate still celebrated in the annals of science, Proust emerged victorious over Berthollet and the *law of definite proportions* drew an impassable frontier between a chemical reaction and a change of physical state, and became the dominating law of all chemistry.

Led by the law of definite proportions and the laws which Dalton and Gay-Lussac were soon to add, chemistry, having broken all ties with physics, made a prodigious development in a short time. The doctrine of affinity was soon forgotten. Such was the triumph that the bitter reproach heaped upon Berthollet for having striven against Proust's ideas is all that is recalled.

At the beginning of his *Leçons de philosophie chimique*, Dumas aroused the distrust of his readers in any return to this doctrine. "Do not come to think," he said to them, "that mechanics and physics has always been very useful. Chemistry has little to gain and much to lose from coming together with physicists at a time when they have nothing else to offer it than their mechanical systems of molecules."

For half a century there was to be neither chemical mechanics nor physical chemistry.

VII

While [260][7] chemists, rejecting any alliance with physicists, multiplied their analyses and syntheses, physicist took up with renewed ardour the study of the conditions in which chemical compounds are generated and destroyed and the effects

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[7] [Duhem's article is continued later in the Journal.]

which accompany this generation and corruption. Faraday and Antoine-César Becquerel determined the laws according to which chemical substances split when subjected to a galvanic current. They inaugurated *Electrochemistry*, which at one time, with Berzelius, had nearly absorbed the whole of chemistry. Hess, Dulong, Abria, Favre and Silbermann measured the amounts of heat released or absorbed during the course of chemical reactions and created *Thermochemistry*.

In 1854 thermochemical investigations led the Dane Julius Thomsen to propose a system of chemical mechanics which became very popular and long-lived.

For Julius Thomsen, the sign of the amount of heat produced by a chemical reaction sufficed to indicate in which sense the reaction occurred. A reaction which released heat could occur spontaneously, and a reaction which absorbed heat was incapable of getting under way itself, and could only be caused by a second reaction which released more heat than the first absorbed. When a chemical system has reached such a state that no [261] further reaction can produce the release of heat, it is no longer possible for it to leave that state and it remains there at equilibrium.

This theory of chemical reactions was not able to encompass changes of physical state. It is all too obvious that a large number of changes of physical state—fusion, vaporisation, dissolution—are produced spontaneously, although they absorb heat. The adherents of the thermochemical system had therefore to renounce one of Berthollet's principal ideas. They had to establish an insuperable line of demarcation between chemical mechanics and physical mechanics, to regard as a nonsense the conception of a physical chemistry.

The distinction between changes of state that observations reveal to us in physical modifications and chemical reactions seemed to them, at first, as a convenient way of avoiding the numerous contradictions of their theory with experiment. But the very flexibility of method, the ease with which it was adapted in the trickiest explanations, the ease with which a single transformation passed from the domain of chemistry to the domain of physics, convinced logical minds better than long arguments that it is fanciful to look for a boundary between changes of physical state and chemical reactions.

Certainly, the sophistry with which the defenders of the thermochemical system have accustomed minds has had an unfortunate influence on the development of science. Nevertheless, the work of Julius Thomsen contained the first germs of a fruitful idea. It was in unifying the old theory of molecular actions with the newly discovered law of equivalence between heat and work that Julius Thomsen had obtained the fundamental theorems of the thermochemical system. In so doing he pointed to the thermodynamic doctrine, the essential dogmas of which Clausius had just formulated, as the source from which chemical mechanics was one day to be derived.

Having [262] just mastered its principles, the young thermodynamics created from all the pieces a theory of change of physical state. Always wary of dubious hypotheses about the intimate nature of bodies, careful to admit into its reasoning only principles taken from the very centre of experience, the new method was not slow in showing that prudence is no obstacle to fruitfulness. Clausius' deductions on the phenomena of vaporisation, those of J. J. Thomson on fusion, and those of Kirchhoff on dissolution, astonished physicists, not, perhaps, so much by the paradoxical character of some of their consequences as by the rigorous precision of the formulas in which these consequences were expressed and by the amply satisfactory confirmation that these formulas received from experiment. Physicists found meticulous agreement between the predictions of the theory and the results of experiment, a *numerical* agreement that they had already encountered with Fresnel's optics and Ampère's electrodynamics, and that they had, since Newton, become accustomed to regard as the mark of sound physics. Thenceforth it was certain that a sure method was available for treating changes of physical state. In order that this method should become a chemical mechanics, it sufficed that Berthollet's main idea was revived and that it was irrefutably established that the laws governing physical changes and the laws governing chemical reactions are of the same nature. That was achieved by the work of Henri Sainte-Claire Deville.

Bringing to light, by extremely ingenious procedures, hitherto unsuspected states of chemical equilibrium, analysing the influence exerted on these equilibrium states by variations in temperature and pressure, showing that this influence resembles in all respects that manifested in better-known physical equilibria, carrying over to reactions whose chemical nature is beyond question the same laws of vaporisation and fusion, finding in these laws the reason why a host of phenomena were previously regarded as strange or aberrant—such was [263] the object of the research of Sainte-Claire Deville and his students, Debray, Troost, Hautefeuille, Caron, Isambert, Ditte and Gernez.

The memorable discoveries that they brought together in connection with the notion of *dissociation* provided a striking demonstration of the truth of these principles.

Pure chemistry has a domain of its own: determining the composition of bodies, grouping them according to their analogies, deriving the formulas of one from that of another in accordance with fixed rules, creating a systematic classification, delimiting gaps and thus predicting new compounds to fill them. These are the operations to which the methods of this *natural science* were adapted. Investigating the conditions in which it is possible to create and destroy substances whose formula it has determined would be to exceed the limits of validity of its procedures. The new problem belongs to the domain of *physical science*; it arose from that discipline, and it falls under the general theory of changes of states. It is to the doctrines already established in the study of vaporisation, of fusion and of dissociation, that the analysis and creation of *chemical mechanics founded on thermodynamics* belonged.

This new science, towards which the efforts of many geniuses have been straining since Newton as though it were a promised land—one Henri Sainte-Claire Deville liked to point out from afar to his disciples. One of them, J. Moutier, was the first to penetrate it. The fruits which he gathered there bear witness to the fecundity of the fields glimpsed by the chemist of the École normale. But the majority of French physicists and chemists refused to follow him, because the high priests of official science had passed [judgement], laying the new country into which Moutier had first opened the way under an interdict, threatening with their excommunication any who moved to colonise it. Once more, the despotism engendered by centralisation had deprived the French genius of the fruits of its discoveries.

VIII

The [264] plant which had grown on our soil was faded and desiccated, but its seeds, dispersed to the four winds, was not long in germinating and bearing an abundant harvest.

In Germany, Horstmann derived a general method for putting the problems of chemical mechanics into equations from some of Clausius' propositions which had remained unused until that time, and this method furnished him with precious information about the dissociation of systems containing mixtures of gases.

At the same time an American, J. Willard Gibbs, seized upon the same propositions of Clausius and developed their consequences with greater generality and breadth than his rival. In a magnificent blooming of the *principle of virtual work* which has, since Lagrange, served to summarise the whole of statics, the collection of these consequences formed a vast doctrine whose laws embraced the most varied kinds of equilibria. These laws governed mechanical equilibria just as well as chemical equilibria, and the equilibria encountered in the study of changes of state as well as electrical equilibria.

The prodigious extension given to statics by Gibbs' investigations came to dynamics from the work of Helmholtz. The formulas which had served until then for discussing the displacements of bodies in space were generalised and complemented to the point of expressing the laws of all changes in the inanimate world: changes of position in space, changes of shape and density, changes of physical state and chemical constitution, and electrical and magnetic changes. From thermodynamics was born a doctrine of extraordinary breadth whose principles claimed to govern all transformations where life had no part; this pure science is *Energetics*.

While Gibbs and Helmholtz were establishing the equations of energetics, others who were more chemists than mathematicians followed the consequences of this new science in the study of reactions. [265] It is fitting to place the two Dutch scientists J. H. van 't Hoff and H. W. Bakhuis Roozboom in the first rank amongst these chemists.

Having condensed in a striking theorem the laws according to which temperature influences chemical equilibria, van 't Hoff began to study very dilute substances and found unforeseen and fruitful analogies between the properties of such substances and the properties of gases.

Bakhuis Roozboom drew the wonderful *Phase Rules* from the midst of algebraic formulas in which Gibbs had condensed them—rules which guide the chemist with certainty in the analysis of the most complicated cases of equilibrium.

The worthy rivals of van 't Hoff, Svante Arrhenius of Uppsala and W. Ostwald of Leipzig, linked the laws of electrochemistry to the ideas of the Dutch scientist about the state of dissolved substances.

IX

Following these pioneers of genius, legions of workers threw themselves into the exploitation of the half-opened mine, and soon each of the veins of physical chemistry furnished innumerable works.

The journals of general chemistry and general physics at first gave refuge to the writings of the physico-chemists. They were not long in becoming cluttered, and the new science called for a new journal devoted to it. In 1887, J. H. van 't Hoff and W. Ostwald founded the *Zeitschrift für physikalische Chemie*, with the aim of publishing the new research in thermochemistry and electrochemistry. This *Zeitschrift* issued one volume each year; from 1889, it issued two; from 1894, three. The opening that it provided for physico-chemical works had become quite narrow, however. The English-speaking countries felt the need for a similar forum, and since 1896, Cornell University, Ithica, [266] has published the *Journal of Physical Chemistry* under the direction of Wilder D. Bancroft and J. F. Trevor.

The discoveries of physical chemistry could not remain confined for very long to the writings of their inventors. They came to penetrate the teaching at universities, where they were not long in taking up a considerable place.

The first department of physical chemistry was instituted at Göttingen by the Prussian government which donated 206,250 francs to it. It is directed by Professor Nernst who teaches with the assistance of two *docenten* and two *assistants*. Moreover, Professor Woldemar Voigt, who teaches mathematical physics at the university of Göttingen, and Professor Ed. Riecke, who teaches experimental physics, neglect neither in their research nor their teaching, the various applications of thermodynamics in chemical mechanics.

Physical chemistry holds a prominent place in the departments of chemistry at Würtzbourg, to which Bavaria has donated 802,500 francs, the department of chemistry and electrochemistry at Darmstadt, which has cost 524,000 francs for the principality of Hesse-Darmstadt, and the department of electrochemistry that the grand-duchy of Bade has joined to the *Polyteknikum* of Carlsruhe, at a price of 750,000 francs. But the finest installation for physical chemistry in Germany is certainly the department that has been inaugurated at the University of Leipzig a year ago. This magnificent laboratory,[8] devoted exclusively to this new branch of science, has cost the government of Saxony 575,000 francs. The directorship has been entrusted to Professor W. Ostwald, who has given the new science such a powerful thrust forward with his teaching, his universally known treatises on *General Chemistry* and *Electrochemistry* and broad and liberal editing of the *Zeitschrift für physikalische Chemie.* He has at his disposition the annual sum of 15,000 francs, "but," he tells me, "it is expected [267] that this sum will be augmented because it hardly suffices to cover all the costs." The laboratory is frequented by 90 students, of which 35 read physical chemistry as their major subject, while the others are beginners who study analytic chemistry.

Berlin has not, as yet, any establishment specifically devoted to physical chemistry, but "some is done everywhere." At the university,[9] Professor Landolt devotes four hours a week to physical chemistry during the winter term. During the same term Professor Hans Jahn devotes three hours a week to electrochemistry, and during the summer term he devotes the same amount of time to physical chemistry. *Privatdocenten* Pringsheim, Arous, Fock and Meyerhoffer deal with physical chemistry from time to time. At the Polytechnic, Professor van Knowe teaches electrochemistry and *privatdocent* Traube teaches physical chemistry. At Mr. Landot's laboratory one section, placed under the direction of Mr. Hans Jahn, is devoted to the new science. A similar section will come into being at the magnificent department to be built for Professor Fischer at a cost of 1,500,000 francs.

But numerous teaching establishments have not sufficed for Berlin. When Helmholtz, like a setting sun whose last rays look the finest, passed without any lapse in the full splendour of his genius to rest with the dead, Berlin wanted to have another prince of chemical mechanics and stole van 't Hoff from Amsterdam.

The Berlin Academy of Science bestows on Professor van 't Hoff a salary of 12,500 francs, and the government supplements that with a chair at the university, with a remuneration of 6,250 francs. It combined the cost of 18,750 francs from the first installation with an annual sum of 3,000 for the maintenance of a laboratory where the professor, together with his assistants Meyerhoffer and Bader, and several students, pursue their research. Germany will certainly not come to regret the welcome that [268] it has extended to its guest. Not content to give each term a course of extreme originality at the university, Mr. van 't Hoff has undertaken research of the greatest interest in the conditions which can have given rise to the various compounds found in the rock salt mines of Stassfurt, which does credit both to the Berlin Academy and its member.

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[8] I owe this information to Professor Ostwald, for which I thank him. Professor Ostwald has published a detailed description of this laboratory under the following title: *Das physikalisch-chemische Institut der Universität Leipzig*, Leipzig, 1898.

[9] I have obtained the following information from Professor J. H. van 't Hoff, to whom I would like to express my gratitude.

On leaving Holland J. H. van 't Hoff left behind him an active teaching programme in physical chemistry,[10] which he had begun at Amsterdam while H. W. Bakhuis Roozboom inaugurated one at Leyden.

Since 1870, the Dutch universities have been obliged to offer autonomous teaching in mineral chemistry and in organic chemistry. Everywhere these two teaching programmes have two chairs, except for the small university of Groningen where a single professor remains in charge of all chemistry.

At the university of Amsterdam, Professor Bakhuis Roozboom, who has replaced J. H. van 't Hoff, deals with mineral chemistry whilst Professor Lobry de Bruyn deals with organic chemistry. The teaching of the theory and practice of physical chemistry is attached to the former chair, and the professor gives expositions of the laws of chemical equilibria. His assistant, E. Cohen, devotes one hour a week to electrochemistry, to photochemistry and rates of reaction; the cycle of his course covers two years. Finally, *privatdocent* van Laar deals with physical chemistry from a mathematical point of view with one lecture per week.

Mr. E. Cohen directs the practical work of the chemistry students, who devote approximately two and a half years to the general study of chemistry and physical chemistry before embarking on the preparation of their theses. In addition, the students receive a solid preparation in physics; for two years they follow the course in mathematical physics given [269] by the illustrious Professor van der Waals and receive practical teaching on heat, light and electricity in his laboratory.

The organisation at the university of Leyden differs a little from that at the university of Amsterdam. Mr. van Bemmelen, director of the department of mineral chemistry only gives elementary teaching in chemical equilibria. But theoretical chemistry is taught by Mr. Schreinemakers, lecturer, one of the most brilliant pupils of Mr. Bakhuis Roozboom whom he succeeded. *Privatdocent* Stortenbeker complements this with a course on electrochemistry. Mr. Schreinemakers directs research in physical chemistry which should become doctoral theses. In addition, the Professor of physics, Mr. Kamerlingh Onnes, gives a course in thermodynamics for chemistry students who, as in Amsterdam, practice in the manipulations relevant to the various branches of physics.

Physical chemistry is not looked upon favourably at the Academy of Utrecht; but this is counterbalanced by its not being neglected at the small university of Groningen. Although the unique Professor of chemistry, Mr. Hollmann, is particularly engaged in organic research, he gives refuge in his teaching to some elementary chapters of physical chemistry. The lecturer, Mr. Wind, complements this with a course in thermodynamics and electrochemistry.

Finally, at the Polytechnic School at Delft the professor of inorganic chemistry, Mr. Aronsten, gives a course in theoretical chemistry to "technologists" and mineral

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[10] H. W. Bakhuis Roozboom has sent me the following information on the teaching of physical chemistry in Holland, which I would like to take this opportunity of acknowledging.

engineers which takes two years. Furthermore, the addition of a department of electrochemistry is under way at this school.

Although physical chemistry has not been developed as strongly in England as in certain countries in continental Europe, an industrialist, Mr. Mond, has just endowed the Royal Society of London with a laboratory for research in physical chemistry. He has donated 950,000 francs for the purchase and installation of furniture when the laboratory is ready. He has added to this a further sum of 1,500,000 francs whose back interest serves to finance research. If we add that this laboratory has been placed under the direction of Lord Rayleigh and M. Dewar, we [270] might well foresee what science can expect from this truly princely donation of Mr. Mond's.

The young American universities, much more so than the European universities, regard physical chemistry as an extremely important science. I will here speak only of one of them, Cornell university, established at Ithica in the state of New York. Two professors are in charge of the *Department of Physical Chemistry*, Mr. Wilder D. Bancroft and Mr. J.-E. Trevor. I open the programme of courses for the academic year 1897-1898 and see that, each week, Professor Bancroft devotes one hour to qualitative physical chemistry and two hours to electrochemistry, while Professor Trevor devotes three hours to lectures on mathematical chemistry and to the reading of classical treatises concerned with this science, three hours to the historical study of thermodynamics and one hour to applications of dynamics to physical chemistry. In addition, Messrs. Trevor and Bancroft meet with the most advanced students once a week for joint critical study of recent works in physical chemistry. Mr. Bancroft directs the laboratory research, and the two professors edit the *Journal of physical Chemistry*, one issue of which leaves the university presses each month.

X

Why this extraordinary activity? Why, in both the old and the new world, these costly laboratories? Why all this time, all this effort, devoted to the study and teaching of physical chemistry? It would seem that the time has come to realise Humboldt's prophecy: "The countries which fail to have recourse to the luminaries of science will see their prosperity be inevitably jeopardised as the neighbouring nations are developed and fortified under the influence of the arts and the sciences." Humboldt's native country has understood this truth, and because it was the most [271] academic nation of the world, it has become the most formidable industrial power.

While France failed to recognise the Strasbourg chemist Gerhardt's ingenious ideas, and those of Laurent, the first dean of our Faculty of Sciences at Bordeaux, while it wore down the activities of their disciples in paltry discussions and cantankerous persecution, while it prevented the entry of their doctrines into the schools, while the Sorbonne had to be coaxed a long time before opening the doors of its lecture rooms to Wurtz, Germany, in the wake of Hofmann,[11] became enthusiastic over the new chemistry and flung the doors of its laboratories, more richer and numerous by the day, wide open to him. Today, in its innumerable factories, engineers—nearly all university doctors—make organic compounds, colouring materials and pharmaceutical substances for the whole world. In the year that has just gone, the world paid *half a billion francs* to Germany for the chemical products it received from them. The export of French chemical products was far from attaining half this sum.

The East and Italy cultivated madder from time immemorial. During the last century the Persian Althen introduced the cultivation of this plant into the [papal state of the] comtat Venaissin, where it was soon developed on a large scale. Around 1870 the *Département* of Vaucluse and the neighbouring *Départments* produced 25 million kilograms of madder root, representing about eighteen millions francs. Since 1872, this production has waned from year to year, and in 1879 it was reduced to 500,000 kilograms. In the volume entitled *French agricultural statistics, published by the Ministry of Agriculture—General results from the decennial inquiry of 1882*, it can be read that "the cultivation of madder has disappeared ...."

What has happened to it? What plague has ravaged the countryside around Avignon?

The dyestuff from the root of madder is a well-defined chemical substance, alizarin. Laurent, the founder of the Faculty of Sciences of Bordeaux, was the first to investigate how to derive this substance from other organic products. [272] His unavailing efforts were continued by others, and in 1868 two German chemists, Groche and Libermann, demonstrated to the Chemical Society of Berlin that alizarin is easily derived from a product, until that time without value, contained in abundance in the residues from the scrubbing of lighting gas, *anthracine*.

Following the consequences of this small laboratory reaction, in 1869, barely a year after its discovery, artificial alizarin was already being produced in six establishments. In 1873, 90,000 kilograms of alizarin paste were produced. In 1876, Germany alone produced nearly four million kilograms. In 1877, the industry delivered 7,500,000 kilograms of alizarin, representing twenty five million francs. Germany had furnished 85% of this production. Of the eighteen factories contributing to this production, twelve were in Germany, two in Switzerland, two in England, one in Austria and one in France. In 1895, Germany exported 8,927,600 kilograms of artificial alizarin, representing the enormous sum of 14,507,500 Fr. In the same year, France, which only exported 99,300 kilograms of madder root, representing 60,984 francs, bought from abroad madder for 240,840 francs and artificial alizarin for 790,790 francs.

Alizarin and the dyestuffs derived from it are not alone in giving rise to this sad comparison. The other artificial colouring materials give rise to similar reflections.

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[11] [Duhem writes "Hoffmann," but is presumably referring to August Wilhelm von Hofmann (1818–1892).]

In 1895, Germany delivered to the world from its thirty factories 25,160,500 kilograms of artificial colouring materials other than alizarin, representing 93,452,500 francs. This amounted to four fifths of the total world production. To this production of artificial colouring materials on the surface of the globe, *France's contribution is barely a quarter: yet of the twelve factories which furnish this contribution, eight are branches of German or Swiss factories.*

Let us not be mistaken about the causes of this incredible disparity. "Attempts have been made to conceal this deficiency by attributing shortcomings to our law of patents, to the exorbitant toll on alcohol, on free exchange, and I know not what. [273] No, one of the causes of this downfall, the principal one, is the misunderstanding, the progressive discord, between the scientific element and industry. It is the indifference that our men of science have witnessed in this respect. It is, finally, the obstinacy with which our scientific officials have opposed the adoption of novel conceptions introduced into the science of chemistry by Gerhardt and his successors, conceptions which have had the effect of renovating and making new and invigorating strides abroad ... Mineral chemistry, on the other hand, being little influenced by questions of doctrine, has always been in favour in France and progressed under the direction of Sainte-Claire Deville, Pelouze, Frémy and Debray. Likewise, that part of the large chemical industry which has not derived much from theories has not been jeopardised in France ... But the industry producing organic products, that which is directly inspired by the theories to which we have just referred, is blighted in our country, while it has reached full bloom in Germany."[12] It is in these terms that one of the men to have done the most, in France, to renew the fruitful alliance between science and the chemical industry, Mr. Haller, professor at the University of Nancy, appreciates the deplorable consequences of the obstinate and routine passion with which the official scientists fought against the reform of organic chemistry.

XI

Let us beware: if the same routine, if the same hatred of everything that contains a new idea, the same horror of everything that requires a new intellectual effort, were to arrest any longer the launch of physical chemistry and electrochemistry in France, [274] then the truth, outraged by those whose mission is to serve it, would once more take revenge on us, inflicting a new industrial disaster. This time, the industry for the large scale production of mineral products would undoubtedly be struck.

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[12] HALLER, "Science et Industrie" *Bulletin de la Société industrielle de l'Est*, année 1897, 2nd. fascicule. The reader will find a lot of statistics and valuable information in this essay and in the following writings by the same author; "L'Industrie chimique; l'Enseignement chimique et les Universités" *Revue générale des Sciences*, t. VIII, p. 226, 1897. — *L'Enseignement pratique de la chimie dans nos Universités*, Paris, Masson et C^{o}, 1898.

In fact, the new ideas which dominate physical chemistry and electrochemistry profoundly transform the procedures in certain branches of industry. Let us fix our attention for a moment on electrochemistry.

Aluminium was virtually unknown before the work of Deville, which gave him a very lofty prize in making the preparation of this metal very easy. With the electric and electrolytic processes it has become a commonly used material. From 1891 to 1896, the production of this metal by the only American factory, *the Pittsburg reduction company*, went from 76,237 kilograms to 589,670 kilograms, while the price per kilogram fell from 8.27 Fr. to 4.11 Fr. Moreover, in 1895 the factory at Neuhausen produced 650 tonnes of it and the French factories at Froges and La Praz produced around 100 tonnes.

Acting as an intense source of heat in the electric furnace, the galvanic current can serve for the production of a whole range of products, still unknown yesterday, but today of industrial importance. In 1893, while hoping to produce diamond, Acheson obtained a carbide of silicon, *carborundum*, whose hardness makes it a substitute for emery. At that time the annual production of emery corundum was around 1,700 tonnes, valued at 425 francs per tonne. In 1895, the industry produced no more than 385 tonnes of emery, and to make up for it, 600 tonnes of carborundum was manufactured at 2,500 francs a tonne

It is still by the very high temperature that it produces that the electric current plays its part in the production, more important by the day, of the source of acetylene gas, calcium carbide. But more so than the electric furnace, reactions which are really electrolytic, and in particular, the electrolysis of sodium chloride and potassium chloride, are undoubtedly those which will give rise to [275] a veritable revolution in industry's major chemical products.[13]

Electrolysis already produces, at the factories in Vallorbes and Saint-Michel de Maurienne in France and at Månsbo in Sweden, practically all the chlorates used. Electrolytic potash is beginning to hold an important place in the market. But among the discoveries in chemistry to find application in these last years, perhaps nothing will have such grave consequences as the automation of the electrolytic [production of] soda. Not only can the new method of production considerably change the price of recovering products for the large-scale chemical industry; it yields twice as much chlorine for the same weight of soda as the Leblanc process. An outlet was needed for this excess of chlorine, which the needs of the commerce in hypochlorites and chlorates do not suffice to absorb. But soon the idea presented itself of using it in the oxidation of sulphurous acid for the preparation of sulphuric acid.

Who cannot see the economic consequences of such a chemical revolution? The two major chemical industries, the soda industry and the sulphuric acid industry, no

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[13] See A. BUISINE, "Revue des perfectionnements récents apportés à la fabrication des grands produits chimiques" *Bulletin de la Société d'encouragement pour l'industrie nationale*, janvier 1896.

longer in need of heat but of electrical energy, will leave the regions where coal lies beneath the ground—the regions where the factories of Lille and Sainte-Gobain have flourished—for regions where waterfalls promise cheap electrical energy, the Alps and the Pyrenees.

Moreover, the emigration has begun. Read the statistics of the electrochemical factories established some years ago on the French side of the Alps:

At la Bathie, L. Robert's factory, which has 2,500 horse power at its disposal, uses 1,000 in the manufacture of calcium carbide. The Comapagnie internationale du carborundum uses a further 1,000 horse power.

Establishments are still given over to the manufacture of calcium carbide [276] at Bellegarde, where the Compagnie des carbures uses 600 horse power, at Saint-Béron, where the Société du gaz acétylène has at its disposal 4,000 horse power of which it uses 2,000, and at Notre-Dame de Briançon, where the Société des carbures has at its disposal 5,000 horse power and uses 3,000, at Epierre, where Messrs. Rochette brothers use 1,200 horse power, at Séchilienne, where the Société française des carbures has 3,500 horse power at its disposal and puts 1,200 to work.

The production of aluminium is added to that of calcium carbide at the factories of La Praz, where 7,000 horse power are used by the Société électométallurgique, which has 13,000 horse power at its disposal. At Saint-Michel, the Société industrielle de l'aluminium uses 2,000 horse power in the preparation of this metal.

At Lancey, Messrs. Corbin and C^{o} devote 200 horse power to the bleaching of paper pulp. At Chedde, 12,000 horse power are used for the manufacture of alkaline chlorates and perchlorates. Finally, at Gavel the Société des soudières, which has at its disposal 5,000 horse power, uses 2,500 in the manufacture of soda, chlorine and hypochlorites.

Is this sudden development of the electrochemical industry in Savoy and Dauphiné not enough to assure us of the state of the teaching of electrochemistry in France? Alas, no! It is not in France, but in the foreign universities and polytechnics schools, at Carlsruhe and Zurich, that the majority of the engineers at these factories have acquired the knowledge with which they exploit the waterfalls of our water courses and the seams in our soil. And in the wake of foreign education, foreign personnel enter our factories, foreign workers and foreign machinery.[14]

Why does the university at Grenoble not emulate [277] the polytechnic at Zurich? Is it for want of the men? The dean of the Faculty of Sciences, having made his debut by creating, in the footsteps of Favre, the thermic study of the pile, has taken an unrivalled place in physical chemistry by establishing what the whole world calls *Raoult's Laws*. His maître de conférences [university teacher], an old student of Bordeaux, Mr. Chavestelon, had already conducted important research on

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[14] I have seen, in the middle of Bretagne, a mining project of the first importance, where the shareholders were French but the director, also French, had studied in Belgium. The engineer, the foreman and the employees were all Belgian, and needless to say, all the machinery came from Belgian factories.

acetylenic carbides. Mr. Paul Janet had, with a very sure and shrewd sense, inaugurated there, without means of support, a course in industrial electricity that Mr. Pionchon pursues with so much talent and devotion—and those from Bordeaux known how he taught. What did the French State, the State which held at that time the responsibility for our scientific development and the protection of our industrial prosperity, do to encourage the teaching of electrophysics at Grenoble and to create the teaching of electrochemistry? It gave a yearly subvention of 1,300 francs.

XII

The state has not as yet created a single course in physical chemistry. During the budget discussion of 1895[15] Mr. Denys Cochin, having given a remarkably clear exposition of the importance of teaching in physical chemistry, added "It is time, I believe, to give such teaching in Paris, under a special chair, by a special professor, and it is for this that I address the Chamber; the expense is not great, only 6,000 francs."—Despite the opposition, though quite spiritless, of the Minister of Public Instruction and the chairman of the Budget Commission, the money Mr. Denys Cochin asked for was voted through. Created under the name *Cours complémentaire de chimie mathématique*, and confided to a geometer already destined to die, Mr. Gustave Robin, the teaching advocated by Mr. Denys Cochin has been taken up last year under the title *physical chemistry*. Endowed with a small laboratory, and confided to a young [278] physicist, Mr. Jean Perrin, who understands the importance of his mission and who has the firm will to accomplish it, this course will not be long in bearing fruit.

It cannot suffice for all the needs of France, however. Mr. Haller has thought that at Nancy the teaching of physical chemistry and electrochemistry should be broad and frankly directed towards industrial applications. While one of his auxiliaries, Mr. Müller, pursues his lectures and researches in this direction, Mr. Haller has led a pressing appeal on his private initiative. Already, the generosity of industry in the East has made possible the foundation of a school of brewing. It is now proposed to adjoin a department of electrochemistry to the department of chemistry at Nancy. 400,000 francs is required; Messrs. Solvay, "the kings of soda," opened the subscription with a princely donation of 100,000 francs, following another donation of 100,000 for the electrophysical laboratory. Today the subscription to the department of electrochemistry has reached 275,000 francs. Neither the state, nor the town, nor the Département has participated in the construction of these buildings. The town donated the ground, which is valued at 50,000 francs. "The new establishment has a roof," Mr. Haller writes to me; "we hope to be able to move in and occupy it at the beginning of next term."

Is the supplementary course in physical chemistry in Paris and the department of electrochemistry at Nancy all that France can offer in the domain of physical

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[15] Chambre de Députés, session of 13 February, 1895.

chemistry? Surely not. Will our great universities continue to be deprived of teaching of such importance? Cannot Lille provide young engineers experienced in the methods of the new science for the chemical factories surrounding the town? Will not Grenoble allow its teaching in electrophysics and electrochemistry to develop in proportion to the blossoming industry in the region of the Alps? Will Lyon and Marseilles be deprived of the chemical establishments on which the knowledge they have a right to demand of a higher education depends? Bordeaux, at the foot of the Pyrenees, whose torrents will, some day, be swallowed up, like the torrents of the Alps, in the turbines of electrochemical establishments, Bordeaux, will it not prepare itself henceforth for the role it will have to play when industry invades Béarn and the Basque country?

We should not, perhaps, think of building everywhere departments comparable to the department of chemistry at Nancy. Though indispensable for Nancy, such an installation is not, perhaps, necessary everywhere. More modest measures would suffice in most universities to maintain the teaching of physical chemistry at the level it should attain. When giving each of them its autonomous magisterial chair, resolutely separate organic and mineral chemistry. While the former is naturally associated with the teaching of agricultural and physiological chemistry, make the latter complete with the teaching of physical chemistry. Complement it by borrowing appropriate courses in heat and electricity from physics. As endorsement of this course, combine a certificate of *physical chemistry* which, together with certificates in *general chemistry* and *applied chemistry*, constitute a truly useful bachelor's degree for young people who go into the chemical industry. This is what should be done in the large universities without delay.

This combination, more modest than that adopted in Göttingen, Leipzig or Nancy, has proved itself. It is, in fact, what has been achieved at the universities of Amsterdam and Leyden, and it is well known what van 't Hoff and Bakhuis Roozboom have achieved with modest resources. Moreover, this combination has many advantages, which Mr. Roozboom has indicated to me in communicating the following reflections alluding to Holland, but which apply just as well to several of our universities: "With the limited number of students that we have here, is it preferable to entrust physical chemistry to a particular professor, aided by a special assistant? I do not have a firm conviction about this. The arrangement I have described for you has, in my eyes, the great advantage that young people acquire a varied knowledge. This is an important advantage in a small country like [280] ours where it is not possible to decide, before completing one's studies, whether to devote oneself to this or that branch. In any case, I would always insist on the necessity of giving considerable time to works of pure inorganic chemistry."

The programme that we have just outlined is *a minimum which it is high time was enacted.* Who will make the sacrifices—quite moderate—necessary to realise this? First, the State. In France, the state has taken practically the whole of higher education under its wing. The rights which it has reserved for itself entail duties. One of them, among the most urgent, is to ensure the expansion of a doctrine as important for science as it is for industry. Those who are entrusted with the interests of French education have allowed the egalitarians[16] to check the development of organic chemistry in France and committed a mistake which costs us a hundred million per year. Let them not commit a similar mistake today! To obtain from Parliament the financing, the little increase, which would assure the survival of our chemical education is a task worthy of whoever presides over the destinies of our universities.

But this sum cannot come without a certain delay, and the need is pressing. One might therefore follow the course taken at Nancy, and the *Départements*, towns, universities and private individuals could make a generous attack, in the conviction that chemical education above all else forges the arms for the economic war. That I think I have established in this article, and I add by way of conclusion the words delivered by Mr. Bardoux from the Senate rostrum:[17]

"For my part, I consider that it is much more important to have a superior education at the height of scientific progress than several kilometres of railway of mostly local interest, and that the more a country develops its higher education, the more it can act and have influence in the whole world."

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[16] *équivalentistes.*

[17] Session of Tuesday, 7 July, 1896.

ESSAY 6

THE WORK OF J. H. VAN 'T HOFF, IN CONNECTION WITH A RECENT BOOK* [1]

I

The prodigious development of Physical Chemistry will undoubtedly remain one of its characteristics, and not the least beautiful, as the nineteenth century draws to a close. The Dutch Schools have played a most important role in this development. Not content, in Leyden, to follow with patience and admirable sagacity his investigations into the hydration of colloidal substances, Professor van Bemmelen looked favourably upon the activity of his *lector*, Bakhuis Roozboom. He exhumed from the midst of Gibbs' algebraic formulas *the phase law*[2] and the properties of transition points, transforming these theorems into powerful instruments of research and, both alone and with his pupils, Schreinemakers and Stortenbeker, disentangled the most complicated chemical equilibria. At Amsterdam, while J. H. van der Waals was penetrating deeply into the problem of the liquefaction of gas and [6] of the continuity between the liquid and gaseous states, J. H. van 't Hoff was enlarging all the branches of Physical Chemistry by his discoveries.

The principles on which Physical Chemistry rests threaten the old systems of cosmology with a revolution, and the consequences of this science have brought about the prospect of an upheaval in the procedures of the chemical industry.[3] A nation which aspires to supremacy both in the intellectual and in the economic

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* Originally published as "L'Oeuvre de M. J. H. van 't Hoff, a propos d'un livre récent," *Revue des questions scientifiques*, 47 (1900), 5-27.

[1] *Leçons de Chimie-Physique*, given at the university of Berlin by J. H. van 't Hoff, member of the Berlin Academy of Sciences, ordinary professor at the university and director of the Institute of physics at Charlottenbourg. – The work is translated from the German by Mr. Corvisy, *Professeur agrégé* at the School of Saint-Omer. First part: *La Dynamique chimique*. Second part: *La Statique chimique*. 2 vol. in 8°. Paris, A. Hermann, 1898 and 1899.

[2] See the July 1898 issue of this *Revue* [translated in this volume as "The Phase Law"].

[3] We refer the reader who wants to inform himself on this point to our brochure: *Une science nouvelle, la Chimie-Physique* (Paris, A. Hermann, 1899) [translated in this volume as "A New Science: Physical Chemistry"].

spheres must, of necessity, lay claim to be at the forefront of Physical Chemistry, and to achieve this place, must assure itself of the assistance of a guide capable of leading it there. Germany therefore took J. H. van 't Hoff from Amsterdam and brought him to Berlin.

The Berlin Academy of Sciences received van 't Hoff as one of its members and granted him a pension. The government entrusted him with the teaching at the university with the title of ordinary professor, assured him a laboratory and made him director of the Charlottenbourg Institute of Physics. During this time, Bakhuis Roozboom succeeded van 't Hoff in the chair at Amsterdam, and at Leyden, Schreinemakers followed after his master.

The Berlin Academy of Sciences will certainly not regret the eagerness with which they appointed the knowledgeable Dutch scientist, nor the generosity with which they treated him. On the one hand, he has communicated original work of the greatest interest which he has successfully conducted in his new laboratories; and on the other, he has given fruitful teaching in the new ideas.

In his new Charlottenbourg laboratories, van 't Hoff has hitherto devoted himself to that branch of Physical Chemistry where his rival, Bakhuis Roozboom, has become famous. The problem of chemical statics which he has tackled, and whose solution has led him [7] to use Gibbs' rules, is certainly one of the most important and one of the most complicated that could be dealt with.

Sea water is, it should not be forgotten, an extremely complex substance in which a range of salts are dissolved. When these salts are deposited on the bottom of a salt marsh as a result of evaporation, they give rise to crystals of the most varied shapes and composition—simple anhydrous salts, simply hydrated salts, and double anhydrous and hydrated salts. All these substances are, in particular, to be found in the great deposit of rock salt at Stassfurt where mineralogists have gathered up, collected and described them. At what temperature and what composition of sea water is each of these salts deposited or redissolved? That is the question, as important for Physical Chemistry as for Geology, whose solution van 't Hoff and his pupils have been directed towards in the light of the phase rule.[4]

Given orally only to the students of the University of Berlin, J. H. van 't Hoff's course will nevertheless profit all those in Europe and America who are interested in Physical Chemistry, for it has, happily, occurred to the illustrious Professor to publish his lectures and Corvisy, Professor at the School of Saint-Omer, has just translated the two volumes which have already appeared into French.

The first volume, entitled, *Dynamique chimique* [chemical dynamics] covers the lectures delivered during the two semesters of the year 1896-1897. The second volume, *Statique chimique* [chemical statics] reproduces the course given during the two semesters of the year 1897-1898.

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[4] The investigations of Mr. van 't Hoff and his pupils are published in *Sitzungsberichte der Berliner Akademie* under the title "Untersuchungen über die Bildungsverhältnisse der oceanischen Salzablagerungen insbesondere des Stassfurter Salzlagers."

Two words of explication on these titles and this division.

What J. H. van 't Hoff calls *Chemical dynamics* [8] is that part of science to which we give the more extended name of *Chemical mechanics*. He studies there both the conditions in which a chemical system remains in equilibrium and the laws to which the speed of reactions is subjected. Static chemistry, on the other hand, is for J. H. van 't Hoff the study of the properties of the chemical individual considered by itself, independently of the conditions in which it is formed or destroyed. The relations between molecular weights and the various physical properties, the constitutional formulas proposed by the atomic theory and stereochemistry, and the laws of crystalline shapes are equally subjects which fall under Chemical statics.

A faithful reflection of the improvised teaching of a man of genius, the *Leçons de Chimie-Physique* brings to life a course with its digressions, its flashbacks, its glimpses of more peripheral ideas. The regularity, the order, the majestic proportions of a treatise should not be expected. Those who are especially struck by logical entailment and the beautiful ordering of a theory will perhaps complain; but those who like to intimately penetrate the intellectual life of a thinker will definitely delight in it. It is not to this book that beginners wishing to acquire elementary knowledge, clearly and precisely arranged, of the principles of Physical chemistry should address themselves. But the inquisitive who like tantalising insights,[5] problems to solve, questions to meditate on, will read it passionately. Were it not for my profound horror of English words which might become naturalised French, I would characterise these lectures by declaring them *suggestive* in the highest degree.

We thought that more than one reader of the *Revue des Questions Scientifiques* would like to see here, if not a summary of all the questions treated in these lectures, then at least a brief exposition of those which carry the personal mark [9] and imprint of the genius of J. H. van 't Hoff. We have chosen to speak for a moment on the three theories to which the Dutch chemist has devoted the greater part of his activity: *stereochemistry*, the *law of displacement of equilibrium by variation in temperature,* and finally, the properties of extremely dilute solutions.

II

We have related here[6] the origins of the atomic notation employed today by all chemists. We have seen the birth of the notion of *substances derived by substitution* of the *same type*. We have seen this notion give rise to that of valency, resulting in the construction of schema chemists call *constitutional formulas* or *developed formulas* [structural formulas].

If the atomic notation has triumphed on all sides over the hostility and prejudice which have for a long time run counter to it, it owes this not only to the numerous

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[5] *aperçus entr'ouverts*.

[6] "Notation Atomique et hypothèses atomistiques" *Revue des Questions scientifiques*, 2nd. series, vol. I, April 1892, pp. 391-454.

syntheses that chemists have accomplished by taking it as their guide, but also, and in the main, perhaps, to the sureness with which it allows the enumeration of all the possible *isomers* of a given compound, and the methods it suggests for producing these isomers.

To a given composition expressed in percentages, to a given molecular weight, and therefore to a given crude formula [compositional formula], there might correspond several different developed formulas. A given number of atoms of each simple substance figures in each of these formulas, but these atoms display different links with one another. These various formulas represent *isomeric* substances with the same composition, and for which the same crude formula corresponds [10] to different physical properties and often enough with different chemical functions too.

Enumerating and forming all the developed formulas which correspond to a given crude formula—in other words, enumerating all the possible isomers of a given substance and displaying their constitutional formulas—then becomes a simple mathematical problem belonging to that part of mathematics which Leibniz has called *analysis sitûs*.[7] These constitutional formulas, once drawn, show from which substances and by which substitutions it is possible to arrive at each of the envisaged isomers, and in this way they guide the chemist towards the realisation of these substances.

Need I recall the striking success of this method? The classification by Kékulé of the fatty series in normal and non-normal alcohols, and in primary, secondary and tertiary alcohols? Or again the classification, more marvellous still, of the derivatives of benzene, prophetically stated and a thousand times verified from this law: all derived bisubstitutes of benzene display three isomeric forms?

Despite its fecundity, more astonishing by the day, the atomic notation ran up against a special category of isomers that it was unable to represent.

Let us take a tartrate, the tartrate of sodium, for example. The substance displays two varieties which, although identical in many of their properties—density, solubility in water—are nicely distinguished from one another by a certain optical characteristic. If a vessel containing a solution of the first variety is placed in the trajectory of a ray of polarised light, the plane of polarisation of the ray turns about this ray *from left to right* at a certain angle. If the same ray is intercepted by the same vessel, containing an equally concentrated solution of the second variety, the plane of polarisation is again rotated about the ray and by the same angle, but *from* [11] *right to left*. The solutions of the two varieties of sodium tartrate has equal *powers of rotation*, but in inverse senses. The first variety is called the *right tartrate* and the second variety the *left tartrate*.

The right sodium tartrate and the left sodium tartrate can both be obtained in crystalline form by evaporation of their respective solutions. The crystals of the two varieties offer, at first glance, the greatest resemblance. If they are examined with care, however, as did Pasteur—and this is one the his most beautiful discoveries—it

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[7] [An old name for topology.]

is soon recognised that a crystal of right tartrate never displays the shape of a solid superimposable on a crystal of left tartrate. The faces on the surface of these two varieties of crystal are so arranged that there exists between the two varieties exactly the same relations as between a right hand and a left hand; or, if one prefers, a crystal of left tartrate is identical with the image of a crystal of right tartrate seen in a mirror.

In organic chemistry there are very many examples of this kind of isomerism which we have just illustrated by studying sodium tartrate.

Now, atomic notation is unable to represent this kind of isomerism. From sodium tartrate, for example, it is not possible to obtain two different developed formulas. Whatever substitution is applied to this substance, the atoms of carbon, hydrogen, oxygen and sodium are always found in the same number and linked to one another in the same manner.

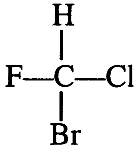
Could the atomic notation not be substituted by another more perfect notation capable of more penetration which, without losing any of the old advantages of the notation, put into correspondence different schemas for the two isomers endowed with the powers of rotation in inverse senses—for what are nowadays called *optical antipodes*? This is the question which Le Bel in France and J. H. van 't Hoff in Holland sought to resolve more or less [12] simultaneously.

Clearly guided by the crystallographic work of Pasteur, they sought to construct for each of the two optical antipodes symbols of constitution such that the symbol for the one would be the reflection in a mirror of the symbol of the other. To succeed, they could not be content with the notions employed up to that time in constitutional formulas, where only the nature of the various atoms and the bonds that they exchange with one another were taken into consideration. When one of the old constitutional formulas is reflected in a mirror, the image and the object display the same atoms exchanging the same bonds. From the point of view of *analysis sitûs*, the given formula and the reflected formula were identical. Le Bel and van 't Hoff had, therefore, of necessity to add to the elements of representation borrowed from *analysis sitûs* employed up to that time, a new element which was borrowed from geometry. This is what they did.

Instead of representing the four valences with which an atom of carbon is endowed in most organic compounds by four lines issuing from a point, they adopted the representation of them as four lines issuing from each of the four vertices of a *tetrahedron*.

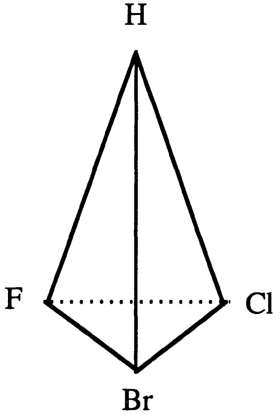
Then it is easily seen that all substances where two or more valences of the tetrahedral carbon atom are saturated by identical atoms or groups of atoms will be represented by a schema which is exactly superimposable on its image in a mirror. But this will not be the case when the four valences of tetrahedral carbon are saturated by four different atoms or four different groups of atoms. In that case, by suitably arranging the symbols of the four atoms at the vertices of a tetrahedron, two figures are obtained which are symmetric with one another but which are not superimposable.

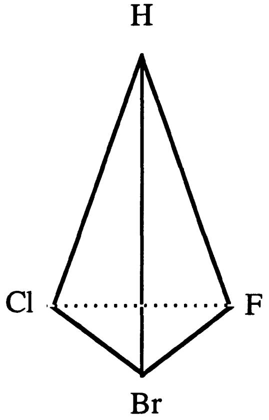
Let [13] us suppose, for example, that the four valences of the carbon atom are saturated by an atom of hydrogen, an atom of chlorine, an atom of bromine and an atom of fluorine. We are dealing with a compound, chlorobromofluoromethane, to which the old atomic notation attributes the developed formula



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{F{-}C{-}Cl} \\ | \\ \mathrm{Br} \end{array}$$

and which does not allow for any isomerism. *Stereochemistry*, on the other hand, can represent this compound equally well by two symmetric, but non-superimposable, formulas which are as follows:





These two formulas are capable of representing two optical antipodes, and there do, in fact, exist two chlorobromofluoromethanes endowed with equal powers of rotation, the one being the inverse of the other.

The use of a tetrahedral symbol to represent the quadrivalent atom of carbon therefore allows, in certain cases, for the construction of two symbols, symmetric with one another but non-superimposable, for a substance of the same composition and the same chemical constitution. Does this procedure furnish [14] a satisfactory representation of the phenomenon of isomerism where the two isomers have the same, but inverse, rotatory powers? To respond affirmatively to this question is precisely to establish the following two laws:

1st. *In all the cases in which a chemical compound can occur under two forms, the one the optical antipode of the other, stereochemistry can represent the constitution of the substance by two symmetric, but non-superimposable, schemas.*

2nd. *In all the cases in which stereochemistry represents the constitution of a substance by two symmetric, but non-superimposable, schemas, this substance occurs under two isomeric forms, the one the optical antipode of the other.*

The verification of the first law presents hardly any difficulties. This verification can be said to be contemporaneous with the debut of stereochemistry or, more exactly, that it is what created stereochemistry. It is because it is possible to put each of a pair of optical antipodes discovered by chemistry into correspondence with two symmetrical and non-superimposable schemas that Le Bel and J. H. van 't Hoff have proposed stereochemistry as a general theory.

The verification of the second law is more difficult, but renders the theory all the more convincing. This verification itself comprises two parts.

In the first place, all substances endowed with the rotatory power, and therefore represented by a stereochemical symbol not superimposable on its symmetric counterpart, suppose the existence of a second substance having precisely this symmetric counterpart as a symbol which will be the optical antipode of the first. If, therefore, chemistry furnishes us with a substance endowed with rotatory power and turning the plane of polarisation from left to right, like *glucose*, which is also called *dextrose*, it should equally furnish us with a substance, isomeric with the former and turning the plane of polarisation from right to left. All dextrose presupposes a *laevulose*. [15] The search for the optical antipodes of all substances endowed with rotatory power should be successful. Investigations along these lines by Pasteur have already met with success, and since the work of the great crystallographer, research is reaching completion on a large number of couples of optical antipodes.

In the second place, all substances whose constitutional formula can, in stereochemistry, take two symmetric and non-superimposable dispositions should be endowed with a rotatory power and display two optical isomers inverse to one another. Now, it very frequently happens that the synthesis of such a substance fails to yield a substance endowed with rotatory power at all, but a substance which is deprived of this rotatory power or, as is often said, *inactive*. Such facts are grave objections to the theory of stereochemistry which it had to resolve, and which it happily succeeded in doing with the aid of ideas created by Pasteur.

It may well happen that the substance which appears to be inactive is in reality a mixture of equal amounts of the two optical antipodes. When a solution of such a substance is evaporated, not just one kind of crystal is obtained but two, the crystals of the one kind being symmetric with the crystals of the other kind although they are not superimposable. It suffices to sort out the crystals, separating the two kinds, and redissolving them separately to obtain two solutions endowed with the power of rotation, the one the optical inverse of the other.

It might also happen that the inactive substance actually obtained is a chemical combination drawn together, molecule by molecule, by the two optical antipodes that were to be obtained. In that case, the evaporation of the solution does not yield two kinds of crystal; the crystals obtained are all of the same shape, any one of which being identical with its mirror image. Pasteur has already shown that inactive salts known [16] under the name *racemates* resulted from the combination of equal weights of right tartrate and left tartrate, and gave the name *racemic compound* to inactive substances generated from two optical antipodes combining molecule by molecule. Dividing inactive substances that stereochemistry regards as racemic compounds into their two optically inverse components should be the aim pursued by the upholders of the new doctrine. They have persevered in their efforts towards this end, guided by very ingenious methods. Their efforts have frequently been crowned with success, and have won stereochemical representation the distinction of fruitfulness which alone fully justifies scientific symbolisms—a distinction which won general support for its precursor, the atomic notation. Not only has it served to classify truths already known; it has also been the instrument of discovery.

I have just mentioned the words *scientific symbolism*, and in the foregoing, faithful to the ideas which I developed here in connection with the atomic notation, I have in fact assigned as the proper object of stereochemistry the creation of a *notation*, the construction of *schemas* appropriate to *represent* truths of the experimental order. I have attributed to these schemas no relationship with the constitution of matter itself, no power of revealing the *quid proprium*[8] of chemical combinations. Does my way of seeing things conform in this respect to that of J. H. van 't Hoff? Does the knowledgeable professor of Amsterdam and Berlin agree with my invincible scepticism regarding the real existence of molecules and atoms? Or is he not, on the contrary, convinced that at the foundation of chemical combination there is a structure, an edifice, whose material is the indestructible atoms of compound substances? Is he convinced that chemical research can gradually unveil for us the plan of this edifice, and that the theory of [17] tetrahedral carbon leads us to knowledge of this plan? This I would not dare to deny, because van 't Hoff nowhere in his book gives the stereochemical representations for the simple symbols. I would no more dare to affirm this either, for fear of taking literally what might be intended figuratively.

Whatever the case, if I have not rendered all his thought, I am conscious of not having attributed to him anything he does not think, and what I have attributed to him is enough to assure him the admiration of all chemists.

III

Although the first great idea of J. H. van 't Hoff belongs to doctrines where some claim to recognise attempts at penetrating to the very heart of matter and divining its

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[8] characteristic or essential feature.

intimate structure, while others would only see symbols appropriate for representing and classifying the facts, the second discovery of the great physicist cannot give rise to the same divergence of interpretation. It belongs, in fact, to the theories of thermodynamics where it is proposed to reduce the laws governing the changes of state of bodies to a small number of abstract principles expressed in the clear language of algebra, but where no claim is made to give to these laws more certitude or more penetration than the experimental method confers on them.

For centuries it was known that some chemical reactions release heat and others absorb it. As soon as chemistry began to take notice of these principles, it was understood that the opposition between *exothermic* and *endothermic* reactions must be a very profound opposition which should be characterised by features other than the sign of the amount of heat brought into play. But what are these characteristics? [18] Chemists have taken a century of fix them with precision; the history of the views expressed on this matter falls into three periods.

The ever celebrated memoir of Lavoisier and Laplace dealing with heat belongs to the first period. For these two physicists, all reactions which released heat are combinations, and all reactions which absorb heat are decompositions. Should certain decompositions appear to release heat, that is, consequently, an illusion. The decomposition which in reality absorbs a certain amount of heat is accompanied by combination which releases a still greater amount of heat which masks the effect of the first reaction.

Long in favour, this theory had to disappear when Favre and Silbermann demonstrated that certain decompositions, perfectly isolated from all combination, were accompanied by a release of heat. It then seemed necessary to accept that an exothermic reaction could be a decomposition, and that an endothermic reaction could be a combination, and an opposition of a different nature was sought between exothermic and endothermic reactions.

The theory of thermochemistry, proposed in the middle of the century by Julius Thomsen, consisted essentially of distinguishing exothermic from endothermic reactions by a new characteristic. According to this theory, exothermic reactions are the only ones which could be produced directly. Endothermic reactions are impossible by themselves; if such a reaction is to be produced, it is necessary to produce an exothermic reaction at the same temperature releasing more heat than the first absorbs.

Thermochemistry, at first triumphant, was opposed by experimental contradictions which became gradually more precise and numerous. Examples of self-sustaining reactions which absorb heat were seen to multiply, [19] and despite the desperate efforts of its advocates,[9] Thermochemistry had to disappear from the field of science.

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[9] See "Thermochimie, à propos d'un livre récent de M. Marcelin Berthelot" *Revue des Questions Scientifiques*, 2nd. series, vol. XII, October 1897, pp. 361-92 [translated in this volume as "Thermochemistry"].

Then Thermodynamics proposed to contrast exothermic and endothermic reactions in a third way.

The new contrast was first noted for a rather special case by J. Moutier.

It was known that equilibrium is established at each temperature in a vessel in which a liquid coexists with its vapour, when the pressure attains a certain value, being the saturated vapour pressure for this temperature. Inversely, under each pressure, there is a temperature which assures equilibrium in the body of the system; this is the boiling point under this pressure.

As stated by H. Sainte-Claire Deville and first demonstrated by H. Debray, there exists many systems susceptible of chemical reaction where the conditions of equilibrium are governed by similar laws. These systems are those which are today designated with the epithet *univariants*.[10] At each temperature, equilibrium is assured by one value of the pressure, the *transformation pressure* relative to this temperature. Under each pressure, equilibrium is produced at a certain temperature, being the transformation point relative to this pressure.

This said, here is the very simple law stated by J. Moutier: *Under a given pressure and at a temperature below the transformation point relative to this pressure, only exothermic reactions can be produced in the system; at a temperature above the transformation point,* [20] *only endothermic reactions can be produced.*

The law is very simple, but rich in consequences.

Let us suppose that the temperature is gradually lowered until it has fallen beyond the transformation point of each of the systems that can be met with; no longer will exothermic reactions be observed, just as thermochemistry would have it. Thermochemistry thus appears as the *chemistry of low temperatures*.

Let us suppose, on the other hand, that the temperature is raised so as to pass the transformation point of all systems; all the possible reactions would be endothermic. The fundamental law of the old thermochemistry will be replaced by the inverse proposition. It can be understood how H. Sainte-Claire Deville, in creating the *chemistry of high temperatures*, has brought about the fall of thermochemistry and the advent of the new chemical mechanics.

But we state here these solemn consequences in an entirely general form, and J. Moutier had only established them for a particular class of systems, the univariant systems. Are they true for the other systems? It is this question which is addressed by the second great discovery of J. H. van 't Hoff, the *principle of the displacement of equilibrium by variation of temperature*. This principle was first stated by van 't Hoff a few years after Moutier's investigations, but these, virtually ignored by French scientists, exerted no influence on the ideas of the chemist from Amsterdam.

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[10] See "La Loi des Phases, à propos d'un livre récent de M. Wilder D. Bancroft" *Revue des Questions Scientifiques*, 2nd. series, vol. XIV, July 1898, pp. 54-82) [translated in this volume as "The Phase Law"].

Complementing J. Moutier's law exactly, van 't Hoff's law applies to all chemical systems except for univariant ones. Here is the statement of this law:

A chemical system is in stable equilibrium at a certain [21] temperature, and its composition determined. Let us raise the temperature a little; the equilibrium of the system is first disturbed; a small reaction is produced there which, finally, brings the system to a state of equilibrium and fixes its composition appropriate to the new temperature. Now, *the reaction thus produced is always an endothermic reaction.*

Let us suppose that our chemical system encloses an exothermic compound mixed with the elements capable of generating it. At a certain temperature the system, in stable equilibrium, contains a certain amount of the compound substance. Let us raise the temperature. A certain reaction would be produced which will give the system its new equilibrium composition, and since this reaction must be endothermic, it necessarily consists in the destruction of a part of the compound substance. A chemical system enclosing an exothermic compound mixed with its elements at stable equilibrium therefore contains an amount of the compound reduced in proportion to how much the temperature is raised.

On the other hand, a chemical system enclosing an endothermic compound mixed with its elements and in stable equilibrium contains a greater amount the higher the temperature.

It can be seen from this that at very low temperatures exothermic compounds are in stable equilibrium and cannot be decomposed. Endothermic compounds, by contrast, cannot be formed at the expense of their elements which are in stable equilibrium. The predictions of thermodynamics are verified; according to the striking formulation of J. H. van 't Hoff, *the principle of maximum work is true at absolute zero.*

On the contrary, as the temperature rises, exothermic compounds are gradually destroyed and endothermic compounds are formed at [22] the expense of their elements. Given this, at very high temperatures these dissociations of exothermic compounds and these syntheses of endothermic compounds—the claim to fame of the School of H. Sainte-Claire Deville, and insurmountable stumbling block for thermochemistry—yield brilliant confirmations of van 't Hoff's principle.

The generality of Moutier's and van 't Hoff's laws was not apparent from the first. In the absence of other evidence, the century of efforts and gropings which preceded the discovery of these laws bears witness to their elusive character. Nicely verified at higher temperatures, they are, in fact, latent and, as it were, dormant, at lower temperatures. Undoubtedly, no reaction is ever observed which contradicts them, but a great number of reactions whose possibility they pointed to were not produced. States of equilibria subject to the laws of Moutier and van 't Hoff are associated with a host of equilibrium states that the laws do not predict. About these *states of false equilibria* we will perhaps one day speak to the readers of the *Revue des Questions Scientifiques*. To speak of them now would lead us too far afield, away from the regions discovered by J. H. van 't Hoff.

IV

Let us penetrate into the third of these regions and say a few words about the investigations of the Dutch scientist into the properties of extremely dilute solutions.

There exists a striking analogy between the laws governing extremely dilute solutions and the laws governing gases which have achieved that state of extreme rarefaction called the perfect state.

The laws of the perfect gas state, to which are given the names of Mariotte and Gay-Lussac, are known. [23] If the volume occupied by 1 gramme of a perfect gas is multiplied by the pressure it supports and the product divided by the absolute temperature, a number is obtained which retains the same value whatever the circumstances of the gas. The value of this number is characteristic of the nature of the gas studied.

Let us take an extremely dilute solution, for example of water slightly sugared, where a very small amount of cane sugar is distributed throughout a very large mass of water. In what way is it possible to apply to this solution propositions analogous to those of Mariotte and Gay-Lussac? And how is it possible in the first place to discern in this solution magnitudes analogous to those in terms of which the gas laws are conveyed?

The absolute temperature retains the same significance in both cases. There is no difficulty in speaking of the volume occupied by 1 gr. of dissolved cane sugar; it is the volume of the solution which contains 1 gr. of cane sugar or, what comes to the same thing since the solution is very diluted, the number of litres of water within which this gramme of cane sugar has been distributed. But what of the magnitude which will play the role played by pressure in the study of perfect gases?

Everyone knows Dutrochet's famous experiment, the classic demonstration of the phenomena of *osmosis*.

A solution of gelatine in water fills a vessel whose base is made of an animal or vegetable membrane. This base separates the gelatine solution from a bath of pure water. The membrane is impermeable to gelatine, which remains confined to the vessel where it was first placed, but on the other hand, it is permeable to water. Pure water which was outside the vessel containing the solution traverses the membrane and penetrates into the solution which it dilutes more and more.

So [24] it is, at least in Dutrochet's experiment where the solution and the pure water are both subjected to atmospheric pressure. But if the two liquids are subjected to different pressures, the experiment can present several aspects.

Let us suppose, for example, that the pure water does not support any pressure while the gelatine solution supports a pressure which can be varied at will. Furthermore, let us suppose that the temperature and the concentration of the solution are well determined. If the pressure exerted on the solution is less than a certain value, whatever the nature of the membrane, the pure water penetrates into the solution and dilutes it. If, on the other hand, the pressure on the solution exceeds this same value, the solution expels water and becomes more concentrated. Finally, if the pressure supported by the solution has precisely this value, no liquid is exchanged between the pure water and the solution by transversing the membrane.

The value of the pressure which maintains this state of equilibrium between the pure water and the gelatine solution is called the *osmotic pressure* of a solution of gelatine having the given temperature and concentration.

It is possible to define in this way the osmotic pressure of an aqueous solution of any substance provided it is possible to prepare a membrane impermeable to the substance and permeable to water, and ingenious procedures allow the realisation of such *semi-permeable partitions.*

Osmotic pressure is the magnitude which plays the role in the study of extremely dilute solutions that pressure plays in the study of perfect gases. Here, in fact, is the law stated by van 't Hoff:

On multiplying the volume of water used to dissolve a gramme of a certain substance by the osmotic pressure of the dilute solution and dividing the product obtained by the absolute temperature, a number is obtained which depends neither [25] *on the temperature nor the concentration of the solution, at least so long as this concentration remains very small. The value of this number is characteristic of the dissolved substance.*

The laws of Mariotte and Gay-Lussac are completed by a third law for perfect gases, the law of Avogadro and Ampère. On multiplying the volume occupied by a gramme of gas by the pressure it supports and dividing the product by the absolute temperature, a number is obtained which retains, for each gas, an invariable value. But this value changes from one gas to another; it is, for each gas, inversely proportional to the molecular weight of the gas. This proposition is what Avogadro and Ampère's law consists in. The importance of this law, and the use to which it is put in fixing the molecular weights of many compounds, is well known in chemistry.

Now, as with Mariotte and Gay-Lussac laws, van 't Hoff has extended this law of Avogadro and Ampère to extremely dilute solutions. If the volume in which 1 gr. of a dissolved substance is distributed is multiplied by the osmotic pressure of the solution and if this product is divided by the absolute temperature, a number is obtained which depends only on the nature of the substance dissolved. *This number is inversely proportional to the molecular weight of the dissolved substance.*

Like Avogadro and Ampère's law, this law could serve in Chemistry to determine the molecular weights of a large number of compounds were the measure of osmotic pressure of a solution is open to precise and easy experimental methods. In reality, things are not so because the preceding law, whose great interest from the theoretical point of view is apparent, cannot be employed directly.

But from this law thermodynamics deduces various consequences which are very well suited to the fixation of molecular [26] weights. We will cite just one, that used most.

Let us take a large number of substances soluble in water. With each of these substances, we form a dilute aqueous solution. We suppose that all these solutions encompass the same mass of water, one kilogramme, for example, and the same mass of dissolved substance, for example, a gramme. Although 0° is the freezing point of pure water, none of these solutions solidify at 0°; for each of them, the freezing point is found to be below 0°.

But the reduction in the freezing point will not be the same for all of these solutions, and its magnitude will be inversely proportional to the molecular weight of the dissolved substance for each of these solutions.

As J. H. van 't Hoff has shown, this proposition can be deduced from the law of Avogadro and Ampère extended to dilute solutions. But what is more, it can be established by direct experimental determinations of the kind that have been discovered by Raoult, Dean of the Faculty of Sciences at Grenoble. The experimental study of freezing points of dilute solutions thus provided one of the most convincing demonstrations of J. H. van 't Hoff's ideas.

But there is more. The determination of the freezing point of a solution has become, thanks above all to the ingenious procedures conceived by Raoult, one of the most easy and most precise operations of physics. Since then, the law governing the lowering of freezing points of dilute solutions has been transformed into a suitable method for fixing the molecular weights of many chemical compounds, the *cryoscopic method.*

The analogy between the laws governing extremely dilute solutions and the laws to which perfect gases are subjected leads to many consequences, raising interesting remarks and leading to numerous [27] discussions. Of these consequences, these remarks and these discussions it is impossible for us to speak here. We are obliged to present, in this sober sketch, van 't Hoff's idea completely bare and, so to say, reduced to its skeleton. We have done the same regarding stereochemistry and the displacement of equilibrium by the variation of temperature. Nevertheless, we think enough has been said for our reader to glimpse what a profound and daring thinker van 't Hoff is—and sufficiently little not to reveal too much of these *Leçons de Chimie-Physique* where fruitful thoughts, original and ingenious insights are crammed together around some masterful ideas.

ESSAY 7

ON SOME RECENT EXTENSIONS OF STATICS AND DYNAMICS*

I

ON THE DEVELOPMENT WHICH PHYSICAL THEORIES HAVE UNDERGONE

Among the important intellectual events of the last twenty-five years, there is, we believe, one which particularly merits attention. We are speaking of the profound change which our ideas about rational Mechanics have undergone. The generally accepted notions on the nature and role of this science have been overthrown, and from this upheaval Mechanics has emerged rejuvenated, more powerful than before and capable of reigning over an incomparably more extended domain.

Before the period of which we are now speaking, Mechanics was the study of *motion*, in the restricted sense that the scholastics characterised with the words *local motion*. It was limited to analysing change of position of figures delimiting the various parts of matter. Among the properties of matter, this alone was reducible to geometric elements, leading mathematicians to conclude, with Descartes, that this alone is capable of being expressed in the language of algebra and analysis.

The other properties of bodies—[being in] a solid or liquid state, a state of chemical combination or decomposition, a state [131] of heating, of illumination, of electrification, of magnetisation—do not appear to our senses as aggregates of geometric elements. Such properties are therefore not amenable to calculation, and their study can only constitute a mathematical theory on one condition: that of penetrating further into the knowledge of bodies than our senses authorise by the foolhardy way of hypothesis—that of supposing that, under the non-geometric properties that our perceptions reveal, combinations of shapes and movements

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* Originally published as "Sur quelques extensions récentes de la statique et de la dynamique," *Revue des questions scientifiques*, 50 (1901), 130-57.

which would be the essence of these properties. A branch of physics cannot be transformed into a mathematical theory unless it becomes a mechanical theory.

This principle has guided the efforts of physicist-geometers for a century. Their efforts were, at first, admirably fruitful; but they finally came up against difficulties which looked very much as though they were insoluble. Restricting ourselves to the most well known, let us merely cite these two: the difficulty of conceiving an ether capable of remaining at stable equilibrium and at the same time propagating purely transverse oscillations of light; and the difficulty of conceiving a calorific movement which is compatible with Clausius' inequality.

Instead of pursuing these—perhaps insurmountable—obstacles which barred the path that had been followed up to that point, a good many physicists have turned back in search of some broader and more certain route. They undertook to examine afresh the foundations of physical theories and to determine what conditions are necessary for such a theory being amenable to translation into mathematical language. They recognised that it was by no means essential for this purpose that physical properties should be replaced by assemblages of shapes and movements, that the states and qualities might not be explained, but symbolised by numbers and figures, and finally, that these numbers and [132] figures allow for the constitution of a science of which the old rational Mechanics was no more than the first chapter and most simple [part], of a science encompassing within its laws not only local movement, but all kinds of change of state or quality.

The Society for Science in Brussels had actively involved itself in this evolution of physical theories. In its beginnings, it supported the work of R. P. Carbonnelle, convinced and competent advocate of the theories which reduced everything in the material world to shape and motion. Later, it had been the first to welcome the attempts at rehabilitating qualities into physics. It seems to me that there is no better way for me to participate in its jubilee celebrations than to examine some of the extensions and transformations that Statics and Dynamics has undergone.

II

EXTENSION OF THE PRINCIPLE OF VIRTUAL SPEEDS

Since the end of the 18th century, Statics has been condensed into a principle of great generality, whose final form had been given by Lagrange, the *Principle of virtual motion*. The equilibrium conditions of a mechanical system are obtained by expressing that in all virtual displacements of the system, the forces applied to it effect zero work. These forces fall into two groups—forces exerted by external bodies on the system, and internal forces which the various parts of the system exert on one another. The work done by the internal forces is, in all circumstances, the decrease in a certain function F of the state of the system, the function which Gauss called the internal potential of the system. Thus, if dT_e is the external work [133] performed by a virtual displacement and dF the increase that the displacement imposes on the internal potential, the equilibrium conditions of the system are obtained by writing

$$dT_e - dF = 0 \tag{1}$$

for every virtual displacement.

The revolution which has transformed and extended the domain of rational Mechanics has particularly enlarged the import of this principle. This progress has been due principally to the labours of Massieu, J. Willard Gibbs, Maxwell and Helmholtz.

Each system is assigned a function depending on all the variable quantities that fix the mechanical, physical and chemical state of the system: coordinates and masses of the various material points, solid, liquid or gaseous state, chemical composition, temperature, electrical charge and magnetisation. Following Gibbs' terminology, this function can be called the internal *thermodynamic potential of the system*. All the conditions of equilibrium of the system are obtained with the aid of this function by expressing all the virtual modifications of the system achieved without varying the temperature and verifying the equality

$$dT_e - dF = 0.$$

In this proposition, the words take on a broader, more comprehensive sense than in the old Statics. The virtual modification at issue here is not a simple displacement; it is a change that can involve not only the position and motion of the various parts of the system, but also their physical and chemical properties. The state of equilibrium is no longer simply a state in which the system remains immobile in space, but a state not undergoing any chemical reaction, nor any change of physical state, nor variation of its various properties. Finally, the external work is no longer reduced [134] simply to work of certain external *forces*; other elements figure too, under the more comprehensive name of *actions*, which are to symbols for various qualities what forces are to coordinates of material points. The product of an action and a variation of the variable to which it is related is an amount of work.

An essential precaution should be observed in the application of this principle, however. The variable quantities which symbolise the physical properties of the system must be chosen in a certain way. It is necessary that in a virtual modification in which the temperature of the system is varied without changing the value of any other of these variables, the virtual work of external actions should be identically zero. The properties of the system are then said to be represented by *normal variables*.

Thus generalised, the principle of Statics exhibits a marvellous fecundity. Not only is all that is given by the principle of virtual motion, understood in Lagrange's sense, contained in the new proposition; it furnishes straightforwardly the laws of a host of equilibrium states that could not even be conceived by the old Mechanics.

First and foremost, it is appropriate to mention the laws of equilibrium which bring to a halt changes of physical state and chemical reactions. *Chemical Statics*, the object of so much efforts since the time of Berthollet, is constituted by it. The laws it so nicely formulates, their simplicity, the naturalness of the notions that it employs, make it a valuable guide to the experimenter in the intricacies of compositions and decompositions. Its most obstinate adversaries are now obliged to recognise this, thanks to the admirable work of Bakhuis Roozboom, van 't Hoff and their students.

But mechanical Statics and chemical Statics are not the only things that depend on the new principle of virtual speeds; [135] electrical Statics and magnetic Statics should also be added, as well as the law of the distribution of electricity in homogeneous and heterogeneous conducting bodies, in electrolytes and in dielectrics, and the law of distribution of magnetism in perfectly soft bodies, which are now established by a rigorous and uniform method.

III

D'ALEMBERT'S PRINCIPLE AND VISCOSITY

Having thus secured the principles of Statics by a considerable extension of the principle of virtual speed, physicists became preoccupied with similarly extending the principles of Dynamics. This extension followed quite different courses, according as mechanical, chemical and even electrical Dynamics were at issue.

We will not treat electrical Dynamics here—not that this branch of science does not merit engaging our attention, but on the contrary because its importance and complexity requires too long and detailed discussion for this brief exposition. We therefore restrict ourselves to examining mechanical and chemical Dynamics.

D'Alembert enunciated a famous principle which allows the passage from Statics to Dynamics. We will briefly recall the statement of this principle.

Each elementary mass *dm* of the system has, at the instant *t*, an acceleration whose components are γ_x, γ_y, and γ_z. The vector whose components are

$$-\gamma_x dm,\ -\gamma_y dm,\ -\gamma_z dm$$

is called the inertial force applied to mass *dm*.

In [136] order to find the equations of motion of the system at the instant *t*, it suffices to show that the system would be at equilibrium if it were subjected not only to the external forces which really act on it, but also the forces of inertia.

If, therefore, the work effected by these forces of inertia during an arbitrary virtual displacement of the system is denoted by dT_j, then all the laws of motion are condensed in this single formula:

The equality

$$dT_e + dT_j - dF = 0 \tag{2}$$

is verified at each instant t for all virtual displacements of the system. In the case where the mechanical system studied is entirely determined by the knowledge of n independent variables $\alpha, \beta, \ldots, \lambda$, Lagrange put the work of the inertial forces in a useful form. Let us suppose that

$$\alpha' = \frac{d\alpha}{dt}, \quad \beta' = \frac{d\beta}{dt}, \quad \ldots, \quad \lambda' = \frac{d\lambda}{dt}. \tag{3}$$

The kinetic energy $\mathfrak{Z}$[1] of the system is a function of the variables $\alpha, \beta, \ldots, \lambda$ and the variables $\alpha', \beta', \ldots, \lambda'$, quadratic in respect of these latter variables. Putting

$$\begin{cases} J_\alpha = \dfrac{\delta\mathfrak{Z}}{\delta\alpha} - \dfrac{d}{dt}\dfrac{\delta\mathfrak{Z}}{\delta\alpha'}, \\ J_\beta = \dfrac{\delta\mathfrak{Z}}{\delta\beta} - \dfrac{d}{dt}\dfrac{\delta\mathfrak{Z}}{\delta\beta'}, \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ J_\lambda = \dfrac{\delta\mathfrak{Z}}{\delta\lambda} - \dfrac{d}{dt}\dfrac{\delta\mathfrak{Z}}{\delta\lambda'}, \end{cases} \tag{4}$$

the work of the inertial forces then takes the form

$$dT_j = J_\alpha\delta\alpha + J_\beta\delta\beta + \ldots J_\lambda\delta\lambda. \tag{5}$$

D'Alembert's principle can now be extended to the new Mechanics.

Let [137] us suppose that a system is defined by the *normal* variables $\alpha, \beta, \ldots, \lambda$ which, together with temperature, fix not only the shape and position of the various parts, but also all the physical properties of the parts. The kinetic energy will still be a function of the variables $\alpha, \beta, \ldots, \lambda$ and the variables $\alpha', \beta', \ldots, \lambda'$, quadratic in respect of the latter. Nothing will stand in the way of forming the equalities (4), the quantities $J_\alpha, J_\beta, \ldots J_\lambda$ and calling them *inertial actions* relative to the variables $\alpha, \beta, \ldots, \lambda$. Nothing will stand in the way of postulating, at each instant of motion of the system, the exactitude of the equality (2) for all virtual and isothermic modifications.

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[1] [For typographical reasons, this symbol is used instead of Duhem's $\mathfrak{T}$.]

Such an extension will allow the laws of motion of certain systems to be obtained in logical fashion—laws which the old Mechanics could not realise without subterfuge, such as the laws of motion for compressible fluids.

Will this extension suffice to constitute the new Dynamics? Some quite simple reflections show that this is not so.

In the new Mechanics, the word *motion* has a much more extended sense than in the old Mechanics. It does not merely designate the local movement which, at various instants during its duration, involves one and the same body occupying different positions; it also designates all changes of physical or chemical properties accomplished during this time.

As a result of the new sense of the word *movement*, a system can be in motion although its various parts occupy invariable positions in space.

Let us take, for example, a perfectly closed glass receptacle filled with hydrogen and chlorine, and expose it to light of a very low intensity. No displacement manifests itself in the system; each elementary volume cut out in space contains at every instant the [138] same matter. Yet the properties of this matter will change from one instant to another. The hydrogen and chlorine are combined and their mixture will gradually be transformed into hydrochloric acid. The system will be the seat of a *chemical movement* which will not be accompanied by any local movement.

Some of the variables which define the state of a system can therefore change in value without any part of the system undergoing any displacement. If α is such a variable, neither α nor α' will figure in the expression for the kinetic energy, $\mathfrak{T}$. Therefore, according to formula (4), the inertial action corresponding to J_α will be zero, and the variable α will be a *variable without inertia.*

Let us suppose that the state of a system is entirely fixed by knowledge of the temperature and one variable without inertia—such is our mixture of hydrogen and chlorine.

For such a system, equation (2), which contains all the laws of motion, is reduced to equation (1), which contains all the laws of equilibrium. Such a system will therefore be found at each instant to remain in a state of equilibrium if the temperature and the external actions remain indefinitely as they are at that instant.

Now, experience shows us that there is a whole group of systems to which this law is certainly inapplicable. Such a system is far from immediately attaining the state of equilibrium compatible with the prevailing external conditions. When a constant temperature is maintained, and when the external actions to which it is subjected are invariable, it is transformed, during the course of a very long time, before coming to equilibrium. The mixture of hydrogen and chlorine that we have taken as our example is a case of this sort.

It is therefore clear that d'Alembert's principle, accepted without modification, does not sanction passing from generalised Statics to generalised Dynamics.

The [139] necessity of modifying d'Alembert's principle by the introduction, in equation (2), of terms which are identically zero for a system at equilibrium and which are, nevertheless, distinct from inertial work, has been known since 1822 when Navier sought to give an account of the properties of viscous fluids. It is Navier's idea that we will enlarge upon[2] by introducing into equation (2) a term dT_v, which we will call the *virtual work of viscosity*, and putting this equation in the form

$$dT_e + dT_j + dT_v - dF = 0. \tag{6}$$

Which essential hypotheses will we formulate regarding this virtual work of viscosity?

We suppose, in the first place, that it is of the form

$$dT_v = V_\alpha \delta\alpha + V_\beta \delta\beta + \ldots + V_\lambda \delta\lambda, \tag{7}$$

V_α, V_β, ... V_λ being the *actions of viscosity* relative to the variables $\alpha, \beta, \ldots, \lambda$.

Regarding each of these actions, we will suppose that it is a function of the quantities $\alpha, \beta, \ldots, \lambda, T$ and also the quantities $\alpha', \beta', \ldots, \lambda'$. We will admit that the action of viscosity is zero when the latter quantities are all zero. Finally, we will make this essential hypothesis: In each real modification of the system the actions of viscosity cannot effect a positive work, so that it always holds that [140]

$$V_\alpha \alpha' + V_\beta \beta' + \ldots + V_\lambda \lambda' \leq 0. \tag{8}$$

In virtue of this last hypothesis, the actions of viscosity should be classed among the *passive resistances.*

Thus complemented, d'Alembert's principle illuminates more than one branch of Physics. Not only is the viscous movement of fluids found to be put into equations by a more regular route than Navier's method. Not only are the equations for the diffusion of fluids devoid of all suppositions borrowed from molecular and kinetic doctrines. Chemical Dynamics also ceases to be an enigma and takes its place in general Mechanics.

The laws which govern chemical reactions and regulate their speed seem not to have any analogy with the laws which determine the local movement of bodies—the purely mechanical phenomena such as the fall of heavy bodies and the path of the

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[2] On this subject, see P. Duhem, "Commentaire aux principes de la Thermodynamique," 3rd. part *Journal de Mathématiques pures et appliquées*, 4th. series, vol. X, p. 203; 1894.—"Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques" *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux*, 5th. series, Vol. II, 1896.—L. Natanson, "Sur les lois des phénoménes irréversibles" *Bulletin de L'Académie des Sciences de Cracovie*, mars 1896.—"Sur les propriétés thermocinétiques des dissolutions" *Ibid.*, July 1898 and July 1899.—*Zeitschrift für physikalische Chemie*, Vol. XXX, p. 681, 1899.—"Ueber thermokinetische Eigenschaften thermodynamischer Potentiale" *Zeitschrift für physikalische Chemie*, Vol. XXIV, p. 302, 1897.

stars. Today, the chain which unites these very diverse phenomena is visible. If these phenomena seem to be unconnected, it is because they lie at the two extremes of this chain. The mechanical motions whose laws the creators of Dynamics, Galileo and Newton, fixed are movements for which actions of viscosity only play a negligible role in comparison with inertial actions. The most simple chemical reactions are, on the contrary, movements which are barely sensitive to inertial actions, but where actions of viscosity dominate.

IV

SYSTEMS WITH FRICTION

The actions of viscosity are annulled at the same time as the speeds α', β', ..., λ'. They therefore play no role [141] in the conditions of equilibrium, and the statics of systems endowed with viscosity does not differ from the statics of systems which have been provided for.

Now this statics, however general it might be, is not broad enough. Observation presents us with a number of systems whose states of equilibrium escape these laws.

Let us suppose that *A*, *B*, ... , *L* are the external actions relative to the variables α, β, ..., λ. The equality (1) could, more explicitly, be replaced by the equalities

$$\begin{cases} A = \dfrac{\delta}{\delta\alpha} F(\alpha,\beta,\ldots,\lambda,T), \\ B = \dfrac{\delta}{\delta\beta} F(\alpha,\beta,\ldots,\lambda,T), \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ L = \dfrac{\delta}{\delta\lambda} F(\alpha,\beta,\ldots,\lambda,T). \end{cases} \tag{9}$$

These equations, which are the *equations of equilibrium* of the system, allow the following proposition:

A system defined by the absolute temperature *T* and the normal variables α, β, ..., λ is maintained at equilibrium by the external actions determined *without ambiguity* as a function of the variables α, β, ..., λ, *T*.

Solving the equations (9) for α, β, ..., λ yields

$$\begin{cases} \alpha = h_\alpha F(\alpha,\beta,\ldots,\lambda,T), \\ \beta = h_\beta F(\alpha,\beta,\ldots,\lambda,T), \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ \lambda = h_\lambda F(\alpha,\beta,\ldots,\lambda,T). \end{cases} \tag{10}$$

The functions h_α, h_β, ..., h_λ may, for a given system of values A, B, ... , L, T, have a limited or an unlimited number of determinations. But even if each system of values A, B, ... , L, T were to correspond to an infinity of [142] systems of values of h_α, h_β, ..., h_λ, these systems do not constitute a continuous ensemble.

Let us therefore suppose the material system maintains a temperature T and is subject to external actions A, B, ... , L, and let us look for the state of equilibrium it will take up under these conditions. We may be able to find, as the solution to the problem, a single equilibrium state. We may be able to find several, or an infinity, of them. But we will certainly not be able to find a *continuous set* of equilibrium states.

Now this result is contrary to a whole range of information that the experimental study of chemical statics furnishes us with.

Let us take, for example, a system at 200°C containing water vapour and the elements of this water vapour, oxygen and hydrogen, mixed under an invariable atmospheric pressure. Whatever the fraction of the gaseous mixture which has passed into the state of combination, and whatever fraction remains free, the system is at equilibrium. We can thus observe, at the same temperature of 200°C and under the same atmospheric pressure, an infinity of equilibrium states of the system, *and these states of equilibrium form a continuous set.*

These chemical equilibria that escape the laws of Statics condensed in equation (1) have analogues among purely mechanical equilibria.

Let us consider, for example, a body which slides on an inclined plane. According to the theorems of classical Mechanics, this body cannot be at equilibrium under the action of weight. In reality, for a given body and inclined plane of a given nature, there will be equilibrium in all cases where the inclination of the plane is less than a certain limit. In order to explain this contradiction, it is said that the body rubs against the plane and that *classical Mechanics does not take account of friction.*

The theory of friction is then developed from special hypotheses, and this is what we are told:

Let [143] N designate the pressure of the body on the inclined plane, and f a positive coefficient that depends on the nature of the body and the nature of the plane. In order that the body be at equilibrium on the inclined plane, it is necessary and sufficient that the component of the weight of the body along the line of greatest slope does not exceed fN.

Let P be the weight of the body and α the angle of inclination of the plane with the horizontal. The pressure N has the value $P\cos\alpha$, and the component of the weight along the line of greatest slope of the plane is $P\sin\alpha$. The condition of equilibrium is therefore

$$P\sin\alpha \leq f P\cos\alpha$$

or

$$\tan\alpha \leq f.$$

The analysis of this example or of any other analogous example justifies the following proposition;

The conditions of equilibrium of a system with friction is expressed not by equations between the acting forces and the variables, but by inequalities. Consequently, when the acting forces are given, the state of equilibrium of the system is not determined; it is possible to observe an infinity of equilibrium states forming a continuous set.

Can the equilibria due to friction that we have just considered and the chemical equilibria that we have treated a moment ago be explained by transforming and enlarging the principles of Mechanics? It was not this hypothesis that physicists dwelled upon first.

A wide-spread opinion regarding the phenomena of friction is the following:

The equations of Mechanics, written without mention of friction, are general; but in the course of [developing] our theories we apply them to very abstract bodies [144], very different from those presented to us in experience. We treat perfectly rigid, perfectly polished solids, whereas natural solids are always more or less deformable, more or less rough, from which the discrepancies between the predictions of Mechanics and the results of observation arise.

These discrepancies all disappear if, instead of applying the equations of Mechanics to very simplified abstractions in order to represent, even roughly, the properties of natural bodies, we take account of the roughness and deformations of these bodies in making the application. If, therefore, in order to eliminate these discrepancies, we introduce a new term into the equations of Statics and Dynamics, it is not that we regard these equations as incomplete and imperfect. It is only to take account in one go, by the introduction of this *fictive* term, of the varied and complex actions which explain friction—actions whose direct and detailed study would be impossible.

The view that we have just presented is, in part, justified. The most familiar observations show that an important part of the effects that are attributed to friction is attributable to roughness and deformations of the surfaces in contact. To be convinced of the point, it suffices to note that friction decreases the harder and more highly polished the body is. But is friction only an appearance? Besides fictive friction, the effect resulting from deformations and roughness, is there no real friction subsisting when bodies in contact are perfectly rigid and perfectly smooth? These are questions to which it would be rash to reply one way or the other.

So, even though friction will always be a pure fiction in the domain of the old Mechanics, doubt cannot be cast on the innumerable chemical equilibria that cannot be brought into agreement with the equality (1).

It [145] is therefore appropriate to introduce a new modification, a new extension, into the essential laws of Statics and Dynamics.

This is how the laws should be modified and enlarged.[3]

With the notation that figured in the equalities (4) to (9), the equality (6) can be clarified and furnishes the following relations:

$$\left\{\begin{array}{l} A - \dfrac{\delta}{\delta\alpha}F + J_{\alpha} + V_{\alpha} = 0, \\ B - \dfrac{\delta}{\delta\beta}F + J_{\beta} + V_{\beta} = 0, \\ \dots\dots\dots\dots\dots\dots \\ L - \dfrac{\delta}{\delta\lambda}F + J_{\lambda} + V_{\lambda} = 0. \end{array}\right. \qquad (11)$$

These are the relations that go to complete the new terms.

Let $|\alpha'|$ designate the *absolute value* of $\alpha' = d\alpha/dt$; the ratio $\alpha'/|\alpha'|$ will be equal to $+1$ if α' is positive and -1 if α' is negative. Let

$$F_{\alpha}, F_{\beta}, \dots F_{\lambda}$$

represent the magnitudes which depend on the following variables:

$$\alpha, \beta, \dots, \lambda, T,$$

$$\alpha', \beta', \dots, \lambda',$$

$$\mathrm{A, B, \dots, L},$$

and replace the equalities (11) with the more general equalities [146]

$$\left\{\begin{array}{l} A - \dfrac{\delta}{\delta\alpha}F + J_{\alpha} + V_{\alpha} + F_{\alpha}\dfrac{\alpha'}{|\alpha'|} = 0, \\ B - \dfrac{\delta}{\delta\beta}F + J_{\beta} + V_{\beta} + F_{\beta}\dfrac{\beta'}{|\beta'|} = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots \\ L - \dfrac{\delta}{\delta\lambda}F + J_{\lambda} + V_{\lambda} + F_{\lambda}\dfrac{\lambda'}{|\lambda'|} = 0. \end{array}\right. \qquad (12)$$

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[3] P. Duhem, "Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques" *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux,* 5th. series, Vol. II, 1896.

These are the equations of motion for a system endowed with viscosity and *friction.*

Furthermore, a new hypothesis completing the foregoing consists of admitting that the actions of friction, F_α, F_β, $\dots F_\lambda$ are never positive:

$$F_\alpha \leq 0, \; F_\beta \leq 0, \; \dots \; F_\lambda \leq 0. \tag{13}$$

The equations of motion are incorporated into the conditions of equilibrium; if Φ_α, Φ_β, $\dots\Phi_\lambda$ are the values taken by F_α, F_β, $\dots F_\lambda$ when all the quantities α', β', $\dots$, λ' become equal to 0, the system is at equilibrium whenever it holds that

$$\begin{cases} \Phi_\alpha \leq A - \dfrac{\delta F}{\delta \alpha} \leq -\Phi_\alpha, \\ \Phi_\beta \leq B - \dfrac{\delta F}{\delta \beta} \leq -\Phi_\beta, \\ \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \; \cdot \\ \Phi_\lambda \leq B - \dfrac{\delta F}{\delta \lambda} \leq -\Phi_\lambda. \end{cases} \tag{14}$$

If temperature T and external actions A, B, $\dots$, L are ascribed, it is seen that, in general, there is an infinity of equilibrium states of the system and *these equilibrium states form a continuous set.*

The laws that we have just stated, at least those of them that are essential, embody conditions of equilibrium and motion of mechanical systems endowed with friction. Moreover, they complete chemical Statics and Dynamics. Many of the peculiarities [147] presented by chemical equilibria are explained and classified. The influence of the variation of temperature on reactions is subjected to precise rules which are supported by a great deal of experimental work and in particular, the beautiful research of H. Pélabon on the dissociation of hydrogen sulphide and selenium hydride, of Hélier on the combustion of hydrogen, carbon monoxide and methane, and of Jouniaux on the reduction of silver chloride by hydrogen. Finally, the theory of explosions is beginning to assume a rational form.

V

STATICS OF SYSTEMS EXHIBITING HYSTERESIS

The consideration of the actions of friction allows the reduction of a large number of mechanical and chemical phenomena to general Mechanics. But this extension of Mechanics is not the only one that experiment obliges us to consider.

Experiment reveals to us many systems that are susceptible to permanent modification: elastic bodies for which pulling, bending and twisting result in permanent deformations; glass and metals which, after heating, retain a permanent dilation; sulphur, metals and alloys whose properties vary with quenching and annealing; and iron and steel capable of retaining a remnant of magnetism after removal from a magnetic field. These various effects display mutual analogies which were already recognised by Coulomb and Biot, which G. Wiedemann brought to light is a striking way, and which Ewing emphasised by coining a particular word, the word *hysteresis*, for the property [148] of retaining a permanent modification, whatever its nature.

The Statics of systems affected by hysteresis cannot be incorporated into the Statics of systems without friction, nor into the Statics of systems with friction.

Let us take a system at equilibrium at a certain temperature and under given external action. Suppose the temperature and the external actions are varied extremely slowly, in such a way that the system is at each instant in a state very close to equilibrium, and let us follow the change which this state undergoes.

If the system lacks friction, the set of equilibrium states thus obtained possesses a quite remarkable property: it is *reversible*. Let us, in accordance with a certain law, vary the collection of values of the temperature and the external actions. The system passes through a determinate series of states. If the collection of values of the temperature and the external actions then takes on the same determinations once more, but in the inverse order, then the system retraces, in inverse order, exactly the same states. When the temperature and the external actions return once more to their original values at the beginning of the modification, the system is returned to its original state.

Matters are quite different when the system is affected by friction. In that case, the gradual variation imposed on the temperature and the external actions will, in general, not result in any change of state of the system. Only when the variation attains a certain magnitude does the system undergo modification.

Systems capable of permanent modification clearly distinguish themselves both from systems without friction and systems with friction.

However little the temperature of, and the external actions on, a system susceptible of permanent modification might, with extreme slowness, be altered, [149] the equilibrium state of the system is altered. This is an essential difference between such a system and a system with friction.

If the temperature and the external actions are subjected to a certain variation with extreme slowness, then if the same variation is imposed in the inverse order, the modification undergone by the system under consideration does not reverse. At the start, it passes through a set of states, and on the return it passes through another set of states which is not the first run through in reverse order. When the temperature and the external actions assume their initial values, the system does not, in general, return to its original state; it retains a *permanent modification*.

The Statics of systems capable of permanent modification cannot therefore be subsumed under the Statics of systems without friction nor under the Statics of systems with friction. It must constitute a third Statics, distinct from the first two.

In order to briefly sketch the principles of the Statics of systems capable of permanent modification or, in other words, affected by *hysteresis*, we will consider a system defined by a single variable, α, in addition to the absolute temperature T.

If the system displayed neither friction nor hysteresis, and were thus subsumed under the Statics described in §II, all equilibrium states of the system would be given by the equality (1) which can still be written

$$A = \frac{\delta}{\delta\alpha} F(\alpha, T).$$

When A and T vary with infinite slowness, the magnitude α will vary in such a way that the preceding equality holds. The infinitely small variations dA, dT and $d\alpha$ of the three magnitudes will be connected by the relation

$$dA = \frac{\delta^2 F}{\delta\alpha^2} d\alpha + \frac{\delta^2 F}{\delta\alpha\delta t} dT \tag{15}$$

[150] Such a modification would evidently be reversible, because if the signs of dA and dT are changed without changing their absolute values, $d\alpha$ will change sign without changing its absolute value.

This would no longer be the case if the infinitely small modification were subjected, not to the relation (15), but to the relation

$$dA = \frac{\delta^2 F(\alpha, T)}{\delta\alpha^2} d\alpha + \frac{\delta^2 F(\alpha, T)}{\delta\alpha\delta T} dT + f(\alpha, A, T)|d\alpha|, \tag{16}$$

where $|d\alpha|$ designates the absolute value of $d\alpha$.

If dA and dT change sign without changing their absolute value, it cannot happen that $d\alpha$ simply changes sign without changing absolute value. If, after varying the temperature and the external action, both are returned to their initial value, the system does not in general return to its initial state; it retains a permanent modification.

The equality (16), or better the equalities that can be extracted by extending the same principle to systems which depend on an arbitrary number of variables, serve as the basis of the Statics of systems affected by permanent modifications.[4]

This new branch of general Statics encompasses a considerable number of facts.

These include, in the first place, all the facts of magnetic hysteresis, so well studied by Ewing and his imitators.

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[4] See P. Duhem, "Sur les déformations permanentes et hystérèsis," five Memoirs, *Mémoires in-4° de l'Académie de Belgique*, Vol. LIV and Vol. LVI, 1894 – 1898.—"Die dauernde Aenderungen und die Thermodynamik," eight Memoirs, *Zeitschrift für physikalische Chemie*, Vols. XXII, XXIII, XXVIII, XXXIII, XXXIV, XXXVII, 1897-1901.

In the second place, there is a large number of permanent elastic deformations produced by pulling, bending and twisting.

The [151] permanent changes produced in bodies by variations of temperature and designated by the terms *quenching* and *annealing* are illuminated and ordered by the new Statics. Not only does it render the properties of iron and steel less mysterious; it conforms in the minutest detail to the modifications of sulphur, which has been the object of Gernez's meticulous research, to the permanent dilations and contractions of glass, unravelled by the considerable work of L. Marchis, to the curious anomalies of nickel steel discovered by Ch. Ed. Guillaume, and to the permanent variations of electrical resistance studied by Chevalier.

The absorption of water vapour by colloidal substances observed over the course of long years by Van Bemmelen revealed to this experimentalist laws which also depend on the new Statics.

VI

THE DYNAMICS OF SYSTEMS EXHIBITING HYSTERESIS

It can be said that this new Statics gives a precise account of all the permanent modifications produced by the slow variation of external actions.

When these variations become rapid, the laws governing these modifications are altered. A large number of experiments, among them those of E. Lenoble, show that the law of elongation of a charged wire depends to a high degree on the speed of variation of the charge. The cycle of magnetic hysteresis of soft iron in a field subject to a rapid periodic variation changes in shape and position with change in the period of variation of the field.

These and many other observations show that [152] after formulating the Statics of systems affected by hysteresis, it is appropriate to construct the Dynamics of such systems.

The first idea to present itself was of simply bringing in d'Alembert's principle to deal with systems affected by hysteresis, and replacing the external action relative to each variable by the sum of this external action and the inertial action relative to the same variable. Consequently, the equality (16) is replaced by the equality

$$d(A+J_\alpha) = \frac{\delta^2 F(\alpha,T)}{\delta\alpha^2}d\alpha + \frac{\delta^2 F(\alpha,T)}{\delta\alpha\delta T}dT + f(\alpha,A+J_\alpha,T)|d\alpha|. \quad (17)$$

The dynamics of systems of hysteresis based on such a principle are sufficient to account for facts which would have escaped Statics. It provides, for example, a correct explanation of the damping undergone by the oscillations of a twisted wire.

It falls short of being what could be regarded as sufficient, however.

For a system without inertia, such a dynamics does not differ from Statics. If the magnitude α, which determines the properties of the system, does not entail any change of position for the various parts of the system by its variations, then the modifications undergone by the system are independent of the greater or lesser rapidity with which the temperature and external actions change. Thus, the changes in magnetisation of a piece of iron would be the same for the same variation of intensity of the field, whether this variation were slow or rapid.

This is not what experience teaches us, which contradicts the principle of Dynamics just outlined.

This contradiction and analogous contradictions would [153] be avoided if what was extended to systems affected by hysteresis were not d'Alembert's principle in its original form, but the modified d'Alembert principle outlined in §III for accommodating viscosity.

Thus, in order to pass from the Statics of systems affected by hysteresis to the Dynamics of such systems, we must substitute for the external action A to which each variable refers the sum of this action A, the action of inertia J_α and the action of viscosity V_α to which the same variable refers. In particular, we do not substitute equality (17) for equality (16), but the equality

$$d(A+J_\alpha+V_\alpha) = \frac{\delta^2 F(\alpha,T)}{\delta\alpha^2}d\alpha + \frac{\delta^2 F(\alpha,T)}{\delta\alpha\delta T}dT + f(\alpha,A+J_\alpha+V_\alpha,T)\,|d\alpha|. \quad (18)$$

In most cases, the action of viscosity V_α can be given the very simple form expressed by the equality

$$V_\alpha = -v(\alpha, T)\,\alpha', \quad (19)$$

where $v(\alpha, T)$ is a positive *coefficient of viscosity.*

We are now in possession of a Dynamics capable of encompassing the laws of motion of a system affected by hysteresis. This new Dynamics[5] shows how the deformations of an elastic body depend on the greater or lesser rapidity with which the external actions are varied. It allows for the complete discussion of changes in shape and position undergone during the hysteresis cycle when a piece of iron is placed in a field periodically oscillating between two given limits, however the period of oscillation of the field is changed.

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[5] This Dynamics is the subject of a memoir presented to the Royal Belgian Academy on 7 May, 1901.

VII

THERMAL PHENOMENA

General [154] Mechanics, some of whose principal branches we have just outlined, offers an advantage over the old Mechanics to which we have yet to draw attention.

The old Mechanics, exclusively devoted to the analysis of local movement, knew nothing of absorption and release of heat. This is not the case with the new Mechanics, which is not content to make precise the laws according to which the properties of material systems are preserved or modified; it also studies the exchange of heat accompanying all modifications.

The formulas which govern these exchanges of heat all depend, in fact, on the same magnitude, the *internal energy* $U(\alpha, \beta, \ldots, \lambda, T)$ of the system studied. Now the internal energy is very simply connected to the internal potential $F(\alpha, \beta, \ldots, \lambda, T)$ on which the equilibrium and movement of the system always depend. If E denotes the mechanical equivalent of heat, the following relation obtains between these two functions:

$$EU = F - T\frac{\delta F}{\delta T}. \tag{20}$$

Mechanical and thermal properties are thus seen to depend on the same doctrine that justly deserves its traditional name, *Thermodynamics*.

Among the general consequences which such a reconciliation furnishes, we begin by citing those concerning closed cycles. They justify and make precise certain of Clausius' brilliant insights.

Let [155] us consider a system which runs through a closed cycle and, in order not to get involved in irrelevant complications, let us suppose that in each state the temperature of the system is uniform. Let T designate this uniform value of the absolute temperature, and dQ the infinitesimally small quantity of heat released by the system during an elementary modification beginning at the instant when the temperature has the value T. Let us form, for the entire cycle, the integral

$$\int \frac{dQ}{T}$$

and let us study its properties for various kinds of system.

We will address systems *without friction* and *without hysteresis* first.

First, let us suppose that such a system traverses a closed cycle with infinite slowness. The cycle will be a set of equilibrium states. It will, moreover, be *reversible*. For such a cycle, we can write the equality

$$\int \frac{dQ}{T} = 0. \tag{21}$$

We can still write this equality if the cycle is described with a certain speed, but on condition that the actions of viscosity do no work in any of the elementary modifications constituting the cycle. This condition will be fulfilled if the system is not affected by viscosity, if it is one of those to which d'Alembert's principle can be applied in its original form. It will also be fulfilled under certain specific modifications of a viscous system.

But in general, in a viscous system which is transformed with a certain speed, the actions of viscosity do a certain work and this work is always negative. In that case, for a closed cycle described by [156] such a system, the equality (21) must be replaced by the inequality

$$\int \frac{dQ}{T} > 0. \tag{22}$$

We must also apply this inequality to a close cycle described by a system *with friction.*

Conditions (21) and (22) take a particularly simple form when the temperature remains invariable during the course of the cycle, in which case the cycle is said to be isothermic. The equality (21) becomes

$$\int dQ = 0; \tag{23}$$

The equality (22) becomes

$$\int dQ > 0. \tag{24}$$

But the principle of the conservation of energy in turn transforms the equality (23) and the inequality (24). If T_e is the work done by the external actions during the course of the cycle, and if $\mathfrak{J}_0$ is the initial value of the kinetic energy of the system and $\mathfrak{J}_1$ its final value, then the equality (23) can be written

$$T_e = \mathfrak{J}_1 - \mathfrak{J}_0, \tag{25}$$

while the inequality (24) can be written

$$T_e > \mathfrak{J}_1 - \mathfrak{J}_0. \tag{26}$$

This latter inequality can be regarded as expressing the *impossibility of perpetual motion.*

Clausius' inequality cannot be applied to just any closed cycle traversed by a system affected [157] by hysteresis.[6] Nevertheless, the inequality (24) remains applicable to all isothermic cycles traversed by such a system. Thus Hysteresis, like viscosity and friction, is not compatible with the possibility of perpetual motion.

The impossibility of a *perpetuum mobile,* taken by Sadi Carnot as the basis of his *Reflections on the motive power of heat,* remains one of the corner stones of the new Mechanics.

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[6] P. Duhem, "Die Ungleichung von Clausius und die Hysteresis" *Zeitschrift für physikalische Chemie,* Vol. XXXVII, p. 91, 1901.

ESSAY 8

ON BODIES AND MIXTURES OR COMBINATIONS*

In what is about to follow, we will represent a *body* as a linearly connected space filled, *in a continuous manner*, by a certain *matter*.

The notion of *matter* is reduced, however, in our mathematical scheme, to the following:

When two three-dimensional figures C and C′ are said to be *two distinct positions of the same body*, it is accepted that between each point M of figure C and each point M′ of figure C′ there exists a certain unequivocal correspondence which is expressed by this sentence: *The matter which was in* M *when the body occupied position* C *is to be found at* M′ *when it occupies* position C′.

We will not be discussing whether bodies are *in reality* continuous or formed of disjointed parts separated by the void—whether the disjointed parts have finite dimensions, albeit very small, or whether they are simple points. All such questions on the subject of the real constitution of bodies are not the object of Physics, but of Metaphysics; they have given and continue to give rise to lively debates between diverse schools of philosophy.

Physics seeks only to construe, by means of notions borrowed from Mathematics, a logical system which provides an approximate image of the laws relating to bodies. In order to [14] construct such a system, we are entirely free to represent a body, which our senses perceive as continuous, either by a continuous distribution of matter in a certain space, or by a discontinuous collection of very small atoms.

The latter mode of representation has been adopted by many theoreticians of physics. Poisson, in particular, employed it in systematic fashion because he believed he saw there the expression of the real constitution of bodies. Without wishing here to examine all the objections which confront this way of dealing with Physics, there is at least one that we can draw attention to now. The formulas to which it immediately leads always involve extensive sums of a very large number of disjoint, very small masses in very close proximity. To render these formulas

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* Section 2 (pp. 13-6) of Chapter 1, entitled "Preliminary Definitions," from *Traité d'énergétique ou de thermodynamique générale*, Gauthier-Villers, Paris (1911); 2 vols.

manageable in Analysis and, at the same time, to extract from them results which can be translated into experimental language, it is necessary to replace these sums, by means of a calculus of approximation, with integrals over continuous space, *spreading out*, as it were, the putative disjoint masses in some such way that their matter fills the intermediate spaces. In this way the continuity which was first rejected is restored to matter after the event. Now this conversion of sums to integrals is a very delicate and very tricky mathematical operation. It is difficult to bring it to a successful conclusion without avoiding tedious procedures. Besides, it always entails many entirely gratuitous hypotheses about the order of magnitude of molecules and their separations.

These difficulties are avoided by representing matter directly as continuous. Conducive as this mode of representation is in all branches of Physics to a simpler, clearer and more elegant theory than atomic or molecular representations afford, we will adopt it in preference to the latter without thereby claiming anything about the real constitution of bodies.

Let us consider two bodies A and B which, at a certain instant t, occupy regions a and b having no part in common. These two bodies are not always and necessarily located in distinct regions. The matter of which they are made might at one instant t', distinct from t, either earlier or later than t, furnish a continuous [15] unique body C occupying region c in such a way that each element w of the space within c, at the instant t', encloses a part of the matter which, at the instant t, formed the body A, as well as a part of the matter which, at the same instant t, formed the body B. The first of these two quantities occupied, at the instant t, an element of volume v of the region a and the second occupied, at the same instant t, an element of volume v' of the region b.

In the situation just described, the body C is said to result either from the *mixture*, or the *combination*, of bodies A and B.

Many physicists refuse to admit the possibility of combination or mixture as we have just defined it. They regard as impossible this intimate penetration by which the matter filling each element of volume of the continuous body C results from the confusion[1] of the matter that includes an element of the continuous body A and the matter that includes an element of the continuous body B. It is this impossibility that they call the *impenetrability of matter*.

For these physicists, the words *mixture* and *combination* in truth only represent appearances.

When we think we see the two bodies A and B blended into a new body C, the extremely small parts which form the discontinuous collections constituting each of these two bodies remain, in fact, distinct from one another. The small parts of body A are simply interposed between the small parts of body B, without the region occupied by one of the parts of body A having any part in common with the region

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[1] [I.e. in the sense of "mixture in which the distinction of the elements is lost" (*Shorter Oxford Dictionary*, 1993 ed.).]

occupied by one of the parts of body B. When sea salt is dissolved in water, the molecules of the sea salt are interposed between the molecules of water without penetrating them. In sulphur dioxide, each atom of sulphur is flanked by two atoms of oxygen, but these atoms are not in any way mixed.

In reality, do things conform to this latter theory, as is the view of the atomic and Cartesian school,[2] or do they conform to the former, as [16] the peripatetic doctrine would have it? This question comes under the heading of Metaphysics and not of Physics. In order to construct a symbolic representation of natural laws, which is its proper concern, theoretical Physics is free to adopt one or other mode of representation of mixture and combination. We will opt for the former because it always gives rise to simpler arguments and more elegant calculations.

Let us consider a body C formed by the mixing of two bodies A and B. The matter which, at the instant t, fills the element of volume w of the body C is composed of a part p of the matter which forms body A and a part q of the matter which forms body B. At a different time t', these two parts p and q are not necessarily united with one another in the same element of volume; the matter constituting the part p might fill an element of volume w' where it is either free or unified with a part q', different from q, of the matter of body B. At the same time, the matter which constitutes the part q might fill another element of volume w'' where it is either free or unified with a part p'', different from p, of the matter of body A.

Thus, when a body C is a mixture of two bodies, the matter filling each element of volume of this body is formed from the confusion of two quantities[3] taken from two different bodies and *these two quantities might be animated by different movements,* so that at each point of the mixture, at each instant, there might be occasion to consider two different speeds, each of these speeds being relative to one of the bodies which constitutes the mixture.

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[2] See, on this matter, P. Duhem, *Le mixte et la combinaison chimique: Essai sur l'évolution d'une idée*, Paris, 1902. [Translated here as *Mixture and Chemical Combination.*]

[3] *parties.* [The sense of "quantity" used here is not that of "magnitude" but of a particular body of matter.]

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