

# THERMO- DYNAMICS OF SMALL SYSTEMS

(Parts I and II)

The background of the cover features a complex abstract design. It consists of several overlapping shapes: a large blue bell-shaped curve at the top, a pink bell-shaped curve below it, and two pink shapes on the left and right sides that resemble the tails of a distribution curve. These shapes overlap to create various shades of blue and pink. The author's name is centered within a white, horizontally-oriented oval shape that overlaps the central part of the design.

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Terrell L. Hill

TWO VOLUMES BOUND AS ONE

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# THERMODYNAMICS OF SMALL SYSTEMS

PART I

To Julie, Lynn, and Ernie



## PREFACE

Small system thermodynamics should be of interest to three classes of readers: (1) experimentalists working with colloidal particles, polymers, or macromolecules; (2) theoreticians concerned with the preceding fields or with the statistical mechanics of any kind of finite system; (3) those with an interest in thermodynamics per se.

Part I contains the first six chapters of a projected total of fifteen chapters. A combined edition of Parts I and II should follow the present book in about a year.

This work is previously unpublished except for one paper in the *Journal of Chemical Physics*, a copy of which is appended. The research has been supported in part by grants from the Heart Institute of the U.S. Public Health Service, the National Science Foundation, and the Alfred P. Sloan Foundation.

There are several reasons why the first six chapters are being brought out separately at this time. First, the author hopes that this branch of thermodynamics will find application in experimental work. These applications should be expedited by the present edition. Second, readers with a borderline interest in the subject will probably find that Part I provides an adequate treatment for their needs. Third, small system thermodynamics might well serve as a special topic toward the end of a thermodynamics course. The first six chapters would furnish more than sufficient material for this purpose. Fourth, and most important, comments made by readers of Part I should result in improvements in the combined volume.

As presently planned, Chapters 7 to 15 will be concerned with the following subjects:

- Chapter 7. Environmental Variables  $N_1, \mu_2, p, T$
- Chapter 8. Environmental Variables  $N, V, T$
- Chapter 9. Environmental Variables  $N, V, E$
- Chapter 10. Environmental Variables  $\mu, p, T$
- Chapter 11. Electric and Magnetic Fields
- Chapter 12. Spherical Drops and Bubbles
- Chapter 13. Polydisperse Systems

Chapter 14. Higher Moments of Distribution Functions

Chapter 15. Difference Equations and Very Small Systems

The reader will find a brief discussion of some of these topics (Chapters 8, 9, 10, 12, and 14) in the appended *Journal of Chemical Physics* article.

The irreversible thermodynamics of small systems appears to be an interesting problem which we are investigating, but this subject will probably not be included in the combined volume.

This is a book on thermodynamics, not statistical mechanics. However, because of the present lack of experimental examples, it has been necessary to use statistical mechanical models for most of the illustrations. These have been selected primarily for their simplicity. There are in the literature a number of rather sophisticated statistical mechanical treatments of small systems which have not been mentioned.

As just implied, the statistical mechanics of small systems is not at all a new subject. But a parallel *thermodynamics* of small systems has been lacking. Our primary object here is to fill this gap.

Even the combined edition of this book will not be exhaustive. Many details and topics will be omitted. With few exceptions, experimental and theoretical applications are left to the future. The author hopes that this work represents the beginning of the subject, not the end.

The reader is assumed to have a good background in classical thermodynamics. Specifically, we shall be concerned here primarily with the so-called thermodynamics of open systems, that is, systems with variable mass and composition. An acquaintance with statistical mechanics will be found of considerable help, especially with the examples. But the main argument is purely thermodynamic in nature and the statistical mechanics can be omitted if necessary.

We shall occasionally use the following reference abbreviations:

S.M.: T. L. Hill, "Statistical Mechanics," McGraw-Hill, New York, 1956.

S.T.: T. L. Hill, "Statistical Thermodynamics," Addison-Wesley, Reading, Mass., 1960.

J.C.P.: T. L. Hill, *J. Chem. Phys.*, **36**, 3182 (1962).

The author is very much indebted to Drs. E. Menefee, A. Silberberg, and D. Stigter for reading the manuscript and making valuable suggestions.

T.L.H.

Eugene, Oregon  
July 1962



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## INTRODUCTION

In ordinary thermodynamics, thermodynamic functions are defined and mathematical interrelations between these functions are derived for *macroscopic* (strictly, infinite) systems only. Our main object in this book is to extend the range of validity of these definitions and interrelations to include small, nonmacroscopic systems (e.g., a single macromolecule or colloidal particle).

Let us turn immediately to a simple illustration. Suppose a certain one-component macroscopic solid has a Gibbs free energy  $F = Nf(p, T)$  where  $N$  = number of molecules in the sample and  $f$  is a function of  $p$  and  $T$  only. Several typical interrelations between thermodynamic functions are then

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{p, T} = \frac{F}{N} \quad (1-1)$$

and

$$-S = \left( \frac{\partial F}{\partial T} \right)_{N, p} = N \left( \frac{\partial f}{\partial T} \right)_p, \quad \left( \frac{\partial \mu}{\partial T} \right)_p = -\frac{S}{N}, \quad (1-2)$$

where  $\mu$  = chemical potential and  $S$  = entropy. Now consider a colloidal particle of the same solid, small enough that correction terms must be added to  $F$ . For example, suppose

$$F = Nf(p, T) + a(p, T)N^{2/3} + b(T) \ln N + c(p, T). \quad (1-3)$$

The term in  $N^{2/3}$  is a surface free energy, while the last two terms might be due, among other things, to rotation of the colloidal particle. In the limit  $N \rightarrow \infty$ ,  $F \rightarrow Nf$ , the macroscopic relationship.<sup>1</sup> But when the system (the colloidal particle) is small and all terms in Eq. (1-3) are retained, macroscopic thermodynamics is no longer applicable and equations such as (1-1) and (1-2) are no longer correct. Hence our aim is to generalize the equations of thermodynamics so that they will be valid for small systems like the one represented by Eq. (1-3) and will go over into ordinary thermodynamic equations as a limiting case (macroscopic system). Thus, we shall see in Section 1-3

<sup>1</sup> In referring to a mathematical expression, "macroscopic" will always imply the asymptotic relation in the limit  $N \rightarrow \infty$  (or  $V \rightarrow \infty$ , etc.).

and Chapter 2, for the above example, that two different chemical potentials  $\hat{\mu}$  and  $\mu$  must be defined (they become equal in a macroscopic system) and that we have, instead of Eqs. (1-1) and (1-2),

$$\hat{\mu} = \frac{F}{N}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{p, T}, \quad \left( \frac{\partial \hat{\mu}}{\partial N} \right)_{p, T} = \frac{\mu - \hat{\mu}}{N},$$

$$\left( \frac{\partial \hat{\mu}}{\partial T} \right)_{N, p} = -\frac{S}{N}, \quad \left( \frac{\partial \mu}{\partial T} \right)_{N, p} = -\left( \frac{\partial S}{\partial N} \right)_{p, T}.$$

In addition to "small" terms of order  $N^{2/3}$  and  $\ln N$ , as in Eq. (1-3), other typical small terms are of order  $N^{1/2}$  (surface of a two-dimensional system),  $N^{1/3}$  (second-order surface effect in three dimensions), unity ("surface" of a one-dimensional system or a small system without surfaces), etc. Small system effects will be particularly noticeable at phase transitions and in critical regions.

**ENSEMBLE OF SMALL SYSTEMS.** Macroscopic thermodynamics will of course apply to a large sample of small systems (e.g., a macromolecular solution), and macroscopic thermodynamic functions are well defined for such a sample. But we wish to pursue thermodynamics on a smaller scale here: we are interested in thermodynamic functions and interrelationships for a *single* small system, including, in general, variations in the size of the system (e.g.,  $N$ , the degree of polymerization or aggregation,  $V$ , the volume, etc.). Allowance for these variations in size is, indeed, the important new feature which would not be included in a conventional macroscopic thermodynamic treatment of a large sample of small systems where only the *number* of small systems (macromolecules, etc.) would be varied. Section 2-3 will make this particularly clear.

Our point of departure in the thermodynamics of small systems will in fact be to start with the macroscopic thermodynamics of a large sample of *independent* small systems (an "ensemble") and introduce  $N$ ,  $V$ , or other such assigned properties of the small systems as variable parameters. The use of an ensemble gives us a firm macroscopic starting point. We shall obtain in this way the desired fundamental thermodynamic equations for a small system. These equations will involve mean values of fluctuating extensive properties (e.g., the energy  $E$ ). The mean values will be averages over the ensemble. But experiments will in general be done on "ensembles" of small systems, so that the ensemble average is just what is required

operationally. Conceptually, however, one would like to think as well in terms of time averages for a single small system. For this purpose we have to borrow from statistical mechanics not only the above idea of using an ensemble but also the fundamental postulate that the time average of a property for a single system is equal to the corresponding ensemble average. This is the only new postulate necessary in order to define and use thermodynamic properties for a single small system. Otherwise the foundation of small system thermodynamics is based on macroscopic thermodynamics. From a strictly operational point of view even this postulate is not necessary if we always understand "average" to mean "ensemble average," not "time average." However, the equivalence of these two averages is so well established as a statistical mechanical postulate, for large or small systems, that we shall also adopt the postulate and not make any further distinction between the two averages.

There is no need to postulate the equality of ensemble and time averages in ordinary thermodynamics, because, in effect, it suffices for the ensemble to contain only a single (macroscopic) system.

**APPLICATIONS.** As with macroscopic thermodynamics, we may anticipate two main classes of applications of small system thermodynamics: (1) as an aid in analyzing, classifying, and correlating equilibrium experimental data on "small systems" such as (noninteracting) colloidal particles, liquid droplets, crystallites, macromolecules, polymers, polyelectrolytes, nucleic acids, proteins, etc.; and (2) to verify, stimulate, and provide a framework for statistical mechanical analysis of models of finite (i.e., "small") systems. A well-known experimental and theoretical example is the helix-coil transition in synthetic polypeptides. A single polymer chain is the system in this case. There are very appreciable effects of the degree of polymerization  $N$  on intensive properties of the system (e.g., the fraction of helical content). In macroscopic thermodynamics intensive properties are always independent of the size ( $N$  here) of a system. For a thermodynamic analysis of such size effects one must therefore turn to small system thermodynamics.

An atomic nucleus is a small system of nucleons and an atom is a small system of electrons. Thermodynamics might be of interest for such systems under extreme conditions of temperature.

Experimental small systems, with possible rare exceptions, are

“condensed” systems: a small solid or liquid particle; a macromolecule; etc. A small system which is a gas is, however, of some interest as a theoretical model (see Section 8-1, for example).

Statistical mechanics is not restricted to macroscopic systems,<sup>1</sup> and examples of the evaluation of statistical mechanical partition functions and other properties for finite systems have been fairly commonplace. However, a general corresponding small system thermodynamic framework has been lacking.<sup>2</sup> The applicability of statistical mechanical ensemble theory to small systems as well as large suggests strongly that a parallel thermodynamics should exist.

Examples of both the above-mentioned classes of applications, (1) and (2), will be considered in some detail in later chapters.

Implicit in the above discussion of applications is the following rather obvious remark, which, however, needs emphasizing. Small system thermodynamics can provide equations, especially differential equations, *connecting* thermodynamic functions, but the functions themselves must be measured experimentally or calculated from molecular theory (statistical mechanics). The same comment is of course true of macroscopic thermodynamics.

**OPERATIONAL DIFFERENCES.** There are some important respects in which experimental small thermodynamic systems differ operationally from macroscopic systems. (a) In general, as already mentioned, measurements are not made on a single small system, but on a large number of small systems. An example is a very dilute solution of a macromolecule: the “small system” is one macromolecule; the solution contains many macromolecules; but the solution must be very dilute so that the systems do not interact with each other. (b) A macroscopic system immersed in a reservoir may exchange heat, molecules, etc., with the reservoir, but the intermolecular interaction between the system and the reservoir at the surface of contact can be neglected in the thermodynamics of the system. This is in general no longer the case for a small system immersed in a solvent (the reservoir). The discussion we give in this introductory chapter does not include solvent effects explicitly. But in Chapter 2 and later chapters we shall see that the equations we obtain here are usually valid even

<sup>1</sup> See, for example, S.M., pp. 97–98 and Appendix 9, and S.T., Secs. 3-4 and 7-2.

<sup>2</sup> The special case of surface effects in drops and bubbles has of course been treated by Gibbs and others (see Chap. 12).



when solvent effects are present. All that is required is a reinterpretation of the meaning of various symbols. (c) Certain properties which can be varied at will, experimentally, in a macroscopic system cannot be so varied with a small system. An example is the volume of a colloidal particle. Another is the length of, or mechanical force  $f$  on, a free elastic macromolecule in solution. The only operationally possible case is that of  $f = \text{constant} = 0$ . There are, of course, no such restrictions in investigating the theoretical properties of a statistical mechanical model of a small system.

**DIFFERENCES IN THERMODYNAMIC TREATMENT.** We have already noted a few differences in the thermodynamic treatment of small and macroscopic systems (ensembles, size effects on intensive properties, etc.). There are two further important differences, which we now want to mention. First, consider, say, a macroscopic system of  $N$  molecules, volume  $V$ , immersed in a heat bath at  $T$ . Consider the same system at  $V$  and  $T$ , but in contact with a reservoir of molecules with the value of the chemical potential  $\mu$  chosen so that the mean  $\bar{N}$  has the same numerical value as  $N$  above. Then all thermodynamic functions, and all equations connecting the functions, are the same in the two cases. This is an illustration of the well-known fact that properties and equations in macroscopic thermodynamics are *independent of "environment"* (i.e., isothermal, isobaric, open, isolated, etc.). We shall see below that this is not the case with small systems: it is useful to give a separate discussion for each "environment," and the thermodynamic functions are different in each case. Of course, these differences are not of "macroscopic order"; they are significant for small systems but become negligible if the size of the system is increased indefinitely.

Section 1-4 shows that it is possible to derive a single set of thermodynamic equations applicable to all environments. This is an important result in principle, but for most purposes it is not the most convenient or illuminating approach.

Each environment, incidentally, can be characterized by its "environmental variables." For example, these variables in the two cases mentioned above are  $N, V, T$  and  $\mu, V, T$ , respectively.

The second point is the following. Ordinary thermodynamic equations connect mean values of those extensive quantities which fluctuate ( $E, N, V$ , etc., as the case may be). Only mean values are of interest, because fluctuations about the mean values are usually

completely negligible in magnitude relative to the mean values themselves. With small systems, however, fluctuations are larger, and hence higher moments of the probability distributions become of interest, as well as the mean values. In Chapter 14 we show that mean-value thermodynamic equations are the first members of a hierarchy of equations involving moments of different order. The treatment given in Chapter 14 will be thermodynamic, but the motivation and starting point come from statistical mechanics. That is, the connection between probability-distribution moments and thermodynamics must be provided by statistical mechanical ensemble theory.

**CONTINUOUS VARIABLES.** For the most part in this book we shall consider systems which are small enough that macroscopic thermodynamics is no longer adequate but large enough that nonfluctuating extensive properties may be regarded as continuously (not discretely) variable to whatever order of accuracy is required. For example, if we consider binding on a macromolecule with  $B$  binding sites, the usual experimental accuracy would require, for the above purpose, something like  $B \geq 10$  to 20. Intensive variables and (mean values of) fluctuating extensive variables are continuously variable in any case. Ordinarily we shall have in mind the first departures from macroscopic behavior. But in Chapter 3 we shall see that small system thermodynamics can be applied even to a single atom or small molecule as a "system," though there is no particular advantage to this point of view unless the size of the molecule can be varied systematically (e.g., the sequence of normal hydrocarbons). In general, when variations in nonfluctuating extensive properties must be regarded as discrete rather than continuous (e.g., when  $B < 10$  above), differentials of these properties in thermodynamic equations must be replaced by differences. This modification is the subject of Chapter 15.

In the remainder of this chapter, we establish the basic equations for a few of the more important sets of environmental variables. These cases, as well as others, are then carried much further in later chapters, where examples are given. We have rather arbitrarily chosen to give more details here on the  $\mu, V, T$  case, but the  $N, p, T$  case has been selected for the first complete discussion (Chapter 2).

The organization of and topics covered in the rest of the book will be clear from the Contents and Preface.



1-1. ENVIRONMENTAL VARIABLES  $\mu$ ,  $V$ ,  $T$ 

As our first case we consider a small, open, one-component system of volume  $V$  in contact with a heat and molecule reservoir at  $T$  and  $\mu$ . An experimental example would be a spherical colloidal particle or macromolecule with  $B$  surface binding sites ( $B$  is the analogue of  $V$ ), immersed in a solvent at  $T$  containing molecules at  $\mu$  which can be bound on the sites. The bound molecules, characterized by  $\mu$ ,  $B$ ,  $T$ , and not including the colloidal particle itself, are the "system" in this case. This involves the approximation of separability. A monatomic fluid at  $\mu$  and  $T$  in a cubical container of volume  $V$ , with periodic boundary conditions,<sup>1</sup> is a theoretical example.

In order to begin with a firm macroscopic thermodynamic foundation, we consider an ensemble of  $\mathcal{N}$  equivalent, distinguishable, independent systems, each with fixed center of mass, and all characterized by  $\mu$ ,  $V$ ,  $T$ . We let  $\mathcal{N} \rightarrow \infty$ . Hence the ensemble itself is a macroscopic thermodynamic system, however small a single system is. We use distinguishable systems with fixed center of mass to eliminate the translational degrees of freedom of the systems.<sup>2</sup> Thus we shall be concerned, below, with the "internal" thermodynamic properties of a single system. Rotation of the system will often be of negligible importance, or not taken into account, but it need not be excluded.

For the entire ensemble with a fixed value of  $\mathcal{N}$ , as a thermodynamic system, we have from macroscopic thermodynamics that

$$dE_t = T dS_t - p\mathcal{N}dV + \mu dN_t$$

or

$$dS_t = \frac{1}{T} dE_t + \frac{p\mathcal{N}}{T} dV - \frac{\mu}{T} dN_t,$$

where  $t$  = total refers to properties of the whole ensemble. The term  $-p\mathcal{N}dV$  is a conventional work term for the ensemble. Each system has the volume  $V$ , and any volume change  $dV$  is the same for all systems. The pressure  $p$  is a mean pressure (time or ensemble average). It can be defined formally by

$$p \equiv -\frac{1}{\mathcal{N}} \left( \frac{\partial E_t}{\partial V} \right)_{S_t, N_t, \mathcal{N}}.$$

<sup>1</sup> See, for example, B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, **33**, 1439 (1960); J. L. Lebowitz and J. K. Percus, *Phys. Rev.*, **124**, 1673 (1961).

<sup>2</sup> This step provides maximum simplicity but is more restrictive than necessary. We relax this restriction beginning in Chapter 2.

The entropy  $S_t$  is clearly a function not only of  $E_t$ ,  $V$ , and  $N_t$  but also of  $\mathcal{N}$  (or  $E_t$  is a function of  $S_t$ ,  $V$ ,  $N_t$ , and  $\mathcal{N}$ ). For example, if we increase  $\mathcal{N}$ , holding  $E_t$ ,  $V$ , and  $N_t$  constant,  $S_t$  will increase because the  $N_t$  molecules can now spread themselves over a larger number of systems of volume  $V$ . Thus the complete expression is [see also Eq. (1-64)]

$$dE_t = T dS_t - p \mathcal{N} dV + \mu dN_t + X d\mathcal{N} \quad (1-4)$$

or

$$dS_t = \frac{1}{T} dE_t + \frac{p \mathcal{N}}{T} dV - \frac{\mu}{T} dN_t - \frac{X}{T} d\mathcal{N},$$

where

$$X \equiv \left( \frac{\partial E_t}{\partial \mathcal{N}} \right)_{S_t, V, N_t} \quad \text{or} \quad -\frac{X}{T} \equiv \left( \frac{\partial S_t}{\partial \mathcal{N}} \right)_{E_t, V, N_t}.$$

The term  $X d\mathcal{N}$  in Eq. (1-4) may be regarded as another  $pV$  work term, for  $d\mathcal{N}$  implies that we are changing the volume of the ensemble, with  $S_t$  and  $N_t$  constant, by changing the number of available systems of volume  $V$  rather than by changing  $V$  for each of the  $\mathcal{N}$  systems. We therefore define a new pressure  $\hat{p}$  (read “ $p$  hat”) by  $-\hat{p}V \equiv X$ . Clearly  $\hat{p}$  may be considered an “integral” pressure, while  $p$  is a “differential” pressure. A moment’s reflection shows that there is no distinction between  $p$  and  $\hat{p}$  for a macroscopic system ( $V \rightarrow \infty$ ). But  $p$  and  $\hat{p}$  will in general differ for a small system, and both will deviate, by small terms, from the macroscopic pressure which would obtain at the same  $\mu$  and  $T$ .

Now suppose we hold  $\mu$ ,  $V$ ,  $T$  constant and double the value of  $\mathcal{N}$ . That is, we double the size of the ensemble without changing its nature otherwise. Then  $E_t$ ,  $S_t$ , and  $N_t$  will also double in value, while  $p$  and  $X$  remain constant. Hence, for this macroscopic system (the whole ensemble),  $E_t$  is a linear homogeneous function of  $S_t$ ,  $N_t$ , and  $\mathcal{N}$ , if  $\mu$ ,  $V$ , and  $T$  are held constant. The volume  $V$  has the status here of a parameter which is necessary, with  $\mu$  and  $T$ , to characterize completely a small system. On integrating Eq. (1-4), we obtain

$$E_t = TS_t + \mu N_t - \hat{p}V\mathcal{N}. \quad (1-5)$$

Next we define  $\bar{E}$ ,  $\bar{N}$ , and  $S$  by

$$E_t = \mathcal{N}\bar{E}, \quad N_t = \mathcal{N}\bar{N}, \quad S_t = \mathcal{N}S. \quad (1-6)$$

The quantities  $\bar{E}$  and  $\bar{N}$  are time or ensemble average values per system of the ensemble, since  $E$  and  $N$  fluctuate in an environment characterized by  $\mu$ ,  $V$ ,  $T$ .  $\bar{E}$  and  $\bar{N}$  are appropriately considered thermodynamic properties of a single small system. We do not put a bar over  $S$  because it is not an average value in the same sense. That is,  $S$  does not fluctuate in value but is a property of the complete probability distribution (see Section 1-2) in  $E$  and  $N$  for a single system;<sup>1</sup> hence  $S$  has the same value for each system in the ensemble. These comments about  $S$  are extrathermodynamic in nature and not essential to the argument. We shall verify in Section 1-2 that  $S$ , defined by  $S_t/\mathcal{N}$ , has the usual meaning of an entropy in statistical mechanics. The bars over  $E$  and  $N$  are optional but help remind one that, unlike  $V$ ,  $E$  and  $N$  are not environmental variables in this case.

We now return to the definitions in (1-6). Putting these in Eq. (1-5), we have

$$X = -\hat{p}V = \bar{E} - TS - \mu\bar{N}. \quad (1-7)$$

This verifies the statement above that  $p = \hat{p}$  for a macroscopic system, for in this case we know that

$$-pV = \bar{E} - TS - \mu\bar{N} \quad (V \text{ macroscopic}).$$

We substitute Eqs. (1-6) and (1-7) into Eq. (1-4) and find, after cancellation and division by  $\mathcal{N}$ ,

$$d\bar{E} = T dS - p dV + \mu d\bar{N} \quad (1-8)$$

$$dS = \frac{1}{T} d\bar{E} + \frac{p}{T} dV - \frac{\mu}{T} d\bar{N}. \quad (1-9)$$

On comparing Eq. (1-8) term by term with

$$\bar{E} = TS - \hat{p}V + \mu\bar{N}, \quad (1-10)$$

we see that  $\bar{E}$  is *not* a linear homogeneous function of  $S$ ,  $V$ , and  $\bar{N}$  as in macroscopic thermodynamics, since  $p \neq \hat{p}$  in general. This is what we should expect for a small system: if we hold  $\mu$  and  $T$  constant and double the value of  $V$ , because of edge effects, etc., we shall not exactly double the values of other extensive properties as for a macroscopic system. Similarly, intensive properties such as  $\bar{N}/V$ ,  $p$ ,

<sup>1</sup> See S.M., pp. 75-79.

$\hat{p}$ , etc., will change in value (i.e., they are functions of  $\mu$ ,  $T$  and  $V$ ). But in the macroscopic limit  $\hat{p}$  approaches  $p$ ,  $\bar{E}$  becomes a linear homogeneous function of  $S$ ,  $V$  and  $\bar{N}$ , and all intensive properties become functions of  $\mu$  and  $T$  only. Thus, for small systems, we have to abandon the conventional implications of the terms “extensive” and “intensive” properties. We shall still refer to extensive and intensive variables, however, basing the classification on the macroscopic limit.

Equation (1-8) has exactly the same form and physical significance as for a macroscopic system, and this proves to be the case for all environments (see Section 1-3). The essential difference between macroscopic and small system thermodynamics, for a  $\mu$ ,  $V$ ,  $T$  system, is exhibited then in Eq. (1-10), where  $\hat{p}$  occurs instead of  $p$ . Equation (1-10) can be rewritten as

$$\bar{E} = TS - pV + \mu\bar{N} + (p - \hat{p})V, \quad (1-11)$$

where the last term is a correction term which becomes negligible for a macroscopic system.

If we take the differential of both sides of Eq. (1-7) to obtain  $d(\hat{p}V)$  and use Eq. (1-8), we find

$$d(\hat{p}V) = S dT + p dV + \bar{N} d\mu. \quad (1-12)$$

This equation is especially useful since the independent variables are also the environmental variables. From Eq. (1-12), we have

$$\left(\frac{\partial \hat{p}V}{\partial T}\right)_{V, \mu} = S, \quad \left(\frac{\partial \hat{p}V}{\partial V}\right)_{T, \mu} = p, \quad \left(\frac{\partial \hat{p}V}{\partial \mu}\right)_{T, V} = \bar{N}. \quad (1-13)$$

The middle equation shows the integral-differential relation between  $\hat{p}$  and  $p$  already mentioned. For a macroscopic system,

$$\left(\frac{\partial \hat{p}V}{\partial V}\right)_{T, \mu} = \frac{\hat{p}V}{V} = \hat{p} = p.$$

We shall see in Section 1-2, as Eq. (1-12) suggests, that it is  $\hat{p}$  and not  $p$  which is directly related to the grand partition function for a small  $\mu$ ,  $V$ ,  $T$  system.

Equation (1-12) can also be written as

$$d\left(\frac{\hat{p}V}{T}\right) = -\bar{E} d\left(\frac{1}{T}\right) + \frac{p}{T} dV + \bar{N} d\left(\frac{\mu}{T}\right). \quad (1-14)$$

Another fundamental relation follows from Eqs. (1-8) and (1-11):

$$d[(p - \hat{p})V] = -S dT + V dp - \bar{N} d\mu, \quad (1-15)$$

or

$$d\left[\frac{(\hat{p} - p)V}{T}\right] = -\bar{E} d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + \bar{N} d\left(\frac{\mu}{T}\right). \quad (1-16)$$

The left-hand sides of these equations are zero for a macroscopic system: only two of  $T$ ,  $p$ , and  $\mu$  can be independent; there are two "degrees of freedom." We see here that a small system has one more degree of freedom than the corresponding macroscopic system. An equivalent statement was made above when it was noted that intensive properties are functions of  $V$  as well as of  $\mu$  and  $T$ , for a small system.

We conclude this section with a few remarks, which may be helpful, on another way of interpreting Eq. (1-4). The following section will then review the basic statistical mechanical equations for the  $\mu$ ,  $V$ ,  $T$  case. We shall continue both the thermodynamic and statistical mechanical analysis for this environment in Chapter 6.

**ALTERNATIVE INTERPRETATION.** Our point of view so far has been that the first four terms in Eq. (1-4) are typical terms in macroscopic thermodynamics and that the last term,  $X d\mathcal{N}$ , associated with the addition of further systems to the ensemble, is a new kind of term required for completeness and whose inclusion represents the essential step in our argument. But there is an alternative point of view. This is that the equation

$$dE_t = T dS_t + \mu dN_t + X d\mathcal{N} \quad (V \text{ constant})$$

is a typical macroscopic equation for a two-component system with numbers of "molecules"  $N_t$  and  $\mathcal{N}$ . The new feature is then that the second kind of molecule can vary in size, the size parameter being  $V$ . We want to allow in the thermodynamics for variations in this parameter; so we add a term in  $dV$ , with  $-p\mathcal{N} \equiv \partial E_t / \partial V$ , to again obtain Eq. (1-4).

Let us illustrate this with a particular model. Suppose that the small system consists of molecules from a reservoir at  $\mu$  and  $T$ , adsorbed on  $B$  sites on the surface of a distinguishable, independent, spherical colloidal particle with fixed center of mass. The colloidal particle is assumed for simplicity to be unperturbed by adsorbed molecules—it merely furnishes an adsorbing surface. We shall therefore subtract out the thermodynamic properties of the colloidal particles themselves. The size of the colloidal particle can be varied, and hence  $B$  can be varied. For a fixed value of  $B$  we then have

$$dE = T dS + \mu dN_t + \mu' d\mathcal{N}$$

$$dE_0 = T dS_0 + \mu'_0 d\mathcal{N}$$

$$dE_t = T dS_t + \mu dN_t + X d\mathcal{N}$$

$$E_t = E - E_0, \quad S_t = S - S_0, \quad X = \mu' - \mu'_0,$$

where the first equation refers to a macroscopic system of  $N_t$  adsorbed molecules and  $\mathcal{N}$  colloidal particles, the second equation refers to  $\mathcal{N}$  colloidal particles without any adsorbed molecules, and the third equation, the one we are really interested in, is obtained by subtraction and refers to  $N_t$  molecules adsorbed on spherical surfaces each with  $B$  sites. If we now allow variations in  $B$ , we must add to the respective equations the terms  $x dB$  (where  $x \equiv \partial E / \partial B$ ),  $x_0 dB$  (where  $x_0 \equiv \partial E_0 / \partial B$ ), and  $-p\mathcal{N} dB$ , where  $p$  is defined by  $-p\mathcal{N} = x - x_0$ . Thus we again obtain Eq. (1-4), with  $B$  in place of  $V$ .

## 1-2. STATISTICAL MECHANICAL DIGRESSION

We have already remarked, earlier in this chapter, that statistical mechanical ensemble theory is valid for small as well as large systems. It would seem worthwhile, however, to supplement this statement by reviewing a few of the basic equations in at least one case ( $\mu, V, T$ ). When we come to other environments, we shall make use of the corresponding statistical mechanical relations without further discussion.

Before turning to the  $\mu, V, T$  case in particular, let us first verify by a simple argument that  $S$ , defined by  $S_t / \mathcal{N}$ , has the usual meaning of an entropy in statistical mechanics for any environment. Let  $ijk \cdots$  represent a possible quantum state for an ensemble of  $\mathcal{N}$  equivalent, distinguishable, and independent systems, and let  $p_{ijk \cdots}$  be the probability of observing the ensemble in this state. Here  $i$  designates

the state of the first system,  $j$  the second, etc. Since the systems are equivalent and independent,

$$p_{ijk} \dots = p_i p_j p_k \dots,$$

where  $p_i$  is the probability of state  $i$  for the first system, etc. Then

$$\begin{aligned} S_t &= -k \sum_{ijk \dots} p_{ijk} \dots \ln p_{ijk} \dots \\ &= -k \sum_{ijk \dots} p_{ijk} \dots (\ln p_i + \ln p_j + \dots) \\ &= \mathcal{N} (-k \sum_i p_i \ln p_i), \end{aligned}$$

where we have used  $\sum_j p_j = 1$ . Thus  $S = -k \sum_i p_i \ln p_i$ , which is the standard form.<sup>1</sup> This entropy is additive ( $S_t = \mathcal{N}S$ ) irrespective of whether the system is small or large. The entropy  $S$  is not an average value of a mechanical variable, it is not defined for a single quantum state<sup>2</sup>  $i$  (as is a mechanical variable), but, rather, it is a property of the whole probability distribution  $p_1, p_2, \dots$ .

An ensemble of  $\mu, V, T$  systems is itself an open macroscopic system characterized by the independent variables  $\mu, V_t, T$ , where  $V_t = \mathcal{N}V$ . We have then the usual macroscopic relation

$$TS_t - E_t + \mu N_t = kT \ln \Xi_t,$$

where  $\Xi_t$  is the grand partition function for the ensemble of systems. From Eq. (1-5), then,

$$\bar{p}V\mathcal{N} = kT \ln \Xi_t.$$

But because of the independence, equivalence and distinguishability of the systems of the ensemble,<sup>3</sup>  $\Xi_t = \Xi^{\mathcal{N}}$ , where  $\Xi$  is the grand partition function of a single  $\mu, V, T$  system. Hence

$$\bar{p}V = kT \ln \Xi. \quad (1-17)$$

Thus we see that  $\bar{p}$  and not  $p$  is the pressure related to  $\Xi$  in this fundamental equation.

<sup>1</sup> See, for example, S.M., p. 75.

<sup>2</sup> See also L. D. Landau and E. M. Lifshitz, "Statistical Physics", pp. 26 and 350, Addison-Wesley, Reading, Mass., 1958.

<sup>3</sup> See also Section 7-2 of S.T.



We can write  $\Xi$  in the alternative forms

$$\Xi(\mu, V, T) = \sum_{j, N} e^{-E_j(N, V)/kT} e^{N\mu/kT} \quad (1-18)$$

$$= \sum_{E, N} \Omega(N, V, E) e^{-E/kT} e^{N\mu/kT} \quad (1-19)$$

$$= \sum_N Q(N, V, T) e^{N\mu/kT}, \quad (1-20)$$

where  $j$  is an energy state,  $\Omega$  is the degeneracy of the energy level  $E$ , and  $Q$  is the canonical ensemble partition function. The probability of observing the state  $j, N$  is

$$p_{jN} = \frac{e^{-E_j/kT} e^{N\mu/kT}}{\Xi}.$$

Then it is easy to verify that

$$\left( \frac{\partial \ln \Xi}{\partial 1/kT} \right)_{V, \mu/kT} = - \sum_{j, N} p_{jN} E_j(N, V) = -\bar{E} \quad (1-21)$$

$$\left( \frac{\partial \ln \Xi}{\partial \mu/kT} \right)_{V, 1/kT} = \bar{N} \quad (1-22)$$

$$\left( \frac{\partial \ln \Xi}{\partial V} \right)_{1/kT, \mu/kT} = - \frac{1}{kT} \overline{\frac{\partial E_j}{\partial V}} = - \frac{p}{kT} \quad (1-23)$$

and

$$\sum_{j, N} p_{jN} \ln p_{jN} = -\ln \Xi + \frac{\mu \bar{N}}{kT} - \frac{\bar{E}}{kT} = -\frac{S}{k},$$

in agreement with Eqs. (1-10) and (1-14). All the above equations, starting with (1-18), are formally unchanged from macroscopic statistical mechanics. The difference lies in the fact that for a small system  $\ln \Xi$  is equal to  $\bar{p}V/kT$  and not  $pV/kT$ .

### 1-3. OTHER ENVIRONMENTS

In this section we give a very brief introduction to a few other cases. Each of these will be pursued at some length in a later chapter.



ENVIRONMENTAL VARIABLES  $N$ ,  $p$ ,  $T$ . This is a closed one-component system in contact with a heat bath, and at pressure  $p$ . Some examples would be a small colloidal particle or crystallite made up of  $N$  molecules or a linear hydrocarbon molecule with  $N$  carbon atoms, both in an inert solvent. Another example is an incompressible linear macromolecule consisting of  $N$  monomers, each of which can exist in two or more states of different length (e.g., the helix-coil transition in synthetic polypeptides and polynucleotides). Here  $V$  = length, which fluctuates, and  $p$  = force on chain = 0, since the chain has free ends in solution. As already mentioned earlier in this chapter, there is no experimental way to vary the force here. Alternatively, the different states may be regarded as different components, with an isomeric chemical equilibrium between them (Chapter 5).

Formally this case is the same as the  $\mu$ ,  $V$ ,  $T$  case just discussed because there are two intensive variables and one extensive variable. As we shall see, we need only replace  $\mu$  by  $-p$ ,  $\bar{N}$  by  $\bar{V}$ ,  $-p$  by  $\mu$ ,  $-\bar{p}$  by  $\hat{\mu}$ , and  $V$  by  $N$ .

For an ensemble of  $N$ ,  $p$ ,  $T$  systems, the analogue of Eq. (1-4) is [see also Eq. (1-65)],

$$dE_t = T dS_t - p dV_t + \mu \mathcal{N} dN + X d\mathcal{N}, \quad (1-24)$$

where

$$X \equiv \left( \frac{\partial E_t}{\partial \mathcal{N}} \right)_{S_t, V_t, N}.$$

The physical significance of the  $X d\mathcal{N}$  term is that we are adding systems to the ensemble, each containing  $N$  molecules, in such a way that  $S_t = \mathcal{N}S$  and  $V_t = \mathcal{N}\bar{V}$  are held constant. This is a chemical potential type of term; so we define  $\hat{\mu}$  by  $\hat{\mu}N \equiv X$ . Whereas  $\mu$  is a "differential" chemical potential (molecules are added to the ensemble by changing  $N$  in each of the  $\mathcal{N}$  systems),  $\hat{\mu}$  is an "integral" chemical potential (molecules are added to the ensemble in "packages" of  $N$  each). In general, for a small system,  $\mu$  and  $\hat{\mu}$  differ from each other and from the macroscopic chemical potential at the same  $p$  and  $T$ . Both  $\mu$  and  $\hat{\mu}$  approach this macroscopic value as  $N \rightarrow \infty$ .

Integration of Eq. (1-24),  $T$ ,  $p$ , and  $N$  being held constant, gives

$$E_t = TS_t - pV_t + \hat{\mu}N\mathcal{N}$$

and

$$\bar{E} = TS - p\bar{V} + \hat{\mu}N. \quad (1-25)$$

If we use Eq. (1-25) to eliminate  $X = \hat{\mu}N$  in Eq. (1-24), we find

$$d\bar{E} = T dS - p d\bar{V} + \mu dN. \quad (1-26)$$

Equation (1-25) can also be written as

$$\bar{E} = TS - p\bar{V} + \mu N + (\hat{\mu} - \mu)N. \quad (1-27)$$

The last term vanishes for a macroscopic system.

Other fundamental equations are

$$d(\hat{\mu}N) = -S dT + \bar{V} dp + \mu dN \quad (1-28)$$

$$d[(\hat{\mu} - \mu)N] = -S dT + \bar{V} dp - N d\mu. \quad (1-29)$$

Again we note that there is an extra degree of freedom for a small system.

If we define the Gibbs free energy  $F$  by

$$F \equiv \hat{\mu}N = \bar{E} - TS + p\bar{V} = X, \quad (1-30)$$

then

$$\left(\frac{\partial \hat{\mu}N}{\partial N}\right)_{T, p} = \left(\frac{\partial F}{\partial N}\right)_{T, p} = \mu, \quad (1-31)$$

but  $F/N = \hat{\mu}$ .

The connection with statistical mechanics is

$$-\hat{\mu}N = kT \ln \Delta, \quad (1-32)$$

where

$$\begin{aligned} \Delta(N, p, T) &= \sum_{E, V} \Omega(N, V, E) e^{-E/kT} e^{-pV/kT} \\ &= \sum_V Q(N, V, T) e^{-pV/kT}. \end{aligned}$$

ENVIRONMENTAL VARIABLES  $N_1, N_2, \dots, p, T$ . This is a multi-component  $N, p, T$  system. A binary colloidal particle in an

inert solvent is an example. The extension of Eqs. (1-24) to (1-26) is

$$dE_t = T dS_t - p dV_t + \mu_1 \mathcal{N} dN_1 + \mu_2 \mathcal{N} dN_2 + \cdots + X d\mathcal{N} \quad (1-33)$$

$$E_t = TS_t - pV_t + X\mathcal{N}$$

$$\bar{E} = TS - p\bar{V} + X \quad (1-34)$$

$$d\bar{E} = T dS - p d\bar{V} + \mu_1 dN_1 + \mu_2 dN_2 + \cdots \quad (1-35)$$

$$\bar{E} \neq TS - p\bar{V} + \mu_1 N_1 + \mu_2 N_2 + \cdots.$$

If we define the Gibbs free energy  $F$  by

$$F = \bar{E} - TS + p\bar{V}, \quad (1-36)$$

then  $F = X$  and

$$dF = -S dT + \bar{V} dp + \mu_1 dN_1 + \mu_2 dN_2 + \cdots \quad (1-37)$$

$$\begin{aligned} d[F - (\mu_1 N_1 + \mu_2 N_2 + \cdots)] \\ = -S dT + \bar{V} dp - N_1 d\mu_1 - N_2 d\mu_2 - \cdots. \end{aligned} \quad (1-38)$$

In statistical mechanics,

$$-F = kT \ln \Delta(N_1, N_2, \cdots, p, T). \quad (1-39)$$

It should be noted that there is no particular reason here to define an intensive quantity analogous to  $\hat{\mu}$  or  $\hat{p}$ . This procedure will be useful only when the environmental variables include one and only one extensive variable, as in the  $\mu$ ,  $V$ ,  $T$  and  $N$ ,  $p$ ,  $T$  cases. The intensive "hat" variable is then conjugate to the one extensive variable.

Incidentally, for the physically unrealistic set of environmental variables  $\mu/T$ ,  $p/T$ ,  $E$ , one finds, instead of Eqs. (1-10), (1-14), and (1-16),

$$S = \frac{p}{T} \bar{V} - \frac{\mu}{T} \bar{N} + \frac{1}{\hat{T}} E \quad (1-40)$$

$$d\left(\frac{E}{\hat{T}}\right) = \frac{1}{T} dE - \bar{V} d\left(\frac{p}{T}\right) + \bar{N} d\left(\frac{\mu}{T}\right) \quad (1-41)$$

$$d\left[\left(\frac{1}{\hat{T}} - \frac{1}{T}\right)E\right] = -E d\left(\frac{1}{T}\right) - \bar{V} d\left(\frac{p}{T}\right) + \bar{N} d\left(\frac{\mu}{T}\right). \quad (1-42)$$

ENVIRONMENTAL VARIABLES  $N, V, T$ . This is a closed system at constant volume (area, length, etc.), in contact with a heat bath at  $T$ . This case is important in work with statistical mechanical models of finite systems because the canonical ensemble partition function  $Q(N, V, T)$  is very often used. But this set of environmental variables is not easily realized experimentally on account of the difficulty of holding  $V$  constant in a small system.

For an ensemble of  $N, V, T$  systems we write

$$dE_t = T dS_t - p \mathcal{N} dV + \mu \mathcal{N} dN + X d\mathcal{N}. \quad (1-43)$$

On integrating with  $N, V, T$  held constant, we find

$$E_t = TS_t + X\mathcal{N}, \quad X = \bar{E} - TS.$$

We replace  $X$  in Eq. (1-43) by  $\bar{E} - TS$ , put  $E_t = \mathcal{N}\bar{E}$ ,  $S_t = \mathcal{N}S$ , and obtain

$$d\bar{E} = T dS - p dV + \mu dN, \quad \bar{E} \neq TS - pV + \mu N. \quad (1-44)$$

If we define the Helmholtz free energy  $A$  by

$$A \equiv X = \bar{E} - TS, \quad (1-45)$$

then

$$dA = -S dT - p dV + \mu dN \quad (1-46)$$

$$d(A + pV - \mu N) = -S dT + V dp - N d\mu. \quad (1-47)$$

In statistical mechanics,

$$-A = kT \ln Q(N, V, T). \quad (1-48)$$

At this point let us digress to illustrate qualitatively, with a simple example, the fact that thermodynamic functions for small systems are in general different in different environments. Quantitative examples will arise in later chapters. Let a single small system consist of molecules bound, at  $T$ , on a pair of sites, not more than one molecule per site. Thus, instead of a volume  $V$ , we use  $B$  = number of sites = 2. If both sites are occupied, there is an interaction energy between the two molecules. We consider  $\mathcal{N}$  of these small systems. In one case each system is closed, and we take  $N$  = number of molecules in a system = 1. The environmental variables are then  $N, B$ ,

$T$ . The fact that the system is *very* small is no problem if we do not try to vary  $N$  or  $B$ . In a second case, the systems are open, and we choose  $\mu$  so that  $\bar{N} = 1$ . The environmental variables are  $\mu$ ,  $B$ ,  $T$ . In both cases each system has the same  $N$  or  $\bar{N}$ ,  $B$ , and  $T$ . But other thermodynamic functions for one of these systems are obviously different. For example, consider  $\bar{E}$ . The contribution of the interaction energy to  $\bar{E}$  is exactly zero in the closed case because each system always has  $N = 1$  and never  $N = 2$  (hence, no interaction). But in the open case any system will sometimes have  $N = 0$ ,  $N = 1$ , and  $N = 2$ , with an average of  $\bar{N} = 1$ . Thus there will be a nonzero average interaction energy. Also, it is obvious that  $S_t(\text{open}) > S_t(\text{closed})$ , and therefore  $S(\text{open}) > S(\text{closed})$ , because all the ways of distributing the  $N_t = \mathcal{N}$  molecules among the  $2\mathcal{N}$  sites in the closed case are available in the open case, and many other distributions as well (involving  $N = 0$  and  $N = 2$  for some systems).

ENVIRONMENTAL VARIABLES  $N$ ,  $V$ ,  $E$ . So far we have discussed systems which are partially "open" and partially "closed". That is, some of the environmental variables are extensive ("closed") and some are conjugate intensive ("open") variables. In this subsection and the next we consider the two extreme cases for a one-component system: completely closed (i.e., "isolated," with environmental variables  $N$ ,  $V$ ,  $E$ ); or completely open (environmental variables  $\mu$ ,  $p$ ,  $T$ ). A completely closed system is important theoretically but not experimentally. The related case  $N$ ,  $E$ ,  $p = 0$  is, however, of some interest (e.g., a nonvolatile crystallite in a vacuum).

The analogue of Eq. (1-43) for an ensemble of isolated systems, each with  $N$ ,  $V$ ,  $E$ , is

$$\mathcal{N} dE = T dS_t - p\mathcal{N} dV + \mu\mathcal{N} dN + X d\mathcal{N}. \quad (1-49)$$

Here,  $S_t$  is a linear homogeneous function of  $\mathcal{N}$  when  $E$ ,  $V$ , and  $N$  are held constant. Therefore

$$0 = TS_t + X\mathcal{N}, \quad X = -TS. \quad (1-50)$$

Equation (1-49) then simplifies to

$$dE = T dS - p dV + \mu dN, \quad (1-51)$$

or

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN. \quad (1-52)$$

The connection with statistical mechanics is  $S = k \ln \Omega(N, V, E)$ . In general,  $E \neq TS - pV + \mu N$ . In fact,

$$d(E - TS + pV - \mu N) = -S dT + V dp - N d\mu, \quad (1-53)$$

or

$$d\left(S - \frac{pV}{T} + \frac{\mu N}{T} - \frac{E}{T}\right) = -E d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + N d\left(\frac{\mu}{T}\right). \quad (1-54)$$

ENVIRONMENTAL VARIABLES  $\mu$ ,  $p$ ,  $T$ . Here we have a “completely open” one-component system. This is a particularly important case, both theoretically and experimentally. Examples are a colloidal aggregate in a solvent at  $p$  and  $T$ , the solvent containing molecules of the aggregate at  $\mu$ , or a liquidlike cluster of molecules in a gas near the critical point.

The “ensemble equation” is

$$dE_t = T dS_t - p dV_t + \mu dN_t + X d\mathcal{N}, \quad (1-55)$$

and hence

$$E_t = TS_t - pV_t + \mu N_t + X\mathcal{N} \\ X = \bar{E} - TS + p\bar{V} - \mu\bar{N} \quad (1-56)$$

$$d\bar{E} = T dS - p d\bar{V} + \mu d\bar{N} \quad (1-57)$$

$$dX = -S dT + \bar{V} dp - \bar{N} d\mu \quad (1-58)$$

$$d\left(-\frac{X}{T}\right) = -\bar{E} d\left(\frac{1}{T}\right) - \bar{V} d\left(\frac{p}{T}\right) + \bar{N} d\left(\frac{\mu}{T}\right). \quad (1-59)$$

In a macroscopic system,  $X = 0$ .

The relation to statistical mechanics is

$$-X = kT \ln \Upsilon \quad (1-60)$$

$$\Upsilon = \sum_{N, V, E} \Omega(N, V, E) e^{-E/kT} e^{-pV/kT} e^{N\mu/kT} \quad (1-61)$$

$$= \sum_V \Xi(\mu, V, T) e^{-pV/kT} \quad (1-62)$$

$$= \sum_N \Delta(N, p, T) e^{N\mu/kT}. \quad (1-63)$$

This partition function requires special care when used with a macroscopic system,<sup>1</sup> basically because of the fact that  $T$ ,  $p$ , and  $\mu$  cannot all be independent. But we have already seen with other environments that  $T$ ,  $p$ , and  $\mu$  *can* be independent in the thermodynamics of small systems. We might therefore anticipate that there is no special difficulty in applying  $\Upsilon$  to a completely open small system, and this proves to be the case (Chapter 10).

#### 1-4. GENERAL TREATMENT OF ENVIRONMENTS

First, in this section, we make a few summarizing observations on the above discussion of various environments. We then turn to a single, general treatment applicable to all environments. This will demonstrate that, although thermodynamic *functions* are different for different environments with small systems, the same thermodynamic *equations* are valid for all environments. In other words, the equations derived above for various environments are really all equivalent. However, for most practical purposes, it is both natural and illuminating to pursue a superficially separate analysis for each environment because: (a) as just mentioned, the values of the thermodynamic functions are in general different for each environment; (b) a particular set of independent variables (i.e., the environmental variables) has unique importance operationally and theoretically in each case; (c) a particular statistical mechanical partition function must be used (instead of having an option, as in macroscopic statistical mechanics); and (d) some of the work in later chapters *requires* this type of treatment (e.g., the treatment of solvent effects in Section 2-3, first-order phase transitions, and the higher moment equations in Chapter 14).

In the ensemble equations (1-4), (1-24), (1-43), and (1-55), the extensive but not the intensive environmental variables appear as independent variables. It is worthwhile rewriting these equations so that all environmental variables are independent. This is already the case in Eq. (1-49), incidentally. We have:

$\mu, V, T$ :

$$d(E_t - TS_t - \mu N_t) = -S_t dT - p \mathcal{N} dV - N_t d\mu + X d\mathcal{N} \quad (1-64)$$

$$\begin{aligned} X &= \left[ \frac{\partial(E_t - TS_t - \mu N_t)}{\partial \mathcal{N}} \right]_{\mu, V, T} = \frac{E_t - TS_t - \mu N_t}{\mathcal{N}} \\ &= \bar{E} - TS - \mu \bar{N} = -kT \ln \Xi; \end{aligned}$$

<sup>1</sup> See S.M., pp. 71-75 and Appendixes 2-4.



$N, p, T$ :

$$d(E_t - TS_t + pV_t) = -S_t dT + V_t dp + \mu \mathcal{N} dN + X d\mathcal{N} \quad (1-65)$$

$$\begin{aligned} X &= \left[ \frac{\partial(E_t - TS_t + pV_t)}{\partial \mathcal{N}} \right]_{N, p, T} = \frac{E_t - TS_t + pV_t}{\mathcal{N}} \\ &= \bar{E} - TS + p\bar{V} = -kT \ln \Delta; \end{aligned}$$

$N, V, T$ :

$$d(E_t - TS_t) = -S_t dT - p \mathcal{N} dV + \mu \mathcal{N} dN + X d\mathcal{N} \quad (1-66)$$

$$\begin{aligned} X &= \left[ \frac{\partial(E_t - TS_t)}{\partial \mathcal{N}} \right]_{N, V, T} = \frac{E_t - TS_t}{\mathcal{N}} \\ &= \bar{E} - TS = -kT \ln Q; \end{aligned}$$

$\mu, p, T$ :

$$d(E_t - TS_t + pV_t - \mu N_t) = -S_t dT + V_t dp - N_t d\mu + X d\mathcal{N} \quad (1-67)$$

$$\begin{aligned} X &= \left[ \frac{\partial(E_t - TS_t + pV_t - \mu N_t)}{\partial \mathcal{N}} \right]_{\mu, p, T} = \frac{E_t - TS_t + pV_t - \mu N_t}{\mathcal{N}} \\ &= \bar{E} - TS + p\bar{V} - \mu\bar{N} = -kT \ln \Upsilon. \end{aligned}$$

Finally, from Eq. (1-49) for the  $N, V, E$  case:

$$\begin{aligned} X &= T \left[ \frac{\partial(-S_t)}{\partial \mathcal{N}} \right]_{N, V, E} = \frac{-TS_t}{\mathcal{N}} \\ &= -TS = -kT \ln \Omega. \end{aligned}$$

We see from the above summary that  $X$  is always the thermodynamic "characteristic function" for the environmental variables;  $X$  is equal to  $-kT$  multiplied by the logarithm of the appropriate partition function. This comes about because the Legendre transformation necessary to make the environmental variables independent on the right-hand side of Eqs. (1-64) to (1-67) produces, at the same time, the ensemble characteristic function (for example,  $E_t - TS_t$ ) on the left-hand side.<sup>1</sup>

In the ensemble equations referred to above and rewritten in Eqs. (1-64) to (1-67), systems are added to the ensemble, in defining  $X$ ,

<sup>1</sup> See S.T., p. 31.



holding variables constant which are particularly appropriate to each environment. Although natural, this is an arbitrary procedure. We outline an alternative method here which is the same for all environments. This leads to a single set of thermodynamic equations which we shall make use of, to some extent, in later chapters.

Our procedure is simply to add systems to the ensemble, for *any* environment, as in Eq. (1-55) for a completely open system. We omit bars over  $E$ ,  $V$ , and  $N$  in order to have a single notation for all cases. With or without bars we have, of course,

$$E_t = \mathcal{N}E, \quad V_t = \mathcal{N}V, \quad N_t = \mathcal{N}N, \quad S_t = \mathcal{N}S.$$

Thus we write, for any number of components,

$$dS_t = \frac{1}{T} dE_t + \frac{p}{T} dV_t - \sum_i \frac{\mu_i}{T} dN_{ti} + \mathcal{S} d\mathcal{N} \quad (1-68)$$

or

$$dE_t = T dS_t - p dV_t + \sum_i \mu_i dN_{ti} + \mathcal{E} d\mathcal{N}, \quad (1-69)$$

where

$$\mathcal{S} \equiv \left( \frac{\partial S_t}{\partial \mathcal{N}} \right)_{E_t, V_t, N_{ti}}, \quad \mathcal{E} \equiv \left( \frac{\partial E_t}{\partial \mathcal{N}} \right)_{S_t, V_t, N_{ti}}, \quad \mathcal{S} = -\frac{\mathcal{E}}{T}. \quad (1-70)$$

Obviously  $\mathcal{E}$  and  $\mathcal{S}$  are not independent; we introduced both of them for convenience only. In defining  $\mathcal{S}$ , systems are added to the ensemble holding  $E_t$ ,  $V_t$ , and the  $N_{ti}$  constant. Hence  $E$ ,  $V$ , and the  $N_i$  are decreased as  $\mathcal{N}$  increases. The ensemble is divided into a larger number of smaller "pieces," keeping the total energy, volume, and numbers of molecules the same. In a very general sense, this is a special case of a chemical reaction. If the systems are macroscopic, this division of the ensemble into smaller systems will not affect the value of  $S_t$  at all. In this case  $\mathcal{S}$  vanishes. Analogous remarks can be made about  $\mathcal{E} \equiv \partial E_t / \partial \mathcal{N}$ . The term  $\mathcal{E} d\mathcal{N}$  in Eq. (1-69) might be called the "subdivision energy" and  $\mathcal{E}$  itself the "subdivision potential" (see Chapter 10).  $\mathcal{E}$  may be positive or negative.

Of course  $\mathcal{E}$  is the same as  $X$  in the special case of a completely open system, but we have introduced new notation because we shall use the symbols  $\mathcal{S}$  and  $\mathcal{E}$  for all environments.

On integration of Eq. (1-68) or (1-69), we find

$$E_t = TS_t - pV_t + \sum_i \mu_i N_{it} + \mathcal{E} \mathcal{N}$$

$$E = TS - pV + \sum_i \mu_i N_i + \mathcal{E} \quad (1-71)$$

$$S = \frac{1}{T}E + \frac{p}{T}V - \sum_i \frac{\mu_i}{T}N_i + \mathcal{S}. \quad (1-72)$$

Thus  $\mathcal{E}$  and  $\mathcal{S}$  are correction terms, required for a small system, but equal to zero for a macroscopic system. We also deduce, from Eqs. (1-68) to (1-72),

$$dE = T dS - p dV + \sum_i \mu_i dN_i \quad (1-73)$$

$$d\mathcal{E} = -S dT + V dp - \sum_i N_i d\mu_i \quad (1-74)$$

$$d\mathcal{S} = -E d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + \sum_i N_i d\left(\frac{\mu_i}{T}\right). \quad (1-75)$$

Equations (1-71) to (1-75) are fundamental for a small system and are applicable to any environment. We emphasize again, though, that the thermodynamic functions (for example,  $S$ ,  $\mathcal{E}$ , etc.) will in general be different for different environments. Of course only one of (1-71) and (1-72) and one of (1-73) to (1-75) are independent. Note that the familiar equation (1-73) is valid for a small as well as a large system. This confirms what we found with each of the environments investigated separately, earlier in the chapter. But small system thermodynamics departs from macroscopic thermodynamics in that  $E$  in Eq. (1-73) is not a linear homogeneous function of  $S$ ,  $V$ , and the  $N_i$ . Hence, an extra term  $\mathcal{E}$  occurs in Eq. (1-71). These last two sentences epitomize the whole book.

The connection between the present notation and that of Sections 1-1 and 1-3 is as follows:

$$\mu, V, T: \quad \mathcal{E} = (p - \hat{p})V \quad (1-76)$$

$$N, p, T: \quad \mathcal{E} = (\hat{\mu} - \mu)N \quad (1-77)$$

$$N_1, N_2, \dots, p, T: \quad \mathcal{E} = F - \sum_i \mu_i N_i \quad (1-78)$$

$$N, V, T: \quad \mathcal{E} = A + pV - \mu N. \quad (1-79)$$

The characteristic functions  $X$  are:

$$\mu, V, T: \quad X = -\hat{p}V = -pV + \mathcal{E} = E - TS - \mu N \quad (1-80)$$

$$N, p, T: \quad X = \hat{\mu}N = \mu N + \mathcal{E} = E - TS + pV \quad (1-81)$$

$$N_1, N_2, \dots, p, T: \quad X = F = \sum_i \mu_i N_i + \mathcal{E} = E - TS + pV \quad (1-82)$$

$$N, V, T: \quad X = A = \mu N - pV + \mathcal{E} = E - TS \quad (1-83)$$

$$N, V, E: \quad X = \mu N - pV - E + \mathcal{E} = -TS \quad (1-84)$$

$$\mu, p, T: \quad X = \mathcal{E} = E - TS + pV - \mu N. \quad (1-85)$$

The ensemble equations (1-4), (1-24), etc., in which the symbol  $X$  was introduced, can easily be converted into Eq. (1-69). For example, in Eq. (1-4) we add and subtract a term  $pV d\mathcal{N}$ :

$$\begin{aligned} dE_t &= T dS_t - p\mathcal{N} dV - pV d\mathcal{N} + \mu dN_t + X d\mathcal{N} + pV d\mathcal{N} \\ &= T dS_t - p dV_t + \mu dN_t + (X + pV) d\mathcal{N}, \end{aligned}$$

where  $X + pV = \mathcal{E}$ . Note that

$$\mathcal{E} = \left[ \frac{\partial(E_t - TS_t - \mu N_t)}{\partial \mathcal{N}} \right]_{\mu, T, V}.$$

Similarly,

$$\mathcal{E} = \left[ \frac{\partial(E_t - TS_t + pV_t)}{\partial \mathcal{N}} \right]_{p, T, N_t},$$

etc. These should be compared with the expressions for  $X$  in Eqs. (1-64) and (1-65).

Equation (1-69) can be rewritten in the form

$$\begin{aligned} d(E_t - TS_t + pV_t - \sum_i \mu_i N_{ti}) \\ = -S_t dT + V_t dp - \sum_i N_{ti} d\mu_i + \mathcal{E} d\mathcal{N}. \end{aligned}$$

Then an alternative definition of  $\mathcal{E}$  is

$$\begin{aligned} \mathcal{E} &\equiv \left[ \frac{\partial(E_t - TS_t + pV_t - \sum_i \mu_i N_{ti})}{\partial \mathcal{N}} \right]_{T, p, \mu_i} \\ &= \frac{E_t - TS_t + pV_t - \sum_i \mu_i N_{ti}}{\mathcal{N}} = E - TS + pV - \sum_i \mu_i N_i. \end{aligned}$$

Here  $\mathcal{E}$  is defined by adding systems to the ensemble without changing the nature of the systems, for all the properties of a system are determined by  $T$ ,  $p$ , and the  $\mu_i$ . The above is of course just Eqs. (1-67)ff. restated as applicable to *any* environment.

We conclude with two general comments on environmental variables, etc. Many environments (e.g.,  $N, V, T$  or  $N, V, E$ ) are of no practical interest for experimental work, but may be important in theoretical work. It is particularly appropriate in these cases to use an ensemble of distinguishable systems with fixed center of mass, as in this chapter. For "real" ensembles, however, translational motion, solvent effects, etc., will have to be taken into account, as in Sections 2-3 and 3-3.

If an extensive variable fluctuates, it is not an environmental variable. If it has the same value in every system of the ensemble (we are excluding polydisperse systems here), it is an environmental variable. This is a useful criterion.

# ENVIRONMENTAL VARIABLES $N, p, T$

A brief introduction to this type of system was included in Section 1-3. We continue the discussion here. In Section 2-1 we derive some of the more important thermodynamic equations for a small  $N, p, T$  system. Examples are given in Section 2-2. Then in Section 2-3 we show that solvent effects, which are ignored up to that point, can be taken into account rigorously without altering the formal appearance of the equations of Section 2-1.

In order to be able to measure and vary the pressure on an experimental small system, the system (colloidal particle, macromolecule, etc.) will ordinarily have to be immersed in a solvent. Then the pressure exerted on the solvent will be the pressure on the small system. Also, of course, the temperature of the small system is taken to be that of the solvent. The solvent will be regarded as an inert medium, and not included explicitly, until Section 2-3, where this restriction is removed.

We have just referred to a macromolecule under a pressure  $p$ , with environmental variables  $N, p, T$ . The equations of this chapter also apply to an incompressible macromolecule under a stretching force  $f$ . The environmental variables are  $N, f, T$  for such a system.

A special case is a system under an invariable pressure or force of zero. Examples are a colloidal particle in a rarified gas and a rodlike macromolecule, in a solvent, whose length can change through an alteration in molecular configuration. In the latter case, the length  $\bar{l}$  replaces the volume  $\bar{V}$  as a dependent thermodynamic variable. If the macromolecule has free ends in solution,  $f = 0$ . The helix-coil transition in synthetic polypeptides is a specific example, but not a very good one, for the molecule is rodlike only in the helical regions, and furthermore these regions are oriented in different directions. The contour length is not a suitable variable here because this length is not thermodynamically conjugate to a force  $f$  exerted on the ends of the chain. The end-to-end length along a given direction could be used, but this length does not depend linearly on the fraction of helical content. The most natural and satisfactory way to treat the helix-coil transition is as an isomeric equilibrium (Chapter 5). We

shall, however, consider some simple models in Section 2-2 which are of the helix-coil type. The more complicated situation in which there is binding of an ionic or molecular species on the macromolecule is considered in Chapter 7.

Use of the environmental variable  $N$  implies that the small system is closed. A polymer molecule made up of  $N$  monomers held together by chemical bonds is a clear-cut example. But an aggregate of molecules bound by relatively weak van der Waals forces would be open rather than closed. In this case the environmental variables, at equilibrium, would be  $\mu$ ,  $p$ ,  $T$  (Chapter 10). The criterion distinguishing the two cases is whether or not the system maintains  $N = \text{constant}$ , within experimental error, during the time required for the thermodynamic measurements of interest. Experimental  $N$ ,  $p$ ,  $T$  systems will usually be colloidal aggregates, which are essentially nonvolatile (in a gas) or insoluble (in a solvent), or chemically bonded polymers.

Incidentally, by varying the time of measurement it may be possible to detect *experimentally* the difference in thermodynamic functions for a suitable small system under different environmental conditions.

Although the system is closed here, primary interest attaches to the effects of varying  $N$ . For this, experiments must be done on samples with different values of  $N$ . Polydispersity in  $N$  is dealt with in Chapter 13.

A macromolecule, such as a naturally occurring protein, which is *not* made up of a variable number of identical units may be regarded as an  $N$ ,  $p$ ,  $T$  system with a fixed value of  $N$ . But aside from seeing that thermodynamic functions such as  $\bar{E}$ ,  $S$ ,  $C_p$ , etc., may be defined and interrelated (always with  $N$  constant) for this type of small system, such a case is relatively uninteresting<sup>1</sup> in the present context because the novel features are associated primarily with variations in  $N$ .

## 2-1. THERMODYNAMIC RELATIONS

We have already mentioned in Chapter 1 that small systems have one more degree of freedom than large systems. A consequence of this is that many more thermodynamic relations exist in small system

<sup>1</sup> Unless there is a phase transition (Chapter 5) or binding on the protein molecules (Chapter 10).

thermodynamics than in macroscopic thermodynamics. It is therefore not practical to try to present a complete catalogue of possible equations. We shall try to emphasize, in this and other chapters, those equations which seem to be most important and useful.

It should be clear from Section 1-4 that equations derived for one environment (for example,  $N, p, T$ ) are also valid for all others (for example,  $\mu, V, T$ ) with the same number of components. Thus, for example, we can replace  $\hat{\mu}$  wherever it occurs in the present section by  $(p\bar{V} - \bar{p}\bar{V} + \mu N)/N$ , etc. But there is little point in this. Actually, because of the unique operational importance of the environmental variables as independent variables for a small system, for the most part we shall derive equations in this chapter employing  $N, p, T$  as independent variables, in Chapter 6 the emphasis will be on  $\mu, V, T$  as independent variables, etc. Thus there will not be much overlap among different chapters, and there is no real purpose served in replacing, say,  $\hat{\mu}$  by  $\bar{p}$  when the environmental variables are  $N, p, T$ , etc. Of course, if a universal notation is desired, we would use  $\mathcal{E}$  instead of either  $\hat{\mu}$  or  $\bar{p}$ .

It will prove convenient here and elsewhere to use the notation  $\mu$  and  $\hat{\mu}$  whenever these quantities occur alone, but when they appear as a difference, we shall usually write  $N(\hat{\mu} - \mu) = \mathcal{E}$ .

We continue to use averaging "bars" (over  $E$  and  $V$  in this case) because of their informational content, but we remind the reader that this convention is optional, especially in view of the equivalence of thermodynamic equations in all environments.

For convenience we reproduce the following equations from Section 1-3:

$$d\bar{E} = T dS - p d\bar{V} + \mu dN \quad (2-1)$$

$$\bar{E} = TS - p\bar{V} + \hat{\mu}N \quad (2-2)$$

$$d(\hat{\mu}N) = -S dT + \bar{V} dp + \mu dN \quad (2-3)$$

$$d[N(\hat{\mu} - \mu)] = d\mathcal{E} = -S dT + \bar{V} dp - N d\mu. \quad (2-4)$$

Also, we define

$$H = \bar{E} + p\bar{V} \quad (2-5)$$

$$A = \bar{E} - TS \quad (2-6)$$

$$F = \bar{E} - TS + p\bar{V}. \quad (2-7)$$

We shall use these definitions for all environments (except for the "bars"). In the present case,  $F = N\hat{\mu}$ . We have, further, that

$$dH = T dS + \bar{V} dp + \mu dN \quad (2-8)$$

$$dA = -S dT - p d\bar{V} + \mu dN. \quad (2-9)$$

From Eq. (2-3),

$$\left(\frac{\partial \hat{\mu} N}{\partial T}\right)_{p, N} = -S, \quad \left(\frac{\partial \hat{\mu}}{\partial T}\right)_{p, N} = -\frac{S}{N} \quad (2-10)$$

$$\left(\frac{\partial \hat{\mu} N}{\partial p}\right)_{T, N} = \bar{V}, \quad \left(\frac{\partial \hat{\mu}}{\partial p}\right)_{T, N} = \frac{\bar{V}}{N} \quad (2-11)$$

$$\left(\frac{\partial \hat{\mu} N}{\partial N}\right)_{T, p} = \mu, \quad \left(\frac{\partial \hat{\mu}}{\partial N}\right)_{T, p} = \frac{\mu - \hat{\mu}}{N}. \quad (2-12)$$

Consequently,

$$d\hat{\mu} = -\frac{S}{N} dT + \frac{\bar{V}}{N} dp - \frac{\mathcal{E}}{N^2} dN, \quad (2-13)$$

or

$$(\hat{\mu} - \mu) dN = -S dT + \bar{V} dp - N d\hat{\mu}. \quad (2-14)$$

Next, we want the analogue of Eq. (2-13) for  $d\mu$ . We first write the three Maxwell relations which follow from Eq. (2-3):

$$\begin{aligned} -\left(\frac{\partial S}{\partial p}\right)_{T, N} &= \left(\frac{\partial \bar{V}}{\partial T}\right)_{p, N}, & -\left(\frac{\partial S}{\partial N}\right)_{T, p} &= \left(\frac{\partial \mu}{\partial T}\right)_{p, N}, \\ \left(\frac{\partial \bar{V}}{\partial N}\right)_{T, p} &= \left(\frac{\partial \mu}{\partial p}\right)_{T, N}. \end{aligned} \quad (2-15)$$

We shall also need

$$\left(\frac{\partial \mu}{\partial N}\right)_{T, p} = -\frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, p}, \quad (2-16)$$

from Eq. (2-4). Then, Eqs. (2-15) and (2-16) give

$$d\mu = -\left(\frac{\partial S}{\partial N}\right)_{T, p} dT + \left(\frac{\partial \bar{V}}{\partial N}\right)_{T, p} dp - \frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, p} dN. \quad (2-17)$$



This should be compared with Eq. (2-13).

The differential-integral relation between  $\mu$  and  $\hat{\mu}$  is also evident from

$$\hat{\mu} = \frac{F}{N} = \frac{\bar{E}}{N} - T \frac{S}{N} + p \frac{\bar{V}}{N} = \frac{H}{N} - T \frac{S}{N}, \quad (2-18)$$

$$\begin{aligned} \mu &= \left( \frac{\partial F}{\partial N} \right)_{T, p} = \left( \frac{\partial \bar{E}}{\partial N} \right)_{T, p} - T \left( \frac{\partial S}{\partial N} \right)_{T, p} + p \left( \frac{\partial \bar{V}}{\partial N} \right)_{T, p} \\ &= \left( \frac{\partial H}{\partial N} \right)_{T, p} - T \left( \frac{\partial S}{\partial N} \right)_{T, p} \end{aligned} \quad (2-19)$$

and from

$$\left( \frac{\partial \hat{\mu}/T}{\partial T} \right)_{p, N} = -\frac{1}{T^2} \frac{H}{N}, \quad \left( \frac{\partial \mu/T}{\partial T} \right)_{p, N} = -\frac{1}{T^2} \left( \frac{\partial H}{\partial N} \right)_{T, p}. \quad (2-20)$$

It is helpful here and in other chapters to notice: (a) which terms in an equation are of "macroscopic order" (i.e., are significant in the macroscopic limit) and which terms are "small" (i.e., vanish in the macroscopic limit); and (b) what the macroscopic form of an equation is. Thus, terms involving  $\mathcal{E}$  or  $\hat{\mu} - \mu$  are always "small." The same is true of derivatives of intensive variables holding intensive variables constant, such as  $(\partial \mu / \partial N)_{T, p}$ . Derivatives involving extensive variables holding intensive variables constant are of macroscopic order but become a simple ratio when  $N \rightarrow \infty$ . For example,

$$\lim_{N \rightarrow \infty} \left( \frac{\partial F}{\partial N} \right)_{T, p} = \frac{F}{N}.$$

There are some expressions which are of macroscopic order but which do not appear in ordinary macroscopic thermodynamic equations. These rather resemble indeterminate forms. For example, from Eq. (2-4),

$$\left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, \mu} = -S, \quad \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, \mu} = \bar{V}, \quad \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{T, p} = -N. \quad (2-21)$$

Hence the dependence of the small term  $\mathcal{E}$  on  $T, p$ , and  $\mu$  suffices to determine the *extensive* properties, of macroscopic order, of the

system. Equation (1-75) provides an alternative form for Eqs. (2-21):

$$\begin{aligned} \left( \frac{\partial \mathcal{S}}{\partial 1/T} \right)_{p/T, \mu/T} &= -\bar{E}, & \left( \frac{\partial \mathcal{S}}{\partial p/T} \right)_{1/T, \mu/T} &= -\bar{V}, \\ \left( \frac{\partial \mathcal{S}}{\partial \mu/T} \right)_{1/T, p/T} &= N. \end{aligned} \quad (2-22)$$

Equations (2-21) and (2-22) hold for any environment of a one-component system, if the bars are omitted. They are of course most easily applied to a completely open system (environmental variables  $\mu, p, T$ ).

Let us pursue the above comments a little further. It is natural here to change the independent variables in Eq. (2-4) from  $T, p, \mu$  to  $T, p, N$ . To accomplish this, we substitute Eq. (2-17) for  $d\mu$  in Eq. (2-4) and find

$$d\mathcal{E} = -[S] dT + [\bar{V}] dp + \left( \frac{\partial \mathcal{E}}{\partial N} \right)_{T, p} dN, \quad (2-23)$$

where, for any extensive property  $G$ , we define

$$[G] \equiv G - N \left( \frac{\partial G}{\partial N} \right)_{T, p}. \quad (2-24)$$

Note that *all* terms in Eq. (2-23) are small. From Eq. (2-23) we have

$$\left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, N} = -[S], \quad \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, N} = [\bar{V}]. \quad (2-25)$$

Unlike Eqs. (2-21), the right-hand sides of Eqs. (2-25) are small and not macroscopic.

Equation (2-23) can be rewritten as

$$d[F] = -[S] dT + [\bar{V}] dp + \frac{[N\mu]}{N} dN, \quad (2-26)$$

since  $[F] = \mathcal{E}$ . Also, if we subtract Eq. (2-19) from Eq. (2-18), we can write

$$[F] = [\bar{E}] - T[S] + p[\bar{V}] \quad (2-27)$$

and then

$$d[\bar{E}] = T d[S] - p d[\bar{V}] + \frac{[N\mu]}{N} dN. \quad (2-28)$$

Equations (2-26) to (2-28) are formally similar to Eqs. (2-3), (2-7), and (2-1), respectively, but contain small terms only. Note that in Eq. (2-3) we have  $F/N \neq \mu$  and here also, in Eq. (2-26),

$$\frac{[F]}{N} = \frac{[N\bar{\mu}]}{N} \neq \frac{[N\mu]}{N}.$$

The above equations suggest the use of  $[S]$ ,  $[\bar{V}]$ , etc., as "excess functions" which vanish for macroscopic systems but are nonzero for small systems. That is, these functions would measure departures from macroscopic behavior. However, what appear to be more convenient excess functions will be introduced at the end of this section.

HEAT CAPACITY. Because the ensemble is macroscopic, we have the usual relation  $DQ_t = T dS_t$ , and because the systems of the ensemble are equivalent, distinguishable, and independent, we have, on dividing the above relation by  $\mathcal{N}$ ,  $DQ = T dS$  for one system. We define the heat capacity  $C_p$  by

$$C_p = \left( \frac{DQ}{\partial T} \right)_{p, N}. \quad (2-29)$$

Then, from Eq. (2-8),

$$dH = DQ = C_p dT = T dS \quad (p, N \text{ constant}) \quad (2-30)$$

and

$$C_p = \left( \frac{\partial H}{\partial T} \right)_{p, N}, \quad \frac{C_p}{T} = \left( \frac{\partial S}{\partial T} \right)_{p, N} = - \left( \frac{\partial^2 F}{\partial T^2} \right)_{p, N}, \quad (2-31)$$

just as in macroscopic thermodynamics. These equations can be integrated over a temperature range, in the usual manner.

Other relations, which are easy to derive, are

$$\left( \frac{\partial C_p}{\partial N} \right)_{T, p} = -T \left( \frac{\partial^2 \mu}{\partial T^2} \right)_{p, N} \quad (2-32)$$

$$\frac{C_p}{N} = -T \left( \frac{\partial^2 \hat{\mu}}{\partial T^2} \right)_{p, N} \quad (2-33)$$

and

$$[C_p] = -T \left( \frac{\partial^2 \mathcal{E}}{\partial T^2} \right)_{p, N}. \quad (2-34)$$

**EFFECT OF SIZE ON INTENSIVE VARIABLES.** We bring together here a number of relations showing the effect of size (measured by  $N$ , in this case) on intensive variables, especially with pressure and temperature held constant. As already emphasized in Chapter 1, such effects are characteristic of small systems and are absent in macroscopic systems. We have already seen that

$$\left( \frac{\partial \hat{\mu}}{\partial N} \right)_{T, p} = -\frac{\mathcal{E}}{N^2} \quad \text{and} \quad \left( \frac{\partial \mu}{\partial N} \right)_{T, p} = -\frac{1}{N} \left( \frac{\partial \mathcal{E}}{\partial N} \right)_{T, p}. \quad (2-35)$$

Among other intensive properties of interest are those of the form  $G/N \equiv \alpha$ , where  $G = S, \bar{V}, \bar{E}$ , etc. Since

$$\left( \frac{\partial G}{\partial N} \right)_{T, p} = -\frac{[G]}{N^2}, \quad (2-36)$$

we deduce immediately, from earlier results,

$$\left( \frac{\partial S}{\partial N} \right)_{T, p} = \frac{1}{N^2} \left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, N} \quad (2-37)$$

$$\left( \frac{\partial \bar{V}}{\partial N} \right)_{T, p} = -\frac{1}{N^2} \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, N} \quad (2-38)$$

$$\left( \frac{\partial N/\bar{V}}{\partial N} \right)_{T, p} = \frac{1}{V^2} \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, N} \quad (2-39)$$

$$\left( \frac{\partial \bar{E}}{\partial N} \right)_{T, p} = -\frac{1}{N^2} \left[ \mathcal{E} - T \left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, N} - p \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, N} \right] \quad (2-40)$$

$$\left( \frac{\partial \bar{H}}{\partial N} \right)_{T, p} = -\frac{1}{N^2} \left[ \mathcal{E} - T \left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, N} \right] \quad (2-41)$$

$$\left( \frac{\partial \bar{A}}{\partial N} \right)_{T, p} = -\frac{1}{N^2} \left[ \mathcal{E} - p \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, N} \right] \quad (2-42)$$

$$\left(\frac{\partial c_p}{\partial N}\right)_{T,p} = \frac{T}{N^2} \left(\frac{\partial^2 \mathcal{E}}{\partial T^2}\right)_{p,N} \quad (2-43)$$

Equation (2-41) is a Gibbs-Helmholtz type of equation, since  $\mathcal{E} = [F]$ . Equations (2-20) are other examples of the same type.

We append two other relations, with  $\hat{\mu}$  constant:

$$-S\left(\frac{\partial T}{\partial N}\right)_{\hat{\mu},p} = \bar{V}\left(\frac{\partial p}{\partial N}\right)_{\hat{\mu},T} = \frac{\mathcal{E}}{N}. \quad (2-44)$$

These follow from Eq. (2-13).

It is interesting to note, but not surprising, that it has been possible to express all the effects of size on intensive variables in this subsection in terms of  $\mathcal{E}$  and derivatives of  $\mathcal{E}$ .

EQUATION-OF-STATE RELATIONS AND PHASE TRANSITIONS. Here we look into the question of what kind of information can be deduced from equation-of-state data, that is, from experimental or theoretical relations among  $p$ ,  $\bar{V}$ ,  $T$ , and  $N$ . Examples of systems to which this discussion could be applied are polymer molecules or insoluble colloidal particles suspended in an inert<sup>1</sup> liquid (environmental variables  $N, p, T$ ), and an  $\alpha$ - $\beta$ , or helix-coil, type of transition in a rodlike macromolecule (environmental variables  $N, f, T$ ). In the latter case  $f = \text{constant} = 0$ , and  $\bar{l}$  is approximately linearly related to observable (nonthermodynamic) quantities such as optical rotation. For simplicity in the equations and discussion below we shall use the variables  $p, \bar{V}$ ; these should be read as  $-f, \bar{l}$  when appropriate.

The term "helix-coil transition" implies something akin to a phase transition, though it is not first-order. A first-order transition is, however, possible in  $N, p, T$  systems, for example, melting of solid colloidal particles. Phase transitions will be discussed in some detail in Chapter 5. They will be considered in this chapter only rather incidentally. One general remark might be made here, however. That is, phase transitions in small systems will not be completely "sharp," as they are in macroscopic systems. The transition will always show at least some degree of gradualness in finite systems. Figure 2-1 illustrates this. The  $p$ - $\bar{V}$  curve is "rounded off" at  $A$  and  $B$  and the curve  $AB$  is not horizontal.

<sup>1</sup> This limitation is removed in Sec. 2-3.

We shall need a few more Maxwell relations. These are

$$\begin{aligned}\left(\frac{\partial S}{\partial \bar{V}}\right)_{T, N} &= \left(\frac{\partial p}{\partial T}\right)_{\bar{V}, N}, & -\left(\frac{\partial S}{\partial N}\right)_{T, \bar{V}} &= \left(\frac{\partial \mu}{\partial T}\right)_{\bar{V}, N}, \\ -\left(\frac{\partial p}{\partial N}\right)_{T, \bar{V}} &= \left(\frac{\partial \mu}{\partial \bar{V}}\right)_{T, N},\end{aligned}\quad (2-45)$$

which follow from Eq. (2-9).

There are six different choices of two variables out of  $p$ ,  $\bar{V}$ ,  $T$ , and  $N$ , and hence there are six equation-of-state derivatives (not all independent, of course). Four of these are given in Eqs. (2-15a), (2-15c), (2-45a), and (2-45c). The other two are

$$\left(\frac{\partial \bar{V}}{\partial p}\right)_{T, N} = -\left(\frac{\partial \bar{V}}{\partial T}\right)_{p, N} / \left(\frac{\partial p}{\partial T}\right)_{\bar{V}, N} \quad (2-46)$$

and

$$\left(\frac{\partial T}{\partial N}\right)_{p, \bar{V}} = -\left(\frac{\partial \bar{V}}{\partial N}\right)_{T, p} / \left(\frac{\partial \bar{V}}{\partial T}\right)_{p, N} = \left(\frac{\partial \mu}{\partial S}\right)_{T, N}. \quad (2-47)$$

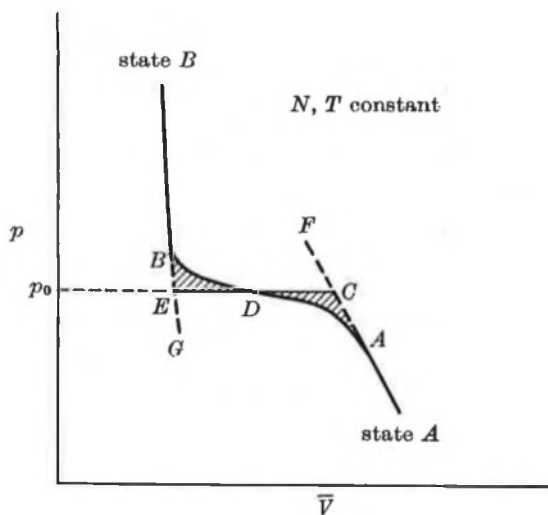


FIGURE 2-1. Schematic  $p$ - $\bar{V}$  isotherm for small system at a temperature such that the macroscopic system has a first-order phase transition.  $BDA$  is the experimental curve.

By use of these six derivatives we can therefore obtain information concerning the isothermal changes of  $S$  and  $\mu$  with  $p$  or  $\bar{V}$ . Equations (2-1) and (2-3) then allow us to extend this list to  $S, \mu, \bar{E}$ , and  $\bar{\mu}$ , and of course also to the composite functions  $H$  and  $A$ . In the helix-coil type of system, only those derivatives involving  $\bar{V}, T$ , and  $N$  with  $p$  constant can be measured experimentally. These occur in Eqs. (2-15a), (2-15c), and (2-47). From the first two of these equations we can learn how  $S$  and  $\mu$  would change with force  $p$  in the neighborhood of  $p = 0$ , if such a force could be exerted. However, the last equation, (2-47), is completely "operational", since  $p$  has been eliminated on the right-hand side.

In practical work one might prefer  $v$  in place of  $\bar{V}$  in the equations referred to above. In this case Eq. (2-15a) becomes

$$-\left(\frac{\partial s}{\partial p}\right)_{T, N} = \left(\frac{\partial v}{\partial T}\right)_{p, N}, \quad (2-48)$$

Eq. (2-15c) goes into Eq. (2-38), Eqs. (2-45a) and (2-45c) become

$$\left(\frac{\partial s}{\partial v}\right)_{T, N} = \left(\frac{\partial p}{\partial T}\right)_{v, N}, \quad \left(\frac{\partial p}{\partial N}\right)_{T, v} = \frac{1}{N^2} \left(\frac{\partial \mathcal{E}}{\partial v}\right)_{T, N}, \quad (2-49)$$

while Eq. (2-47) can be rewritten as

$$\left(\frac{\partial T}{\partial N}\right)_{p, v} = -\frac{1}{N^2} \left(\frac{\partial \mathcal{E}}{\partial s}\right)_{T, N} = -\left[\frac{\partial(\bar{\mu} - \mu)}{\partial S}\right]_{T, N}. \quad (2-50)$$

For a macroscopic system, Eq. (2-45a) or (2-49a) reduces to

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v. \quad (2-51)$$

In a phase transition region,  $p$  is independent of  $v$ . That is,  $p$  is a function of  $T$  only. The left-hand side of the above equation is then a function of  $T$  only, and hence  $s$  is a linear function of  $v$  along the two-phase part of a  $p$ - $v$  isotherm. Equation (2-51) therefore simplifies, in this special case, to

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta S}{\Delta V}, \quad (2-52)$$

which is the Clausius-Clapeyron equation. The symbol  $\Delta$  refers to

the difference between the two ends of the two-phase part of the isotherm.

There can be no *exact* analogues of Eq. (2-52) for a small system because there are no sharply defined end points on experimental curves (see Fig. 2-1, for example). If one wants to be exact, Eq. (2-45a) and similar relations must be used as they stand. However, useful and accurate approximate expressions can be derived, as we shall see in Chapter 5. We confine ourselves here to stating results: Eqs. (2-45a), (2-45c), and (2-47) become

$$\left(\frac{\partial p}{\partial T}\right)_N = \frac{\Delta S}{\Delta \bar{V}}, \quad \left(\frac{\partial p}{\partial N}\right)_T = -\frac{\Delta \mu}{\Delta \bar{V}}, \quad \left(\frac{\partial T}{\partial N}\right)_p = \frac{\Delta \mu}{\Delta S}, \quad (2-53)$$

where  $p$  and the symbol  $\Delta$  are defined by the construction in Fig. 2-1, as follows:<sup>1</sup> we first draw the extrapolations  $AF$  and  $BG$ ; next, the horizontal line [defining  $p$  in Eqs. (2-53)] is located by the condition  $CD = DE$  or from an equal-area theorem as indicated by the shading in the figure; then  $\Delta$  refers to a difference between the metastable states  $C$  and  $E$ . Alternatively, one can make a similar construction on a  $\bar{V}$  versus  $T$  diagram, but in this case there is no equal-area theorem. The basis of the procedure is that  $\Delta \hat{\mu} = 0$ .

**EXCESS QUANTITIES.** Many equations encountered so far in the book contain both small terms and macroscopic terms. Equation (2-4) is an example. It is of some interest to rewrite these equations so that all terms are small, for in this way we obtain a pure "thermodynamics of smallness," so to speak. The most convenient procedure appears to be to define excess quantities relative to the macroscopic state. We do this here for an  $N, p, T$  system.

We define the excess quantity  $G^{(x)}(N, p, T)$  ( $x$  for excess) for any extensive property  $G$  in a small system by<sup>2</sup>

$$G(N, p, T) = G^{(0)}(N, p, T) + G^{(x)}(N, p, T), \quad (2-54)$$

where  $G^{(0)}$  is the value of  $G$  for  $N$  molecules of a macroscopic sample at the same  $p$  and  $T$  as the small system. One can of course write  $G^{(0)}$  as  $Ng^{(0)}$ , where  $g^{(0)} = G^{(0)}/N$  is a function of  $p$  and  $T$  only. Equation

<sup>1</sup> The pressure  $p$  in these equations is labeled  $p_0$  in Fig. 2-1.

<sup>2</sup> Note that the notation here is different from that in J.C.P.



(2-54), as it stands, is suitable for  $\bar{E}$ ,  $S$ , and  $\bar{V}$ , but for  $F$  we have the alternative forms

$$\begin{aligned} F(N, p, T) &= F^{(0)}(N, p, T) + F^{(x)}(N, p, T) \\ \frac{F}{N} &= \hat{\mu}(N, p, T) = \mu^{(0)}(p, T) + \hat{\mu}^{(x)}(N, p, T), \end{aligned} \quad (2-55)$$

and, for  $N\mu$ ,

$$\frac{N\mu}{N} = \mu(N, p, T) = \mu^{(0)}(p, T) + \mu^{(x)}(N, p, T). \quad (2-56)$$

These equations define  $\hat{\mu}^{(x)}$  and  $\mu^{(x)}$ ;  $\mu^{(0)}$  is the macroscopic chemical potential at  $p$  and  $T$ .

We substitute Eqs. (2-54) to (2-56) into Eqs. (2-1) to (2-4), cancel the macroscopic terms, and obtain

$$d\bar{E}^{(x)} = T dS^{(x)} - p d\bar{V}^{(x)} + \mu^{(x)} dN \quad (2-57)$$

$$\bar{E}^{(x)} = T S^{(x)} - p \bar{V}^{(x)} + \hat{\mu}^{(x)} N \quad (2-58)$$

$$d(\hat{\mu}^{(x)} N) = dF^{(x)} = -S^{(x)} dT + \bar{V}^{(x)} dp + \mu^{(x)} dN \quad (2-59)$$

$$d[N(\hat{\mu}^{(x)} - \mu^{(x)})] = d\mathcal{E} = -S^{(x)} dT + \bar{V}^{(x)} dp - N d\mu^{(x)}. \quad (2-60)$$

These equations contain small terms only. They are formally identical with Eqs. (2-1) to (2-4) and can therefore be manipulated in the same way to obtain many further relations. One example is

$$\mu^{(x)} = \hat{\mu}^{(x)} + N \left( \frac{\partial \hat{\mu}^{(x)}}{\partial N} \right)_{p, T}, \quad (2-61)$$

which is the analogue of Eq. (2-12b). Others are

$$d\hat{\mu}^{(x)} = -\frac{S^{(x)}}{N} dT + \frac{\bar{V}^{(x)}}{N} dp - \frac{\mathcal{E}}{N^2} dN \quad (2-62)$$

and

$$d\mu^{(x)} = -\left( \frac{\partial S^{(x)}}{\partial N} \right)_{T, p} dT + \left( \frac{\partial \bar{V}^{(x)}}{\partial N} \right)_{T, p} dp - \frac{1}{N} \left( \frac{\partial \mathcal{E}}{\partial N} \right)_{T, p} dN. \quad (2-63)$$

The possibility of expansion of excess quantities in powers of  $N^{-1}$  may occur to the reader. But, for a discrete variable such as  $N$ , this does not prove to be useful, as will be seen in Chapter 15. An expansion of this sort in  $V^{-1}$  for a  $\mu, V, T$  system is discussed in Chapter 6.

INTEGRATION OF FUNDAMENTAL EQUATION. The equation

$$d\bar{E} = T dS - p d\bar{V} + \mu dN \quad (2-64)$$

for a macroscopic system can be integrated from  $N = 0$  to  $N$ , at constant  $T$  and  $p$ , to yield

$$\bar{E} = TS - p\bar{V} + \mu N \quad (\text{macroscopic}). \quad (2-65)$$

For all values of  $N$ , the sample of matter considered here may be regarded as part of an essentially infinite sample so that there are no edge effects, etc. The analogous integration for a small system may be carried out without complication from  $N$  (small) to  $N^\infty$  (macroscopic), also at constant  $T$  and  $p$ . We obtain

$$\begin{aligned} \bar{E}(N^\infty, p, T) - \bar{E}(N, p, T) &= TS(N^\infty, p, T) - TS(N, p, T) \\ &\quad - p\bar{V}(N^\infty, p, T) + p\bar{V}(N, p, T) + \int_N^{N^\infty} \mu dN. \end{aligned}$$

Using Eq. (2-65), we have

$$\bar{E}(N, p, T) = TS(N, p, T) - p\bar{V}(N, p, T) + \mu^{(0)}(p, T)N^\infty - \int_N^{N^\infty} \mu dN. \quad (2-66)$$

Since the integral of  $\mu dN$  is at constant  $T$  and  $p$ , its value is  $\mu^{(0)}N^\infty - \hat{\mu}(N)N$ , according to Eq. (2-3). Hence Eq. (2-66) becomes

$$\bar{E} = TS - p\bar{V} + \hat{\mu}N, \quad (2-67)$$

in agreement with Eq. (2-2). A similar integration of Eq. (2-57) gives Eq. (2-58).

## 2-2. APPLICATIONS TO THEORETICAL MODELS

In this section we illustrate a few of the above thermodynamic functions and equations with simple theoretical models.

**COLLOIDAL PARTICLE.** As our first example we choose the case referred to at the beginning of Chapter 1. Suppose the Gibbs free energy of a spherical colloidal particle has the form

$$F = N\hat{\mu} = Nf(p, T) + a(p, T)N^{2/3} + b(T) \ln N + c(p, T). \quad (2-68)$$

The term  $Nf$  is the macroscopic term, while  $aN^{2/3}$  is a surface free energy. The constant  $a$  is positive and has the order of magnitude of the surface tension multiplied by the square of the nearest neighbor distance. Equation (80) of J.C.P. gives an explicit partition function leading to terms of this type. A more complete treatment would include an  $N^{1/3}$  term [see Eq. (3-62)]. The last two terms in Eq. (2-68) may be attributed to rotation and translation, as will be clear from Section 3-3. But our point of view here is simply that Eq. (2-68) is an empirical thermodynamic expression applicable to a small colloidal particle.

From Eqs. (2-10) to (2-12), we have

$$-S = \left( \frac{\partial F}{\partial T} \right)_{p, N} = \frac{\partial f}{\partial T} N + \frac{\partial a}{\partial T} N^{2/3} + \frac{db}{dT} \ln N + \frac{\partial c}{\partial T} \quad (2-69)$$

$$\bar{V} = \left( \frac{\partial F}{\partial p} \right)_{T, N} = \frac{\partial f}{\partial p} N + \frac{\partial a}{\partial p} N^{2/3} + \frac{\partial c}{\partial p} \quad (2-70)$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T, p} = f + \frac{2}{3}aN^{-1/3} + bN^{-1}. \quad (2-71)$$

Then

$$\mathcal{E} = N(\hat{\mu} - \mu) = \frac{1}{3}aN^{2/3} + b(\ln N - 1) + c. \quad (2-72)$$

The energy  $\bar{E}$  follows directly from the above functions. The heat

capacity is

$$\begin{aligned} C_p &= -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{p, N} \\ &= -T \left( \frac{\partial^2 f}{\partial T^2} N + \frac{\partial^2 a}{\partial T^2} N^{2/3} + \frac{d^2 b}{dT^2} \ln N + \frac{\partial^2 c}{\partial T^2} \right). \end{aligned} \quad (2-73)$$

These functions can now be used to verify various equations in Section 2-1, for example, Eqs. (2-37), (2-38), etc. This task is left to the reader.

The excess functions are

$$F^{(x)} = N\hat{\mu}^{(x)} = aN^{2/3} + b \ln N + c \quad (2-74)$$

$$\mu^{(x)} = \frac{2}{3}aN^{-1/3} + bN^{-1} \quad (2-75)$$

$$-S^{(x)} = \frac{\partial a}{\partial T} N^{2/3} + \frac{db}{dT} \ln N + \frac{\partial c}{\partial T}, \quad (2-76)$$

etc.

**IDEAL LATTICE GAS.** Consider a lattice of  $B$  identical and distinguishable sites,  $N$  of which are occupied by molecules. These molecules form what is known as a "lattice gas." We omit internal degrees of freedom (vibration, etc.) for simplicity. Also, in an *ideal* lattice gas, we omit intermolecular forces. Hence the only energy possible for the system is  $E = 0$ . We have

$$\Omega(N, B) = \frac{B!}{N!(B-N)!} \quad (2-77)$$

and, from Eq. (1-32),<sup>1</sup>

$$\begin{aligned} \Delta(N, p/kT) &= \sum_{B=N}^{\infty} \Omega(N, B) e^{-pB/kT} \\ &= \frac{x^N}{(1-x)^{N+1}}, \end{aligned}$$

where  $x = e^{-p/kT}$ . Then

$$-\frac{F}{kT} = -\frac{N\hat{\mu}}{kT} = \ln \Delta = N \ln x - (N+1) \ln(1-x), \quad (2-78)$$

<sup>1</sup> See S. M., p. 400, for evaluation of the sum.

and

$$-\frac{\hat{\mu}}{kT} = \ln \frac{x}{1-x} - \frac{1}{N} \ln(1-x). \quad (2-79)$$

Also,

$$-\frac{\mu}{kT} = \left( \frac{\partial F/kT}{\partial N} \right)_x = \ln \frac{x}{1-x} \quad (2-80)$$

$$\mathcal{G} = N(\hat{\mu} - \mu) = kT \ln(1-x) \quad (2-81)$$

$$\bar{B} = \left( \frac{\partial F/kT}{\partial p/kT} \right)_N = \frac{N+x}{1-x} \quad (2-82)$$

or

$$-\ln x = \frac{p}{kT} = -\ln \left( \frac{\bar{B} - N}{1 + \bar{B}} \right).$$

This is the equation of state. The macroscopic limit is

$$\frac{p}{kT} = -\ln \left( 1 - \frac{N}{\bar{B}} \right). \quad (2-83)$$

Note that  $\mu^{(x)} = 0$  but  $\hat{\mu}^{(x)} \neq 0$ .

We find for the entropy, after eliminating  $x$ ,

$$\begin{aligned} \frac{S}{k} &= \frac{p\bar{B}}{kT} - \frac{\hat{\mu}N}{kT} \\ &= (1 + \bar{B}) \ln(1 + \bar{B}) - (1 + N) \ln(1 + N) - (\bar{B} - N) \ln(\bar{B} - N). \end{aligned} \quad (2-84)$$

Stirling's approximation has not been used above. Equations (2-78), (2-79), (2-82), and (2-84) are valid for very small  $N$ , even  $N = 1$ . For example, when  $N = 1$  it is easy, in the limit  $p \rightarrow \infty$  or  $x \rightarrow 0$ , to verify that Eq. (2-84) is consistent with  $S = -k \sum_i p_i \ln p_i$ , for in this limit we need consider only  $B = 1$  and  $B = 2$  [compare Eq. (131) of J.C.P.]. Equations (2-80) and (2-81), on the other hand, involve a differentiation with respect to the discrete variable  $N$  and cannot be taken to arbitrarily small  $N$ . This limitation will be examined in Chapter 15.

In this model there are no edge effects, rotational effects, etc. Deviations from macroscopic behavior are of order unity relative to  $O(N)$  and might be termed "pure" small-number effects. We shall see in Chapter 15 that any errors owing to differentiating with respect to  $N$  are of still smaller order,  $O(N^{-1})$ .

The terms of order  $\ln N$  and, especially,  $O(N^{2/3})$  in the previous example are much larger than the small terms here. Another way to put this is the following. Suppose we want to begin to take into account small terms when their neglect would lead to a 1 per cent error. For a surface (boundary) effect in a three-dimensional system, we would then have

$$\frac{N^{2/3}}{N} = 0.01, \quad \text{or} \quad N = 10^6.$$

Thus a system is "small," by this criterion, when  $N < 10^6$ . For a boundary effect in a two-dimensional system:

$$\frac{N^{1/2}}{N} = 0.01; \quad N < 10^4.$$

For a  $\ln N$  term:

$$\frac{\ln N}{N} = 0.01; \quad N < 600.$$

For a term of order unity (boundary effect in one dimension, or "pure" effect):

$$\frac{1}{N} = 0.01; \quad N < 100.$$

**HELIX-COIL TRANSITION.** We have already mentioned that this subject is best treated in Chapter 5. But an oversimplified rod-like model provides a nice example of an  $N, f, T$  system. We begin with a modified version of one of the special cases treated by Gibbs and DiMarzio.<sup>1</sup>

Consider a rodlike macromolecule containing  $N$  units, each of which can be in two states,  $H$  (helix) and  $C$  (coil). For generality we include the possibility of exerting a force  $f$  on the ends of the chain, although

<sup>1</sup> J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **30**, 271 (1959).

$f = 0$  is the case of most interest. Rotation of the macromolecule is omitted. Let  $q_H(T)$  and  $q_C(T)$  be intrinsic partition functions for  $H$  and  $C$  units, and let the constants  $l_H$  and  $l_C$  be the lengths of a unit ( $l_C > l_H$ ). The total length, for a rod, is then just the sum of the unit lengths.

We investigate first the special case in which coil regions can exist only at the two ends of the chain. That is, the helix can be "un-zipped" from the ends only. A typical sequence of units would then be



If there are  $n$   $H$  units and  $N - n$   $C$  units, the left end ( $\overset{*}{H}$ ) of the  $H$  sequence can be in any one of  $N - n + 1$  locations, for  $1 \leq n \leq N$ . This is a configurational degeneracy. This degeneracy is unity when  $n = 0$ .

The partition function  $\Delta$  is therefore

$$\begin{aligned}\Delta &= \sum_l Q(N, l, T) e^{fl/kT} \\ &= q_C^N e^{Nl_C f/kT} + \sum_{n=1}^N (N - n + 1) q_C^{N-n} q_H^n e^{[(N-n)l_C + nl_H]f/kT},\end{aligned}\quad (2-85)$$

where  $l$  is the total length of the macromolecule. The summation is easy, and we find

$$\Delta(N, f, T) = e^{-N\bar{\mu}/kT} = r_C^N \frac{Nr(1-r) + 1 - 2r + r^{N+2}}{(1-r)^2}, \quad (2-86)$$

where

$$\begin{aligned}r_C &= q_C(T) e^{fl_C/kT}, & r_H &= q_H(T) e^{fl_H/kT}, \\ r(f, T) &= \frac{r_H}{r_C}.\end{aligned}$$

In the macroscopic limit,  $N \rightarrow \infty$ ,

$$\begin{aligned}\ln \Delta &\rightarrow N \ln r_C & \text{if } r < 1, \\ &\rightarrow N \ln r_H & \text{if } r > 1.\end{aligned}\quad (2-87)$$

This model thus predicts a first-order phase transition at  $r = 1$  when

$N = \infty$ . This is a consequence of the fact that the model artificially allows only two  $HC$  boundaries instead of an indefinite number. As is well known,<sup>1</sup> a first-order transition in a one-dimensional system with forces of finite range, treated exactly, can occur only in the double limit  $N \rightarrow \infty$ ,  $T \rightarrow 0$ .

We find, for  $\mu$ ,

$$-\frac{\mu}{kT} = \left( \frac{\partial \ln \Delta}{\partial N} \right)_{T,f} = \ln r_C + \frac{r(1-r) + r^{N+2} \ln r}{Nr(1-r) + 1 - 2r + r^{N+2}}. \quad (2-88)$$

At  $r = 1$ ,

$$-\frac{\hat{\mu}}{kT} = \ln r_C + \frac{1}{N} \ln \frac{N^2 + N + 2}{2} \quad (2-89)$$

$$-\frac{\mu}{kT} = \ln r_C + \frac{2N + 1}{N^2 + N + 2}. \quad (2-90)$$

The mean value of  $n$  is linearly related to  $\bar{l}$  by

$$\bar{l} = (N - \bar{n})l_C + \bar{n}l_H. \quad (2-91)$$

If we write Eq. (2-85) as

$$\Delta = r_C^N \left[ 1 + \sum_{n=1}^N (N - n + 1)r^n \right],$$

then

$$\bar{n} = r \frac{\partial \ln \Delta}{\partial r} \quad (2-92)$$

and

$$\frac{\bar{n}}{N} = \frac{r[N(1-r)(1+r^{N+1}) - 2r + 2r^{N+1}]}{N(1-r)[Nr(1-r) + 1 - 2r + r^{N+2}]}. \quad (2-93)$$

This quantity is the mean fraction of helical units in the chain. It is experimentally observable by optical methods. Figure 2-2 shows a plot of  $\bar{n}/N$  against  $\ln r$ . To illustrate the physical significance of  $\ln r$ , we take  $f = 0$  and suppose that both  $q_C$  and  $q_H$  have simple

<sup>1</sup> See M. E. Baur and L. H. Nosanow, *J. Chem. Phys.*, **37**, 153 (1962), for a recent discussion.



energy (e.g., hydrogen bond in  $H$ ) and entropy (e.g., free rotation in  $C$ ) factors. Then

$$r = \frac{q_H}{q_C} = \frac{\omega_H e^{-\epsilon_H/kT}}{\omega_C e^{-\epsilon_C/kT}},$$

or

$$\ln r = \ln \frac{\omega_H}{\omega_C} + \frac{\epsilon_C - \epsilon_H}{kT},$$

where  $\omega_H/\omega_C < 1$  and  $\epsilon_C - \epsilon_H > 0$ . Thus  $\ln r$  is linearly related to  $1/T$ . A related experimental example is shown in Fig. 2-3.

The value of  $\bar{n}/N$  at  $r = 1$  is

$$\begin{aligned} \frac{\bar{n}}{N} &= \frac{(N+1)(N+2)}{3(N^2+N+2)} \\ &\rightarrow \frac{1}{3} \quad \text{as } N \rightarrow \infty. \end{aligned} \quad (2-94)$$

Only the  $N = \infty$  curve in Fig. 2-2 falls within the province of macroscopic thermodynamics. The other curves are in the domain of small system thermodynamics. The effect of  $N$  on the intensive property  $\bar{n}/N$  is very sizeable in this case.

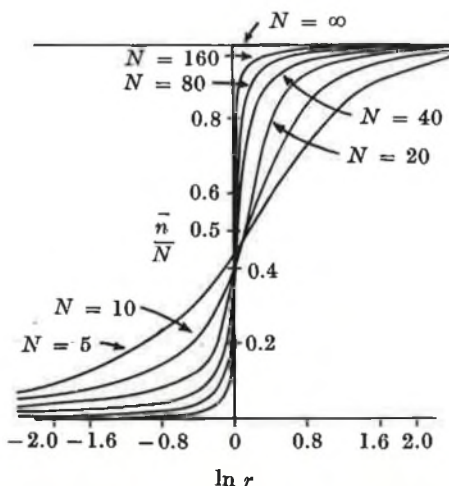


FIGURE 2-2. Mean fraction of helical units as a function of  $\ln r$  (linearly related to  $1/T$ ) for the "unzipper from the ends" model of the helix-coil transition.

Next, for purposes of comparison, let us turn to the simplest possible first-order phase-transition model. For a one-dimensional system this is an even more artificial case than the above zipper model, as we allow only two of the terms in Eq. (2-85):  $n = 0$  or  $n = N$ . This is an "all-or-none" system: all units are  $C$  or all  $H$ . This type of model is, however, physically significant for phase transitions in two- or three-dimensional systems.

We have, in the same notation as above,

$$\begin{aligned}\Delta &= e^{-N\hat{\mu}/kT} = r_C^N + r_H^N \\ &= r_C^N(1 + r^N).\end{aligned}\quad (2-95)$$

The macroscopic limit is again Eq. (2-87). For the chemical potentials we have

$$-\frac{\hat{\mu}}{kT} = \ln r_C + \frac{1}{N} \ln(1 + r^N) \quad (2-96)$$

$$= \ln r_C + \frac{1}{N} \ln 2 \quad \text{when } r = 1;$$

$$-\frac{\mu}{kT} = \ln r_C + \frac{r^N \ln r}{1 + r^N} \quad (2-97)$$

$$= \ln r_C \quad \text{when } r = 1.$$

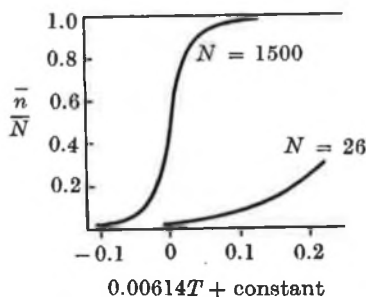


FIGURE 2-3. Mean fraction of helical units as a function of  $T$  for poly- $\gamma$ -benzyl-L-glutamate (smooth curves through experimental points). Data from P. Doty and J. T. Yang, *J. Am. Chem. Soc.*, **78**, 498 (1956). See also B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959). Usually  $\bar{n}/N$  increases with  $1/T$  rather than  $T$ .

The fraction of helical units is

$$\begin{aligned}\frac{\bar{n}}{N} &= \frac{r}{N} \frac{\partial \ln \Delta}{\partial r} = \frac{r^N}{1 + r^N} \\ &= \frac{1}{2} \quad \text{when } r = 1.\end{aligned}\quad (2-98)$$

This quantity is shown as a function of  $\ln r$  in Fig. 2-4. Again there are relatively large effects of  $N$  on the behavior of the system. This is characteristic of a phase transition.

Because of the simplicity of the above results, it is especially easy to check thermodynamic equations with them. Suggested examples, which are left to the reader, are Eqs. (2-20) and (2-38).

Finally, again for comparison, suppose each unit can be  $C$  or  $H$ , independently. The partition function is

$$\Delta = \sum_{n=0}^N \frac{N! r_C^{N-n} r_H^n}{(N-n)! n!} = (r_C + r_H)^N. \quad (2-99)$$

Then

$$\mu = \hat{\mu} = -kT \ln (r_C + r_H), \quad (2-100)$$

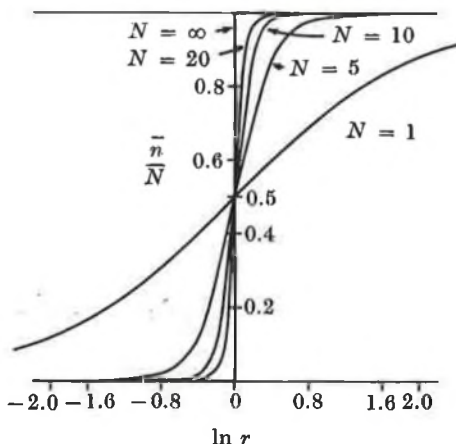


FIGURE 2-4. Mean fraction of helical units as a function of  $\ln r$  (linearly related to  $1/T$ ) for the "all-or-none" model of the helix-coil transition. The  $N = 1$  curve also represents Eq. (2-101).

and

$$\frac{\bar{n}}{N} = \frac{r}{1 + r} \quad (2-101)$$

These expressions for  $\mu$ ,  $\hat{\mu}$ , and  $\bar{n}/N$  are independent of  $N$ : for any  $N$ , this system behaves thermodynamically like a macroscopic system. Equation (2-101) is included in Fig. 2-4.

The three cases considered in this subsection are unrealistic but instructive models of a helix-coil,  $\alpha$ - $\beta$ , or linear Ising system. There are, in reality, cooperative interactions between neighboring units in systems of this type. These interactions are taken into account in an extreme way here by allowing only three sequences (coil-helix-coil) in the zipper model and only one sequence (all coil or all helix) in the phase-transition model. The independent-unit model, on the other hand, does not take interactions between neighboring units into account at all. *Exact* treatments of various finite one-dimensional systems with interactions between neighboring units are well known. Our reason for not including any of these is simply to avoid mathematical complexity in a book devoted primarily to thermodynamics, not statistical mechanics.

### 2-3. SOLVENT EFFECTS

Up to this point, in both Chapter 1 and Chapter 2, our thermodynamic analysis has referred to an ensemble of small systems which are distinguishable and have fixed centers of mass. This approach is particularly appropriate in developing the thermodynamics applicable to statistical mechanical models of finite systems. But experimental small systems will in general be immersed in a solvent, will have translational motion, and hence will be indistinguishable. We therefore have the task of showing that these very fundamental complications can be taken care of without vitiating the work we have done so far.

We shall always restrict our discussions on this subject to small systems which are *isolated* from each other, that is, to an *infinitely dilute* collection (ensemble) of small systems with translational motion. Otherwise the systems would interact and not be independent. The case in which the small systems exist in what would otherwise be a vacuum (i.e., the small systems themselves constitute a dilute one-component gas) is treated in Section 3-3. Here we

consider small systems in a solvent (usually liquid, but it could be gaseous or solid). We shall begin with a one-component solvent, but a multicomponent solvent will be discussed at the end of the section.

The energy  $E$  and volume  $V$  are not possible environmental variables for experimental small systems with translational motion in a closed container. There will be energy exchange owing to collisions with solvent, with other small systems, or the walls. The environmental variable will be  $T$  rather than  $E$ . Also, the volume  $V$  of a small system in this situation is uncontrollable and will fluctuate. The environmental variable will instead be the pressure  $p$  exerted on the solvent and in turn by the solvent on the small systems. If there is no solvent, the pair  $p$ - $V$  is absent from the analysis (see Section 3-3). In special cases, as an approximation, the solvent might be considered to be an inert medium which merely serves to fix the pressure  $p$  and temperature  $T$  of the small systems moving in it. But in general, of course, we have to assume that the solvent interacts with the small systems in some possibly complicated way, including energy, entropy, and volume effects.

ONE-COMPONENT SOLVENT. We are concerned here with a binary macroscopic solution of  $\mathcal{N}$  identical small systems (the "solute") in  $N_1$  molecules of a solvent. The solution is at pressure  $p$  and temperature  $T$ . It is infinitely dilute with respect to the small systems, but still  $\mathcal{N}$  is a very large number, as usual.

Each small system contains  $N$  molecules (or monomers, etc.). From the point of view of macroscopic thermodynamics,  $N$  is a parameter and not one of the usual thermodynamic variables (these are  $p, T, \mathcal{N}, N_1$ ). However, we shall introduce variations in the parameter  $N$ , and it is in fact this step which leads us to something other than ordinary dilute binary-solution thermodynamics.

For the binary solution, we write

$$dE_T = T dS_T - p dV_T + \mu_1 dN_1 + \mu^\square d\mathcal{N} + \mu \mathcal{N} dN. \quad (2-102)$$

All terms but the last are standard in solution thermodynamics. In the last term,  $\mu$  is defined by  $\mu \mathcal{N} \equiv \partial E_T / \partial N$ . The subscript  $T$  (total) refers to the whole solution  $p, T, \mathcal{N}, N_1$ ; the superscript  $\square$  refers to the small systems (solute) at infinite dilution. Now consider the

same solvent ( $p, T, N_1$ ), but with no small systems present ( $\mathcal{N} = 0$ ):

$$dE^* = T dS^* - p dV^* + \mu_1^* dN_1, \quad (2-103)$$

where the asterisk refers to properties in the pure solvent. Since the solution is infinitely dilute,

$$E_T = N_1 \mathbb{E}_1^*(p, T) + \mathcal{N} \tilde{\mathbb{E}}^\square(N, p, T) \quad (2-104)$$

$$V_T = N_1 v_1^*(p, T) + \mathcal{N} \tilde{v}^\square(N, p, T), \quad (2-105)$$

while, for the pure solvent,

$$E^* = N_1 \mathbb{E}_1^*, \quad V^* = N_1 v_1^*,$$

where  $\mathbb{E}_1^*$  and  $v_1^*$  are properties per molecule in the pure solvent; they are also the partial molal (strictly, partial molecular) quantities for the solvent species in the solution in the infinite dilution limit. The quantities  $\tilde{\mathbb{E}}^\square$  and  $\tilde{v}^\square$  are the partial molal energy and volume of the solute in the same limit. We shall introduce the symbol  $\bar{E}$  for  $\tilde{\mathbb{E}}^\square$  and  $\bar{V}$  for  $\tilde{v}^\square$ , below.

The situation is a little more complicated for the free energy  $F_T$  and entropy  $S_T$  of the solution.<sup>1</sup> For the free energy, we have

$$F_T = N_1 \mu_1 \left( p, T, \frac{\mathcal{N}}{N_1} \right) + \mathcal{N} \mu^\square \left( N, p, T, \frac{\mathcal{N}}{N_1} \right) \quad (2-106)$$

$$F^* = N_1 \mu_1^*(p, T),$$

where  $\mu_1$  has the limiting form

$$\mu_1 = \tilde{\mathbb{E}}_1 = \mu_1^*(p, T) - \frac{\mathcal{N} kT}{N_1}. \quad (2-107)$$

The quantity  $\mu^\square$  contains a divergent term  $kT \ln(\mathcal{N}/N_1)$  which we want to subtract out, since it depends only on the number of small systems in the "ensemble," but not on their "intrinsic" properties—which are what we are interested in. We therefore define a new function  $\hat{\mu}(N, p, T)$  by the equation

$$\mu^\square = \tilde{\mathbb{E}}^\square = N \hat{\mu}(N, p, T) + kT \ln \frac{\mathcal{N}}{N_1}. \quad (2-108)$$

<sup>1</sup> See, for example, the series expansions in sec. II of T. L. Hill, *J. Am. Chem. Soc.*, **79**, 4885 (1957).

This function depends not only on  $N, p$ , and  $T$  but also, of course, on the choice of solvent. The same is true of  $\bar{E} = \bar{E}^\square$  and  $\bar{V} = \bar{V}^\square$ , above.

The entropy of the solution is

$$S_T = N_1 \tilde{s}_1 \left( p, T, \frac{\mathcal{N}}{N_1} \right) + \mathcal{N} \tilde{s}^\square \left( N, p, T, \frac{\mathcal{N}}{N_1} \right) \quad (2-109)$$

$$S^* = N_1 s_1^*(p, T).$$

Corresponding to Eq. (2-107), we have

$$\tilde{s}_1 = s_1^*(p, T) + \frac{\mathcal{N}k}{N_1}. \quad (2-110)$$

We now wish to define an "intrinsic" entropy  $S(N, p, T)$  in such a way as to be consistent with Eqs. (2-1) and (2-2), using the definitions of  $\mu$ ,  $\bar{E}$ ,  $\bar{V}$ , and  $\hat{\mu}$  already mentioned. To do this, we first integrate Eqs. (2-102) and (2-103) and subtract:

$$\bar{E}_T - E^* = T(S_T - S^*) - p(V_T - V^*) + (\mu_1 - \mu_1^*)N_1 + \mu^\square \mathcal{N}.$$

Upon employing Eqs. (2-104), (2-105), and (2-107) to (2-110), this becomes<sup>1</sup>

$$\mathcal{N}\bar{E} = T\mathcal{N}\tilde{s}^\square - p\mathcal{N}\bar{V} + \left( N\hat{\mu} + kT \ln \frac{\mathcal{N}}{N_1} \right) \mathcal{N}.$$

We divide this equation by  $\mathcal{N}$  and set the right-hand side equal to  $TS - p\bar{V} + \hat{\mu}N$  [in order to satisfy Eq. (2-2)]. This leads to the following definition of  $S$ :

$$\tilde{s}^\square = S(N, p, T) - k \ln \frac{\mathcal{N}}{N_1}. \quad (2-111)$$

This result might have been anticipated since we are here merely removing the divergent term  $-k \ln(\mathcal{N}/N_1)$  from  $\tilde{s}^\square$ , just as in Eq. (2-108).

<sup>1</sup> This equation also follows directly from

$$\bar{E}^\square = T\tilde{s}^\square - p\bar{V}^\square + \mu^\square.$$

As a check on self-consistency, we subtract Eq. (2-103) from (2-102), use the above definitions and find

$$\begin{aligned} d(\mathcal{N}\bar{E}) = T d\left(\mathcal{N}S - \mathcal{N}k \ln \frac{\mathcal{N}}{N_1} + \mathcal{N}k\right) - p d(\mathcal{N}\bar{V}) \\ - \frac{\mathcal{N}kT}{N_1} dN_1 + \left(\hat{\mu}N + kT \ln \frac{\mathcal{N}}{N_1}\right) d\mathcal{N} + \mu\mathcal{N} dN. \end{aligned}$$

After cancellation of some terms, this simplifies to

$$d(\mathcal{N}\bar{E}) = T d(\mathcal{N}S) - p d(\mathcal{N}\bar{V}) + \hat{\mu}N d\mathcal{N} + \mu\mathcal{N} dN. \quad (2-112)$$

Substitution of

$$\hat{\mu}N = \bar{E} - TS + p\bar{V} \quad (2-113)$$

for  $\hat{\mu}N$  in Eq. (2-112) gives

$$d\bar{E} = T dS - p d\bar{V} + \mu dN. \quad (2-114)$$

Thus we have equations which are formally identical with (2-1) and (2-2), even though solvent is present and the small systems have translational motion. Also, of course, all the deductions made from these equations will be formally identical with the earlier results in Section 2-1. This includes, incidentally, the heat-capacity equations (2-31) to (2-34), in which we identify  $C_p$  with  $\bar{c}_p^\square$ .

The chemical potential  $\hat{\mu}$  is closely related to the standard chemical potential of the solute on the molality basis. For if we write

$$\mu^\square = \mu^\Delta + kT \ln m \quad (m \rightarrow 0),$$

where  $\mu^\Delta$  is the standard chemical potential per solute molecule and  $m$  the solute molality, then comparison with Eq. (2-108) shows that

$$N\hat{\mu} = \mu^\Delta + kT \ln \frac{1000}{M_1}, \quad (2-115)$$

since  $m = 1000\mathcal{N}/M_1N_1$ , where  $M_1$  is the molecular weight of the solvent. In ordinary solution thermodynamics,  $\mu^\Delta$  depends on  $p$ ,  $T$  and the solvent. Here it also depends on the parameter  $N$ . Note that it is  $\hat{\mu}$  and not  $\mu$ , defined in Eq. (2-102), which is so closely related to the macroscopic quantities  $\mu^\square$  and  $\mu^\Delta$ .



Let us summarize the new meanings which must be attached to  $\bar{E}$ ,  $\bar{V}$ , etc.:

$$\bar{E} = \tilde{E}^\square, \quad \bar{V} = \tilde{v}^\square, \quad C_p = \tilde{c}_p^\square, \quad S = \tilde{s}^\square + k \ln \frac{\mathcal{N}}{N_1}, \quad (2-116)$$

$$\hat{\mu} = \frac{1}{N} \left( \mu^\square - kT \ln \frac{\mathcal{N}}{N_1} \right), \quad \mu = \frac{1}{\mathcal{N}} \left( \frac{\partial E_T}{\partial N} \right)_{S_T, V_T, N_1, \mathcal{N}}.$$

The last relation can be rewritten as

$$\begin{aligned} \mu &= \frac{1}{\mathcal{N}} \left( \frac{\partial E_T}{\partial N} \right)_{T, p, N_1, \mathcal{N}} \\ &= \left( \frac{\partial \mu^\square}{\partial N} \right)_{T, p, \mathcal{N}/N_1} = \left( \frac{\partial N \hat{\mu}}{\partial N} \right)_{T, p}, \end{aligned}$$

where we have used Eqs. (2-106) and (2-108). This confirms Eq. (2-12a). We see, then, that, for small systems moving in a solvent, partial molal quantities at infinite dilution play the same role as  $\bar{E}$ ,  $\bar{V}$ , etc., do in Sections 2-1 and 2-2, with the understanding that the divergent  $\ln(\mathcal{N}/N_1)$  terms are not included in  $S$  and  $N\hat{\mu}$ . This is an intuitively reasonable result, since these partial molal quantities measure the average effect on the appropriate extensive property of adding a single small system to the pure solvent.<sup>1</sup> Interactions between small systems and solvent are automatically included in the partial molal quantities. The functions defined in Eqs. (2-116) include contributions from rotation and translation.

It should be noted that the  $\ln(\mathcal{N}/N_1)$  corrections introduced above are operationally well defined and easy to apply in practice.

Because of the fact that the basic thermodynamic equations are formally identical whether the small systems move in a solvent or not, we do not have to keep this distinction in mind in most of our work. It is always understood that the interpretation of  $\bar{E}$ ,  $\bar{V}$ , etc., in Eqs. (2-116) is to be made when necessary.

It was shown in Section 1-4 that a general basic treatment could be given which was applicable to *all* environments. This is no longer

<sup>1</sup> In the special case that the solvent is a very dilute gas,  $\bar{V} = \tilde{v}^\square$  is no longer a measure of the effective "size" of the small system but rather is equal to  $kT/p$ . In general  $\tilde{v}^\square$  is a measure of the size of the small system if this size is large compared with  $v_1^*$ .

the case when the small systems are in a solvent, because many environments are not even possible when solvent is present, for example, those with fixed  $E$  or  $V$ . See also Chapter 7.

In conclusion, we emphasize that there are two distinct thermodynamic levels involved in the above discussion: Eq. (2-102) refers to a macroscopic dilute binary solution of small systems (macromolecules, colloidal particles, etc.) in a solvent; Eqs. (2-113) and (2-114) refer to a single small system (including interaction with solvent). The latter equations themselves go over into macroscopic thermodynamic equations if the small system becomes indefinitely large.

**MIXED SOLVENT.** The solvent may have any number of components, say,  $c$ , without introducing complications. Hence we need give only a very brief discussion of this situation. The solute is again taken as infinitely dilute but the solvent composition (denoted below by  $sc$ ) is arbitrary. The solvent composition may be specified by  $c-1$  intensive variables. Equations (2-102) and (2-103) become

$$dE_T = T dS_T - p dV_T + \sum_{i=1}^c \mu_i dN_i + \mu^\square d\mathcal{N} + \mu \mathcal{N} dN \quad (2-117)$$

$$dE^* = T dS^* - p dV^* + \sum_{i=1}^c \mu_i^* dN_i, \quad (2-118)$$

where

$$E_T = E^* + \mathcal{N} \tilde{E}^\square(N, p, T, sc)$$

$$E^* = \sum_i N_i \tilde{E}_i^*(p, T, sc),$$

with similar equations for the volume. We introduce the symbols  $\tilde{E}$  for  $\tilde{E}^\square$  and  $\tilde{V}$  for  $\tilde{V}^\square$ .

The free energy is

$$F_T = \sum_i N_i \mu_i(p, T, x', sc) + \mathcal{N} \mu^\square(N, p, T, x', sc)$$

$$F^* = \sum_i N_i \mu_i^*(p, T, sc),$$

As before, we define the function  $\hat{\mu}(N, p, T, sc)$  by

$$\mu^\square = N \hat{\mu}(N, p, T, sc) + kT \ln x', \quad (2-119)$$

where

$$x' = \frac{\mathcal{N}}{N_1 + \dots + N_c}.$$

Then it is easy to show (see Section 7-2, for example) that

$$\mu_i = \mu_i^*(p, T, sc) + \left[ (N_1 + \dots + N_c) \frac{\partial \hat{\mu} N}{\partial N_i} - kT \right] x'.$$

The expressions for  $S_T$  and  $S^*$  are similar, with

$$\tilde{s}_i = \tilde{s}_i^* + \left[ - (N_1 + \dots + N_c) \frac{\partial^2 \hat{\mu} N}{\partial T \partial N_i} + k \right] x'$$

$$\tilde{s}^\square = S(N, p, T, sc) - k \ln x'. \quad (2-120)$$

Again Eqs. (2-113) and (2-114) are satisfied (with solvent composition held constant in the latter case) by  $\mu$ ,  $\tilde{E}$ ,  $\tilde{V}$ ,  $\hat{\mu}$ , and  $S$  here defined.

Thus the formal results are the same whether the solvent is mixed or not. Of course the small system thermodynamic functions depend on solvent composition if  $c > 1$ , and this composition (e.g., the ionic strength) may be varied.

**ALTERNATIVE TREATMENT.** It is possible to avoid explicit mention of the thermodynamic properties of the solvent, if desired. To do this, we start with

$$\tilde{E}^\square = T\tilde{s}^\square - p\tilde{v}^\square + \mu^\square. \quad (2-121)$$

We define  $\tilde{E} = \tilde{E}^\square$ ,  $\tilde{V} = \tilde{v}^\square$  and  $\hat{\mu}$  as in Eq. (2-119). We then find that Eq. (2-113) is obtained if we define  $S$  as in Eq. (2-120).

We also have

$$d\mu^\square = -\tilde{s}^\square dT + \tilde{v}^\square dp + \frac{\partial \mu^\square}{\partial x'} dx' + \frac{\partial \mu^\square}{\partial (sc)} d(sc) + \frac{\partial \mu^\square}{\partial N} dN, \quad (2-122)$$

where  $N$  is regarded as a parameter. The other terms are conventional. We define<sup>1</sup>  $\mu$  as  $\partial \mu^\square / \partial N$ . From Eq. (2-119),  $\partial \mu^\square / \partial x' = kT/x'$ .

<sup>1</sup>This can be shown to be equivalent to the definition of  $\mu$  in Eq. (2-117.) See Section 7-2.

We now substitute  $\mu$  and  $kT/x'$  for the appropriate derivatives in Eq. (2-122), and also introduce  $\bar{V}$  for  $\bar{v}^\square$  and Eqs. (2-119) and (2-120) for  $\mu^\square$  and  $\mathfrak{F}^\square$ , respectively. After cancellation of terms, we are left with the desired result:

$$d(\hat{\mu}N) = -S dT + \bar{V} dp + \mu dN \quad (sc \text{ constant}). \quad (2-123)$$

RELATION TO STATISTICAL MECHANICS. We return again to a one-component solvent for simplicity. For theoretical work, one needs the relation between the fundamental thermodynamic function  $N\hat{\mu}$  and statistical mechanics. This connection is provided by "constant-pressure solution theory":<sup>1</sup>

$$N\hat{\mu} = kT \ln \frac{N_1 \Delta_T(N_1, 0, p, T)}{\Delta_T(N_1, 1, p, T)}, \quad (2-124)$$

where

$$\Delta_T(N_1, \mathcal{N}, p, T) = \sum_V Q_T(N_1, \mathcal{N}, V_T, T) e^{-pV_T/kT}. \quad (2-125)$$

The partition functions  $\Delta_T$  and  $Q_T$  refer to the binary macroscopic solution.

<sup>1</sup> T. L. Hill, *J. Am. Chem. Soc.*, **79**, 4885 (1957), and S.T., p. 362. See especially equations (5), (17), (26), (29), (37), and (43) in the first reference.

# ENVIRONMENTAL VARIABLES $N$ , $T$

The previous chapter dealt with the environmental variables  $N$ ,  $p$ ,  $T$ . Here we consider the simpler situation in which the pressure does not appear as a variable (nor does the volume). The respective sections of the present chapter are concerned with the following ways in which this can come about: the small systems are incompressible, as an approximation; the pressure is held constant and never varied; and the small systems form a very dilute gas, with no other molecules present. The thermodynamic equations are formally the same in all these cases. As one would expect, these equations are simplified or degenerate versions of some of those in Chapter 2. Because of this relation to Chapter 2, it is not necessary to give a lengthy analysis here.

## 3-1. INCOMPRESSIBLE SMALL SYSTEM

We start with the  $N$ ,  $p$ ,  $T$  basic equations

$$d\bar{E} = T dS - p d\bar{V} + \mu dN \quad (3-1)$$

$$\bar{E} = TS - p\bar{V} + \mu N, \quad (3-2)$$

from Chapters 1 and 2. It will be recalled that these equations apply whether or not a solvent is present. The special case we consider here is that  $\bar{V}$  is independent of  $p$  and  $T$ ; it is a function of  $N$  only. This will be a useful simplifying approximation for many experimental systems. It is also a commonly used model in statistical mechanics. It is not necessary to assume that  $\bar{V}$  is proportional to  $N$ , though this will of course be the case when  $N \rightarrow \infty$ .

Since  $\bar{V}$  is a function of  $N$  only, we shall eliminate  $\bar{V}$  as an independent variable in Eq. (3-1) by combining the terms  $-p d\bar{V}$  and  $\mu dN$ . Let us write

$$\bar{V} = cf(N), \quad d\bar{V} = c \frac{df}{dN} dN,$$

where  $c$  is a constant and  $f$  a function of  $N$  only. Then Eqs. (3-1) and (3-2) become

$$d\bar{E} = T dS + \mu' dN \quad (3-3)$$

$$\bar{E} = TS + \mu' N, \quad (3-4)$$

where

$$\mu' = \mu - pc \frac{df}{dN} \quad \text{and} \quad \hat{\mu}' = \hat{\mu} - \frac{pcf}{N}. \quad (3-5)$$

According to Eq. (2-11),

$$\left( \frac{\partial N \hat{\mu}}{\partial p} \right)_{T, N} = \bar{V} = cf(N).$$

On integrating this equation we find

$$N \hat{\mu} = cf(N)p + g(N, T),$$

where the integration constant  $g$  is a function of  $N$  and  $T$  only. Therefore  $\hat{\mu}' = g/N$  is a function of  $N$  and  $T$  only. Also,

$$\begin{aligned} \mu &= \left( \frac{\partial N \hat{\mu}}{\partial N} \right)_{T, p} = cp \frac{df}{dN} + \left( \frac{\partial g}{\partial N} \right)_T \\ -S &= \left( \frac{\partial N \hat{\mu}}{\partial T} \right)_{p, N} = \left( \frac{\partial g}{\partial T} \right)_N, \end{aligned}$$

and hence  $S$  and  $\mu' = (\partial g / \partial N)_T$  are likewise functions of  $N$  and  $T$  only. Thus all quantities appearing in Eqs. (3-3) and (3-4) depend only on  $N$  and  $T$ . These equations can be taken, then, as fundamental for an  $N, T$  system.

At this point to conform with other notation, we drop the primes in Eqs. (3-3) and (3-4), but the definitions in Eqs. (3-5) should of course be kept in mind. We have

$$d\bar{E} = T dS + \mu dN \quad (3-6)$$

$$\bar{E} = TS + \mu N = TS + A, \quad (3-7)$$

and therefore

$$d(\hat{\mu}N) = dA = -S dT + \mu dN \quad (3-8)$$

$$d[(\hat{\mu} - \mu)N] = d\mathcal{E} = -S dT - N d\mu \quad (3-9)$$

$$d\hat{\mu} = -\frac{S}{N} dT + \frac{\mu - \hat{\mu}}{N} dN \quad (3-10)$$

$$d\mu = -\left(\frac{\partial S}{\partial N}\right)_T dT - \frac{1}{N}\left(\frac{\partial \mathcal{E}}{\partial N}\right)_T dN. \quad (3-11)$$

These should be compared with Eqs. (2-1) to (2-17). There then follow relations such as

$$\left(\frac{\partial N\hat{\mu}}{\partial T}\right)_N = -S, \quad \left(\frac{\partial N\hat{\mu}}{\partial N}\right)_T = \mu, \quad (3-12)$$

etc. Since Chapter 2 can be used as a guide, there seems little point in pursuing this type of discussion any further.

If the small system absorbs heat with  $N$  (and therefore  $\bar{V}$ ) constant, we have from Eq. (3-1),

$$d\bar{E} = T dS = DQ = C dT \quad (N \text{ constant}), \quad (3-13)$$

where  $C$  is the heat capacity. Thus

$$C = \left(\frac{\partial \bar{E}}{\partial T}\right)_N = T \left(\frac{\partial S}{\partial T}\right)_N. \quad (3-14)$$

The connection with statistical mechanics is

$$N\hat{\mu} = A = -kT \ln Q(N, T). \quad (3-15)$$

*Example. Lattice Model for Polymer Molecules.* Fisher and Hiley<sup>1</sup> have studied a lattice model of a polymer molecule with excluded volume and nearest-neighbor forces arising from polymer-solvent interactions. Exact numerical calculations were made for short chains of up to about  $N = 10$  links. Careful extrapolations were made and shown to be justified for  $N > 10$ . For both plane square

<sup>1</sup> M. E. Fisher and B. J. Hiley, *J. Chem. Phys.*, **34**, 1253 (1961). These authors use the symbol  $\mu$  instead of  $M$  in Eq. (3-16).

and simple cubic lattices the asymptotic ( $N$  large) expression for the free energy of a single polymer chain was found to be of the form

$$A = N\hat{\mu} = -kT[N \ln M(\eta) + \alpha(\eta) \ln N], \quad (3-16)$$

where  $\eta = e^{-V_0/kT}$  and  $V_0$  (a constant) measures the energy of a polymer-polymer contact relative to the energies of polymer-solvent and solvent-solvent contacts. The functions  $M(\eta)$  and  $\alpha(\eta)$  are different for the two lattices and are shown graphically by Fisher and Hiley. The term  $N \ln M$  in Eq. (3-16) is the macroscopic term, while  $\alpha \ln N$  represents the first departure from macroscopic behavior for a small system (finite polymer chain).

From Eq. (3-16) we deduce for other functions

$$\hat{\mu} = -kT[\ln M(\eta) + \alpha(\eta)N^{-1} \ln N] \quad (3-17)$$

$$\mu = \left( \frac{\partial N\hat{\mu}}{\partial N} \right)_T = -kT[\ln M(\eta) + \alpha(\eta)N^{-1}] \quad (3-18)$$

$$\mathcal{E} = N(\hat{\mu} - \mu) = -kT\alpha(\eta)(\ln N - 1). \quad (3-19)$$

Also, from

$$\left( \frac{\partial N\hat{\mu}/kT}{\partial 1/kT} \right)_N = \bar{E},$$

we have

$$\bar{E} = NV_0 \left( \eta \frac{d \ln M}{d\eta} + \eta \frac{d\alpha}{d\eta} \frac{\ln N}{N} \right) \quad (3-20)$$

and then

$$\begin{aligned} \frac{S}{Nk} &= \frac{\bar{E}}{NkT} - \frac{\hat{\mu}}{kT} \\ &= \ln M + T \frac{d \ln M}{dT} + \left( \alpha + T \frac{d\alpha}{dT} \right) \frac{\ln N}{N}. \end{aligned} \quad (3-21)$$

### 3-2. INVARIABLE PRESSURE

Consider a small  $N, p, T$  system for which, for one reason or another,  $p$  is a constant, not to be varied (for example,  $p = 1$  atm). A special



case is  $p = 0$  (or  $f = \text{force} = 0$ , in place of  $p$ ). A solvent may or may not be present (see Chapter 2). We rewrite Eqs. (3-1) and (3-2) in the form

$$d(\bar{E} + p\bar{V}) = dH = T dS + \mu dN \quad (p \text{ constant}) \quad (3-22)$$

$$\bar{E} + p\bar{V} = H = TS + \mu N, \quad (3-23)$$

and then

$$d(N\mu) = -S dT + \mu dN \quad (p \text{ constant}). \quad (3-24)$$

These equations are formally identical with Eqs. (3-6) to (3-8) if we replace  $\bar{E}$  by  $H$ . There is the same identity relative to the heat capacity:

$$dH = T dS = DQ = C_p dT \quad (N, p \text{ constant}). \quad (3-25)$$

These brief remarks are sufficient to show that the formal thermodynamics here is indistinguishable from that in Section 3-1.

### 3-3. DILUTE GAS OF SMALL SYSTEMS

Suppose we have  $\mathcal{N}$  small systems in a volume  $V$  at  $T$ . Each system contains  $N$  monomers, molecules, or units. The concentration  $\mathcal{N}/V$  is sufficiently small that the systems form an ideal gas. The equation of state is  $pV = \mathcal{N}kT$ . In this "ensemble" the small systems have translational motion and are indistinguishable. The situation resembles that in Section 2-3, except that no solvent is present here.

Of the variables  $\mathcal{N}$ ,  $V$ ,  $T$ , and  $N$ , it is obvious that  $\mathcal{N}$  and  $V$  (corresponding to  $\mathcal{N}$  and  $N_1$  in Section 2-3) are not concerned with the "intrinsic" thermodynamics of a single small system, while  $N$  and  $T$  are so concerned. Our object is therefore to define "intrinsic" thermodynamic functions for a small system, with environmental variables  $N$ ,  $T$ , in such a way that the equations connecting the functions are the same as Eqs. (3-6) and (3-7) in Section 3-1.

Examples of small systems of the type under consideration are a normal saturated hydrocarbon molecule containing  $N$  carbon atoms, a colloidal particle of graphite containing  $N$  carbon atoms, etc.

If  $N$  is quite small, say, 5 or 10, difference rather than differential equations are required if we want to vary  $N$  (Chapter 15). If one is content to hold  $N$  constant, then  $N$  can be as small as one pleases,

even  $N = 1$ . In this case the small system can be a single atom or small molecule (see the examples at the end of this section).

We start with a macroscopic equation for the dilute gas of systems (the ensemble):

$$dE_t = T dS_t - p dV + \mu_t d\mathcal{N} + \mu \mathcal{N} dN, \quad (3-26)$$

where all terms are conventional for a macroscopic system except the last. In this term  $N$  is regarded as a parameter on which the macroscopic functions depend [compare Eq. (2-102)], and  $\mu$  is defined by  $\mu \mathcal{N} \equiv \partial E_t / \partial N$ . Integration of Eq. (3-26),  $T$ ,  $p$ ,  $\mu_t$ , and  $N$  being held constant, gives

$$E_t = TS_t - pV + \mu_t \mathcal{N}. \quad (3-27)$$

By analogy with Section 2-3, we want to define the intrinsic functions  $S$  and  $\hat{\mu}$  for a small system in such a way that these quantities are independent of the variables  $\mathcal{N}$  and  $V$ . An equivalent statement is that there are divergent terms in  $\ln \mathcal{N}$  in  $S_t$  and  $\mu_t$  which must be subtracted out in order that the resulting definitions of  $S$  and  $\hat{\mu}$  will be appropriate to a single small system. We do this in a way which allows us to relate our definitions to the conventional definitions of standard free energies and entropies of gases in macroscopic thermodynamics.

We define  $N\hat{\mu} = A$  by<sup>1</sup>

$$\mu_t = N\hat{\mu} + kT \ln \frac{c}{c^\dagger}, \quad (3-28)$$

where  $c = \mathcal{N}/V$  and  $c^\dagger$  is an arbitrarily chosen constant reference value of  $c$ . Of course  $c/c^\dagger = \mathcal{N}/\mathcal{N}^\dagger$ , where  $\mathcal{N}^\dagger$  is a corresponding reference value of  $\mathcal{N}$ . Hence the term in  $\ln c$  is equivalent to the divergent term in  $\ln \mathcal{N}$  referred to above. Ordinarily the quantity

$$\mu_t - kT \ln \frac{c}{c^\dagger}$$

for an ideal gas is a function of  $T$  only, but here it will also depend on the parameter  $N$ . Therefore  $N\hat{\mu}$  is a function of  $N$  and  $T$ .

<sup>1</sup> The general connection between  $N\hat{\mu}$  and statistical mechanics is given in Eq. (3-42), below, if we regard both  $m$  and  $q_i$  as functions of  $N$ .

We now want to define  $S$  so that

$$\bar{E} = TS + N\hat{\mu} = TS + A, \quad (3-29)$$

as in Eq. (3-7). To do this, we rewrite Eq. (3-27) in the form

$$\mathcal{N}\bar{E} = \mathcal{N}TS + \mathcal{N}N\hat{\mu} = TS_t - \mathcal{N}kT + \left(N\hat{\mu} + kT \ln \frac{c}{c^\dagger}\right)\mathcal{N},$$

where we have used  $pV = \mathcal{N}kT$  and defined  $\bar{E}$  by  $E_t = \mathcal{N}\bar{E}$ . This gives<sup>1</sup>

$$S_t = \mathcal{N}S + \mathcal{N}k - \mathcal{N}k \ln \frac{c}{c^\dagger} \quad (c \rightarrow 0) \quad (3-30)$$

for the definition of  $S$ . Clearly  $S$  is a function of  $N$  and  $T$ . As a check on self-consistency, we can substitute  $E_t = \mathcal{N}\bar{E}$  and Eqs. (3-28) and (3-30) for  $\mu_t$  and  $S_t$  in Eq. (3-26) and find, after cancellation,

$$d\bar{E} = T dS + \mu dN. \quad (3-31)$$

Equations (3-8) to (3-12) then follow. This is as far as we need go in the derivation of general small system thermodynamic equations for this case.

The small system functions, defined above, include contributions from rotation and translation.

For practical purposes, the relation between  $N\hat{\mu}$  and the standard free energy per molecule,  $\mu^0$ , should be pointed out. The conventional relation is

$$\mu_t = \mu^0 + kT \ln \frac{p}{p^\dagger} \quad (p \rightarrow 0), \quad (3-32)$$

where  $p^\dagger$  is a constant reference pressure (usually 1 atm). If we equate the right-hand sides of Eqs. (3-28) and (3-32) and use  $p = ckT$ , we obtain

$$N\hat{\mu} = A = \mu^0 + kT \ln \frac{kTc^\dagger}{p^\dagger}. \quad (3-33)$$

Hence  $N\hat{\mu}$  is practically the same as  $\mu^0$ , except for a simple correction.

<sup>1</sup> The definition of  $S$  here has a term  $-k$  not present in Eq. (2-111). This point is referred to further in Section 7-2.

If we choose  $c^\dagger$  to conform with  $p^\dagger$  at  $25^\circ\text{C}$ , that is,  $p^\dagger = 298.15 \text{ } kc^\dagger$ , then

$$N\hat{\mu} = A = \mu^0 + kT \ln \frac{T}{298.15} . \quad (3-34)$$

Similarly, the standard entropy per molecule  $s^0$  is defined by

$$\frac{S_t}{\mathcal{N}} = s^0 - k \ln \frac{p}{p^\dagger} . \quad (3-35)$$

Comparison with Eq. (3-30) shows that

$$S = s^0 - k + k \ln \frac{p^\dagger}{kTc^\dagger} . \quad (3-36)$$

If  $c^\dagger$  is chosen so that  $p^\dagger = 298.15kc^\dagger$  as above, then

$$S = s^0 - k + k \ln \frac{298.15}{T} . \quad (3-37)$$

On combining Eqs. (3-33) and (3-36), we also have

$$\begin{aligned} \bar{E} &= TS + N\hat{\mu} = Ts^0 - kT + \mu^0 \\ &= H^0 - kT = E^0. \end{aligned} \quad (3-38)$$

Thus, if tables of  $\mu^0$  and  $s^0$  are available as functions of  $T$  for a sequence of molecules with different  $N$  values (say, normal saturated hydrocarbons), then  $\hat{\mu}$ ,  $S$ , and  $\bar{E}$  may be found as functions of  $N$  and  $T$ .

*Example. Simple Molecules as Small Systems.* We show here that there is no difficulty in defining thermodynamic functions for a gaseous monatomic, diatomic, or simple polyatomic molecule as a small system.<sup>1</sup> However, this is just a matter of academic interest, since small system thermodynamics hardly seems worth pursuing if the size of the system is not variable. With a small system of fixed size the only environmental variable remaining is  $T$ . Of course the temperature is determined operationally from the macroscopic gas

<sup>1</sup> See also Secs. 3-4 and 7-2 of S.T.

(ensemble) of small systems. Each small system is in a macroscopic heat bath (the remaining  $\mathcal{N} - 1$  small systems of the ensemble) at  $T$ . The basic thermodynamic equations degenerate to

$$d\bar{E} = T dS, \quad A = \bar{E} - TS, \quad dA = -S dT. \quad (3-39)$$

Thus we can speak of an energy, entropy and free energy of a single simple molecule.

For a dilute gas of  $\mathcal{N}$  molecules (small systems) in  $V$ , we write

$$Q = \frac{1}{\mathcal{N}!} q^{\mathcal{N}}, \quad q = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V q_t(T), \quad (3-40)$$

where  $q_t(T)$  is the internal partition function, if any (electronic, nuclear, rotational, vibrational). Then

$$\mu_t = -kT \left( \frac{\partial \ln Q}{\partial \mathcal{N}} \right)_{V, T} = -kT \ln \frac{q}{\mathcal{N}}. \quad (3-41)$$

We set this equal to  $\mu_t$  in Eq. (3-28) and obtain, for the free energy of a small system,

$$A(T) = -kT \ln \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \frac{q_t(T)}{c^t} \right]. \quad (3-42)$$

Then, from  $-S = dA/dT$ ,

$$S(T) = \frac{\bar{E}}{T} - \frac{A}{T},$$

where

$$\bar{E}(T) = \frac{3}{2} kT + kT^2 \frac{d \ln q_t}{dT}. \quad (3-43)$$

*Example. Normal Saturated Hydrocarbon Molecules.* This is a particularly simple illustration of small system thermodynamics. A small system here is a normal saturated hydrocarbon molecule (in the ideal-gas state) containing  $N$   $\text{CH}_2$  groups (the two hydrogen atoms left over at the ends contribute to the end effects below).

It has been found<sup>1</sup> that  $H^0$  for these molecules at 25°C, with  $N > 4$ , relative to the elements in their conventional standard states at 25°C as zero, can be well represented by

$$H^0 = -4.926N - 10.41 \text{ kcal mole}^{-1}, \quad (3-44)$$

where the first term is the macroscopic term (infinitely long hydrocarbon molecule). Therefore, from Eq. (3-38),

$$\bar{E} = -4.926N - 11.00 \text{ kcal mole}^{-1} \quad (25^\circ\text{C}, N > 4). \quad (3-45)$$

Similarly,  $S^0$  (ideal gas at 1 atm) relative to a zero for each molecule at 0°K is

$$S^0 = 9.31N + 37.07 \text{ cal mole}^{-1} \text{ deg}^{-1} \quad (25^\circ\text{C}, N > 4). \quad (3-46)$$

Hence, from Eq. (3-37),

$$S = 9.31N + 35.08 \text{ cal mole}^{-1} \text{ deg}^{-1} \quad (25^\circ\text{C}, N > 4). \quad (3-47)$$

On combining Eqs. (3-45) and (3-47), we have

$$\begin{aligned} N\hat{\mu} &= A = \bar{E} - TS \\ &= -7.70N - 21.46 \text{ kcal mole}^{-1} \quad (25^\circ\text{C}, N > 4), \end{aligned} \quad (3-48)$$

relative to the zeros of heat content and entropy mentioned above. If we write, more generally,

$$N\hat{\mu} = a(T)N + b(T) \quad (3-49)$$

$$S = -\frac{da}{dT}N - \frac{db}{dT}, \quad (3-50)$$

then we see that, at 25°C, in the above units,

$$a = -7.70, \quad b = -21.46, \quad \frac{da}{dT} = -9.31, \quad \frac{db}{dT} = -35.08.$$

<sup>1</sup> See G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics", pp. 520-521, McGraw-Hill, New York, 1961.

We also have

$$\hat{\mu} = -7.70 - 21.46N^{-1} \text{ kcal mole}^{-1} \text{ CH}_2^{-1} \quad (25^\circ\text{C}) \quad (3-51)$$

$$\mu = -7.70 \text{ kcal mole}^{-1} \text{ CH}_2^{-1} \quad (25^\circ\text{C}) \quad (3-52)$$

$$\mathcal{E} = N(\hat{\mu} - \mu) = -21.46 \text{ kcal mole}^{-1} \quad (25^\circ\text{C}). \quad (3-53)$$

The last two relations treat  $N$  as continuously variable and hence assume that  $N$  is not too small (Chapter 15). It is easy to show that the physical significance of the subdivision potential  $\mathcal{E}$  is

$$\mathcal{E} = \left( \frac{\partial \mathcal{N}A}{\partial \mathcal{N}} \right)_{T, \mathcal{N}N} = -\frac{N}{\mathcal{N}} \left( \frac{\partial \mathcal{N}A}{\partial N} \right)_{T, \mathcal{N}N}.$$

This kind of analysis of course adds nothing new to our knowledge of the properties of hydrocarbon molecules. It is merely another way of organizing, classifying, or interconnecting the data, which is all that thermodynamics can do in any case. Our purpose has been to show that a single large hydrocarbon molecule, in the gas phase, can be considered an example of a small thermodynamic system.

*Example. Rigid Linear Aggregate.* The small system in this example is a rigid linear aggregate or polymer of  $N$  units. This is an approximate model for many macromolecules, colloidal particles, etc. The small system is considered in the dilute-gas state here, but the treatment is also valid in the presence of a solvent if the small system is incompressible and the solvent inert.

Each unit has mass  $m$  and length  $a$ . The system has translational and rotational degrees of freedom, but no vibration. The bond energy between units is  $\epsilon$ , a constant (it could be taken a function of temperature). The rotational motion is assumed to be that of a rigid rod (no thickness) of mass  $Nm$ , length  $Na$ , and symmetry number 2. The moment of inertia about the center is  $I = N^3ma^2/12$ .

Then, for a dilute gas of  $\mathcal{N}$  systems in  $V$ ,

$$Q = \frac{1}{\mathcal{N}!} q^{\mathcal{N}}, \quad (3-54)$$

where

$$q = \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} V q_{\text{rot}}(T) e^{-(N-1)\epsilon/kT} \quad (3-55)$$

and

$$q_{\text{rot}} = \frac{4\pi^2 I k T}{h^2} = \frac{\pi^2 k T m a^2 N^3}{3h^2}. \quad (3-56)$$

From Eqs. (3-28) and (3-41), we find

$$N\hat{\mu} = -kT \ln \left[ \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} \frac{\pi^2 k T m a^2 N^3}{3h^2 c^\dagger} \right] + (N-1)\epsilon. \quad (3-57)$$

The macroscopic term in this expression is  $N\epsilon$ , while the small terms are of order  $kT \ln N$  (with contributions from both rotation and translation) and  $kT$ . In the limit  $N \rightarrow \infty$ ,  $\hat{\mu} \rightarrow \epsilon$ . The other thermodynamic functions are found in the usual way and are

$$\mu = \epsilon - \frac{9kT}{2N} \quad (3-58)$$

$$\bar{E} = (N-1)\epsilon + \frac{5}{2}kT \quad (3-59)$$

$$S = k \ln \left[ \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} \frac{\pi^2 k T m a^2 N^3 e^{5/2}}{3h^2 c^\dagger} \right]. \quad (3-60)$$

In the macroscopic limit, for this simple model,

$$\mu \rightarrow \epsilon, \quad \bar{E} \rightarrow N\epsilon, \quad \text{and} \quad S = 0.$$

That is, the entropy is negligible relative to  $O(Nk)$ .

*Example. Spherical Crystallite.* At the beginning of Chapter 1 and in Section 2-2 we referred to a spherical crystallite as a small thermodynamic system. Here we give a somewhat more explicit statistical mechanical discussion. We consider a dilute gas of such crystallites in a volume  $V$  (or they could be dispersed in an inert solvent). Each crystallite contains  $N$  molecules of mass  $m$  and has a volume  $Nv$ , where  $v$  is assumed independent of  $T$  and  $N$  for simplicity. The



moment of inertia about a diameter is

$$I = \frac{2Nm r^2}{5} = \frac{2mN^{5/3}}{5} \left( \frac{3v}{4\pi} \right)^{2/3},$$

where  $r$  = radius.

We use Eq. (3-54) with

$$q = \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} V q_{\text{rot}}(T) j(T) N e^{-a(T) N^{2/3} / k T}, \quad (3-61)$$

where

$$q_{\text{rot}} = \pi^{1/2} \left( \frac{8\pi^2 I k T}{h^2} \right)^{3/2},$$

$j(T)$  is the partition function per molecule in an Einstein model of the bulk crystal, and  $a(T)N^{2/3}$  is the surface free-energy term [see Eq. (2-68)]. Equations (3-28) and (3-41) then lead to

$$N\hat{\mu} = -NkT \ln j(T) + a(T)N^{2/3} - kT \ln \left[ \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{c^\dagger} \left( \frac{8\pi^2 I k T}{h^2} \right)^{3/2} \right]. \quad (3-62)$$

The first term is the macroscopic term, of order  $NkT$ . The surface term is of order  $N^{2/3}kT$ , while translation and rotation both contribute terms of order  $kT \ln N$  and  $kT$ . Actually, in a more complete formulation we would take into account the variation of surface tension with curvature, which, according to Gibbs' treatment, would add terms of order  $N^{1/3}kT$  (more important than  $kT \ln N$ ) and  $kT$ .

Other thermodynamic functions are

$$\mu = -kT \ln j + \frac{2}{3} a N^{-1/3} - \frac{4kT}{N} \quad (3-63)$$

$$\bar{E} = NkT^2 \frac{d \ln j}{dT} + \left( a - T \frac{da}{dT} \right) N^{2/3} + 3kT \quad (3-64)$$

$$S = Nk \left( \ln j + T \frac{d \ln j}{dT} \right) - \frac{da}{dT} N^{2/3} + k \ln \left[ \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} \frac{\pi^{1/2} e^3}{c \dagger} \left( \frac{8\pi^2 I k T}{h^2} \right)^{3/2} \right]. \quad (3-65)$$

The heat capacity  $C$  follows from either  $\partial \bar{E} / \partial T$  or  $T \partial S / \partial T$ .

There have been several theoretical and experimental papers in recent years on the effect of particle size on the heat capacity of solids.<sup>1</sup>

<sup>1</sup> See, for example, the following papers, where further references may be found: E. W. Montroll, *J. Chem. Phys.*, **18**, 183 (1950); G. Jura and K. S. Pitzer, *J. Am. Chem. Soc.*, **74**, 6030 (1952); J. A. Morrison and D. Patterson, *Trans. Faraday Soc.*, **52**, 764 (1956); M. Dupuis, R. Mazo, and L. Onsager, *J. Chem. Phys.*, **33**, 1452 (1960); R. Stratton, *J. Chem. Phys.*, **37**, 2972 (1962).

# ENVIRONMENTAL VARIABLES $N_1, \dots, N_c, p, T$

In this chapter we give a brief account of the thermodynamics of a closed small system of  $c$  components with environmental variables  $N_1, \dots, N_c, p, T$ . A small  $p, T$  system which is open with respect to one or more components ( $\mu_i$  replaces  $N_i$  for such a component) is considered in Chapters 7 and 10. Chemical equilibrium between components is discussed in Chapter 5.

The main experimental application of the present chapter is probably to insoluble or nonvolatile liquid or solid colloidal particles of two or more components. Regular or random copolymers, protein molecules etc., are not cases in point, because the sequence of monomers is "frozen" and not in a dynamic equilibrium. If such a polymer is made with varying degrees of polymerization but with a constant type of composition, it is an  $N, p, T$  system.

## 4-1. GENERAL RELATIONS

The basic equations for this kind of system have been given in Chapter 1 [Eqs. (1-33) to (1-39) and (1-68) to (1-75)]. The most useful of these relations are

$$d\bar{E} = T dS - p d\bar{V} + \sum_{i=1}^c \mu_i dN_i \quad (4-1)$$

$$F = \bar{E} - TS + p\bar{V} = \sum_i \mu_i N_i + \mathcal{E} \quad (4-2)$$

$$dF = -S dT + \bar{V} dp + \sum_i \mu_i dN_i \quad (4-3)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - \sum_i N_i d\mu_i. \quad (4-4)$$

For any extensive property  $G$  we define the partial molal quantity  $\tilde{g}_i$  by

$$\tilde{g}_i = \left( \frac{\partial G}{\partial N_i} \right)_{p, T, N_j}, \quad (4-5)$$

where  $j$  refers to all components except the one indicated in  $\partial N_i$ .

This quantity is a function of  $p, T, N_1, \dots, N_c$ . In a macroscopic system it is a function of  $p, T$ , and  $c - 1$  composition variables. A special case is  $\tilde{F}_i = \mu_i$ . In a one-component small system,

$$\tilde{G} = \left( \frac{\partial G}{\partial N} \right)_{p, T} \neq \frac{G}{N} = g.$$

For any  $G$ ,

$$dG = \left( \frac{\partial G}{\partial p} \right)_{T, N_i} dp + \left( \frac{\partial G}{\partial T} \right)_{p, N_i} dT + \sum_i \tilde{G}_i dN_i, \quad (4-6)$$

where  $N_i$  in the subscript means all the  $N_i$ . We extend the definition of  $[G]$  in Eq. (2-24) as follows:

$$[G] \equiv G - \sum_i N_i \tilde{G}_i. \quad (4-7)$$

This quantity vanishes in a macroscopic system. We have

$$d[G] = \left( \frac{\partial G}{\partial p} \right)_{T, N_i} dp + \left( \frac{\partial G}{\partial T} \right)_{p, N_i} dT - \sum_i N_i d\tilde{G}_i \quad (4-8)$$

$$d[G] = - \sum_i N_i d\tilde{G}_i \quad (p, T \text{ constant}). \quad (4-9)$$

This is a Gibbs–Duhem type of equation. Equation (4-4) is a special case of Eq. (4-8), since  $\mathcal{E} = [F]$ . Another form of Eq. (4-9) is

$$\left( \frac{\partial [G]}{\partial N_k} \right)_{p, T, N_j} = - \sum_i N_i \left( \frac{\partial \tilde{G}_i}{\partial N_k} \right)_{p, T, N_j} = - \sum_i N_i \left( \frac{\partial \tilde{G}_k}{\partial N_i} \right)_{p, T, N_j}. \quad (4-10)$$

The last relation follows from Eq. (4-6):

$$\frac{\partial^2 G}{\partial N_\alpha \partial N_\beta} = \frac{\partial \tilde{G}_\alpha}{\partial N_\beta} = \frac{\partial \tilde{G}_\beta}{\partial N_\alpha}. \quad (4-11)$$

If we put  $G = F$  in

$$d[G] = \frac{\partial [G]}{\partial p} dp + \frac{\partial [G]}{\partial T} dT + \sum_i \frac{\partial [G]}{\partial N_i} dN_i \quad (4-12)$$

and use

$$\frac{\partial[F]}{\partial p} = \bar{V} - \sum_i N_i \frac{\partial \mu_i}{\partial p} = [\bar{V}] \quad (4-13)$$

$$\frac{\partial[F]}{\partial T} = -S - \sum_i N_i \frac{\partial \mu_i}{\partial T} = -[S], \quad (4-14)$$

we have

$$d[F] = d\mathcal{E} = -[S] dT + [\bar{V}] dp + \sum_i [\mu_i] dN_i, \quad (4-15)$$

where

$$\begin{aligned} [\mu_i] &\equiv \left( \frac{\partial[F]}{\partial N_i} \right)_{p, T, N_j} = - \sum_k N_k \left( \frac{\partial \mu_k}{\partial N_i} \right)_{p, T, N_j} \\ &= - \sum_k N_k \left( \frac{\partial \mu_i}{\partial N_k} \right)_{p, T, N_j}. \end{aligned} \quad (4-16)$$

All terms in Eq. (4-15) are small. This is the generalization of Eq. (2-26) to a multicomponent system.

If we differentiate Eq. (4-2) with respect to  $N_i$ , we obtain

$$\mu_i = \tilde{\mathbf{E}}_i - T \tilde{\mathbf{S}}_i + p \tilde{\mathbf{V}}_i, \quad (4-17)$$

and hence

$$\sum_i N_i \mu_i = \sum_i N_i \tilde{\mathbf{E}}_i - T \sum_i N_i \tilde{\mathbf{S}}_i + p \sum_i N_i \tilde{\mathbf{V}}_i. \quad (4-18)$$

We subtract this last result from Eq. (4-2) and find

$$[F] = \mathcal{E} \doteq [\bar{E}] - T[S] + p[\bar{V}]. \quad (4-19)$$

Then, from Eqs. (4-15) and (4-19),

$$d[\bar{E}] = T d[S] - p d[\bar{V}] + \sum_i [\mu_i] dN_i. \quad (4-20)$$

We also have, from Eq. (4-15),

$$d[\mathcal{E}] = -[S] dT + [\bar{V}] dp - \sum_i N_i d[\mu_i], \quad (4-21)$$

where

$$[\mathcal{E}] \equiv \mathcal{E} - \sum_i N_i \left( \frac{\partial \mathcal{E}}{\partial N_i} \right)_{p, T, N_j} = [F] - \sum_i N_i [\mu_i]. \quad (4-22)$$

Equation (4-21) is a higher analogue of Eq. (4-4).

If we subtract Eq. (4-15) from Eq. (4-3), there results

$$d\left(\sum_k N_k \mu_k\right) = -\left(\sum_k N_k \tilde{s}_k\right) dT + \left(\sum_k N_k \tilde{v}_k\right) dp + \sum_i \frac{\partial \sum_k N_k \mu_k}{\partial N_i} dN_i, \quad (4-23)$$

where

$$\frac{\partial \sum_k N_k \mu_k}{\partial N_i} = \mu_i + \sum_k N_k \frac{\partial \mu_k}{\partial N_i} = \mu_i - [\mu_i].$$

For a one-component system, this can easily be transformed into Eq. (2-17). Equations (4-3) and (4-23) are identical for macroscopic systems, but they differ for small systems. The difference is of course just Eq. (4-15).

Next, we find an expression for  $d\mu_k$ . We have, to begin with,

$$d\mu_k = -\tilde{s}_k dT + \tilde{v}_k dp + \sum_i \frac{\partial \mu_k}{\partial N_i} dN_i. \quad (4-24)$$

Let us change variables from  $N_1, \dots, N_c$  to  $N_1, N_2/N_1, \dots, N_c/N_1$ , since  $\mu_k$  is a function of  $p, T$ , and only  $c-1$  composition variables in a macroscopic system. We substitute

$$\frac{\partial \mu_k}{\partial N_1} = -\frac{1}{N_1} \frac{\partial \mathcal{E}}{\partial N_k} - \sum_{i=2}^c \frac{N_i}{N_1} \frac{\partial \mu_k}{\partial N_i},$$

which follows from Eq. (4-16), for  $\partial \mu_k / \partial N_1$  in Eq. (4-24):

$$\begin{aligned} d\mu_k &= -\tilde{s}_k dT + \tilde{v}_k dp - \frac{1}{N_1} \frac{\partial \mathcal{E}}{\partial N_k} dN_1 + \sum_{i=2}^c \frac{\partial \mu_k}{\partial N_i} \left( dN_i - \frac{N_i}{N_1} dN_1 \right) \\ &= -\tilde{s}_k dT + \tilde{v}_k dp - \frac{1}{N_1} \frac{\partial \mathcal{E}}{\partial N_k} dN_1 \\ &\quad + \sum_{i=2}^c \left( \frac{\partial \mu_k}{\partial N_i / N_1} \right)_{p, T, N_1, N_j} d \frac{N_i}{N_1}. \end{aligned} \quad (4-25)$$

Equation (2-17) is the one-component version of this result. When applied to a macroscopic multicomponent system, the term in  $\mathcal{E}$  in Eq. (4-25) drops out.

From Eqs. (4-17) and (4-24):

$$\left(\frac{\partial \mu_k / T}{\partial T}\right)_{p, N_i} = -\frac{\tilde{s}_k}{T} - \frac{\mu_k}{T^2} = -\frac{\tilde{h}_k}{T^2}. \quad (4-26)$$

EFFECT OF SIZE ON INTENSIVE PROPERTIES. Here we investigate the effect of changes in the total number of molecules  $N = N_1 + \dots + N_c$  on intensive properties holding the composition fixed. In this case, for any component:

$$N_i = x_i N, \quad dN_i = x_i dN,$$

where  $x_i$  = mole fraction = constant.

Thus, we find easily from Eqs. (4-16) and (4-24) that

$$\left(\frac{\partial \mu_k}{\partial N}\right)_{p, T, x_i} = -\frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial N_k}\right)_{p, T, N_j}. \quad (4-27)$$

This also follows from Eq. (4-25), since  $dN_1/N_1 = dN/N$ .

Also, for any intensive property of the type  $G = G/N$ , we have from Eq. (4-6),

$$\left(\frac{\partial G}{\partial N}\right)_{p, T, x_i} = \frac{1}{N} \sum_i N_i \tilde{G}_i \quad (4-28)$$

and hence

$$\left(\frac{\partial G}{\partial N}\right)_{p, T, x_i} = -\frac{[G]}{N^2}. \quad (4-29)$$

For example, from Eq. (4-15),

$$\left(\frac{\partial S}{\partial N}\right)_{p, T, x_i} = \frac{1}{N^2} \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p, N_i} \quad (4-30)$$

$$\left(\frac{\partial v}{\partial N}\right)_{p, T, x_i} = -\frac{1}{N^2} \left(\frac{\partial \mathcal{E}}{\partial p}\right)_{T, N_i}. \quad (4-31)$$

As expected, since composition is being held constant, these equations are essentially the same as the corresponding one-component equations (2-36) to (2-38).

**EXCESS QUANTITIES.** For any extensive property  $G$  we define the excess quantity  $G^{(x)}$  by

$$G(N_1, \dots, p, T) = G^{(0)}(N_1, \dots, p, T) + G^{(x)}(N_1, \dots, p, T), \quad (4-32)$$

where  $G^{(0)}$  is the value of  $G$  for  $N_1, \dots, N_c$  molecules from a macroscopic sample at the same pressure, temperature, and composition. We can always write

$$G^{(0)} = N_1 \tilde{G}_1^{(0)} + \dots + N_c \tilde{G}_c^{(0)}, \quad (4-33)$$

where  $\tilde{G}_i^{(0)}$  is a function of  $p, T$ , and  $c - 1$  composition variables. A special case is

$$F^{(0)} = N_1 \mu_1^{(0)} + \dots + N_c \mu_c^{(0)}. \quad (4-34)$$

Differentiation of Eq. (4-32) with respect to  $N_i$  gives

$$\tilde{G}_i = \tilde{G}_i^{(0)} + \tilde{G}_i^{(x)}; \quad \tilde{G}_i^{(x)} \equiv \left( \frac{\partial G^{(x)}}{\partial N_i} \right)_{p, T, N_j} \quad (4-35)$$

$$\mu_i = \mu_i^{(0)} + \mu_i^{(x)} \quad (G = F). \quad (4-36)$$

We substitute Eqs. (4-32) and (4-36) into Eqs. (4-1) to (4-4), cancel macroscopic terms, and obtain the following relations connecting excess functions:

$$d\bar{E}^{(x)} = T dS^{(x)} - p d\bar{V}^{(x)} + \sum_i \mu_i^{(x)} dN_i \quad (4-37)$$

$$F^{(x)} = \bar{E}^{(x)} - T S^{(x)} + p \bar{V}^{(x)} = \sum_i \mu_i^{(x)} N_i + \mathcal{E} \quad (4-38)$$

$$dF^{(x)} = -S^{(x)} dT + \bar{V}^{(x)} dp + \sum_i \mu_i^{(x)} dN_i \quad (4-39)$$

$$d\mathcal{E} = -S^{(x)} dT + \bar{V}^{(x)} dp - \sum_i N_i d\mu_i^{(x)}. \quad (4-40)$$

Also, from Eq. (4-39),

$$d\mu_k^{(x)} = -\tilde{S}_k^{(x)} dT + \tilde{V}_k^{(x)} dp + \sum_i \frac{\partial \mu_k^{(x)}}{\partial N_i} dN_i. \quad (4-41)$$



Equation (4-40) is a Gibbs–Duhem equation. Still another form is

$$\sum_i N_i d\mu_i = \sum_i N_i d\mu_i^{(x)} \quad (p, T \text{ constant}). \quad (4-42)$$

This follows from Eq. (4-4).

## 4.2. SOLVENT EFFECTS

Solvent effects for an  $N, p, T$  system were discussed in Section 2-3. The number of molecules or monomers,  $N$ , per small system appeared in that discussion as a parameter and not as a thermodynamic variable of macroscopic solution thermodynamics. Because of this and the fact that when the small system is multicomponent we still have only one species of system in the ensemble, the extension of the treatment in Section 2-3 to the multicomponent case is very easy.

In Section 2-3 we now understand  $N$  to mean the set  $N_1, \dots, N_c$ , and we read

$$\mu_1 dN_1 + \dots + \mu_c dN_c$$

for  $\mu dN$ , starting in Eq. (2-102). The notation for the solvent must be changed as follows to avoid confusion:

$$N_1 \rightarrow N_1^S, \quad \mu_1 \rightarrow \mu_1^S, \quad \tilde{G}_1 \rightarrow \tilde{G}_1^S.$$

Also, beginning with Eq. (2-108), we put  $F(N_1, \dots, N_c, p, T)$  in place of  $N\hat{\mu}$ . Hence we arrive at

$$F = \bar{E} - TS + p\bar{V} \quad (4-43)$$

$$d\bar{E} = T dS - p d\bar{V} + \sum_i \mu_i dN_i, \quad (4-44)$$

in place of Eqs. (2-113) and (2-114). Equations (4-43) and (4-44) are formally identical with Eqs. (4-1) and (4-2) (no solvent).

The introduction of a mixed solvent here does not present any new features, but the notation for the solvent [Eq. (2-117)] must be changed:

$$N_i \rightarrow N_i^S, \quad \mu_i \rightarrow \mu_i^S, \quad \tilde{G}_i \rightarrow \tilde{G}_i^S.$$

4-3. ENVIRONMENTAL VARIABLES  $N_1, \dots, N_c, T$ 

Chapter 3 was concerned with three cases in which neither the pressure nor the volume appears as an environmental variable. We present brief comments here on the analogous problems for a multi-component small system.

INCOMPRESSIBLE SMALL SYSTEM. We begin with the equations

$$d\mathcal{E} = T dS - p d\bar{V} + \sum_i \mu_i dN_i \quad (4-45)$$

$$F = \mathcal{E} - TS + p\bar{V} = \sum_i \mu_i N_i + \mathcal{E}, \quad (4-46)$$

for an  $N_1, \dots, N_c, p, T$  system. We now suppose, as in Section 3-1, that  $\bar{V}$  is a function of  $N_1, \dots, N_c$  only. Then we write

$$\bar{V} = cf(N_1, \dots, N_c)$$

$$d\bar{V} = \sum_i \frac{d\bar{V}}{dN_i} dN_i = c \sum_i \frac{\partial f}{\partial N_i} dN_i.$$

We put these expressions in Eqs. (4-45) and (4-46) and obtain

$$d\mathcal{E} = T dS + \sum_i \mu'_i dN_i \quad (4-47)$$

$$A' = \mathcal{E} - TS = \sum_i \mu'_i N_i + \mathcal{E}', \quad (4-48)$$

where

$$\mu'_i = \mu_i - pc \frac{\partial f}{\partial N_i} = \mu_i - p\bar{v}_i \quad (4-49)$$

$$\mathcal{E}' = \mathcal{E} - p(\bar{V} - \sum_i N_i \bar{v}_i). \quad (4-50)$$

Note that both  $\mathcal{E}$  and  $\mathcal{E}'$  vanish for a macroscopic system. Equations (4-47) and (4-48) lead to

$$dA' = -S dT + \sum_i \mu'_i dN_i \quad (4-51)$$

$$d\mathcal{E}' = -S dT - \sum_i N_i d\mu'_i. \quad (4-52)$$

From Eq. (4-3), we have

$$\left(\frac{\partial F}{\partial p}\right)_{T, N_i} = \bar{V} = cf(N_1, \dots, N_c).$$

On integration,

$$F = p\bar{V} + g(N_1, \dots, N_c, T),$$

where  $g$  is the integration constant. Therefore

$$A' = F - p\bar{V} = g(N_1, \dots, N_c, T)$$

is a function of  $N_1, \dots, N_c$  and  $T$  only. Hence, from Eq. (4-51),  $S$  and the  $\mu'_i$  are all functions of  $N_1, \dots, N_c$  and  $T$  only. The same is true of  $\mathcal{E}'$ , according to Eq. (4-48).

We can now drop the primes and use (4-47), (4-48), (4-51), and (4-52) as basic equations for an incompressible  $N_1, \dots, N_c, T$  system. An example is given in the next section.

**INVARIABLE PRESSURE.** The extension to a multicomponent system is obvious. The fundamental equations are

$$dH = T dS + \sum_i \mu_i dN_i \quad (p \text{ constant}) \quad (4-53)$$

$$F = H - TS = \sum_i \mu_i N_i + \mathcal{E} \quad (4-54)$$

$$dF = -S dT + \sum_i \mu_i dN_i \quad (p \text{ constant}). \quad (4-55)$$

**DILUTE GAS OF SMALL SYSTEMS.** Section 3-3 is applicable here practically without change. We simply read  $N$  as the set  $N_1, \dots, N_c$ ;  $\mu dN$  becomes  $\sum_i \mu_i dN_i$ ; and we use the symbol  $A$  instead of  $N\hat{\mu}$ .

#### 4.4. BINARY BRAGG-WILLIAMS CRYSTALLITE

As an example, we consider an incompressible colloidal particle of a binary solid solution in the Bragg-Williams (BW) approximation.<sup>1</sup> We include bulk and surface effects only, for simplicity. In the BW approximation, nearest-neighbor interactions are taken into account,

<sup>1</sup> See S.T., pp. 375-379.

but the distributions of the  $N_1$  and  $N_2$  molecules of the two species among the  $N = N_1 + N_2$  sites (interior or surface) is assumed to be random.

Suppose that each surface site has  $z'$  nearest-neighbor sites, while each interior site has  $z$  nearest-neighbor sites ( $z > z'$ ). There are  $N$  sites in the crystallite, of which  $\alpha N^{2/3}$  are on the surface, where  $\alpha$  is a constant depending on the shape of the crystallite, the type of lattice, and the volume per molecule. If a given site is occupied by a molecule of species  $i$  ( $i = 1, 2$ ) and one of its nearest-neighbors sites by a molecule of species  $j$  ( $j = 1, 2$ ), this pair contributes an interaction energy  $w_{ij}$  ( $w_{12} = w_{21}$ ) to the total interaction energy  $W$  of the system. Let  $p_{ij}$  be the probability that any nearest-neighbor pair is occupied in the manner  $ij$  ( $p_{12} = p_{21}$ ). Then, in the BW approximation,

$$p_{11} = \frac{N_1^2}{N^2}, \quad 2p_{12} = \frac{2N_1N_2}{N^2}, \quad p_{22} = \frac{N_2^2}{N^2}.$$

The total number of pairs is

$$\frac{Nz}{2} - \frac{\alpha N^{2/3}(z - z')}{2}.$$

Then

$$W = \left[ \frac{Nz}{2} - \frac{\alpha N^{2/3}(z - z')}{2} \right] (p_{11}w_{11} + 2p_{12}w_{12} + p_{22}w_{22}),$$

or

$$\begin{aligned} -\frac{W}{kT} = & \frac{N_1^2}{N} X_{11} + \frac{N_1N_2}{N} X_{12} + \frac{N_2^2}{N} X_{22} \\ & + \frac{N_1^2}{N^{4/3}} Y_{11} + \frac{N_1N_2}{N^{4/3}} Y_{12} + \frac{N_2^2}{N^{4/3}} Y_{22}, \end{aligned} \quad (4-56)$$

where

$$X_{11} = -\frac{zw_{11}}{2kT}, \quad X_{12} = -\frac{zw_{12}}{kT}, \quad \text{etc.},$$

$$Y_{11} = \frac{\alpha(z - z')w_{11}}{2kT}, \quad Y_{12} = \frac{\alpha(z - z')w_{12}}{kT}, \quad \text{etc.}$$

For the complete partition function of the crystallite we use

$$Q(N_1, N_2, T) = e^{-A/kT} = j_1(T)^{N_1} j_2(T)^{N_2} \frac{N!}{N_1! N_2!} e^{-W/kT}, \quad (4-57)$$

where  $j_1$  and  $j_2$  are vibrational partition functions. In a more refined treatment different vibrational partition functions would be introduced for molecules on the surface.

We find  $\ln Q$  from Eq. (4-57), using the simple Stirling approximation, and then, from Eq. (4-51),

$$\begin{aligned} \frac{\mu_1(x_2, N, T)}{kT} &= \frac{1}{kT} \left( \frac{\partial A}{\partial N_1} \right)_{N_2, T} \\ &= \frac{\mu_1^0(N, T)}{kT} + \ln(1 - x_2) + x_2^2 X \\ &\quad + \frac{1}{3N^{1/3}} [4x_2^2 Y + x_2(Y_{12} - 2Y_{11})], \end{aligned} \quad (4-58)$$

where

$$x_2 = \frac{N_2}{N}$$

$$X = X_{11} + X_{22} - X_{12} = -\frac{z}{2kT} (w_{11} + w_{22} - 2w_{12})$$

$$Y = Y_{11} + Y_{22} - Y_{12} = -\frac{\alpha(z - z')}{z} X$$

and

$$-\frac{\mu_1^0(N, T)}{kT} = \ln j_1 + X_{11} + \frac{2Y_{11}}{3N^{1/3}}.$$

Note that  $Y = 0$  when  $X = 0$ . The reference chemical potential  $\mu_1^0$  is that of pure component 1 ( $x_2 = 0$ ), including a surface term. There is an analogous expression for  $\mu_2(x_2, N, T)$  which follows by symmetry:

$$\begin{aligned} \frac{\mu_2(x_2, N, T)}{kT} &= \frac{\mu_2^0(N, T)}{kT} + \ln x_2 + (1 - x_2)^2 X \\ &\quad + \frac{1}{3N^{1/3}} [4(1 - x_2)^2 Y + (1 - x_2)(Y_{12} - 2Y_{22})]. \end{aligned} \quad (4-59)$$

In the limit  $x_2 \rightarrow 0$ , with  $N$  constant, Eqs. (4-58) and (4-59) become

$$-\left(\frac{\mu_1 - \mu_1^0}{kT}\right) = x_2 \left[ 1 - \frac{1}{3N^{1/3}}(Y_{12} - 2Y_{11}) \right] + O(x_2^2) \quad (4-60)$$

$$\exp\left(\frac{\mu_2 - \mu_2^0}{kT}\right) = x_2 \left\{ \exp \left[ X + \frac{1}{3N^{1/3}}(4Y + Y_{12} - 2Y_{22}) \right] \right\} + O(x_2^2). \quad (4-61)$$

The coefficient of  $x_2$  in Eq. (4-60) is the Raoult's-law slope (this slope is unity in a macroscopic system), while the coefficient of  $x_2$  in Eq. (4-61) is the Henry's-law constant (equal to  $e^X$  for a macroscopic BW system).

The excess chemical potentials, defined in Eq. (4-36), are

$$\frac{\mu_1^{(x)}}{kT} = \frac{1}{3N^{1/3}}[4x_2^2 Y + x_2(Y_{12} - 2Y_{11}) - 2Y_{11}] \quad (4-62)$$

$$\frac{\mu_2^{(x)}}{kT} = \frac{1}{3N^{1/3}}[4(1 - x_2)^2 Y + (1 - x_2)(Y_{12} - 2Y_{22}) - 2Y_{22}]. \quad (4-63)$$

Also, from Eqs. (4-57) to (4-59),

$$\begin{aligned} \frac{\mathcal{E}}{kT} &= \frac{A - N_1\mu_1 - N_2\mu_2}{kT} \\ &= -\frac{N^{2/3}}{3}[(1 - x_2)^2 Y_{11} + x_2(1 - x_2)Y_{12} + x_2^2 Y_{22}] \quad (4-64) \end{aligned}$$

$$= \frac{1}{3} \frac{A^{(x)}}{kT} = \frac{1}{2} \left( \frac{N_1\mu_1^{(x)} + N_2\mu_2^{(x)}}{kT} \right). \quad (4-65)$$

As can easily be verified, the above relations satisfy the following Gibbs-Duhem equations:

$$-\frac{1}{N} \left( \frac{\partial \mathcal{E}}{\partial x_2} \right)_{T, N} = x_1 \left( \frac{\partial \mu_1}{\partial x_2} \right)_{T, N} + x_2 \left( \frac{\partial \mu_2}{\partial x_2} \right)_{T, N} \quad (4-66)$$

$$= x_1 \left( \frac{\partial \mu_1^{(x)}}{\partial x_2} \right)_{T, N} + x_2 \left( \frac{\partial \mu_2^{(x)}}{\partial x_2} \right)_{T, N}. \quad (4-67)$$

Note that, unlike the situation in macroscopic thermodynamics, we cannot integrate Eq. (4-67) to obtain, say,  $\mu_2^{(x)}(x_2)$  from a knowledge of  $\mu_1^{(x)}(x_2)$ . We must know  $\mathcal{E}(x_2)$  as well.

## 4.5. DILUTE AND IDEAL SOLUTIONS

The special cases of dilute and ideal nonelectrolyte solutions deserve some comment. For example, suppose we have a macroscopic dilute or ideal liquid or solid solution and prepare colloidal particles therefrom. What will be the thermodynamic properties of these small systems?

In the logical structure of macroscopic thermodynamics, the basic properties of dilute and ideal solutions are not deduced from the laws of thermodynamics but rather rest on empirical observation or molecular theory. This must be true of small systems as well, but unfortunately there is little experience at present to draw on. However, between the known macroscopic behavior, the example in the preceding section, and intuition, we can probably make the correct assumptions for dilute solution behavior. The ideal-solution case seems less obvious.

**DILUTE SOLUTION.** Let the solvent<sup>1</sup> be component 1 and the solutes components 2, 3, ... . We assume that, in a solution dilute with respect to all solute components, the chemical potential of any solute component has the limiting form

$$\mu_i = \mu_i^\Delta(p, T, N_1) + kT \ln \frac{N_i}{N_1} \quad (i = 2, 3, \dots). \quad (4-68)$$

In the limit  $N_1 \rightarrow \infty$  (macroscopic solution),  $\mu_i^\Delta$  becomes a function of  $p$  and  $T$  only.

An expression for the chemical potential of the solvent can now be deduced from the Gibbs–Duhem equation, (4-4). Let us “prepare” the dilute solution by starting with pure solvent ( $N_1, p, T$ ) and adding solute species in a constant ratio. If the final numbers of solute molecules are  $N_2, N_3, \dots$ , at an intermediate stage they would be  $\alpha N_2, \alpha N_3, \dots$ , where  $0 \leq \alpha \leq 1$ . For arbitrary  $\alpha$ , Eq. (4-4) can be written

$$\frac{\partial \mathcal{E}}{\partial \alpha} = -\alpha \sum_{i \geq 2} N_i \frac{\partial \mu_i}{\partial \alpha} - N_1 \frac{\partial \mu_1}{\partial \alpha}, \quad (4-69)$$

where  $p, T, N_1, N_2, \dots$  are held constant in the derivatives. If we

<sup>1</sup> All these components are components of the small system. The small system itself may be in a macroscopic solvent, as in Section 4-2.

replace  $N_i$  by  $\alpha N_i$  in Eq. (4-68), we find  $\partial\mu_i/\partial\alpha = kT/\alpha$ . We then multiply Eq. (4-69) by  $d\alpha$  and integrate from  $\alpha = 0$  to  $\alpha = 1$ . The result is

$$\begin{aligned}\mu_1 = \mu_1^0(p, T, N_1) - kT \sum_{i \geq 2} \frac{N_i}{N_1} \\ - \frac{1}{N_1} [\mathcal{E}(p, T, N_1, N_2, \dots) - \mathcal{E}(p, T, N_1, 0, 0, \dots)],\end{aligned}\quad (4-70)$$

where  $\mu_1^0$  is the chemical potential of pure component 1. In the macroscopic limit,  $\mu_1^0$  becomes a function of  $p$  and  $T$  only, and the term in  $\mathcal{E}$  vanishes.

It seems reasonable to expect that  $\mathcal{E} - \mathcal{E}(0)$  in Eq. (4-70) may be expanded in a power series in the  $N_i/N_1$ . In the dilute-solution limit under consideration here we retain linear terms only:

$$\mathcal{E} - \mathcal{E}(0) = \sum_{i \geq 2} f_i(p, T, N_1) \frac{N_i}{N_1}, \quad (4-71)$$

where the  $f_i$  are expansion coefficients. Comparison with the definition of  $[\mu_i]$  in Eq. (4-16) shows that  $f_i/N_1$  is just  $[\mu_i]$  evaluated at infinite dilution.

An example is the three-component version of the preceding section. One finds

$$\begin{aligned}\frac{\mu_1}{kT} = \frac{\mu_1^0(N_1, T)}{kT} - \frac{N_2 + N_3}{N_1} + \frac{1}{3N_1^{1/3}} \\ \times \left[ \frac{N_2}{N_1} (Y_{12} - \frac{4}{3} Y_{11}) + \frac{N_3}{N_1} (Y_{13} - \frac{4}{3} Y_{11}) \right].\end{aligned}\quad (4-72)$$

**SOLUTE ACTIVITY COEFFICIENTS.** The functions  $\mu_i^\Delta$  in Eq. (4-68) may be regarded as defined by the properties of the dilute solution. Activity coefficients for the solutes may then be defined for a nondilute solution with the same  $N_1$  in terms of the  $\mu_i$  (non-dilute) and  $\mu_i^\Delta$ :

$$\begin{aligned}\mu_i(p, T, N_1, N_2, \dots) = \mu_i^\Delta(p, T, N_1) + kT \ln \frac{N_i \gamma_i(p, T, N_1, N_2, \dots)}{N_1} \\ (i = 2, 3, \dots).\end{aligned}\quad (4-73)$$



The activity itself is  $a_i \equiv N_i \gamma_i / N_1$ . This is the same procedure as in macroscopic thermodynamics.

**IDEAL SOLUTION.** We assume, in this case, that the chemical potential of component  $i$  can be written as

$$\mu_i = \mu_i^0(p, T, N) + kT \ln x_i + g_i(p, T, N_1, N_2, \dots) \quad (i = 1, 2, \dots), \quad (4-74)$$

where  $x_i = N_i/N$  and  $N = N_1 + N_2 + \dots$ . The quantity  $\mu_i^0(p, T, N)$  is the chemical potential of a small system of  $N$  molecules of pure component  $i$ . The function  $g_i$  must vanish in either of the limits  $N \rightarrow \infty$  or  $x_i \rightarrow 1$ . It is difficult at this writing to be any more informative, with assurance, about  $g_i$ .

The ideal-solution behavior of, say,  $\mu_1$  in the three-component version of Section 4-4 can easily be shown to be<sup>1</sup>

$$\frac{\mu_1}{kT} = \frac{\mu_1^0(N, T)}{kT} + \ln x_1 + \frac{1}{3N^{1/3}} [x_2(Y_{12} - 2Y_{11}) + x_3(Y_{13} - 2Y_{11})]. \quad (4-75)$$

Recall also that in macroscopic thermodynamics the solvent behaves in dilute solution (Raoult's law) in the same way as any component does in an ideal solution. Therefore Eqs. (4-71) and (4-75) both suggest that  $g_i$  might depend linearly on all the  $x_j$ ,  $j \neq i$ . That is,

$$g_i = \sum_{j \neq i} g_{ij}(p, T, N) x_j. \quad (4-76)$$

However, we can see from the following simple example that this surmise does not have general validity.

*Example. Ideal Binary Mixture.* Consider a binary mixture with partition function

$$Q(N_1, N_2, T) = e^{-A/kT} = \frac{j_1(T)^{N_1} j_2(T)^{N_2} N!}{N_1! N_2!}, \quad (4-77)$$

where  $N = N_1 + N_2$ . This is a special case of Eq. (4-57) and is

<sup>1</sup> In the notation of Sec. 4-4, an ideal solution has  $X = Y = 0$ . See the definition of  $Y$  following Eq. (4-58).

closely related to the ideal lattice gas of Eq. (2-77). To find first-order "smallness" effects, we use

$$\ln N! = N \ln N - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi \quad (4-78)$$

and similar expressions for  $\ln N_1!$  and  $\ln N_2!$ , instead of the usual simple Stirling approximation. Then

$$\begin{aligned} \ln Q = & N_1 \ln j_1 + N_2 \ln j_2 + N \ln N - N_1 \ln N_1 \\ & - N_2 \ln N_2 - \frac{1}{2} \ln \frac{2\pi N_1 N_2}{N} \end{aligned} \quad (4-79)$$

$$\frac{\mu_1}{kT} = - \left( \frac{\partial \ln Q}{\partial N_1} \right)_{N_2, T} = - \ln j_1 + \ln x_1 + \frac{1}{2N} \frac{x_2}{1 - x_2}, \quad (4-80)$$

and a similar expression for  $\mu_2/kT$ . We note that the last term in Eq. (4-80) is *not* linear in  $x_2$ , as required by Eq. (4-76).

We also find

$$\frac{\mathcal{E}}{kT} = \frac{A - N_1 \mu_1 - N_2 \mu_2}{kT} = \frac{1}{2} \ln \frac{2\pi N_1 N_2}{Ne}. \quad (4-81)$$

# CHEMICAL AND PHASE EQUILIBRIA

This chapter is essentially a digression in which we treat the important special topics of chemical and phase equilibria in small systems of the types considered in Chapters 2 to 4 (closed; constant  $p$  and  $T$ ). We shall then return in Chapters 6 to 10 to the systematic examination of further sets of environmental variables. There will be supplementary discussion of chemical and phase equilibria in these and later chapters, where appropriate.

## 5-1. SPONTANEOUS PROCESSES AND CRITERIA FOR EQUILIBRIUM

The very brief discussion of this topic which we give here leans heavily on Section 2-3 of S.T., which the reader may wish to consult. As is shown there, the same general argument applies to the environmental variables  $N, V, E$ ;  $N, V, T$ ;  $N, p, T$ ; etc. So we confine our remarks to the case  $N, V, E$ , which is simplest.

Consider a macroscopic ensemble of  $\mathcal{N}$  small systems, each with  $N, V, E$ . Let  $\Omega_1(N, V, E)$  be the number of quantum states accessible to each of the systems in some initial thermodynamic state 1. We consider a process in which each system of the ensemble proceeds spontaneously from the initial state 1 to a final state 2, where the number of accessible quantum states is  $\Omega_2(N, V, E)$ . That is, in the initial thermodynamic state of the ensemble each system is in one (or a linear combination) of the  $\Omega_1$  quantum states, and in the final thermodynamic state each system is in one of the  $\Omega_2$  quantum states.

The case of most interest is  $\Omega_2 > \Omega_1$ , where the final state 2 includes the  $\Omega_1$  quantum states of state 1 plus an additional  $\Omega_2 - \Omega_1$  states made available by the removal of some restraint on accessibility. A second possibility is that  $\Omega_1 > \Omega_2$ , where each system of the ensemble goes spontaneously from one of the initial  $\Omega_1$  states to one of a limited group of  $\Omega_2$  states selected from among the  $\Omega_1$  states. In this latter case, the probability of all the systems in the ensemble proceeding spontaneously from state 1 to state 2 is  $(\Omega_2/\Omega_1)^{\mathcal{N}}$ , which is zero for all practical purposes, since  $\mathcal{N}$  is an extremely large number. Hence the second case is essentially impossible, and we conclude

that real spontaneous processes in an ensemble take place in the direction of *removal* of a restraint,  $\Omega_2 > \Omega_1$ .

An example of the  $\Omega_2 > \Omega_1$  type would be the addition to each small system of a bit of catalyst which makes possible a spontaneous chemical reaction as a result of the elimination or reduction of a free energy of activation by the catalyst. More specifically, in this example, the initial state 1 might be, say, all  $A$  molecules and the final state 2 might be a chemical equilibrium mixture of two isomers,  $A$  and  $B$ .

We can recapitulate as follows. By a "spontaneous" process from state 1 to state 2 in an ensemble we mean that every system in the ensemble proceeds spontaneously from one of  $\Omega_1$  quantum states to one of  $\Omega_2$  quantum states, where  $\Omega_2$  includes the  $\Omega_1$  states plus others made available by removal of a restraint. The entropy change accompanying a spontaneous process in the ensemble is then

$$\Delta S_t = k \ln \left( \frac{\Omega_2}{\Omega_1} \right)^{\mathcal{N}} > 0, \quad (5-1)$$

and, in a single system of the ensemble,

$$\Delta S = \frac{\Delta S_t}{\mathcal{N}} = k \ln \frac{\Omega_2}{\Omega_1} > 0. \quad (5-2)$$

When a restraint is removed and a spontaneous process occurs in an ensemble,  $\Delta S_t$  and  $\Delta S$  for the process are positive. The probability of the *reverse* process taking place spontaneously in the ensemble (i.e., in every system of the ensemble) is virtually zero, as we have already seen. But for any one specified system, this probability is  $\Omega_1/\Omega_2$ , which is of order  $e^{-N}$ . Hence the reverse process might well be observed in a specified single system if  $N$  is quite small. Thus the observation of the direction of a spontaneous process in a single small system will not indicate for certain the direction  $\Delta S > 0$ . To be sure of this direction, we must observe the whole ensemble.

When spontaneous processes are available to the systems of an ensemble,  $S_t$  increases until these processes are exhausted. Then, at equilibrium,  $S_t$  is a maximum, and  $dS_t = 0$ . Thus, in summary,

$$\begin{aligned} dS_t &\geq 0 && (\mathcal{N}, N, V, E \text{ constant}) \\ dS &\geq 0 && (N, V, E \text{ constant}), \end{aligned} \quad (5-3)$$

where the equality holds at equilibrium and the inequality refers to a spontaneous process.

With appropriate environmental variables held constant, minimization of a free energy function replaces maximization of entropy as the criterion of equilibrium, as is well known. We shall encounter applications involving free energy criteria in the next three sections. It will be seen that existence of small system translational motion (and therefore indistinguishability of small systems) and interaction with a solvent do not prove to be troublesome complications.

Incidentally, the form of Eq. (5-1) implies distinguishability of small systems. But this is the only case of interest for an isolated small system (environmental variables  $N$ ,  $V$ ,  $E$ ), because translational motion would allow collisions between small systems and hence exchange of energy. Also, in order to be isolated, the systems cannot be in contact with a solvent ( $E$  and  $V$  would fluctuate in the presence of a solvent).

The relation between the subdivision potential  $\mathcal{E}$  and possible spontaneous changes in the size of the small systems of an ensemble will be discussed in Chapter 10.

## 5-2. CHEMICAL EQUILIBRIUM

In this section we consider the chemical reaction

$$\sum_i \nu_i A_i = 0$$

among species  $A_i$ , in the presence of nonreacting ("solvent") species<sup>1</sup> denoted by subscript  $\alpha$ . The  $\nu_i$  are stoichiometric coefficients. The next section is concerned with the special case  $A_1 \rightleftharpoons A_2$  in the absence of other components (e.g., the helix-coil "reaction"). These two cases do not, of course, exhaust the subject, but they are the only ones we shall include.

The small system of interest here is at  $p$  and  $T$  and is closed with respect to exchange of molecules with the outside. However, molecules of the various species  $i$  appear and disappear because of the chemical reaction.

<sup>1</sup> All these components are components of the small system. The small system itself may be in a macroscopic solvent, as in Section 4-2.

Each system of the ensemble is "prepared" with  $p, T$ , solvent numbers  $N_\alpha$ , and initial reactant numbers  $N_i^0$ . If  $n$  units of reaction take place, the reactant numbers become  $N_i = N_i^0 - \nu_i n$ . There will be fluctuations in the value of  $n$  in different systems, or in the same system at different times, with an average value  $\bar{n}$  and a corresponding average  $\bar{N}_i = N_i^0 - \nu_i \bar{n}$ .

We write for the ensemble, as in Eq. (1-69),

$$dE_t = T dS_t - p dV_t + \sum_i \mu_i dN_{it} + \sum_\alpha \mu_\alpha dN_{t\alpha} + \mathcal{E} d\mathcal{N}. \quad (5-4)$$

Integration followed by division by  $\mathcal{N}$  gives

$$\bar{E} = TS - p\bar{V} + \sum_i \mu_i \bar{N}_i + \sum_\alpha \mu_\alpha N_\alpha + \mathcal{E} \quad (5-5)$$

$$\begin{aligned} F &= \bar{E} - TS + p\bar{V} \\ &= H - TS = \sum_i \mu_i \bar{N}_i + \sum_\alpha \mu_\alpha N_\alpha + \mathcal{E} \\ &= \sum_i \mu_i N_i^0 - \psi \bar{n} + \sum_\alpha \mu_\alpha N_\alpha + \mathcal{E}, \end{aligned} \quad (5-6)$$

where we have introduced  $\psi \equiv \sum_i \nu_i \mu_i$ . The quantities  $n$  and  $\psi$  are the negatives of the "extent of reaction" and "affinity" defined by Prigogine and Defay.<sup>1</sup>

Equation (5-4) can also be written as

$$\begin{aligned} dE_t &= T dS_t - p dV_t + \sum_i \mu_i d(\mathcal{N} N_i^0) - \psi d(\mathcal{N} \bar{n}) \\ &\quad + \sum_\alpha \mu_\alpha d(\mathcal{N} N_\alpha) + \mathcal{E} d\mathcal{N} \end{aligned} \quad (5-7)$$

or

$$dF_t = -\psi \mathcal{N} d\bar{n} \quad (p, T, N_i^0, N_\alpha, \mathcal{N} \text{ constant}), \quad (5-8)$$

where  $N_i^0$  and  $N_\alpha$  mean *all* the  $N_i^0$  and  $N_\alpha$ . The last relation refers to a closed ensemble at constant  $p$  and  $T$ . Under these conditions, the analogue of Eq. (5-3) is

$$\begin{aligned} dF_t &= -\psi \mathcal{N} d\bar{n} \leq 0 & (p, T, N_i^0, N_\alpha, \mathcal{N} \text{ constant}) \\ dF &= -\psi d\bar{n} \leq 0 & (p, T, N_i^0, N_\alpha \text{ constant}). \end{aligned} \quad (5-9)$$

<sup>1</sup> I. Prigogine and R. Defay, "Chemical Thermodynamics", Longmans, Green, New York, 1954. Macroscopic versions of a number of equations derived here may be found in this book.

Thus, when the systems of the ensemble have reached equilibrium with respect to the chemical reaction,  $\psi = 0$ . For a value of  $\psi$  not equal to zero, the systems approach equilibrium spontaneously in such a way that  $\psi$  and  $d\bar{n}$  have the same sign.

In closed experimental small systems at  $p$  and  $T$  in which a chemical reaction can take place, the environmental variables are  $p$ ,  $T$ ,  $N_i^0$ ,  $N_\alpha$ , and  $\psi$ . In actual fact, the only operationally possible value of  $\psi$  is zero. This is closely analogous to the case of the incompressible free macromolecule in solution mentioned several times in Chapter 2, where the environmental variables were  $N$ ,  $f$ ,  $T$ , with  $f = 0$  the only experimentally realizable value of the force.

Actually, the equations of this section are still valid (see Section 1-4) under other environmental conditions, say,  $p$ ,  $T$ ,  $N_i^0$ ,  $N_\alpha$ ,  $n$  or  $V$ ,  $T$ ,  $N_i^0$ ,  $N_\alpha$ ,  $n$ , but these conditions are not attainable in practice. For example, constant  $N_i^0$  and  $n$  imply exactly the same composition at equilibrium in all systems of the ensemble. Such conditions are attainable with theoretical models, however, and a simple example is given at the end of the next section. It will be seen that the equilibrium composition differs by a small term depending on whether  $\psi = \text{constant}$  or  $n = \text{constant}$ . This is to be expected in view of the general rule for small systems: thermodynamic functions depend on environment, but equations connecting the functions do not.

Next, we eliminate  $\mathcal{E}$  between Eqs. (5-4) and (5-5) and obtain

$$d\bar{E} = T dS - p d\bar{V} + \sum_i \mu_i d\bar{N}_i + \sum_\alpha \mu_\alpha dN_\alpha \quad (5-10)$$

$$dF = -S dT + \bar{V} dp + \sum_i \mu_i d\bar{N}_i + \sum_\alpha \mu_\alpha dN_\alpha \quad (5-11)$$

$$= -S dT + \bar{V} dp + \sum_i \mu_i dN_i^0 - \psi d\bar{n} + \sum_\alpha \mu_\alpha dN_\alpha \quad (5-12)$$

$$d(F + \psi\bar{n}) = -S dT + \bar{V} dp + \sum_i \mu_i dN_i^0 + \bar{n} d\psi + \sum_\alpha \mu_\alpha dN_\alpha. \quad (5-13)$$

The last equation has the environmental variables as independent variables. In the notation of Chapter 1,

$$X = F + \psi\bar{n} = \sum_i \mu_i N_i^0 + \sum_\alpha \mu_\alpha N_\alpha + \mathcal{E}. \quad (5-14)$$

The Gibbs–Duhem equation is

$$d\mathcal{E} = -S dT + \bar{V} dp - \sum_i N_i^0 d\mu_i + \bar{n} d\psi - \sum_\alpha N_\alpha d\mu_\alpha. \quad (5-15)$$

There are a number of important differential relations which follow from Eqs. (5-11) to (5-13), especially. We shall set these down as needed below.

**EQUILIBRIUM CONSTANT.** In a solution dilute with respect to all reactants, we assume, as in Eq. (4-68), that  $\mu_i$  has the form

$$\mu_i = \mu_i^\Delta(p, T, N_\alpha) + kT \ln \frac{\bar{N}_i}{\sum_\alpha N_\alpha}. \quad (5-16)$$

Because of the difference in environmental variables, under conditions which are otherwise the same, the functions  $\mu_i^\Delta$  in Eqs. (4-68) and (5-16) differ by a small term. For a nondilute solution with the same  $N_\alpha$ , the nondilute  $\mu_i$  and  $\mu_i^\Delta$  from Eq. (5-16) are then used to define the activity  $a_i$ :

$$\mu_i = \mu_i^\Delta(p, T, N_\alpha) + kT \ln a_i. \quad (5-17)$$

The equilibrium constant for the reaction  $\sum_i \nu_i A_i = 0$  is then defined as the value of

$$K = \prod_i a_i^{\nu_i} \quad (5-18)$$

at equilibrium. From Eq. (5-17), we have

$$\ln K = \sum_i \frac{\mu_i - \mu_i^\Delta}{kT} \nu_i = -\frac{\psi^\Delta}{kT}, \quad (5-19)$$

where

$$\psi^\Delta = \sum_i \nu_i \mu_i^\Delta(p, T, N_\alpha), \quad (5-20)$$

and we have used the fact that  $\psi = 0$  at equilibrium. Both  $\psi^\Delta$  and  $K$  are functions of  $p$ ,  $T$ ,  $N_\alpha$  only.



It is difficult to see how  $\mu_i^\Delta$  for a single species, under present environmental conditions, can be measured experimentally. But  $K$  is an operational quantity, since

$$K = \prod_i \left( \frac{\bar{N}_i}{\sum_\alpha N_\alpha} \right)^{\nu_i} \quad (\psi = 0, \text{ dilute solution}). \quad (5-21)$$

Therefore  $\psi^\Delta$ , a combination of the  $\mu_i^\Delta$ , is also operational.

We now derive expressions for the derivatives of  $K$  with respect to  $T$ ,  $p$ , and  $N_\alpha$ . Since  $K$  is determined by the  $\mu_i^\Delta$  through Eqs. (5-19) and (5-20) and  $\mu_i^\Delta$  is in turn defined by the properties of the dilute solution through Eq. (5-16), we work primarily with Eq. (5-16).

We differentiate both sides of Eq. (5-16) with respect to  $T$ , as follows:

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{p, \bar{N}_j, N_\alpha} = -\tilde{s}_i^\square = \left( \frac{\partial \mu_i^\Delta}{\partial T} \right)_{p, N_\alpha} + \frac{\mu_i - \mu_i^\Delta}{T}, \quad (5-22)$$

where  $\bar{N}_j$  means all the  $\bar{N}_j$  and we use the same definition of partial molal quantities as in Section 4-1, despite the difference in environmental variables. The superscript  $\square$  refers to the fact that the small system is dilute in all the reactants (in Section 2-3 the same symbol meant that a macroscopic solution was dilute in small systems themselves). Then

$$\left( \frac{\partial \ln K}{\partial T} \right)_{p, N_\alpha} = - \left( \frac{\partial \psi^\Delta / kT}{\partial T} \right)_{p, N_\alpha} = \frac{\sum_i \nu_i \tilde{s}_i^\square}{kT} + \frac{\sum_i \nu_i \mu_i}{kT^2} = \frac{\sum_i \nu_i \tilde{H}_i^\square}{kT^2} \quad (5-23)$$

The particular dilute concentrations of reactants chosen in Eqs. (5-22) and (5-23) are arbitrary (that is,  $\psi$  does not have to be zero). The  $\tilde{H}_i^\square$  are independent of these concentrations;  $\tilde{s}_i^\square$  and  $\mu_i$  depend on them separately but not in the combination  $\mu_i + T\tilde{s}_i^\square$ . If we select dilute concentrations at chemical equilibrium, we can write

$$\left( \frac{\partial \ln K}{\partial T} \right)_{p, N_\alpha} = \frac{(\sum_i \nu_i \tilde{s}_i^\square)_{\psi=0}}{kT} = \frac{\sum_i \nu_i \tilde{H}_i^\square}{kT^2}. \quad (5-24)$$

The separate  $\tilde{s}_i^\square$  and  $\tilde{H}_i^\square$  are probably not measurable under the required environmental conditions ( $p$ ,  $T$ ,  $N_i^0$ ,  $N_\alpha$ ,  $\psi$ ). An alternative

operational form of Eq. (5-24) may be obtained as follows. We have

$$dS = \sum_i \frac{\partial S}{\partial \bar{N}_i} d\bar{N}_i = \sum_i \tilde{s}_i d\bar{N}_i \quad (p, T, N_\alpha \text{ constant}).$$

Upon using  $\bar{N}_i = N_i^0 - \nu_i \bar{n}$ , this becomes

$$\left( \frac{\partial S}{\partial \bar{n}} \right)_{p, T, N_i^0, N_\alpha} = - \sum_i \nu_i \tilde{s}_i. \quad (5-25)$$

Now  $T dS_i = DQ_i$  for the ensemble and  $T dS = DQ = DQ_i/\mathcal{N}$  for a single small system, where  $DQ$  is heat absorbed by the system in a reversible process. Therefore, on combining Eqs. (5-24) and (5-25), we have

$$\left( \frac{\partial \ln K}{\partial T} \right)_{p, N_\alpha} = \frac{-(DQ/\partial \bar{n})_{p, T, N_i^0, N_\alpha}^{\square, \psi=0}}{kT^2}. \quad (5-26)$$

Here  $DQ$  is the heat absorbed when the reaction proceeds an infinitesimal extent  $d\bar{n}$  in a closed, dilute system at chemical equilibrium, with  $p$  and  $T$  constant. The change  $d\bar{n}$  may be regarded as having been brought about by a variation  $d\psi$  at  $\psi = 0$ , for example, as the system approaches but has not quite reached chemical equilibrium. We also have

$$\frac{\partial H}{\partial \bar{n}} = - \sum_i \nu_i \tilde{H}_i = T \frac{\partial S}{\partial \bar{n}} - \psi = \frac{DQ}{\partial \bar{n}} - \psi$$

and

$$\left( \frac{\partial H}{\partial \bar{n}} \right)^{\square} = - \sum_i \nu_i \tilde{H}_i^{\square} = \left( \frac{DQ}{\partial \bar{n}} \right)^{\square, \psi} - \psi = \left( \frac{DQ}{\partial \bar{n}} \right)^{\square, \psi=0}. \quad (5-27)$$

Differentiation of both sides of Eq. (5-16) with respect to  $p$  gives

$$\left( \frac{\partial \mu_i}{\partial p} \right)_{T, \bar{N}_i, N_\alpha} = \tilde{v}_i^{\square} = \left( \frac{\partial \mu_i^{\Delta}}{\partial p} \right)_{T, N_\alpha}, \quad (5-28)$$

and hence

$$\left( \frac{\partial \ln K}{\partial p} \right)_{T, N_\alpha} = - \frac{1}{kT} \left( \frac{\partial \psi^{\Delta}}{\partial p} \right)_{T, N_\alpha} = - \frac{\sum_i \nu_i \tilde{v}_i^{\square}}{kT}, \quad (5-29)$$

$$= \frac{(\partial V/\partial \bar{n})_{p, T, N_i^0, N_\alpha}^{\square}}{kT}. \quad (5-30)$$

This volume change  $\partial V/\partial \bar{n}$  is measurable. Equations (5-24), (5-26) and (5-30) are essentially the same as their macroscopic counterparts.

For simplicity, let us now assume that there is only one solvent species, which we still denote by  $\alpha$ . Our object is to derive an equation for  $\partial \ln K/\partial N_\alpha$ , or  $-\partial(\psi^\Delta/kT)/\partial N_\alpha$ . We begin by multiplying Eq. (5-16) by  $\nu_i$  and summing over  $i$ :

$$\psi = \psi^\Delta + kT \sum_i \nu_i \ln \frac{\bar{N}_i}{N_\alpha}. \quad (5-31)$$

We differentiate this equation with respect to  $N_\alpha$ , holding  $p, T, N_j^0$ , and  $\psi$  constant. We use  $\bar{N}_i = N_i^0 - \nu_i \bar{n}$  and regard  $\bar{n}$  as a function of  $p, T, N_j^0, N_\alpha$ , and  $\psi$ . This gives

$$0 = \left( \frac{\partial \psi^\Delta}{\partial N_\alpha} \right)_{p, T} - \frac{kT}{N_\alpha} \sum_i \nu_i - kT \left( \frac{\partial \bar{n}}{\partial N_\alpha} \right)_{p, T, N_i^0, \psi} \sum_i \frac{\nu_i^2}{\bar{N}_i}. \quad (5-32)$$

From Eq. (5-13), we have

$$\begin{aligned} \left( \frac{\partial \bar{n}}{\partial N_\alpha} \right)_{p, T, N_i^0, \psi} &= \left( \frac{\partial \mu_\alpha}{\partial \psi} \right)_{p, T, N_i^0, N_\alpha} \\ &= \left( \frac{\partial \mu_\alpha}{\partial \bar{n}} \right)_{p, T, N_i^0, N_\alpha} \left( \frac{\partial \bar{n}}{\partial \psi} \right)_{p, T, N_i^0, N_\alpha}. \end{aligned} \quad (5-33)$$

Also, from Eq. (5-31),

$$\left( \frac{\partial \psi}{\partial \bar{n}} \right)_{p, T, N_i^0, N_\alpha} = -kT \sum_i \frac{\nu_i^2}{\bar{N}_i}. \quad (5-34)$$

We mention in passing that this equation is related to a statistical mechanical fluctuation formula which will be introduced in the next section [Eq. (5-78)]. We now substitute Eqs. (5-33) and (5-34) in Eq. (5-32) and find

$$\left( \frac{\partial \psi^\Delta}{\partial N_\alpha} \right)_{p, T} = \frac{kT}{N_\alpha} \sum_i \nu_i - \left( \frac{\partial \mu_\alpha}{\partial \bar{n}} \right)_{p, T, N_i^0, N_\alpha}. \quad (5-35)$$

An expression for  $\partial\mu_\alpha/\partial\bar{n}$  follows from the Gibbs-Duhem equation, (5-15):

$$\left(\frac{\partial\mathcal{E}}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha} = - \sum_i N_i^0 \left(\frac{\partial\mu_i}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha} + \bar{n} \left(\frac{\partial\psi}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha} - N_\alpha \left(\frac{\partial\mu_\alpha}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha}. \quad (5-36)$$

We may now eliminate  $\partial\mu_\alpha/\partial\bar{n}$  between Eqs. (5-35) and (5-36), use Eq. (5-34) and

$$\left(\frac{\partial\mu_i}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha} = -\frac{kT\nu_i}{\bar{N}_i} \quad (5-37)$$

to obtain, finally,

$$\begin{aligned} \left(\frac{\partial \ln K}{\partial N_\alpha}\right)_{p,T} &= -\frac{1}{kT} \left(\frac{\partial\psi^\Delta}{\partial N_\alpha}\right)_{p,T} \\ &= -\frac{1}{N_\alpha kT} \left(\frac{\partial\mathcal{E}}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha}^\square. \end{aligned} \quad (5-38)$$

A review of the derivation shows that  $\partial\mathcal{E}/\partial\bar{n}$  is to be measured in the dilute solution but its value is independent of  $\psi$  [that is, like  $(\partial H/\partial\bar{n})^\square$  and unlike  $(\partial S/\partial\bar{n})^\square$ ].

This can be verified from the following alternative derivation (the above derivation is included because some of the intermediate equations are important). As in Eq. (5-25),

$$\left(\frac{\partial\mathcal{E}}{\partial\bar{n}}\right)_{p,T,N_i^0,N_\alpha}^\square = - \sum_j \nu_j \left(\frac{\partial\mathcal{E}}{\partial\bar{N}_j}\right)_{p,T,\bar{N}_j,N_\alpha}^\square. \quad (5-39)$$

Here  $j$  means all  $j \neq i$ . From the last form of Eq. (4-16), using Eq. (5-16),

$$\left(\frac{\partial\mathcal{E}}{\partial\bar{N}_i}\right)_{p,T,\bar{N}_j,N_\alpha}^\square = -kT - N_\alpha \left(\frac{\partial\mu_i}{\partial N_\alpha}\right)_{p,T,\bar{N}_k} = -N_\alpha \left(\frac{\partial\mu_i^\Delta}{\partial N_\alpha}\right)_{p,T}. \quad (5-40)$$

The right-hand side of Eq. (5-40) is a function of  $p$ ,  $T$ , and  $N_\alpha$  only (like  $\bar{h}_i^\square$  and unlike  $\bar{s}_i^\square$ ). Therefore  $(\partial\mathcal{E}/\partial\bar{n})^\square$  in Eq. (5-39) is a function of  $p$ ,  $T$ , and  $N_\alpha$  only. Substitution of Eq. (5-40) into Eq. (5-39) again leads to Eq. (5-38).

The left-hand side of Eq. (5-38) is amenable to experimental determination. This would provide information about  $\mathcal{E}^\square$ .

**EXTENT OF REACTION.** The extent of reaction  $\bar{n}$ , at equilibrium, is in some respects a property similar to  $K$ . Both can be used to follow the progress of a chemical equilibrium. Practical use of the above  $K$  equations presumably will require that the chemical equilibrium be studied in solutions dilute with respect to the  $\bar{N}_i$ . There is no such limitation with  $\bar{n}$ . But, on the other hand,  $\bar{n}$  (at  $\psi = 0$ ) is a function not only of  $p$ ,  $T$ , and  $N_\alpha$ , but also of the  $N_i^\circ$ .

We give in this subsection a few basic equations involving  $\bar{n}$  at constant  $\psi$  (the actual case of interest being  $\psi = 0$ ). Thus, from Eq. (5-13) we have

$$\left(\frac{\partial\bar{n}}{\partial T}\right)_{p, N_i^\circ, N_\alpha, \psi} = -\left(\frac{\partial S}{\partial\psi}\right)_{p, T, N_i^\circ, N_\alpha} \quad (5-41)$$

and

$$\left(\frac{\partial\bar{n}}{\partial p}\right)_{T, N_i^\circ, N_\alpha, \psi} = \left(\frac{\partial\bar{V}}{\partial\psi}\right)_{p, T, N_i^\circ, N_\alpha}. \quad (5-42)$$

Measurement of the left-hand sides of these equations at equilibrium gives values of the derivatives on the right at  $\psi = 0$ . These derivatives cannot be determined directly. By combining Eqs. (5-41) and (5-42), we obtain

$$\left(\frac{\partial p}{\partial T}\right)_{N_i^\circ, N_\alpha, \psi, \bar{n}} = \left(\frac{\partial S}{\partial\bar{V}}\right)_{p, T, N_i^\circ, N_\alpha}. \quad (5-43)$$

The meaning of the derivative on the left is the following:  $p$  and  $T$  are varied simultaneously in such a way that the equilibrium  $\bar{n}$  is maintained at a constant value.

If the temperature is varied while chemical equilibrium is maintained, the accompanying volume change is determined by

$$\left(\frac{\partial\bar{V}}{\partial T}\right)_{p, N_i^\circ, N_\alpha, \psi} = -\left(\frac{\partial S}{\partial p}\right)_{T, N_i^\circ, N_\alpha, \psi}. \quad (5-44)$$

This follows from Eq. (5-13). If we use  $d(F + \psi\bar{n} - p\bar{V})$  instead of (5-13), we can deduce

$$\left(\frac{\partial p}{\partial T}\right)_{\bar{V}, N_i^0, N_\alpha, \psi} = \left(\frac{\partial S}{\partial \bar{V}}\right)_{T, N_i^0, N_\alpha, \psi}. \quad (5-45)$$

Then there is also, of course, the relation

$$\left(\frac{\partial \bar{V}}{\partial p}\right)_{T, N_i^0, N_\alpha, \psi} = -\frac{(\partial \bar{V}/\partial T)_{p, N_i^0, N_\alpha, \psi}}{(\partial p/\partial T)_{\bar{V}, N_i^0, N_\alpha, \psi}}. \quad (5-46)$$

These equations are the analogues of very familiar relations in the macroscopic thermodynamics of one-component systems.

Perhaps of most interest is the effect of the size of the small system on the extent of reaction. Let the solvent have only one component (or keep the solvent composition constant). Now suppose we increase  $N_\alpha$  and all the  $N_i^0$  in the same ratio, keeping  $p$ ,  $T$ , and  $\psi$  constant. Then the quantity  $\bar{n}/N_\alpha$  will vary somewhat in a small system, though it would be constant in a macroscopic system. Thus we require an expression for  $\partial(\bar{n}/N_\alpha)/\partial N_\alpha$  with  $p$ ,  $T$ ,  $\psi$ , and  $N_i^0/N_\alpha$  held constant.

We start with

$$d\bar{n} = \sum_i \frac{\partial \bar{n}}{\partial N_i^0} dN_i^0 + \frac{\partial \bar{n}}{\partial N_\alpha} dN_\alpha \quad (p, T, \psi \text{ constant})$$

and substitute

$$\left(\frac{\partial \bar{n}}{\partial N_i^0}\right)_{p, T, N_j^0, N_\alpha, \psi} = \left(\frac{\partial \mu_i}{\partial \psi}\right)_{p, T, N_k^0, N_\alpha} \quad (5-47)$$

$$\left(\frac{\partial \bar{n}}{\partial N_\alpha}\right)_{p, T, N_i^0, \psi} = \left(\frac{\partial \mu_\alpha}{\partial \psi}\right)_{p, T, N_i^0, N_\alpha} \quad (5-48)$$

$$dN_i^0 = N_\alpha d\left(\frac{N_i^0}{N_\alpha}\right) + \frac{N_i^0}{N_\alpha} dN_\alpha.$$

This leads to

$$\left(\frac{\partial \bar{n}}{\partial N_\alpha}\right)_{p, T, \psi, N_i^0/N_\alpha} = \frac{1}{N_\alpha} \sum_i N_i^0 \frac{\partial \mu_i}{\partial \psi} + \frac{\partial \mu_\alpha}{\partial \psi}.$$

Then

$$\frac{\partial \bar{n}/N_\alpha}{\partial N_\alpha} = -\frac{\bar{n}}{N_\alpha^2} + \frac{1}{N_\alpha} \frac{\partial \bar{n}}{\partial N_\alpha}$$

and the Gibbs-Duhem equation, (5-15), give the final result

$$\left( \frac{\partial \bar{n}/N_\alpha}{\partial N_\alpha} \right)_{p, T, \psi, N_i^0/N_\alpha} = -\frac{1}{N_\alpha^2} \left( \frac{\partial \mathcal{E}}{\partial \psi} \right)_{p, T, N_i^0, N_\alpha} \quad (5-49)$$

$$= -\frac{1}{N_\alpha^2} \left( \frac{\partial \mathcal{E}}{\partial \bar{n}} \right)_{p, T, N_i^0, N_\alpha} \left( \frac{\partial \bar{n}}{\partial \psi} \right)_{p, T, N_i^0, N_\alpha} \quad (5-50)$$

A general fluctuation formula for  $\partial \bar{n}/\partial \psi$  is given in Eq. (5-78). Comparison of Eq. (5-50) with Eq. (5-38), and use of Eq. (5-34), shows that, in a dilute solution,

$$\left( \frac{\partial \ln K}{\partial N_\alpha} \right)_{p, T} = -N_\alpha \left( \sum_i \frac{v_i^2}{\bar{N}_i} \right) \left( \frac{\partial \bar{n}/N_\alpha}{\partial N_\alpha} \right)_{p, T, \psi, N_i^0/N_\alpha} \quad (5-51)$$

When the size of the system is increased as above, how must the temperature change in order to maintain  $\bar{n}/N_\alpha$  constant? Equation (5-41) can be rewritten as

$$\left( \frac{\partial \bar{n}/N_\alpha}{\partial T} \right)_{p, \psi, N_\alpha, N_i^0/N_\alpha} = -\frac{1}{N_\alpha} \left( \frac{\partial S}{\partial \psi} \right)_{p, T, N_i^0, N_\alpha}$$

Then this relation may be combined with Eq. (5-49) to yield the desired result,

$$\left( \frac{\partial T}{\partial N_\alpha} \right)_{p, \psi, N_i^0/N_\alpha, \bar{n}/N_\alpha} = -\frac{1}{N_\alpha} \left( \frac{\partial \mathcal{E}}{\partial S} \right)_{p, T, N_i^0, N_\alpha} \quad (5-52)$$

In an analogous way we also find

$$\left( \frac{\partial p}{\partial N_\alpha} \right)_{T, \psi, N_i^0/N_\alpha, \bar{n}/N_\alpha} = \frac{1}{N_\alpha} \left( \frac{\partial \mathcal{E}}{\partial \bar{V}} \right)_{p, T, N_i^0, N_\alpha} \quad (5-53)$$

**DILUTE GAS OF SMALL SYSTEMS.** We have already seen in Section 3-3 and at the end of Section 4-3 that the thermodynamic equations

applicable to small systems forming a very dilute gas are formally the same as for an ensemble of distinguishable systems, except that  $p$ - $V$  terms and effects are missing. From the nature of the argument which starts with Eq. (5-4) we may anticipate a similar immediate extension of equations derived so far in this section to the case of a chemical reaction taking place in the small systems of a dilute gas. Again, of course,  $p$ - $V$  effects and dependencies have to be omitted.

There are, however, two fundamental points which should be verified. One is that  $-\psi d\bar{n} \leq 0$  is still the criterion for chemical equilibrium. The other is that the entropy  $S$ , as defined in Eq. (3-30), is still related to the reversible heat of the chemical reaction per system by  $DQ = T dS$ . This is used in Eq. (5-26).

The extension of Eq. (3-26) needed here is

$$\begin{aligned} dE_t &= T dS_t - p dV + \mu_t d\mathcal{N} + \mathcal{N} \left( \sum_i \mu_i d\bar{N}_i + \sum_\alpha \mu_\alpha dN_\alpha \right) \\ &= T dS_t - p dV + \mu_t d\mathcal{N} + \mathcal{N} \left( \sum_i \mu'_i dN_i^0 - \psi d\bar{n} + \sum_\alpha \mu_\alpha dN_\alpha \right). \end{aligned} \quad (5-54)$$

When the dilute gas of small systems is held at constant  $T$ ,  $V$ ,  $\mathcal{N}$ ,  $N_i^0$ , and  $N_\alpha$ , and the chemical reaction is the only possible spontaneous process, we have, from Eq. (5-54),

$$dA_t = d(E_t - TS_t) = -\mathcal{N}\psi d\bar{n} \leq 0.$$

From the definition of  $S$  in Eq. (3-30),

$$A_t = \mathcal{N}\bar{E} - \mathcal{N}TS - \mathcal{N}kT + \mathcal{N}kT \ln \frac{c}{c^\dagger},$$

where  $c = \mathcal{N}/V$  and  $c^\dagger$  is a constant. Therefore, with  $T$ ,  $V$ ,  $\mathcal{N}$ ,  $N_i^0$ , and  $N_\alpha$  constant,

$$dA_t = \mathcal{N} d(\bar{E} - TS) = \mathcal{N} dA$$

and hence

$$dA = -\psi d\bar{n} \leq 0 \quad (T, N_i^0, N_\alpha \text{ constant}). \quad (5-55)$$

This verifies that  $\psi = 0$  is the criterion for chemical equilibrium.

Equation (3-31) is converted here into Eq. (5-10) with the  $p d\bar{V}$  term omitted. In Eqs. (5-11) to (5-15),  $F$  is replaced by  $A$  and  $\bar{V} dp$  is omitted. In Eqs. (5-23) to (5-27),  $H$  and  $\bar{H}_t$  become  $\bar{E}$  and  $\bar{E}_t$ .



When the closed ensemble ( $\mathcal{N}$ ,  $N_i^0$ ,  $N_\alpha$  constant) at constant  $V$  absorbs heat,

$$DQ_t = T dS_t = T d\left(\mathcal{N}S + \mathcal{N}k - \mathcal{N}k \ln \frac{c}{c^\dagger}\right) = \mathcal{N}T dS.$$

The heat absorbed per system is  $DQ = DQ_t/\mathcal{N}$ , and hence  $DQ = T dS$  as assumed in Eqs. (5-26) and (5-27).

**SMALL SYSTEMS IN SOLVENT.** If a chemical reaction takes place in small systems immersed in a solvent (see Sections 2-3 and 4-2), Eqs. (5-5), (5-6), and (5-10) to (5-53) are all unchanged in formal appearance. But we should again verify that  $-\psi d\bar{n} \leq 0$  and  $DQ = T dS$  for a chemical reaction.

Equation (2-102) for the dilute solution of small systems in solvent becomes, for the present problem,

$$\begin{aligned} dE_T = T dS_T - p dV_T + \mu_1 dN_1^S + \mu^\square d\mathcal{N} \\ + \mathcal{N} \left( \sum_i \mu_i dN_i^0 - \psi d\bar{n} + \sum_\alpha \mu_\alpha dN_\alpha \right). \end{aligned} \quad (5-56)$$

When the chemical reaction occurs spontaneously in the closed ensemble ( $N_1^S, \mathcal{N}$ ,  $N_i^0$ ,  $N_\alpha$  constant) at constant  $T$  and  $p$ ,

$$dF_T = d(E_T - TS_T + pV_T) = -\mathcal{N} \psi d\bar{n} \leq 0.$$

In the notation of Section 2-3,  $F^*(p, T, N_1^S)$  is the Gibbs free energy of the pure solvent. Using the definitions of  $\bar{E}$  and  $\bar{V}$ , and Eqs. (2-109) to (2-111),

$$\begin{aligned} F_T - F^* &= (E_T - E^*) + p(V_T - V^*) - T(S_T - S^*) \\ &= \mathcal{N} \bar{E} + p\mathcal{N} \bar{V} - \mathcal{N}kT - \mathcal{N}TS + \mathcal{N}kT \ln \frac{\mathcal{N}}{N_1^S}. \end{aligned}$$

When  $T$ ,  $p$ ,  $N_1^S$ , and  $\mathcal{N}$  are all constant, as above,

$$dF_T = d(F_T - F^*) = \mathcal{N} d(\bar{E} + p\bar{V} - TS) = \mathcal{N} dF$$

and hence

$$dF = -\psi d\bar{n} \leq 0 \quad (p, T, N_i^0, N_\alpha \text{ constant}), \quad (5-57)$$

just as in Eq. (5-9).

When the closed ( $N_1^S, \mathcal{N}, N_t, N_\alpha$  constant) dilute solution absorbs heat,  $T dS_T = DQ_T$ . Similarly, for the closed solvent ( $N_1^S$  constant),  $T dS^* = DQ^*$ . Then

$$\begin{aligned} T d(S_T - S^*) &= T d\left(\mathcal{N}k + \mathcal{N}S - \mathcal{N}k \ln \frac{\mathcal{N}}{N_1^S}\right) \\ &= \mathcal{N}T dS = DQ_T - DQ^* \\ &\quad (N_1^S, \mathcal{N}, N_t^0, N_\alpha \text{ constant}). \end{aligned}$$

For the process of interest in, and described following, Eq. (5-26) (chemical reaction at constant  $p$  and  $T$ ),  $DQ^* = 0$ . Then  $DQ = DQ_T/\mathcal{N} = T dS$ .

### 5-3. ISOMERIC EQUILIBRIUM IN TWO-COMPONENT SYSTEM

We consider a very special case of a chemical equilibrium in this section. A small system at  $p$  and  $T$  has two components only, with total number of molecules  $N$ ; the two components are in isomeric equilibrium with each other,  $A_1 \rightleftharpoons A_2$ . The main application we have in mind is to a linear macromolecule of  $N$  monomers or units, each of which can exist in two states  $A_1$  or  $A_2$ .

The helix-coil transition is an example. A given unit is in the helical form or the coil (nonhelical) form. This transition is not a phase transition in reality, but it may become one in sufficiently crude theoretical models [see Eq. (2-87), for example]. The most direct, general thermodynamic treatment of a transition of this type is as an isomeric chemical equilibrium. The same problem is treated as an  $N, f, T$  system (omitting  $p$ ) in Section 2-2, but this approach involves some unnecessary arbitrariness in the introduction of the length of the macromolecule and the lengths of the two units. Also, if rotation of the macromolecule is included, states with  $f \neq 0$  become rather artificial.

At chemical equilibrium between the two isomers  $A_1$  and  $A_2$ , the system is formally a one-component system with environmental variables  $N, p, T$ . If desired, the equilibrium can be ignored and the equations of Chapter 2 applied. In fact, any one-component system may be regarded as an equilibrium isomeric mixture of substates of one kind or another. If no information is available about the isomeric composition at equilibrium, the equilibrium is not taken into account in the thermodynamics. Here we assume that there is some

method of determining the equilibrium composition of the  $A_1$ ,  $A_2$  mixture, and hence we consider the reaction explicitly. The thermodynamics is more informative in this case than it would be if the reaction were ignored. In the helix-coil example, optical methods are generally used to estimate the fraction of helical content at equilibrium.

We use the general approach of the previous section. The environmental variables are  $N$ ,  $p$ ,  $T$ ,  $\psi$ , where the only operationally achievable value of  $\psi$  is again  $\psi = 0$  (equilibrium).

The basic equations (5-4) to (5-15) all apply to this special case. We make the following specific choice of notation:  $N_1^0 = 0$ ,  $N_2^0 = N$ ,  $\nu_1 = -1$ ,  $\nu_2 = +1$ ,  $N_1 = n$ ,  $N_2 = N - n$ ,  $\psi = \mu_2 - \mu_1$ . Then the fundamental equations of most interest are

$$F = H - TS = \mu_1 \bar{N}_1 + \mu_2 \bar{N}_2 + \mathcal{E} \quad (5-58)$$

$$F = \mu_2 N - \psi \bar{n} + \mathcal{E} \quad (5-59)$$

$$X = F + \psi \bar{n} = \mu_2 N + \mathcal{E} \quad (5-60)$$

$$dF = -S dT + \bar{V} dp + \mu_1 d\bar{N}_1 + \mu_2 d\bar{N}_2 \quad (5-61)$$

$$dF = -S dT + \bar{V} dp + \mu_2 dN - \psi d\bar{n} \quad (5-62)$$

$$d(F + \psi \bar{n}) = -S dT + \bar{V} dp + \mu_2 dN + \bar{n} d\psi \quad (5-63)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - N d\mu_2 + \bar{n} d\psi. \quad (5-64)$$

Many relations between derivatives follow from these equations. We shall indicate some of these below as they are required.

**EQUILIBRIUM CONSTANT.** We define an equilibrium constant here which may be of use with statistical mechanical models but which would ordinarily be not measurable for a small system. Hence the discussion will be very brief. Let  $\mu_1^0(p, T, N)$  be the chemical potential of component 1 when the system is pure 1, and let  $\mu_1(p, T, N, \psi)$  be the chemical potential of component 1 in general. Then define the activity  $a_1$  in terms of  $\mu_1^0$  and  $\mu_1$  as follows:

$$\mu_1(p, T, N, \psi) = \mu_1^0(p, T, N) + kT \ln a_1. \quad (5-65)$$

Similarly,

$$\mu_2(p, T, N, \psi) = \mu_2^0(p, T, N) + kT \ln a_2. \quad (5-66)$$

We define  $K$  as the ratio  $a_2/a_1$  when  $\psi = 0$ . Then

$$\ln K = -\left(\frac{\mu_2^0 - \mu_1^0}{kT}\right). \quad (5-67)$$

Thus  $K$  is a function of  $p$ ,  $T$ , and  $N$ . Its value depends on the properties of the two pure components. The two activities and the equilibrium constant will generally be nonoperational quantities because of the difficulty of forming the pure systems for study at arbitrary  $p$ ,  $T$ , and  $N$  (unless a catalyst is required, the systems will spontaneously approach the equilibrium mixture and fluctuate about it).

We can easily obtain the derivatives of  $\ln K$  with respect to  $T$ ,  $p$ , and  $N$ , from Eqs. (2-15c), (2-16), (2-20b), and (5-67):

$$\left(\frac{\partial \ln K}{\partial T}\right)_{p, N} = \frac{1}{kT^2} \left[ \left(\frac{\partial H_2^0}{\partial N}\right)_{p, T} - \left(\frac{\partial H_1^0}{\partial N}\right)_{p, T} \right] \quad (5-68)$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_{T, N} = -\frac{1}{kT} \left[ \left(\frac{\partial \bar{V}_2^0}{\partial N}\right)_{p, T} - \left(\frac{\partial \bar{V}_1^0}{\partial N}\right)_{p, T} \right] \quad (5-69)$$

$$\left(\frac{\partial \ln K}{\partial N}\right)_{p, T} = \frac{1}{NkT} \left[ \left(\frac{\partial \mathcal{E}_2^0}{\partial N}\right)_{p, T} - \left(\frac{\partial \mathcal{E}_1^0}{\partial N}\right)_{p, T} \right], \quad (5-70)$$

where the superscript zero on  $H$ ,  $\bar{V}$ , and  $\mathcal{E}$  refers to a pure component.

**ALTERNATIVE EQUILIBRIUM CONSTANT.** A much more practical constant is

$$K' = \frac{\bar{N}_2}{\bar{N}_1} = \frac{N - \bar{n}}{\bar{n}} \quad \text{at } \psi = 0. \quad (5-71)$$

Although no activity coefficients are included in this definition, this is a true "thermodynamic" equilibrium constant in the usual sense that  $K'$  is a function of  $p$  and  $T$  only for a macroscopic system (and a function of  $p$ ,  $T$ , and  $N$  only for a small system). This is a consequence of the special nature of the system: there are only two components, and they are in chemical equilibrium with each other. Thus, at equilibrium (small system),

$$\mu_1(p, T, \bar{n}/N, N) = \mu_2(p, T, \bar{n}/N, N).$$

This relation determines the mean equilibrium composition  $\bar{n}/N$ , and therefore  $K'$ , as a function of  $p$ ,  $T$ , and  $N$ . For given  $p$ ,  $T$ , and  $N$ , and hence for a given  $K'$ , there is only one equilibrium composition possible. This is not characteristic of chemical reactions in general (see Section 5-2, for example), of course: an infinite number of compositions are consistent with the same value of  $K$  [see Eq. (5-18), for example].

In general  $\bar{n}$  is a function of  $p$ ,  $T$ ,  $N$ , and  $\psi$ . At  $\psi = 0$ , it is a function of  $p$ ,  $T$ , and  $N$  only. To obtain the properties of  $K'$ , we begin with those of  $\bar{n}$ .

From Eq. (5-63) we have immediately

$$\left(\frac{\partial \bar{n}}{\partial T}\right)_{p, N, \psi} = -\left(\frac{\partial S}{\partial \psi}\right)_{p, T, N}, \quad \left(\frac{\partial \bar{n}}{\partial p}\right)_{T, N, \psi} = \left(\frac{\partial \bar{V}}{\partial \psi}\right)_{p, T, N},$$

$$\left(\frac{\partial \bar{n}}{\partial N}\right)_{p, T, \psi} = \left(\frac{\partial \mu_2}{\partial \psi}\right)_{p, T, N}. \quad (5-72)$$

Another derivative which we shall encounter is  $(\partial \bar{n}/\partial \psi)_{p, T, N}$ . There is an exact statistical mechanical relation between  $\partial \bar{n}/\partial \psi$  and fluctuations of  $n$  about the mean value  $\bar{n}$ . This relation is particularly significant in small systems where fluctuations are important. The appropriate partition function<sup>1</sup> is

$$Y(p, T, N, \psi) = \sum_{n=0}^N e^{-n\psi/kT} \Delta(N, n, p, T), \quad (5-73)$$

where  $\Delta$  is the usual  $p$ ,  $T$ ,  $N_1$ ,  $N_2$  partition function [see Eq. (1-32)], but with independent variables  $N$  and  $n$ :  $N_1 = n$ ,  $N_2 = N - n$ . The relation to thermodynamics is

$$F + \psi \bar{n} = \mu_2 N + \mathcal{E} = -kT \ln Y. \quad (5-74)$$

It then follows that

$$\left(\frac{\partial \bar{n}}{\partial \psi}\right)_{p, T, N} = -\frac{\overline{n^2} - \bar{n}^2}{kT}, \quad (5-75)$$

which is the desired relation.

<sup>1</sup> See S.M., p. 294, and T. L. Hill, *J. Am. Chem. Soc.*, **79**, 4885 (1957), (eq. 54).

We should digress to point out that the same general relationships hold in Section 5-2 [see especially Eqs. (5-13) and (5-14)]:

$$Y(p, T, N_i^0, N_\alpha, \psi) = \sum_n e^{-n\psi/kT} \Delta(N_i^0, N_\alpha, n, p, T) \quad (5-76)$$

$$X = F + \psi\bar{n} = -kT \ln Y \quad (5-77)$$

$$\left(\frac{\partial \bar{n}}{\partial \psi}\right)_{p, T, N_i^0, N_\alpha} = -\frac{\overline{n^2} - \bar{n}^2}{kT}. \quad (5-78)$$

We had no occasion to use this general formula in the previous section because we needed only the special relation (5-34) for a dilute solution. Combining Eqs. (5-34) and (5-78) shows that

$$\overline{n^2} - \bar{n}^2 = \left(\sum_i \frac{v_i^2}{\bar{N}_i}\right)^{-1}. \quad (5-79)$$

The simplest example would be an isomeric equilibrium  $A_1 \rightleftharpoons A_2$ , occurring in a solvent. Then<sup>1</sup>

$$\overline{n^2} - \bar{n}^2 = \frac{\bar{N}_1 \bar{N}_2}{\bar{N}_1 + \bar{N}_2} \quad (\text{dilute solution}). \quad (5-80)$$

Let us now turn to  $K' = (N - \bar{n})/\bar{n}$ . We shall treat  $K'$  formally as a function of  $\psi$  as well as of  $p$ ,  $T$ , and  $N$ , with the understanding that evaluation of the various expressions at  $\psi = 0$  is always the case of real interest. For the temperature derivative of  $\ln K'$ , we find

$$\left(\frac{\partial \ln K'}{\partial T}\right)_{p, N, \psi} = -\frac{N}{\bar{n}(N - \bar{n})} \left(\frac{\partial \bar{n}}{\partial T}\right)_{p, N, \psi}, \quad (5-81)$$

where we can make the substitution, from Eq. (5-72a),

$$\left(\frac{\partial \bar{n}}{\partial T}\right)_{p, N, \psi} = -\left(\frac{\partial S}{\partial \bar{n}}\right)_{p, T, N} \left(\frac{\partial \bar{n}}{\partial \psi}\right)_{p, T, N}. \quad (5-82)$$

The thermodynamic quantity  $\partial \bar{n}/\partial \psi$  may be retained here, or it can be replaced by  $-(\overline{n^2} - \bar{n}^2)/kT$ . Neither of these quantities is directly measurable for a small system, by thermodynamic methods.

<sup>1</sup> This equation is also derived in S.T., p. 182, for a dilute gas.

Also, in Eq. (5-82), there are alternative expressions for  $\partial S/\partial \bar{n}$ . Thus, we have

$$\left(\frac{\partial F}{\partial \bar{n}}\right)_{p, T, N} = -\psi = \left(\frac{\partial H}{\partial \bar{n}}\right)_{p, T, N} - T\left(\frac{\partial S}{\partial \bar{n}}\right)_{p, T, N}$$

and hence

$$\left(\frac{\partial H}{\partial \bar{n}}\right)_{p, T, N} = T\left(\frac{\partial S}{\partial \bar{n}}\right)_{p, T, N} = \left(\frac{DQ}{\partial \bar{n}}\right)_{p, T, N} \quad \text{at } \psi = 0, \quad (5-83)$$

where  $DQ$  is the heat absorbed when the reaction proceeds an extent  $dn$  at  $\psi = 0$ , with  $p$ ,  $T$ , and  $N$  constant.

We may define partial molal quantities as in Section 4-1 for this binary system. Hence, still other expressions for  $\partial S/\partial \bar{n}$  are

$$\left(\frac{\partial S}{\partial \bar{n}}\right)_{p, T, N} = -(\tilde{s}_2 - \tilde{s}_1) = -\frac{\tilde{H}_2 - \tilde{H}_1}{T} \quad \text{at } \psi = 0. \quad (5-84)$$

In summary,

$$\left(\frac{\partial \ln K'}{\partial T}\right)_{p, N, \psi} = \frac{\Delta H}{kT^2} \left[ \frac{N(\bar{x}_1^2 - \bar{x}_1'^2)}{\bar{x}_1(1 - \bar{x}_1)} \right] \quad (\psi = 0), \quad (5-85)$$

where

$$\Delta H = \tilde{H}_2 - \tilde{H}_1 = T(\tilde{s}_2 - \tilde{s}_1) = -\left(\frac{DQ}{\partial \bar{n}}\right)_{p, T, N} \quad (\psi = 0) \quad (5-86)$$

and  $x_1 = n/N = N_1/N$ .

The quantity in square brackets in Eq. (5-85) is of order unity [compare Eq. (5-80), where this same expression is exactly unity]. If  $K' = (1 - \bar{x}_1)/\bar{x}_1$  can be measured by some analytical method and  $\Delta H$  obtained calorimetrically,  $\bar{x}_1^2 - \bar{x}_1'^2$  may then be calculated from Eq. (5-85). It is clearly incorrect to measure  $\partial \ln K'/\partial T$  and then to compute the "heat of the reaction" from the conventional expression  $\partial \ln K'/\partial T = \text{"heat"}/kT^2$ .

In exactly the same way we find

$$\left(\frac{\partial \ln K'}{\partial p}\right)_{T, N, \psi} = \frac{1}{kT} \left(\frac{\partial \bar{V}}{\partial \bar{n}}\right)_{p, T, N} \left[ \frac{N(\bar{x}_1^2 - \bar{x}_1'^2)}{\bar{x}_1(1 - \bar{x}_1)} \right], \quad (5-87)$$

where we can put

$$\left(\frac{\partial \bar{V}}{\partial \bar{n}}\right)_{p, T, N} = -(\bar{v}_2 - \bar{v}_1).$$

Again,  $\partial \ln K' / \partial p$  and  $\partial \bar{V} / \partial \bar{n}$  may in principle be measured and  $\bar{x}_1^2 - \bar{x}_1^2$  then calculated.

A possibly useful equation results on combining Eqs. (5-85) and (5-87):

$$\frac{\Delta H}{T} \left(\frac{\partial \ln K'}{\partial p}\right)_{T, N, \psi} = \left(\frac{\partial \bar{V}}{\partial \bar{n}}\right)_{p, T, N} \left(\frac{\partial \ln K'}{\partial T}\right)_{p, N, \psi} \quad (\psi = 0). \quad (5-88)$$

If three of the four factors appearing here can be measured, the fourth may then be calculated. A closely related equation is

$$\left(\frac{\partial p}{\partial T}\right)_{N, K', \psi} = \left(\frac{\partial p}{\partial T}\right)_{N, \bar{n}, \psi} = - \frac{(\partial \bar{n} / \partial T)_{p, N, \psi}}{(\partial \bar{n} / \partial p)_{T, N, \psi}} = \left(\frac{\partial S}{\partial \bar{V}}\right)_{p, T, N}. \quad (5-89)$$

Here  $p$  and  $T$  are varied in such a way as to keep  $\bar{n}$  constant, at  $\psi = 0$ . This is a special case of Eq. (5-43).

Next, we consider the dependence of  $\ln K'$  on  $N$ . From  $K' = (N - \bar{n}) / \bar{n}$  and Eq. (5-72c), we find

$$\left(\frac{\partial \ln K'}{\partial N}\right)_{p, T, \psi} = \frac{\bar{n} - N(\partial \mu_2 / \partial \bar{n})_{p, T, N} (\partial \bar{n} / \partial \psi)_{p, T, N}}{(N - \bar{n}) \bar{n}} \quad (5-90)$$

$$= \frac{1}{N} \left\{ \frac{1}{1 - \bar{x}_1} + \frac{1}{kT} \left(\frac{\partial \mu_2}{\partial \bar{x}_1}\right)_{p, T, N} \left[ \frac{N(\bar{x}_1^2 - \bar{x}_1^2)}{\bar{x}_1(1 - \bar{x}_1)} \right] \right\}. \quad (5-91)$$

The quantity  $\{ \}$  vanishes for a macroscopic system since, in Eq. (5-90),

$$\frac{\bar{n}}{N} - \left(\frac{\partial \mu_2}{\partial \psi}\right)_{p, T, N} = \frac{\bar{n}}{N} - \left(\frac{\partial \bar{n}}{\partial N}\right)_{p, T, \psi} = \frac{\bar{n}}{N} - \frac{\bar{n}}{N} = 0.$$

A more compact expression than (5-91) follows on use of the Gibbs-Duhem equation:

$$\left(\frac{\partial \mathcal{E}}{\partial \bar{n}}\right)_{p, T, N} = -N \left(\frac{\partial \mu_2}{\partial \bar{n}}\right)_{p, T, N} + \bar{n} \left(\frac{\partial \psi}{\partial \bar{n}}\right)_{p, T, N}. \quad (5-92)$$



Elimination of  $\partial\mu_2/\partial\bar{n}$  between Eqs. (5-90) and (5-92) gives

$$\left(\frac{\partial \ln K'}{\partial N}\right)_{p, T, \psi} = -\frac{1}{NkT} \left(\frac{\partial \mathcal{E}}{\partial \bar{n}}\right)_{p, T, N} \left[ \frac{N(\bar{x}_1^2 - \bar{x}_1)}{\bar{x}_1(1 - \bar{x}_1)} \right]. \quad (5-93)$$

We found Eq. (5-89) by combining Eqs. (5-81) and (5-87). There are two further relations of this type. From Eqs. (5-81), (5-82), and (5-93):

$$\begin{aligned} \left(\frac{\partial T}{\partial N}\right)_{p, K', \psi} &= \left(\frac{\partial T}{\partial N}\right)_{p, \bar{x}_1, \psi} = -\frac{(\partial \ln K'/\partial N)_{p, T, \psi}}{(\partial \ln K'/\partial T)_{p, N, \psi}} \\ &= -\frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial S}\right)_{p, T, N}. \end{aligned} \quad (5-94)$$

In this equation  $T$  and  $N$  are simultaneously varied so that  $\bar{x}_1 = \bar{n}/N$  remains constant. The derivative  $\partial T/\partial N$  can be evaluated, for example, from data on the fraction of helical content (say,  $\bar{x}_1$ ) in synthetic polypeptides as a function of temperature and degree of polymerization ( $N$ ). Similarly, from Eqs. (5-87) and (5-93):

$$\left(\frac{\partial p}{\partial N}\right)_{T, K', \psi} = \left(\frac{\partial p}{\partial N}\right)_{T, \bar{x}_1, \psi} = \frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial \bar{V}}\right)_{p, T, N}. \quad (5-95)$$

Derivatives of  $\bar{x}_1$  itself instead of  $\ln K'$  may be of use. These are:

$$\left(\frac{\partial \bar{x}_1}{\partial T}\right)_{p, N, \psi} = -\frac{1}{N} \frac{\partial S}{\partial \psi} = -\frac{1}{N} \frac{\partial S}{\partial \bar{n}} \frac{\partial \bar{n}}{\partial \psi} \quad (5-96)$$

$$\left(\frac{\partial \bar{x}_1}{\partial p}\right)_{T, N, \psi} = \frac{1}{N} \frac{\partial \bar{V}}{\partial \psi} = \frac{1}{N} \frac{\partial \bar{V}}{\partial \bar{n}} \frac{\partial \bar{n}}{\partial \psi} \quad (5-97)$$

$$\left(\frac{\partial \bar{x}_1}{\partial N}\right)_{p, T, \psi} = -\frac{1}{N^2} \frac{\partial \mathcal{E}}{\partial \psi} = -\frac{1}{N^2} \frac{\partial \mathcal{E}}{\partial \bar{n}} \frac{\partial \bar{n}}{\partial \psi}, \quad (5-98)$$

where all derivatives on the right-hand side are with constant  $p, T, N$ .

A few other relations of possible interest are the following:

$$\left(\frac{\partial S}{\partial \bar{n}}\right)_{p, T, N} = \left(\frac{\partial \psi}{\partial T}\right)_{p, N, \bar{n}}, \quad \left(\frac{\partial \mu_2}{\partial \bar{n}}\right)_{p, T, N} = -\left(\frac{\partial \psi}{\partial N}\right)_{p, T, \bar{n}}, \quad (5-99)$$

and

$$\left(\frac{\partial T}{\partial N}\right)_{p, \bar{n}, \psi} = \left(\frac{\partial \mu_2}{\partial S}\right)_{p, T, N} \quad (5-100)$$

Equations (5-99) follow from Eq. (5-62), and Eq. (5-100) from Eqs. (5-72a) and (5-72c).

*Example. Helix-Coil Transition.* Our object here is simply to translate the “unzipper-from-the-ends” model of the helix-coil transition from the  $N, f, T$  language of Eq. (2-85) to the present, equivalent  $N, \psi, T$  language. Component 1 is  $H$  (helix) and component 2 is  $C$  (coil). Hence  $\bar{x}_1 = \bar{n}/N$  is the fraction of helical units. We put  $l_C = 0$  and  $l_H f = -\psi$ . The partition function  $\Delta$  of Eq. (2-85) then becomes

$$\begin{aligned} Y(T, N, \psi) &= \sum_{n=0}^N e^{-n\psi/kT} Q(N, n, T) \\ &= q_C^N + \sum_{n=1}^N (N - n + 1) q_C^{N-n} q_H^n e^{-n\psi/kT}, \end{aligned} \quad (5-101)$$

$$= q_C^N \frac{Nr(1-r) + 1 - 2r + r^{N+2}}{(1-r)^2}, \quad (5-102)$$

where

$$r(\psi, T) = \frac{q_H(T)e^{-\psi/kT}}{q_C(T)}. \quad (5-103)$$

The basic thermodynamic equations are

$$A + \psi \bar{n} = \mu_2 N + \mathcal{E} = -kT \ln Y \quad (5-104)$$

$$d(A + \psi \bar{n}) = -S dT + \mu_2 dN + \bar{n} d\psi \quad (5-105)$$

$$d\mathcal{E} = -S dT - N d\mu_2 + \bar{n} d\psi. \quad (5-106)$$

Equation (2-93) for  $\bar{n}/N$  is obtained just as before, while in Eq. (2-88) we replace  $\mu$  by  $\mu_2$  and  $r_C$  by  $q_C$ .

It should be possible soon to apply the equations of this section to experimental data on the helix-coil transition in synthetic polypeptides. These data are being accumulated in the laboratories of M. Goodman and E. Katchalsky, for example.

*Example. Ideal Binary Mixture.* Suppose an isomeric reaction takes place between the two components in the model represented by Eq. (4-77). Except for different notation, this is also the model in Eq. (2-99) (independent helix and coil units).

Equations (5-101) and (5-104) to (5-106) are applicable here, with

$$Q(N, n, T) = \frac{j_1(T)^n j_2(T)^{N-n} N!}{n!(N-n)!} \quad (5-107)$$

Thus

$$Y = (j_2 + j_1 e^{-\psi/kT})^N \quad (5-108)$$

and

$$\frac{\bar{n}}{N} = \frac{j_1 e^{-\psi/kT}}{j_2 + j_1 e^{-\psi/kT}} \quad (5-109)$$

At equilibrium ( $\psi = 0$ ),

$$\frac{\bar{n}}{N} = \frac{j_1}{j_1 + j_2}, \quad \frac{N - \bar{n}}{\bar{n}} = \frac{j_2}{j_1} = K'(T). \quad (5-110)$$

In this special case,  $K'$  is independent of  $N$ .

We find from Eqs. (5-75) and (5-109) that

$$\frac{\overline{n^2} - \bar{n}^2}{\bar{n}^2} = \frac{N - \bar{n}}{N\bar{n}} = \frac{K'(T)}{N}, \quad (5-111)$$

which is the same as Eq. (5-80).

The operationally significant environmental variables are  $T$ ,  $N$ ,  $\psi = 0$ , as in the above analysis. There are fluctuations, in each small system, about the mean composition. In Eq. (5-111), we have calculated the extent of these fluctuations. It is of some theoretical interest to compare with this a hypothetical ensemble of systems with nonfluctuating composition, at equilibrium. That is, the environmental variables are  $T$ ,  $N_1$ ,  $N_2$ , with  $N_1$  and  $N_2$  adjusted so that  $\mu_1 = \mu_2$ . That this is the equilibrium condition follows from Eq. (5-9) and the fact that thermodynamic equations (though not

functions) for small systems are independent of environment. Equation (4-80) gives  $\mu_1$ , and there is a symmetrical expression for  $\mu_2$ . Equating  $\mu_1$  and  $\mu_2$  leads to

$$x_2 = \bar{x}_2 - \frac{1 - 2\bar{x}_2}{2N} + O(N^{-2}), \quad (5-112)$$

where  $x_2$  is the equilibrium mole fraction of component 2 for a  $T, N_1, N_2$  system, while  $\bar{x}_2 = (N - \bar{n})/N$  is the same quantity for a  $T, N, \psi$  system [that is,  $\bar{x}_2 = j_2/(j_1 + j_2)$ ]. Equation (5-112) shows that the two equilibrium compositions differ for a small system and that the existence of composition fluctuations shifts the equilibrium in the direction of the dilute component.

#### 5-4. FIRST-ORDER PHASE TRANSITIONS IN $N, p, T$ SYSTEMS

An experimental macroscopic system may show discontinuities in various thermodynamic functions below a critical temperature, corresponding to a first-order phase transition. In theoretical work, these discontinuities are "sharp" only in the limit of an infinite system. Small systems will exhibit, instead, more or less gradual changes which approach discontinuities more closely the larger the system.

The exact treatment of first-order phase transitions is an important topic in macroscopic thermodynamics. This topic exists, as an exact branch of thermodynamics, only by virtue of the occurrence of sharp discontinuities in properties in macroscopic systems. Since such discontinuities are absent in small systems, there is no corresponding exact thermodynamics of first-order phase transitions.

From a formalistic and rigorous point of view, the thermodynamics of a *single-phase* small system should be used under all circumstances. If a phase transition is known to occur in a macroscopic system, it is ignored in the corresponding small system. Thus, for example, the treatment of a one-phase  $N, p, T$  system in Chapter 2 is valid for a small  $N, p, T$  system whether or not the infinite system shows phase transitions.

Of course, even in macroscopic thermodynamics it is quite legitimate to take a similar "black-box" attitude and ignore the possible existence of more than one phase in a system. In this case any phase transition which does in fact occur will be correctly taken into account implicitly, though not explicitly. Actually, the derivation of Eq. (2-52) from Eq. (2-51) is an example of the "implicit" point of

view. But for a small system there is no choice: an *exact* treatment must take care of any phase transition implicitly; an exact, explicit analysis does not exist because of the absence of any discontinuities or sharply defined points or regions.

The above comments are, of course, purely thermodynamic in nature. One can investigate the nature of a phase transition, in various ways, exactly and explicitly, for  $N$  finite or infinite, by a statistical mechanical analysis of a model.

Contrary to the above rather sterile position concerning the exact thermodynamics of phase transitions in small systems, it is possible to give an explicit, *approximate* thermodynamic treatment of first-order phase transitions in a small  $N, p, T$  system. Furthermore, this approximation is probably excellent except near the critical point or for  $N$  too small. The remainder of this section will be devoted to this subject.

Phase transitions with other environmental variables will be discussed in later chapters. It should be mentioned here, though, that the  $\mu, V, T$  case (Chapter 6) is formally identical with the present  $N, p, T$  case. Thus the examples in Chapter 6 supplement those in the present section.

There is one other general comment which should be made. If a small system is in a phase equilibrium with a macroscopic system, this equilibrium is already taken into account by the assignment of environmental variables. For example, a small  $\mu, V, T$  system is in equilibrium with some macroscopic reservoir of molecules, say, a solution, at chemical potential  $\mu$ . It is for the above reason, also, that one does not speak of, say, the vapor pressure of an  $N, p, T$  system. If a small  $p, T$  system is in equilibrium with a macroscopic vapor, then it is a  $\mu, p, T$  system, not an  $N, p, T$  system.

NATURE OF THE "TWO-STATE" APPROXIMATION. This approximation, once established, will be handled by thermodynamic methods. But the argument justifying the approximation comes from statistical mechanics.<sup>1</sup>

<sup>1</sup> The following discussion is based on appendix 9 of S.M. The reader interested in a more detailed argument should consult this reference. A  $\mu, V, T$  system, with  $P(N)$ , is discussed in S.M., instead of an  $N, p, T$  system, with  $P(V)$ . But these two cases are formally identical. See also T. L. Hill, *J. Chem. Phys.*, **23**, 812 (1955).

The normalized probability that an  $N, p, T$  system will be observed to have a volume  $V$  is

$$P(V) = \frac{Q(N, V, T)e^{-pV/kT}}{\Delta}, \quad (5-113)$$

where  $\Delta$  is the  $N, p, T$  partition function,

$$\Delta(N, p, T) = \sum_V Q(N, V, T)e^{-pV/kT}. \quad (5-114)$$

At an "ordinary" point (i.e., not near a critical point or phase transition) the function  $P(V)$  has a single peak about  $\bar{V}$ , as shown in Fig. 5-1a. For a macroscopic system, the peak in Fig. 5-1a approaches a  $\delta$  function. But, for a small system, the fluctuations in  $V$  about  $\bar{V}$  become appreciable. At a critical point,  $P(V)$  probably has a flat top, as shown schematically in Fig. 5-1b. At the middle of a phase transition (phases  $A$  and  $B$ ;  $\bar{V}_A > \bar{V}_B$ ), on the other hand,  $P(V)$  has two separated peaks, as in Fig. 5-1c. These become  $\delta$  functions at  $\bar{V}_A$  and  $\bar{V}_B$  for a macroscopic system. In the transition region, but not at its middle, the two peaks remain at  $\bar{V}_A$  and  $\bar{V}_B$ , but they have different heights and areas.

According to Fig. 5-1c, an  $N, p, T$  system in a phase-transition region may be observed to have a volume near  $\bar{V}_A$  or near  $\bar{V}_B$  (the range of fluctuations about these values depends on the size of system, just as in Fig. 5-1a), but the probability of observing intermediate values of  $V$ , say,  $V = \bar{V}$ , is negligible. Thus the phase-transition region may be regarded as a composite of two "ordinary" states  $A$  and  $B$ . A given system in the ensemble may be assumed to be

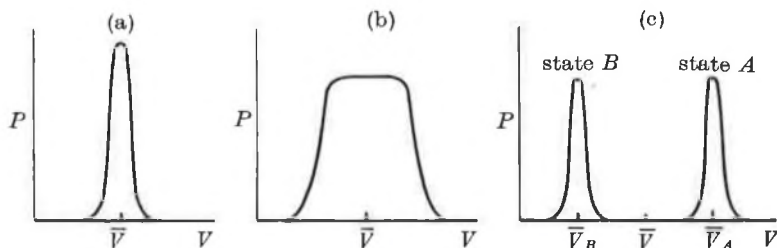


FIGURE 5-1. The function  $P(V)$ . (a) At an "ordinary point"; (b) at a critical point; (c) at the middle of a first-order phase transition. In all these curves  $N, p$  and  $T$  are constant.

either in state  $A$  or in state  $B$ , but not in an intermediate state. This is the origin of the term "two-state approximation."

The physical reason why intermediate states are unimportant is that, while states  $A$  and  $B$  are both pure phases, an intermediate state, say,  $V = \bar{V}$ , must have both phases  $A$  and  $B$  present, with an *interface* between them. The interface contributes an extra free energy to the system and introduces a corresponding unfavorable Boltzmann factor. Specifically, for a three-dimensional system, in the notation of Fig. 5-1c,

$$\frac{P(\bar{V}_A)}{P(\bar{V})} = O(e^{aN^{2/3}/kT}), \quad (5-115)$$

where  $a$  is a positive constant of order  $kT$ , proportional to the interfacial tension, and  $N^{2/3}$  is the approximate number of molecules at the interface. The magnitude of the ratio in Eq. (5-115) determines the degree of validity of the two-state approximation. The ratio is not large if  $N$  is very small or if the system is near a critical point (where  $a \rightarrow 0$ ). In a two-dimensional system,  $N^{2/3}$  is replaced by  $N^{1/2}$ . In a one-dimensional system, this quantity becomes  $N^{0/1}$ , or unity. A one-dimensional system with forces of finite range does not exhibit a first-order transition, as is well known. At a "transition" in a one-dimensional system, according to Eq. (5-115),  $P(V)$  will have more or less of a flat top as in Fig. 5-1b, and the two-state approximation is not applicable.

There are many approximate statistical mechanical theories of phase transitions which lead to a  $p$ - $V$  or  $\mu$ - $N$  "loop" from the canonical ensemble. These theories are characterized by the fact that the system, in the canonical ensemble, is always forced to have a uniform density throughout  $V$ : two phases are never present at the same time. In the  $N, p, T$  ensemble for such a theory, the function  $P(V)$  appears as in Fig. 5-1c. It is easy to show that

$$\frac{P(\bar{V}_A)}{P(\bar{V})} = O(e^N) \quad (5-116)$$

except near the critical point, where a flat top as in Fig. 5-1b is found (see also Fig. 6-7). Thus the two-state approximation may be employed with theories of this type except when  $N$  is very small or near a critical point.

**SOME DEDUCTIONS FROM THE APPROXIMATION.** We now accept the two-state approximation and deduce some of its thermodynamic consequences. The observed small system  $p$ - $\bar{V}$  curve is shown schematically as  $ADB$  in Fig. 5-2. The same curve is included in Fig. 5-3 along with the schematic  $N = \infty$  curve, which shows a sharp transition. In Fig. 5-2,  $ACF$  is the extrapolation of the state  $A$  curve, or  $ACF$  may possibly be available as a metastable experimental curve. This is the way the system would behave, based on the state  $A$  peak only in Fig. 5-1c: all systems in the ensemble stay in state  $A$ . The extrapolation is well defined for a theoretical model, but it may be somewhat ambiguous if only an experimental curve  $ADB$  is available. In this case, the theorems deduced below will aid in locating the correct extrapolation. The same comments apply, of course, to the extrapolation  $BEG$ .

Let  $F_A = N\hat{\mu}_A$  and  $F_B = N\hat{\mu}_B$  be the Gibbs free energies of states  $A$  (curve  $ACF$  in Fig. 5-2) and  $B$  ( $BEG$  in Fig. 5-2), respectively. Both  $F_A$  and  $F_B$  are functions of  $N$ ,  $p$ , and  $T$ , but we shall be concerned for the moment only with the  $p$  dependence ( $N$  and  $T$  held constant). Consider an ensemble of  $\mathcal{N}$  distinguishable  $N$ ,  $p$ ,  $T$  systems. Each system, in the present approximation, can be either

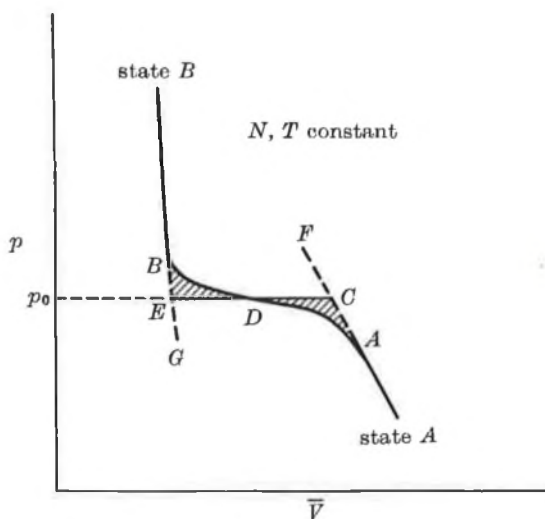


FIGURE 5-2. Schematic  $p$ - $\bar{V}$  isotherm for small system at a temperature such that the macroscopic system has a first-order phase transition.  $BDA$  is the experimental curve.



in state  $A$  or in state  $B$ . If  $\mathcal{N}_A$  systems are in state  $A$  and  $\mathcal{N}_B$  in state  $B$ , then the total Gibbs free energy of the ensemble is

$$F_t = \mathcal{N}_A F_A + \mathcal{N}_B F_B - kT \ln \frac{\mathcal{N}!}{\mathcal{N}_A! \mathcal{N}_B!} = \mathcal{N} F = \mathcal{N} N \hat{F}, \quad (5-117)$$

where the factorial expression is the number of different arrangements of the  $A$  and  $B$  systems.

The equilibrium value of  $\mathcal{N}_A$  may be found by minimizing  $F_t$  with respect to  $\mathcal{N}_A$ , holding  $p$ ,  $T$ ,  $N$ , and  $\mathcal{N}$  constant. We put  $\mathcal{N}_B = \mathcal{N} - \mathcal{N}_A$ , use the simple Stirling approximation (since  $\mathcal{N} \rightarrow \infty$ ), and find

$$\frac{\mathcal{N}_A}{\mathcal{N}_B} = \frac{e^{-F_A/kT}}{e^{-F_B/kT}} = \left( \frac{e^{-\hat{\mu}_A/kT}}{e^{-\hat{\mu}_B/kT}} \right)^N. \quad (5-118)$$

Here  $\hat{\mu}_A$  and  $\hat{\mu}_B$  are considered known functions of  $p$  ( $N$  and  $T$  constant). Thus, for any  $p$ , we can calculate  $\mathcal{N}_A/\mathcal{N}_B$ . If  $p$  is chosen so that  $\hat{\mu}_A = \hat{\mu}_B$  exactly, then  $\mathcal{N}_A = \mathcal{N}_B$ . We denote this value of  $p$  by  $p_0$ . If  $p$  is slightly different from  $p_0$  so that, say,  $\hat{\mu}_B > \hat{\mu}_A$  by a very small fraction of  $kT$ , then, according to Eq. (5-118),  $\mathcal{N}_A \gg \mathcal{N}_B$  when  $N$  is very large, and essentially all systems are in state  $A$ . The

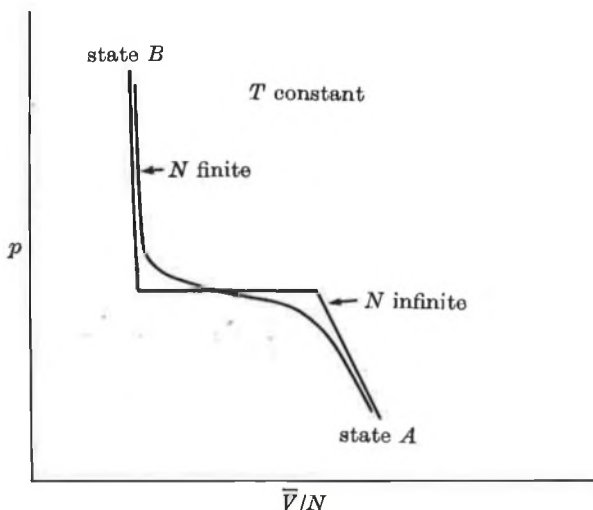


FIGURE 5-3. "Sharp" phase transition in an infinite system and the corresponding somewhat smoothed-out transition in a finite system.

form of Eq. (5-118) thus makes it clear how the large magnitude of  $N$  in a macroscopic system leads to the discontinuous behavior shown by the “ $N$  infinite” curve in Fig. 5-3. On the other hand, when  $N$  is small, say, 20, or 100, or 1000, the transition from  $\mathcal{N}_A = \mathcal{N}_B$  at  $p = p_0$  to  $\mathcal{N}_A \cong \mathcal{N}$  or  $\mathcal{N}_B \cong \mathcal{N}$  as  $p$  is decreased or increased, respectively, is more gradual. The smaller the value of  $N$ , the greater the range in  $p$  over which the transition is extended.

The equilibrium between state  $A$  and state  $B$ , for small  $N$ , is intermediate in nature between an isomeric chemical equilibrium ( $N = 1$ ) and a macroscopic phase equilibrium ( $N = \infty$ ). Fluctuations about the equilibrium value of  $\mathcal{N}_A$  are negligible, incidentally, because  $\mathcal{N} \rightarrow \infty$ .

The pressure  $p_0$  is a function of  $N$  and  $T$ . As  $N \rightarrow \infty$ ,  $p_0$  approaches the pressure at which the two macroscopic phases are in equilibrium at temperature  $T$ .

From Eq. (5-117) we can write

$$F(N, p, T) = P_A F_A + P_B F_B + kT(P_A \ln P_A + P_B \ln P_B), \quad (5-119)$$

where  $P_A = \mathcal{N}_A/\mathcal{N}$  is the probability of a system being in state  $A$  and  $P_B = 1 - P_A$ . In this equation,  $F_A$  and  $F_B$  are functions of  $N$ ,  $p$ , and  $T$ , as are also  $P_A$  and  $P_B$  through Eq. (5-118). We also have, on division by  $N$ ,

$$\hat{\mu}(N, p, T) = P_A \hat{\mu}_A + P_B \hat{\mu}_B + \frac{kT}{N}(P_A \ln P_A + P_B \ln P_B). \quad (5-120)$$

If we now differentiate Eq. (5-119) with respect to  $p$ , using

$$\left(\frac{\partial F_A}{\partial p}\right)_{N, T} = \bar{V}_A, \quad \left(\frac{\partial F_B}{\partial p}\right)_{N, T} = \bar{V}_B,$$

and

$$\begin{aligned} \left(\frac{\partial P_A}{\partial p}\right)_{N, T} &= \frac{1}{kT}(\bar{V}_B - \bar{V}_A)P_A P_B \\ \left(\frac{\partial P_B}{\partial p}\right)_{N, T} &= \frac{1}{kT}(\bar{V}_A - \bar{V}_B)P_A P_B, \end{aligned} \quad (5-121)$$

which follow from Eq. (5-118), we find

$$\left(\frac{\partial F}{\partial p}\right)_{N,T} = \bar{V} = P_A \bar{V}_A + P_B \bar{V}_B \quad (5-122)$$

as expected. Similarly,

$$\left(\frac{\partial F}{\partial N}\right)_{p,T} = \mu = P_A \mu_A + P_B \mu_B. \quad (5-123)$$

Thus the experimental curve  $\bar{V}(p)$  in Fig. 5-2 ( $ADB$ ) is a simple linear combination of the extrapolated or metastable curves  $\bar{V}_A(p)$  ( $ACF$ ) and  $\bar{V}_B(p)$  ( $BEG$ ), with weights  $P_A(p)$  and  $P_B(p)$  from Eq. (5-118): the ensemble is a mixture of systems in state  $A$  and state  $B$ .

In particular, at  $p = p_0$ ,  $\bar{V}$  is midway between  $\bar{V}_A$  and  $\bar{V}_B$ :

$$\bar{V}(p_0) = \frac{1}{2} \bar{V}_A(p_0) + \frac{1}{2} \bar{V}_B(p_0). \quad (5-124)$$

Thus we have the following *theorem*: if the experimental curve  $\bar{V}(p)$  and the extrapolated curves  $\bar{V}_A(p)$  and  $\bar{V}_B(p)$  are available, then adjustment of a line segment parallel to the  $\bar{V}$  axis, which connects the two extrapolated curves, until the line segment is bisected by the  $\bar{V}(p)$  curve will locate that value of  $p$ ,  $p_0$ , at which  $\hat{\mu}_A = \hat{\mu}_B$ . For example, in Fig. 5-2,  $D$  bisects the line  $EC$ , and  $\hat{\mu}_A$  at  $C$  is equal to  $\hat{\mu}_B$  at  $E$ .

It should be noted: that the theorem is based on the two-state approximation; that the equality of  $\hat{\mu}_A$  and  $\hat{\mu}_B$  resembles the macroscopic phase equilibrium condition, but here  $C$  and  $E$  are not points on the experimental curve  $ADB$ ; that this theorem is an "equal-distance" (that is,  $ED = DC$ ) theorem in contrast to the well-known Maxwell "equal-area" theorem; and that metastable but not unstable parts of curves are involved.

Earlier in this chapter we found that  $\mu$  is fundamental in determining chemical equilibria in small systems, while here we see that phase equilibria depend on  $\hat{\mu}$ . The reason is obvious: in the former case individual molecules change their state, while in the latter whole systems change their state (in the two-state approximation).

Figure 5-4 shows a schematic plot of  $\hat{\mu}$  against  $p$ , as calculated from Eq. (5-120). The labeling is the same as in Fig. 5-2. Thus  $AF$  is the

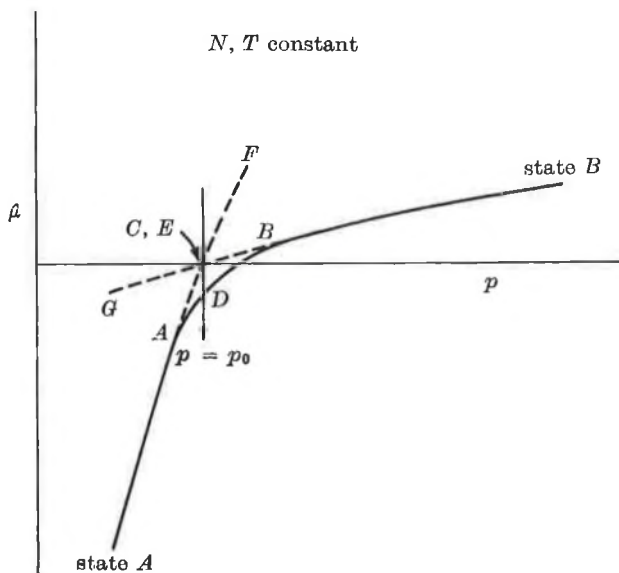


FIGURE 5-4. Schematic plot of  $\hat{\mu}$  against  $p$ . The labeling is the same as in Fig. 5-2.

function  $\hat{\mu}_A(p)$ , while  $BG$  is  $\hat{\mu}_B(p)$ . The observed curve  $ADB$  in Fig. 5-4 approaches  $ACEB$  more closely as  $N \rightarrow \infty$  (of course the curves  $AC$  and  $EB$  would themselves change somewhat as  $N \rightarrow \infty$ , as implied by Fig. 5-3). This can be put quantitatively: according to Eq. (5-120), the distance  $CD$  in Fig. 5-4 is  $(kT/N) \ln 2$ .

In addition to the equal-distance theorem, there is also an equal-area theorem, which we now state and prove. The *theorem* is the following: the line segment defined in the equal-distance theorem (i.e., placed so that it is bisected by the experimental curve) will produce two equal areas between the extrapolated and experimental curves (i.e., area  $ACD$  = area  $BED$  in Fig. 5-2). The proof is very simple. Let  $p_A$  be any pressure at or below point  $A$  in Fig. 5-2. At such a pressure extrapolated ( $ACF$ ) and experimental ( $ADB$ ) curves have merged. Similarly, let  $p_B$  be any pressure at or above point  $B$  in Fig. 5-2. Then we have to show that

$$\int_{p_A}^{p_0} (\bar{V}_A - \bar{V}) dp = \int_{p_0}^{p_B} (\bar{V} - \bar{V}_B) dp, \quad (5-125)$$

or

$$\int_{p_A}^{p_0} \bar{V}_A dp + \int_{p_0}^{p_B} \bar{V}_B dp = \int_{p_A}^{p_B} \bar{V} dp,$$

or

$$F_A(p_0) - F_A(p_A) + F_B(p_B) - F_B(p_0) = F(p_B) - F(p_A).$$

But by the equal-distance theorem,  $F_A(p_0) = F_B(p_0)$ . Also,  $F_A(p_A) = F(p_A)$  since  $P_A = 1$  at  $p = p_A$  in Eq. (5-119). Similarly,  $F_B(p_B) = F(p_B)$ . Hence the theorem is proved. The converse follows by reversing the argument: if the areas are made equal, then the pressure thus defined is that at which  $\hat{\mu}_A = \hat{\mu}_B$ .

We now have two independent ways of finding the pressure  $p = p_0$  at which  $\hat{\mu}_A = \hat{\mu}_B$ : we can adjust the line  $EC$  so that it is bisected by the experimental curve; or we can adjust it so that two equal areas  $ACD$  and  $BED$  are formed. If the extrapolations are uncertain, the redundancy in these two methods can be used as a check to correct the extrapolations.

Still another check is available. If we differentiate Eq. (5-122) with respect to  $p$ , using Eq. (5-121), we obtain

$$\left(\frac{\partial \bar{V}}{\partial p}\right)_{N,T} = P_A \left(\frac{\partial \bar{V}_A}{\partial p}\right)_{N,T} + P_B \left(\frac{\partial \bar{V}_B}{\partial p}\right)_{N,T} - \frac{P_A P_B}{kT} (\bar{V}_A - \bar{V}_B)^2. \quad (5-126)$$

All quantities appearing in this equation are known if  $\bar{V}(p)$ ,  $\bar{V}_A(p)$ , and  $\bar{V}_B(p)$  are given, since  $P_A = (\bar{V} - \bar{V}_B)/(\bar{V}_A - \bar{V}_B)$  and  $P_B = 1 - P_A$ . Equation (5-126) also follows from the fluctuation relation

$$\overline{\bar{V}^2} - \bar{V}^2 = P_A(\overline{\bar{V}_A^2} - \bar{V}_A^2) + P_B(\overline{\bar{V}_B^2} - \bar{V}_B^2) + P_A P_B (\bar{V}_A - \bar{V}_B)^2, \quad (5-127)$$

which is a consequence of the two-state approximation. At  $p = p_0$ ,

$$\frac{\partial \bar{V}}{\partial p} = \frac{1}{2} \frac{\partial \bar{V}_A}{\partial p} + \frac{1}{2} \frac{\partial \bar{V}_B}{\partial p} - \frac{N(\bar{V}_A - \bar{V}_B)^2}{4kT}, \quad (5-128)$$

where  $\bar{v} = \bar{V}/N$ , etc. The last term on the right is larger than the other two terms, which will often be negligible, by a factor of order  $N$ . This equation could be used to verify the correctness of the

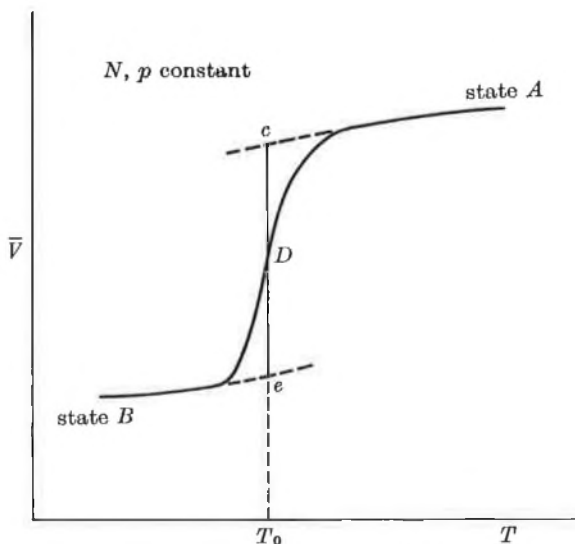


FIGURE 5-5. Equal-distance theorem in a  $\bar{V}$ - $T$  plot ( $cD = De$ ).

extrapolations, or it might even serve as a method for estimating  $N$  [that is, solve Eq. (5-128) for  $N$ ], in cases where  $N$  is unknown.

According to Eq. (5-128), and as illustrated in Fig. 5-2, a finite system has a finite slope in a  $p$ - $\bar{V}$  diagram at a first-order transition. But, with  $N$  held constant and finite, Eq. (5-128) predicts that this slope will approach zero as  $T \rightarrow 0$ .

Ordinarily one will be dealing with a system, at finite  $N$ , which is known to have a first-order phase transition at infinite  $N$ . But there may be cases where the infinite system has not been studied and an observed fairly sharp transition at finite  $N$  may or may not represent a first-order transition. In this event, on the assumption that one has some confidence in the extrapolations, the self-consistency of (a) the equal-distance theorem, (b) the equal-area theorem, and (c) Eq. (5-128) may be used as a test (necessary condition) for a first-order transition. For example,  $p_0$  might be located by method (a) and then (b) and (c) checked at this  $p_0$ .

If we hold  $N$  and  $p$  constant and regard all the quantities appearing in Eq. (5-122) as functions of  $T$ , then clearly

$$\bar{V}(T_0) = \frac{1}{2}\bar{V}_A(T_0) + \frac{1}{2}\bar{V}_B(T_0), \quad (5-129)$$

where  $T_0$  is that value of  $T$  at which  $\hat{\mu}_A = \hat{\mu}_B$ . Thus the equal-distance theorem is also applicable to a  $\bar{V}$  versus  $T$  diagram, as in Fig. 5-5. There is, however, no equal-area theorem on such a diagram.

It is easy to show that a linear relation, as in Eq. (5-122) for  $\bar{V}$ , also exists for  $H$  and  $\bar{E}$ . For the entropy,

$$\begin{aligned} S &= P_A S_A + P_B S_B - k(P_A \ln P_A + P_B \ln P_B) \\ &= \frac{1}{2} S_A + \frac{1}{2} S_B + k \ln 2 \quad \text{when } \hat{\mu}_A = \hat{\mu}_B. \end{aligned}$$

According to this last relation, we do not have an exact equal distance theorem on an  $S$  versus  $T$  diagram ( $p$  and  $N$  constant), but the final term is negligible for  $N$  not too small ( $S$  is of order  $Nk$ ). There is, however, an exact equal area theorem on such a diagram.

**SYSTEMS IN SOLVENT OR GAS.** In Eq. (5-117) we made explicit use of the distinguishability of the systems of the ensemble. Is the argument in the above subsection still valid when the systems are moving freely in solvent or gas, as in Sections 2-3 and 3-3? The answer is "yes," as one would expect intuitively. We show this for the solvent case only, since the argument for a gas is very similar.

The small systems represent a dilute single component in the solvent. But in the two-state approximation we may also take the alternative but equivalent point of view that there are two small system components  $A$  and  $B$  in equilibrium with each other. Equation (2-102) becomes, in this case,

$$\begin{aligned} dE_T &= T dS_T - p dV_T + \mu_1 dN_1 + \mu_A^\square d\mathcal{N}_A + \mu_B^\square d\mathcal{N}_B \\ &\quad + (\mu_A \mathcal{N}_A + \mu_B \mathcal{N}_B) dN, \end{aligned} \quad (5-130)$$

and hence

$$dF_T = (\mu_A^\square - \mu_B^\square) d\mathcal{N}_A \leq 0 \quad (T, p, N_1, \mathcal{N}, N \text{ constant}). \quad (5-131)$$

The equilibrium condition is  $\mu_A^\square = \mu_B^\square$ . Just as in Eq. (2-108), we have

$$\mu_A^\square = N\hat{\mu}_A(N, p, T) + kT \ln \frac{\mathcal{N}_A}{N_1} \quad (5-132)$$

and a similar expression for  $\mu_B^\square$ . The equilibrium condition therefore again leads to Eq. (5-118).

Let us equate the equivalent quantities  $\mathcal{N}\mu^\square$  (one-component point of view) and  $\mathcal{N}_A\mu_A^\square + \mathcal{N}_B\mu_B^\square$  (two-component equilibrium point of view):

$$\mathcal{N}\left(N\hat{\mu} + kT \ln \frac{\mathcal{N}}{N_1}\right) = \mathcal{N}_A\left(N\hat{\mu}_A + kT \ln \frac{\mathcal{N}_A}{N_1}\right) + \mathcal{N}_B\left(N\hat{\mu}_B + kT \ln \frac{\mathcal{N}_B}{N_1}\right). \quad (5-133)$$

After cancellation of the terms in  $N_1$ , this becomes identical with Eq. (5-119) or (5-120). Similarly,

$$\mu\mathcal{N} = \mu_A\mathcal{N}_A + \mu_B\mathcal{N}_B, \quad (5-134)$$

as in Eq. (5-123).

The fact that the basic equations (5-118) to (5-120) are again obtained taken together with the results already found in Section 2-3, assures us that the argument of the preceding subsection (and the following one) is unaltered when the small systems are in a solvent. A similar statement can be made about a dilute gas of small systems.

**EQUATIONS OF THE CLAUSIUS-CLAPEYRON TYPE.** Using the theorems discussed above, we can locate points (*C* and *E* in Fig. 5-2) on the two extrapolated or metastable curves at which  $\hat{\mu}_A = \hat{\mu}_B$ . The two states represented by points *C* and *E* have the same values of  $N$ ,  $p$ ,  $T$ , and  $\hat{\mu}$ . If conditions are varied, the equality of these four variables at *C* and *E* must be maintained. Thus variations in  $N$ ,  $p$ , and  $T$  must satisfy  $d\hat{\mu}_A = d\hat{\mu}_B$ ; hence only two of  $N$ ,  $p$ , and  $T$  are independent.

It should be emphasized that we are discussing here the "equilibrium" between points on two metastable curves for a small system. Or, on the equilibrium curve, we are considering the point  $\mathcal{N}_A = \mathcal{N}_B$  only. Because the system is small, there is an additional independent variable  $N$  which does not appear in the corresponding macroscopic problem.

From  $d\hat{\mu}_A = d\hat{\mu}_B$  and Eq. (2-13) we have<sup>1</sup>

$$\begin{aligned} -s_A dT + v_A dp + \left(\frac{\mu_A - \hat{\mu}_A}{N}\right) dN \\ = -s_B dT + v_B dp + \left(\frac{\mu_B - \hat{\mu}_B}{N}\right) dN, \end{aligned} \quad (5-135)$$

<sup>1</sup> The pressure  $p$  in Eqs. (5-135) to (5-140) is denoted by  $p_0$  above and in Figure 5-2.



where  $s_A = S_A/N$ , etc. Then

$$\left(\frac{\partial p}{\partial T}\right)_N = \frac{\Delta s}{\Delta v} = \frac{\Delta H}{T \Delta v} \quad (5-136)$$

$$\left(\frac{\partial T}{\partial N}\right)_p = \frac{\Delta \mu}{N \Delta s} = \frac{\Delta \mu}{\Delta S} = -\frac{T \Delta \mathcal{E}}{N \Delta H} \quad (5-137)$$

$$\left(\frac{\partial p}{\partial N}\right)_T = -\frac{\Delta \mu}{N \Delta v} = -\frac{\Delta \mu}{\Delta \bar{v}} = \frac{\Delta \mathcal{E}}{N \Delta \bar{v}}, \quad (5-138)$$

where  $\Delta$  means the value at point  $C$  (state  $A$ ) minus the value at point  $E$  (state  $B$ ) and where we have used

$$N\hat{\mu} = H - TS, \quad \Delta\hat{\mu} = 0, \quad \Delta H = T \Delta S \quad (5-139)$$

$$\mathcal{E} = N(\hat{\mu} - \mu), \quad \Delta \mathcal{E} = -N \Delta \mu. \quad (5-140)$$

Equation (5-136) resembles the familiar Clausius-Clapeyron equation, but Eqs. (5-137) and (5-138) are new for small systems. The left-hand sides of Eqs. (5-136) to (5-138) are measurable, as is also  $\Delta v$ . Hence  $\Delta s$  and  $\Delta \mu$  may be calculated.

Since the process  $B \rightarrow A$  referred to above occurs in a closed system at constant  $p$  and  $T$ , the reversible heat  $Q = \Delta H = T \Delta S$ . But this would not ordinarily be an operational heat, because two metastable states are involved and the solvent is not included.

If the transition occurs to an infinitesimal extent *along* the *stable* equilibrium path (by varying  $p$  or  $T$ ), and if we include the solvent, as we must, experimentally, when a solvent is present, then

$$DQ_T = T dS_T \quad (N_1, \mathcal{N}, N \text{ constant}),$$

where the subscript  $T$  refers to the macroscopic solution in the preceding subsection. Then it is easy to show that

$$\begin{aligned} \left(\frac{DQ_T}{\partial p}\right)_{T, N_1, \mathcal{N}, N} &= \Delta H \left(\frac{\partial \mathcal{N}_A}{\partial p}\right)_{T, N_1, \mathcal{N}, N} \\ &\quad + T \left(\frac{\partial S_T}{\partial p}\right)_{T, N_1, \mathcal{N}_A, \mathcal{N}_B, N}, \end{aligned}$$

where  $\partial \mathcal{N}_A / \partial p$  is given by Eq. (5-121a) and this is the equilibrium-path  $\Delta H$ . The first term represents heat absorbed by small systems

undergoing the transition. The second term gives the heat absorbed at constant solution composition. One can measure the sum but not the separate terms. Similarly, when the temperature is varied,

$$\left(\frac{DQ_T}{\partial T}\right)_{p, N_1, \mathcal{N}, N} = \Delta H \left(\frac{\partial \mathcal{N}_A}{\partial T}\right)_{p, N_1, \mathcal{N}, N} + T \left(\frac{\partial S_T}{\partial T}\right)_{p, N_1, \mathcal{N}_A, \mathcal{N}_B, N}$$

where

$$\frac{\partial \mathcal{N}_A}{\partial T} = \frac{\mathcal{N} P_A P_B \Delta H}{kT^2}.$$

Both contributions to  $DQ_T/\partial T$  are positive.  $\Delta H = T\Delta S$  only when  $\mathcal{N}_A = \mathcal{N}_B$ .

Only two of Eqs. (5-136) to (5-138) are independent, in view of

$$\left(\frac{\partial p}{\partial T}\right)_N = -\frac{(\partial p/\partial N)_T}{(\partial T/\partial N)_p}. \quad (5-141)$$

Another interrelation of possible interest is

$$\frac{\partial^2 p}{\partial T \partial N} = \left(\frac{\partial \Delta s/\Delta v}{\partial N}\right)_T = -\frac{1}{N} \left(\frac{\partial \Delta \mu/\Delta v}{\partial T}\right)_N. \quad (5-142)$$

If we take the direction of the transition such that  $\Delta s > 0$  (that is, state  $A$  is the high-temperature phase, as in Fig. 5-5), then  $(\partial p/\partial T)_N$  has the same sign as  $\Delta v$  and  $(\partial T/\partial N)_p$  has the same sign as  $\Delta \mu$ .

There are nine other relations similar to Eqs. (5-136) to (5-138) which follow from  $dp_A(\hat{\mu}, T, N) = dp_B(\hat{\mu}, T, N)$ ,  $dT_A = dT_B$ , and  $dN_A = dN_B$ , but they are not very important. An example, from  $dp_A = dp_B$ , is

$$\left(\frac{\partial \hat{\mu}}{\partial T}\right)_N = -\frac{\Delta(s/v)}{\Delta(1/v)}. \quad (5-143)$$

*Simple Example.* Here we consider the simplest conceivable illustration of the two-state approximation. Suppose  $A$  and  $B$  are two condensed phases with  $v_A$  and  $v_B$ ,  $v_A > v_B$ , independent of  $p$  and  $N$ .

Therefore, in Fig. 5-2, the curves  $ACF$  and  $BEG$  are both vertical lines. Also, in Fig. 5-4,  $ACF$  and  $BEG$  are straight lines with slopes  $v_A$  and  $v_B$ , respectively. Let  $\hat{\mu}$  be the common value of  $\hat{\mu}_A$  and  $\hat{\mu}_B$  when  $p = p_0$  ( $p_0$  is also assumed independent of  $N$ ). Then integration of  $\partial\hat{\mu}_A/\partial p = v_A$  gives

$$\hat{\mu}_A = \hat{\mu} + v_A(p - p_0).$$

Similarly,

$$\hat{\mu}_B = \hat{\mu} + v_B(p - p_0).$$

Equation (5-118) becomes

$$\frac{P_A}{1 - P_A} = \exp \left[ -\frac{N(v_A - v_B)(p - p_0)}{kT} \right]. \quad (5-144)$$

Because  $v_A$  and  $v_B$  are assumed independent of  $N$ , the only  $N$  dependence on the right-hand side is that explicitly indicated. Since  $P_A = (v - v_B)/(v_A - v_B)$ , a plot (Fig. 5-6) of

$$\frac{(v_A - v_B)(p - p_0)}{kT} \quad \text{versus} \quad \frac{v - v_B}{v_A - v_B} \quad (5-145)$$

can easily be calculated from Eq. (5-144). This is essentially a  $p$  versus  $v$  diagram for this simple model, corresponding to Fig. 5-2. Several values of  $N$  are included in the figure, which demonstrates quantitatively how the transition becomes sharper as  $N$  increases.

Comparison shows that Eqs. (2-98) ("all-or-none" helix-coil model) and (5-144) are formally identical. This is not surprising in view of the models. The correspondences in the two equations are:

$$P_A \leftrightarrow \frac{\bar{n}}{N}, \quad \exp \left[ -\frac{(v_A - v_B)(p - p_0)}{kT} \right] \leftrightarrow r.$$

Thus Fig. 5-6 is also a plot of  $-\ln r$  against  $\bar{n}/N$ . Hence, Figs. 2-4 and 5-6 are identical except for a rotation of one figure by  $90^\circ$ .

Further details on this model are given in Section 6-2.

*Example. Crystallite Melting.* We investigate next the effect of the size of a crystallite on the temperature and pressure at which it melts. The pressure could be exerted by an inert fluid reservoir in

which the small systems are insoluble. We use a simplified version of the model in Eqs. (2-68) to (2-71), for both solid and liquid, in that the only small term we retain is the surface term [see also Eqs. (3-61)ff.]. We shall seek only first-order departures from macroscopic behavior.

Suppose  $p_\infty$  and  $T_\infty$  are values of  $p$  and  $T$  at which the two macroscopic phases are in equilibrium. We consider first the effect of a finite  $N$  on the equilibrium  $T$ , holding  $p$  constant at  $p_\infty$ . We use Eq. (5-137) for this purpose. From Eq. (2-71) we have

$$\Delta\mu = \Delta f(p_\infty, T) + \frac{2}{3}N^{-1/3} \Delta a(p_\infty, T), \quad (5-146)$$

where  $\Delta\mu = \mu_L - \mu_S$  ( $L$  = liquid,  $S$  = solid), etc. The temperature here is the equilibrium  $T$ : this is the value of  $T$  at which the two

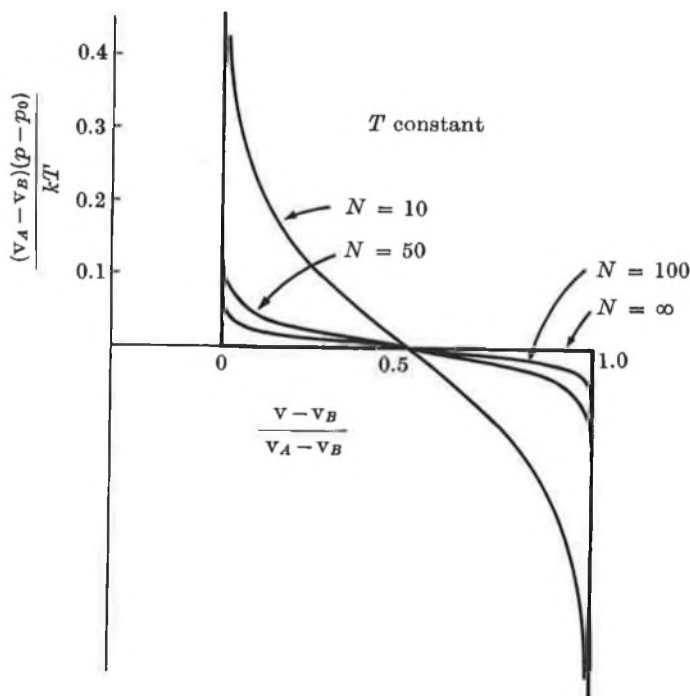


FIGURE 5-6. Plot of (essentially)  $p$  versus  $v$  in a simple model of a first-order phase transition.

metastable states are in equilibrium ( $\hat{\mu}_L = \hat{\mu}_S$ ) at the given  $N$  and  $p_\infty$ ; it is also the value of  $T$  at which half of the crystallites have melted at  $N$  and  $p_\infty$ . We also have, from Eq. (2-68),

$$\Delta\hat{\mu} = 0 = \Delta f(p_\infty, T) + N^{-1/3} \Delta a(p_\infty, T). \quad (5-147)$$

It should be noted that  $\Delta f(p_\infty, T_\infty) = 0$  but  $\Delta f(p_\infty, T) \neq 0$ . On elimination of  $\Delta f$  between Eqs. (5-146) and (5-147), we obtain

$$\Delta\mu = -\frac{1}{3}N^{-1/3} \Delta a(p_\infty, T). \quad (5-148)$$

Equation (2-69) gives

$$\Delta s = -\frac{\partial \Delta f(p_\infty, T)}{\partial T} - N^{-1/3} \frac{\partial \Delta a(p_\infty, T)}{\partial T}. \quad (5-149)$$

We may now substitute Eqs. (5-148) and (5-149) into Eq. (5-137). But we are interested in first-order effects only. Hence we expand  $\Delta a$  and  $\partial \Delta f / \partial T$  about  $T_\infty$  and keep just the first terms, and we omit the  $N^{-1/3}$  term in  $\Delta s$ . With these simplifications,

$$\left(\frac{\partial T}{\partial N}\right)_{p_\infty} = -\frac{N^{-4/3} \Delta a(p_\infty, T_\infty)}{3 \Delta s_\infty}, \quad (5-150)$$

where  $\Delta s_\infty = -(\partial \Delta f / \partial T)_\infty$  is the macroscopic entropy of fusion. Integration of this equation gives the desired result,

$$T = T_\infty + \frac{N^{-1/3} \Delta a(p_\infty, T_\infty)}{\Delta s_\infty}. \quad (5-151)$$

An alternative simpler derivation of Eq. (5-151) is the following. In Eq. (5-147), expand  $\Delta f$  about  $T_\infty$ :

$$\begin{aligned} \Delta f(p_\infty, T) &= \left(\frac{\partial \Delta f}{\partial T}\right)_{T_\infty} (T - T_\infty) + \dots \\ &= -\Delta s_\infty (T - T_\infty) + \dots \end{aligned}$$

We also expand  $\Delta a$  about  $T_\infty$  and keep the leading term only. Equation (5-147) then becomes identical with Eq. (5-151).

Completely analogous arguments lead to

$$p = p_\infty - \frac{N^{-1/3} \Delta a(p_\infty, T_\infty)}{\Delta v_\infty} \quad (5-152)$$

for the first-order effect of  $N$  on the equilibrium pressure at constant  $T = T_\infty$ .

Now  $a$  is proportional to the surface tension<sup>1</sup>  $\gamma$ . In fact, we may set the surface free energy  $aN^{2/3}$  in Eq. (2-68) equal to  $\gamma\mathcal{A}$ , where  $\mathcal{A}$  is the surface area. If we assume a spherical shape for the crystallite,

$$aN^{2/3} = \gamma\mathcal{A} = \gamma(6\pi^{1/2}Nv)^{2/3}$$

or

$$\begin{aligned} a &= \gamma(6\pi^{1/2}v)^{2/3} \\ \Delta a &= 6^{2/3}\pi^{1/3}\Delta(\gamma v^{2/3}). \end{aligned} \tag{5-153}$$

Suppose, as an example,  $\gamma_S$  is sufficiently larger than  $\gamma_L$  to make  $\Delta a$  negative. Since  $\Delta s_\infty$  is positive, Eq. (5-151) then predicts that the crystallite has a lower melting point than the bulk solid. If  $\Delta a > 0$ , the crystallite melting point will be higher than that of the bulk solid. As for the rough order of magnitude of the effect,  $\Delta a$  is of order  $kT$ ,  $\Delta s_\infty$  is of order  $k$ , and hence the correction term in Eq. (5-151) is of order  $TN^{-1/3}$ . It could easily be larger than this by a factor of 100 or more.

If  $\Delta a$  is negative and  $\Delta v_\infty$  positive, Eq. (5-152) predicts that the pressure on a crystallite must be increased in order to maintain its melting point at the bulk value  $T_\infty$ . The order of magnitude of the correction term is  $pN^{-1/3}$ .

<sup>1</sup> Strictly, interfacial tension between small system and inert fluid.

# ENVIRONMENTAL VARIABLES $\mu$ , $V$ , $T$

We shall be concerned in this chapter with a one-component open system in a heat bath. Thus, two of the environmental variables are  $\mu$  and  $T$ . As the third variable we choose the volume (or area, length, etc.): each small system has the same volume  $V$  which, however, can be varied. There are fluctuations in  $N$  and  $E$ , but not  $V$ .

This case is not an important one experimentally because in general it is not possible to hold the volume (area, length) of a small system constant. Instead, the pressure will usually be the experimentally controllable variable, via a solvent, with the volume fluctuating. This corresponds to a  $\mu$ ,  $p$ ,  $T$  system, which we treat in Chapter 10. A special case, also considered in Chapter 10, is a  $\mu$ ,  $T$  system for which neither  $p$  nor  $V$  is an environmental variable (compare Chapter 3).

There are some experimental systems which may, as an approximation, be considered  $\mu$ ,  $V$ ,  $T$  systems. Examples are the binding, adsorption, or absorption of molecules within or on the surface of a colloidal particle, or on a polymer molecule. The approximation is to regard the colloidal particle or polymer molecule as an inert material which merely provides the force field for binding, and is not otherwise included in the thermodynamics. The bound molecules form the one-component system of interest. However, the proper and rigorous way to treat such a system is as a *two*-component system with environmental variables  $N_1$ ,  $\mu_2$ ,  $p$ ,  $T$  or  $N_1$ ,  $\mu_2$ ,  $T$  (Chapter 7).

Although  $\mu$ ,  $V$ ,  $T$  systems hold little interest for experimentalists, they are of considerable importance in theoretical work. The appropriate partition function is the grand partition function (see Section 1-2), which is extensively used in statistical mechanics.

We do not treat solvent effects or a dilute gas of  $\mu$ ,  $V$ ,  $T$  systems because these cases do not arise experimentally.

## 6-1. TRANSCRIPTION OF CHAPTER 2 AND SECTION 5-4 TO $\mu$ , $V$ , $T$ CASE

Sections 1-1 and 1-2, and part of Section 1-4, have already been devoted to  $\mu$ ,  $V$ ,  $T$  systems. The reader may wish to review this

material. However, Chapter 2 and Section 5-4, both of which are concerned with  $N, p, T$  systems, will be of most use here because a formal equivalence between pairs of variables can be established in the  $\mu, V, T$  and  $N, p, T$  cases. This equivalence permits a simple transcription or translation of almost all the equations of Chapter 2 and Section 5-4 into equations appropriate to  $\mu, V, T$  systems. The essential point is that the sets  $\mu, V, T$  and  $N, p, T$  both have one extensive and two intensive variables.

Let us rewrite Eqs. (1-7), (1-8), (2-1), and (2-2) as follows:

$$N, p, T: \quad d\bar{E} = T dS - p d\bar{V} + \mu dN \quad (6-1)$$

$$\mu, V, T: \quad d\bar{E} = T dS + \mu d\bar{N} - p dV \quad (6-2)$$

$$N, p, T: \quad \bar{E} = TS - p\bar{V} + \mu N \quad (6-3)$$

$$\mu, V, T: \quad \bar{E} = TS + \mu\bar{N} - pV. \quad (6-4)$$

It is obvious that any relations deduced in Chapter 2 from Eqs. (6-1) and (6-3) for  $N, p, T$  systems will also follow from Eqs. (6-2) and (6-4) for  $\mu, V, T$  systems, if we establish the following correspondences:

$$\begin{aligned} \bar{E} &\rightarrow \bar{E}, & T &\rightarrow T, & S &\rightarrow S \\ N &\rightarrow V, & \bar{V} &\rightarrow \bar{N} \\ \mu &\rightarrow -p, & \hat{\mu} &\rightarrow -\hat{p}, & p &\rightarrow -\mu, \end{aligned} \quad (6-5)$$

where, in each pair, the  $N, p, T$  variable is on the left and the  $\mu, V, T$  variable is on the right. With the above recipe or code one can immediately transcribe the equations of Chapter 2 into  $\mu, V, T$  notation. Hence there is no need to present an independent, lengthy treatment of the  $\mu, V, T$  case. Instead, the interested reader should go through Chapter 2 and Section 5-4 systematically and make a mental or written transcription of the  $N, p, T$  equations. We shall confine ourselves in the remainder of this section to brief notes and examples which will be of assistance in this task.

If we introduce the notation, for a  $\mu, V, T$  system,

$$J \equiv -\hat{p}V \quad \text{and} \quad L \equiv \bar{E} - \mu\bar{N} = TS - \hat{p}V,$$

then we have the further correspondences,

$$\begin{aligned} F &= N\hat{\mu} \rightarrow -\hat{p}V = J \\ H &= \bar{E} + p\bar{V} \rightarrow L. \end{aligned} \quad (6-6)$$



Also,

$$\begin{aligned} A &= \bar{E} - TS \rightarrow A = \bar{E} - TS \\ \mathcal{E} &= N(\hat{\mu} - \mu) \rightarrow V(p - \hat{p}) = \mathcal{E}. \end{aligned} \quad (6-7)$$

Equations (2-3), (2-4), (2-13), and (2-17) become, for example,

$$d(\hat{p}V) = -dJ = S dT + p dV + \bar{N} d\mu \quad (6-8)$$

$$d[(p - \hat{p})V] = d\mathcal{E} = -S dT + V dp - \bar{N} d\mu \quad (6-9)$$

$$d\hat{p} = \frac{S}{V} dT + \frac{\bar{N}}{V} d\mu + \frac{\mathcal{E}}{V^2} dV \quad (6-10)$$

$$dp = \left(\frac{\partial S}{\partial V}\right)_{T, \mu} dT + \left(\frac{\partial \bar{N}}{\partial V}\right)_{T, \mu} d\mu + \frac{1}{V} \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, \mu} dV. \quad (6-11)$$

Equations (2-21) and (2-22) transcribe into themselves (except for the bar on  $N$  instead of  $V$ ), as we should expect from Section 1-4.

To avoid confusion we have to introduce new notation in the equivalent of Eq. (2-23):

$$d\mathcal{E} = -\{S\} dT - \{\bar{N}\} d\mu + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, \mu} dV \quad (6-12)$$

where

$$\{G\} \equiv G - V \left(\frac{\partial G}{\partial V}\right)_{T, \mu} \quad (6-13)$$

$$[G] \rightarrow \{\text{trans } G\} \quad (6-14)$$

and  $\text{trans } G$  means the transcription of  $G$ . For example,

$$\mathcal{E} = [F] \rightarrow \{J\} = \mathcal{E}. \quad (6-15)$$

We can define the "heat capacity"  $C_\mu$  formally by

$$dL = C_\mu dT = T dS \quad (\mu, V \text{ constant}). \quad (6-16)$$

The transcription of Eqs. (2-31) to (2-34) follows, using  $C_p \rightarrow C_\mu$ . But we *cannot* include  $DQ$  in Eq. (6-16), and hence  $C_\mu$  is not an operational heat capacity, because  $DQ = T dS$  only if  $\bar{N}$  is held constant.<sup>1</sup>

<sup>1</sup> The macroscopic relation  $DQ = T dS$  holds for a closed system. If we consider a closed ensemble of  $\mathcal{N}$  open systems,  $DQ_t = T dS_t$  ( $N_t$  constant) and hence  $DQ = T dS$  ( $\bar{N}$  constant) for a small, open system.

Beginning with Eq. (2-36) we need the correspondence

$$G = \frac{G}{N} \rightarrow \frac{\text{trans } G}{V} . \quad (6-17)$$

For example, Eq. (2-38) becomes

$$\left( \frac{\partial \bar{N}/V}{\partial V} \right)_{T, \mu} = \frac{1}{V^2} \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{T, V} . \quad (6-18)$$

Equations (2-45) transcribe into themselves, except for the bar on  $N$  instead of  $V$ . The phase-transition equations (2-53) will be discussed below in connection with Section 5-4.

The "excess equations" (2-54) to (2-63) transform without complication, using the following. (1) The definition of  $G^{(x)}$  is now<sup>1</sup>

$$G(\mu, V, T) = G^{(0)}(\mu, V, T) + G^{(x)}(\mu, V, T), \quad (6-19)$$

where  $G^{(0)}/V$  is a property of the macroscopic system at  $\mu$  and  $T$  and is a function of  $\mu$  and  $T$  only. (2) We have the additional correspondences:

$$\begin{aligned} G^{(x)} &\rightarrow (\text{trans } G)^{(x)} \\ \mu^{(x)} &\rightarrow -p^{(x)} \\ \hat{\mu}^{(x)} &\rightarrow -\hat{p}^{(x)}. \end{aligned} \quad (6-20)$$

In general  $G^{(x)}$  might include terms proportional to  $V^{2/3}$ ,  $\ln V$ , etc., so that a power-series expansion of  $G^{(x)}$  is not to be expected. But in the special case of an idealized system with a continuously variable  $V$  and without "edges" (e.g., the surface of a sphere or a system with periodic boundary conditions), an expansion in powers of  $V^{-1}$  might exist. If this is the case, we can write

$$G = Vg^{(0)}(\mu, T) + g^{(1)}(\mu, T) + V^{-1}g^{(2)}(\mu, T) + \cdots \quad (6-21)$$

$$p = p^{(0)}(\mu, T) + V^{-1}p^{(1)}(\mu, T) + V^{-2}p^{(2)}(\mu, T) + \cdots \quad (6-22)$$

$$\hat{p} = p^{(0)}(\mu, T) + V^{-1}\hat{p}^{(1)}(\mu, T) + V^{-2}\hat{p}^{(2)}(\mu, T) + \cdots, \quad (6-23)$$

where  $g^{(0)} \equiv G^{(0)}/V$ . The smaller the system, the more terms must

<sup>1</sup> This notation is not the same as in J.C.P.

be retained in the series. Then Eq. (6-4) leads to a hierarchy of equations:

$$\begin{aligned} e^{(0)} &= Ts^{(0)} + \mu n^{(0)} - p^{(0)} & (\text{macroscopic}) \\ e^{(1)} &= Ts^{(1)} + \mu n^{(1)} - \hat{p}^{(1)} \\ e^{(2)} &= Ts^{(2)} + \mu n^{(2)} - \hat{p}^{(2)}, \end{aligned} \quad (6-24)$$

etc. Succeeding levels of the hierarchy refer to "smaller" effects. Similarly, from Eq. (6-2),

$$\begin{aligned} de^{(0)} &= T ds^{(0)} + \mu dn^{(0)} & (\text{macroscopic}) \\ de^{(1)} &= T ds^{(1)} + \mu dn^{(1)}, \end{aligned} \quad (6-25)$$

etc., and

$$p^{(1)} = 0, \quad p^{(2)} = -\hat{p}^{(2)}, \quad p^{(3)} = -2\hat{p}^{(3)}, \quad \text{etc.} \quad (6-26)$$

We have here made use of the fact that  $e^{(1)}$ ,  $e^{(2)}$ , etc., are independent of  $V$ . Equations (6-26) follow, as well, from Eqs. (6-22), (6-23), and  $p = \partial \hat{p} V / \partial V$ . Another set of equations may be deduced from (6-10):

$$\begin{aligned} dp^{(0)} &= s^{(0)} dT + n^{(0)} d\mu & (\text{macroscopic}) \\ d\hat{p}^{(1)} &= s^{(1)} dT + n^{(1)} d\mu, \end{aligned} \quad (6-27)$$

etc. It is easy to verify that Eqs. (6-24), (6-25), and (6-27) are self-consistent. According to Eq. (6-27),

$$s^{(i)} = \left( \frac{\partial \hat{p}^{(i)}}{\partial T} \right)_{\mu}, \quad n^{(i)} = \left( \frac{\partial \hat{p}^{(i)}}{\partial \mu} \right)_T. \quad (6-28)$$

Two expansions of interest are

$$\mathcal{E} = -(\hat{p}^{(1)} + 2V^{-1}\hat{p}^{(2)} + 3V^{-2}\hat{p}^{(3)} + \dots) \quad (6-29)$$

$$\{G\} = g^{(1)} + 2V^{-1}g^{(2)} + 3V^{-2}g^{(3)} + \dots. \quad (6-30)$$

It is easy to show, from Eqs. (6-24) and (6-25), that

$$d(e^{(i)}V) = T d(s^{(i)}V) - \hat{p}^{(i)} dV + \mu d(n^{(i)}V). \quad (6-31)$$

Note that  $\hat{p}^{(i)}$  occurs in this equation, and not  $p^{(i)}$ . At any level  $i$  of

the hierarchy, the functions  $e^{(i)}V$ ,  $s^{(i)}V$ , and  $n^{(i)}V$  are linear homogeneous functions of  $V$ , at constant  $\mu$  and  $T$ , as in macroscopic thermodynamics. Hence, on integration,

$$e^{(i)}V = Ts^{(i)}V - \hat{p}^{(i)}V + \mu n^{(i)}V,$$

in agreement with Eq. (6-24).

PHASE TRANSITIONS. Turning to Section 5-4, we can continue to transcribe results from the  $N, p, T$  case to  $\mu, V, T$ . The probability function is now

$$P(N) = \frac{Q(N, V, T)e^{N\mu/kT}}{\Xi} \quad (6-32)$$

where

$$\Xi = e^{\hat{p}V/kT} = \sum_N Q(N, V, T)e^{N\mu/kT}. \quad (6-33)$$

The behavior of  $P(N)$  is completely analogous to that of  $P(V)$ , as we have already pointed out in Section 5-4.

An ensemble of  $\mathcal{N}$  distinguishable  $\mu, V, T$  systems is itself a macroscopic system characterized by  $\mu, V, T$ . The equilibrium value of  $\mathcal{N}_A$  is found by minimizing the following function with respect to  $\mathcal{N}_A$ , holding  $\mathcal{N}, \mu, V, T$  constant:

$$\begin{aligned} E_t - TS_t - \mu N_t &= \mathcal{N}_A(\bar{E}_A - TS_A - \mu\bar{N}_A) + \mathcal{N}_B(\bar{E}_B - TS_B - \mu\bar{N}_B) \\ &\quad - kT \ln \frac{\mathcal{N}!}{\mathcal{N}_A!\mathcal{N}_B!} \\ &= \mathcal{N}_A(-\hat{p}_A V) + \mathcal{N}_B(-\hat{p}_B V) - kT \ln \frac{\mathcal{N}!}{\mathcal{N}_A!\mathcal{N}_B!}. \end{aligned} \quad (6-34)$$

We find

$$\frac{\mathcal{N}_A}{\mathcal{N}_B} = \frac{e^{-J_A/kT}}{e^{-J_B/kT}} = \left( \frac{e^{\hat{p}_A/kT}}{e^{\hat{p}_B/kT}} \right)^V. \quad (6-35)$$

The value of  $\mu$  which, for given  $V$  and  $T$ , leads to  $\hat{p}_A = \hat{p}_B$  and hence  $\mathcal{N}_A = \mathcal{N}_B$  is denoted by  $\mu_0$ .

We again have equal distance and equal area theorems, as shown schematically in Fig. 6-1 ( $XY = YZ$ ). Figure 6-2 presents the corresponding schematic plot of  $\hat{p}$  against  $\mu$ . The distance  $XY$  in the latter figure is equal to  $(kT/V) \ln 2$ .

Equation (5-128) transcribes into

$$\frac{\partial(\bar{N}/V)}{\partial\mu} = \frac{1}{2} \frac{\partial(\bar{N}_A/V)}{\partial\mu} + \frac{1}{2} \frac{\partial(\bar{N}_B/V)}{\partial\mu} + \frac{V[(\bar{N}_A/V) - (\bar{N}_B/V)]^2}{4kT}. \quad (6-36)$$

Points  $X$  and  $Z$  in Fig. 6-1 have the same values of  $\hat{p}$ ,  $\mu$ ,  $V$ , and  $T$ . If  $\mu$ ,  $V$ , and  $T$  are varied,  $d\hat{p}_A = d\hat{p}_B$ :

$$\frac{S_A}{V} dT + \frac{\bar{N}_A}{V} d\mu + \frac{(p_A - \hat{p}_A)}{V} dV = \frac{S_B}{V} dT + \frac{\bar{N}_B}{V} d\mu + \frac{(p_B - \hat{p}_B)}{V} dV. \quad (6-37)$$

Then

$$\left(\frac{\partial\mu}{\partial T}\right)_V = -\frac{\Delta S}{\Delta\bar{N}} = -\frac{\Delta L}{T \Delta\bar{N}} \quad (6-38)$$

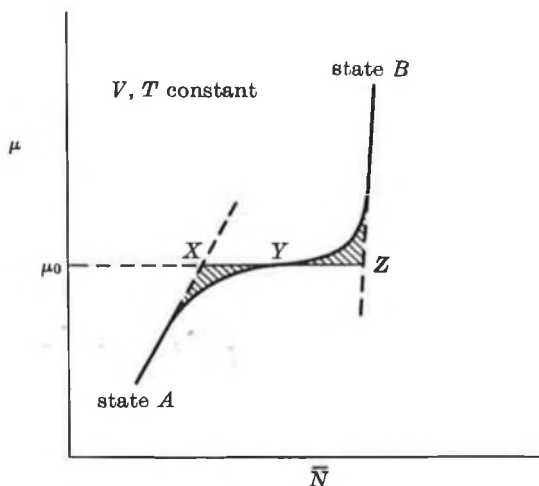


FIGURE 6-1. Schematic  $\mu$ - $\bar{N}$  isotherm for small system at a temperature such that the macroscopic system has a first-order phase transition.

$$\left(\frac{\partial T}{\partial V}\right)_{\mu} = -\frac{\Delta p}{\Delta S} = -\frac{T \Delta \mathcal{E}}{V \Delta L} \quad (6-39)$$

$$\left(\frac{\partial \mu}{\partial V}\right)_T = -\frac{\Delta p}{\Delta \bar{N}} = -\frac{\Delta \mathcal{E}}{V \Delta \bar{N}}, \quad (6-40)$$

where

$$\begin{aligned} -\hat{p}V &= L - TS, & \Delta \hat{p} &= 0, & \Delta L &= T \Delta S \\ \mathcal{E} &= (p - \hat{p})V, & \Delta \mathcal{E} &= V \Delta p. \end{aligned} \quad (6-41)$$

We cannot set  $T \Delta S$  equal to a heat of transition  $Q$  here because  $\Delta \bar{N} \neq 0$ . In fact, for the same reason, the value of  $\Delta S$  depends on the arbitrary choice of the zero of entropy. But of course Eqs. (6-38) and (6-39) are not invalidated by a change in the zero of entropy because there are compensating changes in  $L$  and  $\mu$ .

There are nine other relations which follow from  $d\mu_A = d\mu_B$ ,  $dT_A = dT_B$ , and  $dV_A = dV_B$ . Thus, as also indicated in Section 5-4, there are a total of  $3 \times 4 = 12$  Clausius-Clapeyron equations in either case ( $N, p, T$  or  $\mu, V, T$ ). These two sets degenerate into the same  $1 \times 3 = 3$  equations for a macroscopic system:

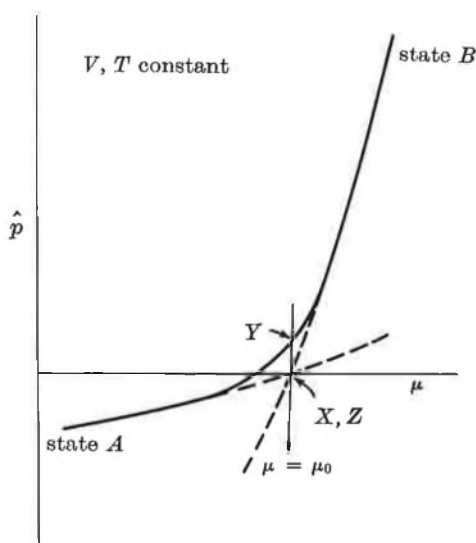


FIGURE 6-2. Schematic plot of  $\hat{p}$  against  $\mu$ . The labeling is the same as in Fig. 6-1.

$$\frac{dp}{dT} = \frac{\Delta(S/N)}{\Delta(V/N)}, \quad \frac{d\mu}{dT} = -\frac{\Delta(S/V)}{\Delta(N/V)}, \quad \frac{dp}{d\mu} = \frac{\Delta(N/S)}{\Delta(V/S)}. \quad (6-42)$$

GENERALIZATIONS. There are two obvious generalizations of a  $\mu, V, T$  system which should at least be mentioned briefly. First, there is an open system of  $c$  components with environmental variables  $\mu_1, \mu_2, \dots, \mu_c, V, T$ . Because there is only one extensive variable, it is still useful to introduce the two pressures,  $p$  and  $\bar{p}$ . The fundamental equations are

$$d\bar{E} = T dS - p dV + \sum_i \mu_i d\bar{N}_i \quad (6-43)$$

$$\bar{E} = TS - \bar{p}V + \sum_i \mu_i \bar{N}_i \quad (6-44)$$

$$d(\bar{p}V) = S dT + p dV + \sum_i \bar{N}_i d\mu_i \quad (6-45)$$

$$d[(p - \bar{p})V] = d\mathcal{E} = -S dT + V dp - \sum_i \bar{N}_i d\mu_i. \quad (6-46)$$

The other case is an open one-component system with several "external variables." If we denote these by  $V_1, V_2, \dots$ , then

$$d\bar{E} = T dS - \sum_j p_j dV_j + \mu d\bar{N} \quad (6-47)$$

$$\bar{E} = TS - \sum_j p_j V_j + \mu \bar{N} + \mathcal{E} \quad (6-48)$$

$$d(\sum_j p_j V_j - \mathcal{E}) = S dT + \sum_j p_j dV_j + \bar{N} d\mu \quad (6-49)$$

$$d\mathcal{E} = -S dT + \sum_j V_j dp_j - \bar{N} d\mu. \quad (6-50)$$

Examples are:  $V_1$  = volume,  $V_2$  = length;  $V_1$  = length,  $V_2$  = width (two-dimensional system); etc. We can introduce the thermodynamics of shape in this way. The same can be done for a closed system  $(N, V_1, V_2, \dots, T)$ . Of course, with experimental macromolecules in solution, etc., the shape is not controllable: it adjusts itself to minimize the free energy or other appropriate function, with fluctuations about a mean shape. Thus, for example, instead of environmental variables  $V_1$  = volume and  $V_2$  = length for a cylindrical macromolecule in solution, we would use  $p_1$  = pressure and  $p_2$  = force = 0 (this corresponds to a minimization with respect to  $V_2$ ).

## 6-2. APPLICATIONS TO THEORETICAL MODELS

**IDEAL LATTICE GAS.** Reference should be made to Eqs. (2-77) to (2-84) for notation and for comparison with  $N, p/T$  results on the same system.

The properties of an ideal lattice gas are particularly simple in a  $\mu/T, B$  system. We have

$$\Xi = e^{\hat{p}B/kT} = \sum_{N=0}^B \frac{B! \lambda^N}{N!(B-N)!} = (1 + \lambda)^B, \quad (6-51)$$

where  $\lambda = e^{\mu/kT}$ . Then

$$\frac{\hat{p}B}{kT} = B \ln(1 + \lambda), \quad \frac{\hat{p}}{kT} = \ln(1 + \lambda) \quad (6-52)$$

$$\frac{p}{kT} = \frac{1}{kT} \left( \frac{\partial \hat{p}B}{\partial B} \right)_{\mu, T} = \ln(1 + \lambda) \quad (6-53)$$

$$\hat{p}^{(x)} = 0, \quad p^{(x)} = 0, \quad \mathcal{E} = 0. \quad (6-54)$$

Also,

$$\bar{N} = \left( \frac{\partial \hat{p}B}{\partial \mu} \right)_{T, B} = \frac{B\lambda}{1 + \lambda}, \quad \lambda = \frac{\bar{N}}{B - \bar{N}} \quad (6-55)$$

$$\frac{\hat{p}}{kT} = \frac{p}{kT} = -\ln \left( 1 - \frac{\bar{N}}{B} \right). \quad (6-56)$$

The entropy is

$$\begin{aligned} \frac{S}{k} &= \frac{\hat{p}B}{kT} - \frac{\bar{N}\mu}{kT} \\ &= B \ln B - (B - \bar{N}) \ln(B - \bar{N}) - \bar{N} \ln \bar{N}, \end{aligned} \quad (6-57)$$

without approximation.

The unique feature here is that all of these expressions are the same in both finite and macroscopic systems. However, the relations above involving  $p$  depend on a differentiation with respect to  $B$ , a discrete variable. Hence these relations cannot be extended to arbitrarily small  $B$  (see Chapter 15).



PHASE TRANSITION IN BRAGG-WILLIAMS LATTICE GAS. Consider the binding of molecules from a reservoir at  $\mu$  and  $T$  on the surface of, say, a spherical colloidal particle with  $B$  uniformly distributed binding sites. The bound molecules at  $\mu, T$ , and  $B$ , which is proportional to the area, form the system of interest. Because we are concerned with a spherical surface, there are no "edge effects"—only the effects of small values of  $B$ . Another very similar system is the adsorption of a gas on a finely divided powder. Unlike the ideal lattice gas just discussed, we now wish to take into account intermolecular interactions. We use the Bragg-Williams approximation for maximum simplicity.

The canonical ensemble partition function, in this approximation, is

$$Q(N, B, T) = \frac{B! j^N}{N!(B - N)!} e^{-\alpha N^2/B}, \quad (6-58)$$

where  $\alpha = zw/2kT$ ,  $z$  = nearest-neighbor number of sites,  $w$  = nearest-neighbor pair interaction energy, and  $j$  = partition function of a bound molecule at a site. We take  $j = 1$  below for simplicity.

Critical and phase-transition behavior becomes possible when  $w$  is negative. The critical temperature, for the infinite system, can be shown to be given by  $\alpha_c = zw/2kT_c = -2$ .

A few properties of this system, using Eqs. (6-32) and (6-33), have been calculated numerically.<sup>1</sup> Computations for  $B = 10$  and 20 were carried out by complete summation, while for  $B = 100$  and 200 numerical integration with intervals of  $\Delta N = 5$  was used.

Figures 6-3 and 6-4 present  $\mu/kT$  versus  $\bar{\rho} = \bar{N}/B$  curves for  $T < T_c$  and  $T = T_c$ , respectively. A first-order phase transition occurs in the former case. Incidentally, equal-distance and equal-area theorems are automatically satisfied in Fig. 6-3 because of symmetry. The equation of state ( $\bar{p}/kT$  versus  $1/\bar{\rho}$ ) corresponding to Fig. 6-3 is shown in Fig. 6-5.

Figures 6-6 and 6-7 show the probability  $P$  that a system contains  $N$  molecules, plotted as a function of  $\rho = N/B$ . These figures serve as a good illustration of the basis of the two-state approximation for sufficiently large  $B$ , and  $T$  not too near  $T_c$ .

<sup>1</sup> T. L. Hill, *J. Phys. Chem.*, **57**, 324 (1953). See also Appendix 9 of S.M.

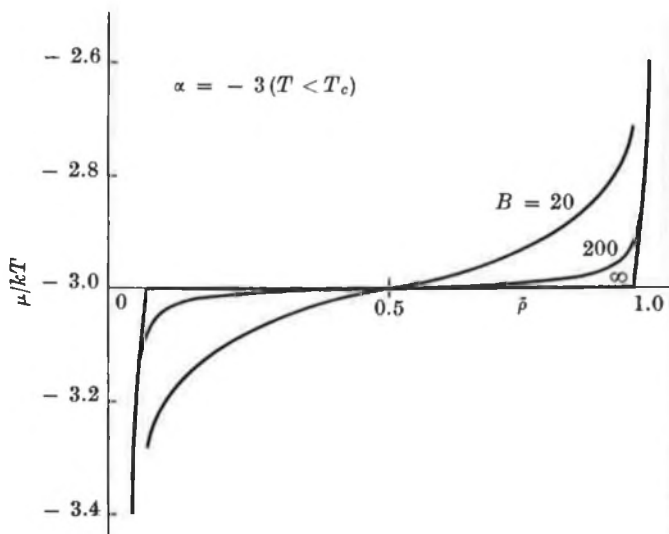


FIGURE 6-3. Phase transition in Bragg-Williams lattice gas for finite  $\mu, B, T$  system (i.e., the grand partition function has been used), with  $\bar{\rho} = \bar{N}/B$ .

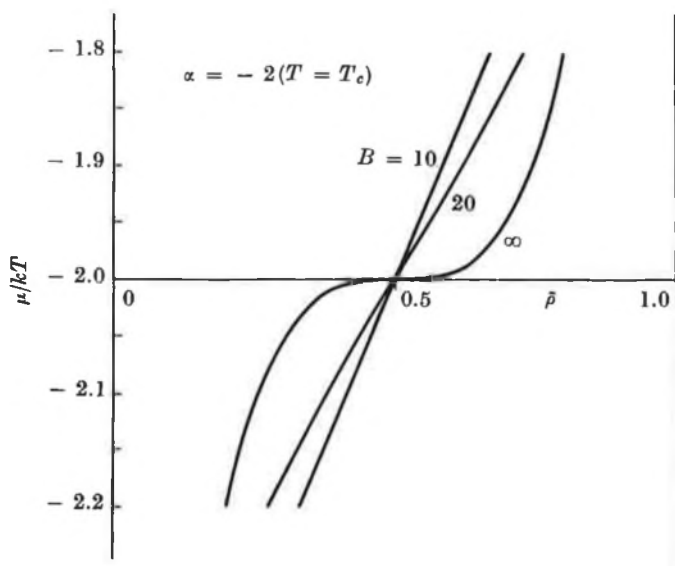


FIGURE 6-4. Same system as in Fig. 6-3 but the temperature is the macroscopic critical temperature.

BRAGG-WILLIAMS LATTICE GAS AT ORDINARY POINT. This is the same model as above but here our object is to examine an "ordinary point" (i.e., outside of phase transition and critical regions) analytically for first departures from macroscopic behavior.

For a macroscopic system we can use Stirling's simple approximation and replace  $\ln \Xi$  by the logarithm of the maximum term in  $\Xi$ . That is, there is essentially a  $\delta$  function at the maximum term when  $B \rightarrow \infty$ . When the system is not quite large enough for this procedure to be valid, we have to use

$$\ln N! = N \ln N - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi \quad (6-59)$$

and replace the  $\delta$  function by a Gaussian distribution. This will give us the first-order departure from macroscopic behavior.

Let us define the function  $R(\mu, B, T, N)$  by  $R \equiv Qe^{N\mu/kT}$ . Using Eqs. (6-58) and (6-59), we have

$$\begin{aligned} \ln R = & B \ln B + \frac{1}{2} \ln B - N \ln N - \frac{1}{2} \ln N - \frac{1}{2} \ln 2\pi \\ & - (B - N) \ln(B - N) - \frac{1}{2} \ln(B - N) - \frac{\alpha N^2}{B} + \frac{N\mu}{kT} \end{aligned} \quad (6-60)$$

$$\begin{aligned} \left( \frac{\partial \ln R}{\partial N} \right)_{\mu, B, T} = 0 = & -\ln N^* - \frac{1}{2N^*} + \ln(B - N^*) + \frac{1}{2(B - N^*)} \\ & + \frac{\mu}{kT} - \frac{2\alpha N^*}{B} \end{aligned} \quad (6-61)$$

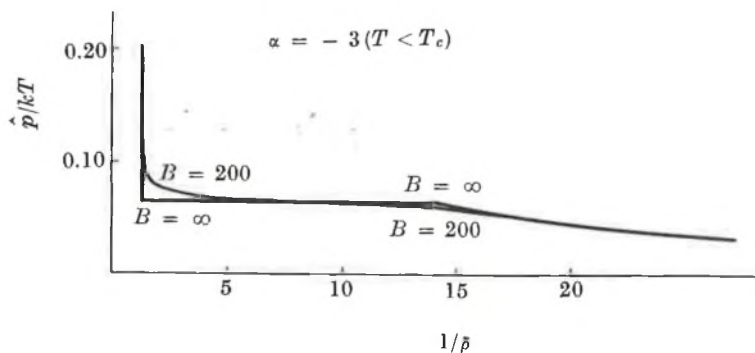


FIGURE 6-5. Equation of state corresponding to Fig. 6-3.

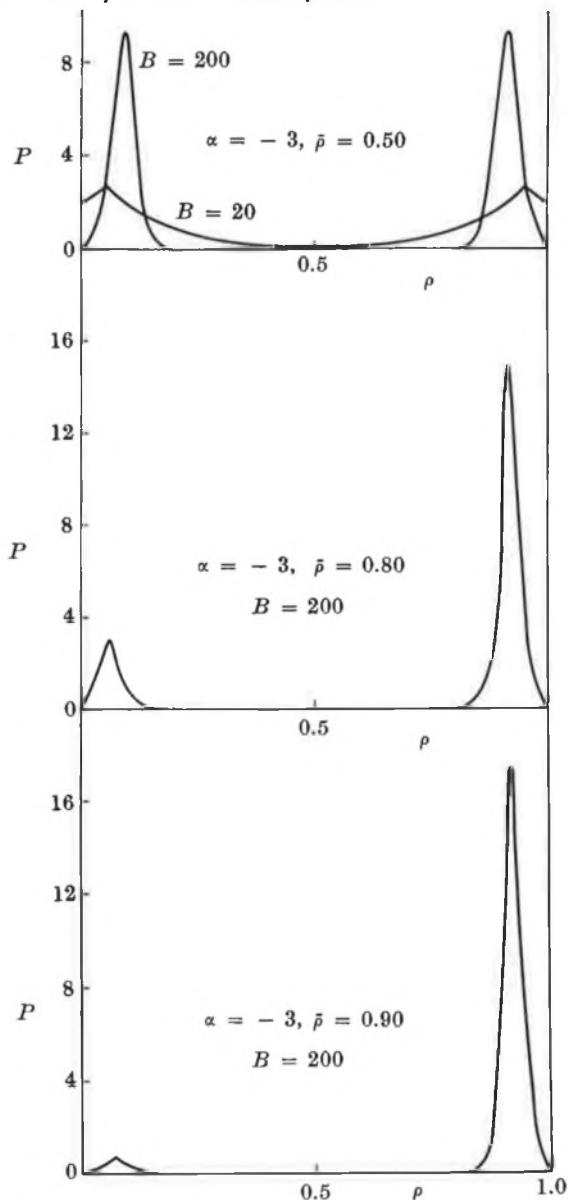


FIGURE 6-6. Probability  $P$  that the system in Fig. 6-3 contains  $N$  molecules, plotted against  $\rho = N/B$ , for different values of  $\bar{p}$ . The two peaks correspond to the two phases in the phase equilibrium. The two-state approximation is clearly appropriate for  $B = 200$  but not for  $B = 20$ .

$$\left( \frac{\partial^2 \ln R}{\partial N^2} \right)_{\substack{\mu, B, T \\ N=N^*}} = -\frac{1}{N^*} + \frac{1}{2N^{*2}} - \frac{1}{B - N^*} + \frac{1}{2(B - N^*)^2} - \frac{2\alpha}{B}, \quad (6-62)$$

where  $N^*$  is that value of  $N$  giving the maximum  $\ln R$ . Equation (6-61) provides us with  $N^*(\mu, B, T)$ . Then the desired Gaussian distribution is

$$R(N) = R(N^*)e^{-\beta(N-N^*)^2}$$

where

$$\beta = -\frac{1}{2} \left( \frac{\partial^2 \ln R}{\partial N^2} \right)_{N=N^*}.$$

Equation (6-62) gives  $\beta$  as a function of  $N^*, B, T$  and hence as a function of  $\mu, B, T$  using  $N^*(\mu, B, T)$  from Eq. (6-61). It follows that

$$\Xi = \int_{-\infty}^{+\infty} R(N^*)e^{-\beta(N-N^*)^2} d(N - N^*) = \frac{R(N^*)\pi^{1/2}}{\beta^{1/2}}$$

or

$$\ln \Xi = \ln R(N^*) + \frac{1}{2} \ln \pi - \frac{1}{2} \ln \beta(N^*, B, T). \quad (6-63)$$

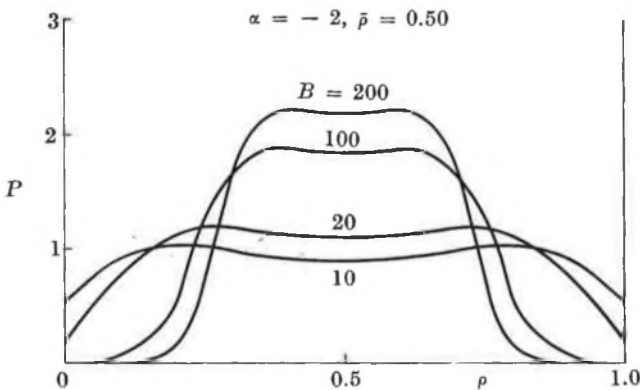


FIGURE 6-7. Same as Fig. 6-6 but the temperature is the macroscopic critical temperature. The two-state approximation is clearly inappropriate here.

We can now use Eqs. (6-8) and (6-33) to find any property of interest. For example, we obtain

$$\frac{\hat{p}}{kT} = \ln \frac{B}{B - N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B - 2N^*}{2B(B - N^*)} - \frac{1}{2B} \ln \left[ \frac{B^2 + 2\alpha N^*(B - N^*)}{B^2} \right] \quad (6-64)$$

$$\frac{p}{kT} = \ln \frac{B}{B - N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B - 2N^*}{2B(B - N^*)} \quad (6-65)$$

$$\bar{\rho} = \frac{\bar{N}}{B} = \frac{N^*}{B} + \frac{B^2(B - 2N^*)}{2[B^2 + 2\alpha N^*(B - N^*)]^2}. \quad (6-66)$$

Terms of order unity are placed first, followed by terms of order  $B^{-1}$ . The work here is not sufficient to obtain  $O(B^{-2})$ .

The macroscopic properties  $p^{(0)}$  and  $\bar{N}^{(0)}$  are given by

$$\frac{p^{(0)}}{kT} = \ln \frac{B}{B - N^\dagger} + \frac{\alpha N^{\dagger 2}}{B^2}, \quad \bar{N}^{(0)} = N^\dagger, \quad (6-67)$$

where  $N^\dagger(\mu, B, T)$  is determined by [see Eq. (6-61)]

$$0 = -\ln N^\dagger + \ln(B - N^\dagger) + \frac{\mu}{kT} - \frac{2\alpha N^\dagger}{B}. \quad (6-68)$$

One can then show that, contrary to the superficial appearance of Eq. (6-65),

$$\frac{p}{kT} = \frac{p^{(0)}}{kT} + O(B^{-2}) \quad (6-69)$$

whereas

$$\frac{\hat{p}}{kT} = \frac{p^{(0)}}{kT} + O(B^{-1}). \quad (6-70)$$

This is verified by Eq. (6-26), which shows that if  $\hat{p}/kT$  has a term in  $B^{-1}$ , the  $B^{-1}$  term is missing in  $p/kT$ .

As a check on self-consistency we can calculate both sides of Eq. (6-18) for this model and find the result

$$B \left( \frac{\partial \bar{p}}{\partial B} \right)_{T, \mu} = \frac{\alpha N^*(B - N^*)(B - 2N^*)}{[B^2 + 2\alpha N^*(B - N^*)]^2} = O(B^{-1}). \quad (6-71)$$

This order of magnitude is expected from Eqs. (6-21) (with  $G = \bar{N}$ ) and (6-28b).

**SIMPLE PHASE-TRANSITION MODEL.** In Eqs. (5-144) and (5-145) we considered a very simple model of a phase transition in an  $N, p, T$  system. We discuss the corresponding model here in somewhat more detail, again using a thermodynamic approach. Essentially the same example is treated in Eqs. (40) to (49) of J.C.P. from a statistical mechanical point of view.<sup>1</sup>

Consider an idealized, small  $\mu, B, T$  system which can exist in two states characterized by  $\hat{p}_1$  and  $\hat{p}_2$ , assumed independent of  $B$ , and densities  $\rho_1$  and  $\rho_2$ , assumed independent of  $B$  and  $\mu$ . We take  $\rho_1 > \rho_2$  for definiteness. Let  $\mu_0$  be the value of  $\mu$  for which  $\hat{p}_1 = \hat{p}_2$ . Then  $\mu_0$  is a function of  $T$  only. Let  $\hat{p}_0$  be the value of  $\hat{p}_1$  and  $\hat{p}_2$  at  $\mu = \mu_0$ . Then  $\hat{p}_0$  is also a function of  $T$  only. On integrating  $\partial \hat{p} / \partial \mu = \bar{\rho}$  for states 1 and 2,

$$\begin{aligned} \hat{p}_1 &= \hat{p}_0 + \rho_1(\mu - \mu_0) \\ \hat{p}_2 &= \hat{p}_0 + \rho_2(\mu - \mu_0). \end{aligned} \quad (6-72)$$

Equations (6-35) and (6-72) lead to

$$\frac{P_1}{1 - P_1} = \exp \left[ \frac{B(\rho_1 - \rho_2)(\mu - \mu_0)}{kT} \right]. \quad (6-73)$$

<sup>1</sup> (a) In J.C.P. we took  $\rho_2 > \rho_1$  and  $\hat{p}_1 + \hat{p}_2 = 1$ .

(b) The two-state approximation is analyzed in Section 5-4 by thermodynamic methods. The same results could have been obtained using statistical mechanical language. The starting point is

$$\begin{aligned} e^{-F/kT} &= \Delta = \Delta_A + \Delta_B = e^{-F_A/kT} + e^{-F_B/kT} \\ P_A &= \Delta_A / \Delta. \end{aligned}$$

(c) The present example is a special case of the two-state approximation. In the  $N, p, T$  case,  $P(V)$  consists of two  $\delta$  functions (compare Fig. 5-1c).

We define

$$x = \frac{\lambda}{\lambda_0} = e^{(\mu - \mu_0)/kT}.$$

Then on solving Eq. (6-73) for  $P_1$ , we find

$$P_1 = \frac{x^{\rho_1 B}}{x^{\rho_1 B} + x^{\rho_2 B}} \quad (6-74)$$

and

$$\bar{\rho} = P_1 \rho_1 + P_2 \rho_2 = \frac{\rho_1 x^{\rho_1 B} + \rho_2 x^{\rho_2 B}}{x^{\rho_1 B} + x^{\rho_2 B}} \quad (6-75)$$

$$P_1 = \frac{\bar{\rho} - \rho_2}{\rho_1 - \rho_2}. \quad (6-76)$$

Note from Eqs. (5-144) and (6-73) that Fig. 5-6 is also a plot of

$$-\frac{(\rho_1 - \rho_2)(\mu - \mu_0)}{kT} \quad \text{versus} \quad \frac{\bar{\rho} - \rho_2}{\rho_1 - \rho_2},$$

for  $B = 10, 50$ , etc. This is essentially  $-\mu$  plotted against  $\bar{\rho}$  (compare Figs. 6-1 and 6-3). The equal-distance and equal-area theorems are automatically satisfied in this example by virtue of symmetry.

In Fig. 6-6 (Bragg-Williams lattice gas), the maxima in  $P(N)$  for  $B = 200$  occur at  $\rho_1 = 0.93$  and  $\rho_2 = 0.07$ . If we replace the two peaks in this figure by  $\delta$  functions at  $\rho_1$  and  $\rho_2$ , we can calculate approximately the curve of  $(\mu - \mu_0)/kT$  against  $\bar{\rho}$ , for  $B = 200$ , using Eq. (6-73). This curve is indistinguishable from that shown in Fig. 6-3 for  $B = 200$  except very near  $\rho_1$  and  $\rho_2$  (the approximation makes states 1 and 2 incompressible).

The transcription of Eq. (5-120) gives an expression for  $\hat{p}$ . Substitution of Eqs. (6-72) and (6-74) into this expression results in

$$\hat{p} = \hat{p}_0(T) + \frac{kT}{B} \ln(x^{\rho_1 B} + x^{\rho_2 B}). \quad (6-77)$$

If we define  $p_0$  as the value of  $\hat{p}$  at  $x = 1$ , then

$$\hat{p} = p_0(B, T) + \frac{kT}{B} \ln \frac{(x^{\rho_1 B} + x^{\rho_2 B})}{2} \quad (6-78)$$



where<sup>1</sup>

$$p_0(B, T) = \hat{p}_0(T) + \frac{kT}{B} \ln 2.$$

Using  $p = \partial(\hat{p}B)/\partial B$  for states 1 and 2, we deduce from Eqs. (6-72):

$$p_1 = \hat{p}_1, \quad p_2 = \hat{p}_2 \quad (6-79)$$

$$p = P_1 p_1 + P_2 p_2 = \hat{p}_0 + \bar{\rho} kT \ln x. \quad (6-80)$$

The last result also follows on differentiating  $\hat{p}B$ , using Eq. (6-77). Then

$$\begin{aligned} \mathcal{E} &= (p - \hat{p})B \\ &= kT [\bar{\rho} B \ln x - \ln(x^{\rho_1 B} + x^{\rho_2 B})]. \end{aligned} \quad (6-81)$$

When  $B \rightarrow \infty$ , the last term becomes  $\rho_1 B \ln x$  for  $x > 1$  and  $\rho_2 B \ln x$  for  $x < 1$ ; also,  $\bar{\rho} \rightarrow \rho_1$  or  $\rho_2$ , respectively. Hence  $\mathcal{E} \rightarrow 0$  as  $B \rightarrow \infty$ .

For a macroscopic system, both of Eqs. (6-77) and (6-80) become

$$\begin{aligned} p^{(0)} - \hat{p}_0(T) &= \rho_1(\mu - \mu_0) \quad (\mu > \mu_0) \\ &= \rho_2(\mu - \mu_0) \quad (\mu < \mu_0) \end{aligned} \quad (6-82)$$

as expected.

Using Eq. (6-75) for  $\bar{\rho}$ , it is easy to verify the statistical mechanical relation

$$x \left( \frac{\partial \bar{\rho}}{\partial x} \right)_{T, B} = (\bar{\rho}^2 - \bar{\rho}^2) B. \quad (6-83)$$

At  $x = 1$ ,

$$\begin{aligned} \bar{\rho} &= \frac{1}{2}(\rho_1 + \rho_2), \quad \bar{\rho}^2 = \frac{1}{2}(\rho_1^2 + \rho_2^2) \\ x \left( \frac{\partial \bar{\rho}}{\partial x} \right)_{T, B} &= \frac{B}{4}(\rho_1 - \rho_2)^2 = O(B). \end{aligned} \quad (6-84)$$

This is verified by Eq. (6-36).

<sup>1</sup> It is incorrectly assumed in J.C.P. that  $p_0$  (called  $p_T$  there) is a function of  $T$  only.

As a check on self-consistency, we can evaluate both sides of Eq. (6-18). We find

$$\left(\frac{\partial \bar{\rho}}{\partial B}\right)_{T, \mu} = (\bar{\rho}^2 - \bar{\rho}^2) \ln x = O(1). \quad (6-85)$$

This is a much larger effect, because of the phase transition, than in Eq. (6-71). Also, on combining Eqs. (6-83) and (6-85), we have

$$\begin{aligned} \left(\frac{\partial \mu/kT}{\partial B}\right)_{T, \bar{\rho}} &= -\left(\frac{\partial \bar{\rho}}{\partial B}\right)_{T, \mu} \left(\frac{\partial \mu/kT}{\partial \bar{\rho}}\right)_{T, B} \\ &= -\frac{\ln x}{B} = \left(\frac{\partial \ln x}{\partial B}\right)_{T, \bar{\rho}}. \end{aligned} \quad (6-86)$$

Integration of Eq. (6-86) leads to the conclusion that  $x^B$  is some function of  $\bar{\rho}$  and  $T$ , in agreement with Eq. (6-75).

INTERACTING PARTICLES IN A "PERIODIC" CUBE. This is an important but very complicated problem on which much careful work has been done. Because of the complications, we shall not discuss it here. The interested reader should consult the original literature.<sup>1</sup> The same problem for an  $N, V, T$  system is referred to on p. 198 of Part II.

<sup>1</sup> See, for example, J. L. Lebowitz and J. K. Percus, *Phys. Rev.*, **124**, 1673 (1961); I. Oppenheim and P. Mazur, *Physica*, **23**, 216 (1957).

## Thermodynamics of Small Systems\* †

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It is shown in this paper that the differential equations of macroscopic thermodynamics can be generalized in such a way that they apply as well to small (i.e., nonmacroscopic) systems. Conventional thermodynamic relations then follow from the present treatment as a limiting case (large system). As with macroscopic thermodynamics, there are two main classes of applications: (1) as an aid in analyzing, classifying, and correlating equilibrium experimental data on "small systems" such as noninteracting colloid particles, liquid droplets, crystallites, macromolecules, polymers, polyelectrolytes, nucleic acids, proteins, etc.; and (2) to verify, stimulate, and provide a framework for statistical mechanical analysis of models of finite (i.e., "small") systems. A well-known experimental and theoretical example (in which there are sizable effects of chain length) is the helix-coil transition in synthetic polypeptides and polynucleotides. Unlike macroscopic thermodynamics, thermodynamic functions are different for different environments (open, closed, isothermal, isobaric, etc.). Although it is possible to derive a single set of

thermodynamic equations applicable to all environments, it proves useful to give a separate analysis for each environment. Several cases are discussed, and a few simple statistical mechanical models are used for purposes of illustration. The partition function for a "completely open" small system can be used without any special technique such as is required when this partition function is applied to a macroscopic system. Solvent effects are discussed and details are given in one case. The present method provides an invariant treatment of the spherical interface of a drop or bubble, independent of any choice of dividing surface. Usually, only mean values of fluctuating extensive variables appear in thermodynamic equations. This is justified in macroscopic thermodynamics because fluctuations are generally unimportant. The situation is different for small systems and we derive, in one case, a hierarchy of thermodynamic equations involving higher moments of the probability distribution of fluctuating extensive properties.

## I. INTRODUCTION

ORDINARY thermodynamics applies only to macroscopic (strictly, infinite) systems. Our object is to try to extend thermodynamics, insofar as possible, to include "small" (i.e., nonmacroscopic) systems. The equations we obtain here are more general than those of ordinary thermodynamics: They apply to macroscopic systems as a limiting case.

It turns out (as is clear from Sec. II) that many special cases need to be considered, and that numerous examples are helpful. In this paper we discuss certain selected cases and results obtained thus far. A more suitable medium for a detailed and systematic account of the subject would appear to be a short monograph, and this is in preparation.<sup>1</sup>

As in ordinary thermodynamics, there are two kinds of application of this work: (a) to experimental systems such as colloidal particles, aggregates, polymers, macromolecules, etc. (not large enough to be considered macroscopic); and (b) to statistical mechanical models of "finite" (small) systems. We include a few simple examples of type (b) in Sec. II.

The most important practical aim of macroscopic thermodynamics is to derive equations which provide interconnections between various thermodynamic functions. The same is true of "small system thermodynamics." This is essentially the only topic (together with examples) considered in this paper. Perhaps the

most obvious "interconnections" of interest here are those showing how the size of the small system affects various intensive properties of the system. There is no such effect in a macroscopic system.

There are some important respects in which experimental small thermodynamic systems differ operationally from macroscopic systems. (a) In general, measurements are not made on a single small system but on a large number of small systems. An example is a very dilute solution of a macromolecule: the "small system" is one macromolecule; the solution contains many macromolecules; but the solution must be very dilute so that the systems do not interact with each other. (b) A macroscopic system immersed in a reservoir may exchange heat, molecules, etc., with the reservoir, but the intermolecular interaction between the system and the reservoir at the surface of contact is of negligible order. This is, in general, no longer the case for a small system immersed in a solvent (the reservoir). The discussion we give in Sec. II does not include solvent effects explicitly, and applies essentially to small systems (e.g., a macromolecule, colloidal particle, or aggregate) in the gas phase or in an inert solvent. But in Sec. III we illustrate the fact that the equations of Sec. II are formally valid even when solvent effects are present. All that is required is a reinterpretation of the meaning of various symbols. (c) Certain properties which can be varied experimentally at will for a macroscopic system cannot be so varied with a small system. An example is the volume of a colloidal particle. Another is the length of, or force  $f$  on, an elastic macromolecule in solution. The only operationally possible case is that of  $f = \text{constant} = 0$ . There are, of course, no such restrictions when investigating the theoretical properties of a statistical

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† A very brief summary of this work was presented at an American Chemical Society meeting, Washington, D. C., March 23, 1962.

‡ T. L. Hill, *Thermodynamics of Small Systems* (W. A. Benjamin, Inc., New York), in preparation.

mechanical model of a small system. We ignore this question in Sec. II but return to it in Sec. III.

Consider a *macroscopic* system of  $N$  molecules, volume  $V$ , immersed in a heat bath at  $T$ . Consider the same system at  $V$  and  $T$ , but in contact with a reservoir of molecules, with the value of the chemical potential  $\mu$  chosen so that  $\bar{N}$  has the same value as  $N$  above. Then all thermodynamic functions, and all equations connecting the functions, are the same in the two cases. This is an illustration of the well-known fact that properties and equations in macroscopic thermodynamics are *independent of "environment"* (i.e., isothermal, isobaric, open, isolated, etc.). We see below that this is not the case with small systems: it is useful to give a separate discussion (Sec. II) for each "environment," and the thermodynamic functions are different in each case. Of course, these differences are not of "macroscopic order"; they exist only for small systems and disappear if the size of the system is increased indefinitely. Section IIG shows that it is possible to derive a single set of thermodynamic equations applicable to all environments; but for most purposes this does not appear to be the most convenient approach.

Ordinary thermodynamic equations connect mean values of fluctuating extensive quantities ( $E$ ,  $N$ ,  $V$ , etc., as the case may be). Only mean values are of interest because fluctuations about the mean values are ordinarily completely negligible in magnitude, relative to the mean values themselves. With small systems, fluctuations are larger and hence higher moments of the probability distributions become of interest, as well as do the mean values. In Sec. V we show that mean-value thermodynamic equations are the first members of a hierarchy of equations involving moments of different order. The treatment given in Sec. V will be thermodynamic, but the motivation and starting point comes from statistical mechanics. That is, the connection between probability distribution moments and thermodynamics must be provided by statistical mechanical ensemble theory.

In this paper we consider systems which are small enough that macroscopic thermodynamics is no longer adequate but large enough that nonfluctuating extensive properties may be regarded as continuously (not discretely) variable to whatever order of accuracy is required. For example, if we consider binding on a macromolecule with  $B$  binding sites, the usual experimental accuracy would require, for the above purpose, something like  $B \geq 10-20$ . Intensive variables and (mean values of) fluctuating extensive variables are continuously variable in any case. For the most part, in this paper, we have in mind the first departures from macroscopic behavior.

In the longer account of this problem to be published elsewhere,<sup>1</sup> the treatment given here will be expanded considerably and the following additional topics discussed, among others: calorimetry; small systems in

the gas phase; rotation and translation; multicomponent small systems; chemical and phase equilibria; semi-open small systems (e.g., binding on a macromolecule); electric and magnetic fields; polydisperse systems; discrete variables (very small systems); and irreversible thermodynamics of small systems.

## II. PARTICULAR CHOICES OF THERMODYNAMIC ENVIRONMENT

### A. Small System with $\mu$ , $V$ , $T$

Here we consider a one-component system of volume  $V$  in contact with a heat and molecule reservoir at  $T$  and  $\mu$ . An example would be a spherical protein molecule with  $B$  binding sites ( $B$  is the analog of  $V$ ), immersed in a solvent at  $T$  containing molecules at  $\mu$  which can be bound on the sites (the bound molecules, characterized by  $\mu$ ,  $B$ ,  $T$ , are the "system" in this case). Let  $\bar{p}$  be the (mean) pressure conjugate to  $V$  (i.e.,  $\bar{p}dV$  is a conventional work term). The system is small, so we cannot simply assume that usual thermodynamic equations, for example

$$dE = TdS - \bar{p}dV + \mu dN,$$

are valid.

In order to begin with a firm macroscopic thermodynamic foundation, we consider an ensemble of  $\mathcal{N}$  equivalent, distinguishable, independent systems, each with fixed center of mass, and all characterized by  $\mu$ ,  $V$ ,  $T$ . We let  $\mathcal{N} \rightarrow \infty$  and hence the ensemble itself is a macroscopic thermodynamic system, however small a single system is. We use distinguishable systems with fixed center of mass to eliminate the translational degrees of freedom of the whole system.<sup>2</sup> Thus we will be left with the "internal" thermodynamic properties of a single system. Rotation of the whole system will often be of negligible importance, but it is not excluded.<sup>1</sup> We do not include rotation in any of the simple statistical models used in the present paper.

For an ensemble with constant  $\mathcal{N}$ , we have from macroscopic thermodynamics that

$$dE_t = TdS_t - \bar{p}dV + \mu dN_t,$$

where  $t$ =total refers to properties of the whole ensemble. But  $S_t$  is clearly a function not only of  $E_t$ ,  $V$ , and  $N_t$ , but also of  $\mathcal{N}$  (or  $E_t$  is a function of  $S_t$ ,  $V$ ,  $N_t$ , and  $\mathcal{N}$ ). Thus the complete expression is

$$dE_t = TdS_t - \bar{p}dV + \mu dN_t + Xd\mathcal{N}, \quad (1)$$

where

$$X \equiv (\partial E_t / \partial \mathcal{N})_{S_t, V, N_t} \quad \text{or} \quad -X/T \equiv (\partial S_t / \partial \mathcal{N})_{E_t, V, N_t}.$$

Now suppose we hold  $\mu$ ,  $V$ ,  $T$  constant and double the value of  $\mathcal{N}$ . Then  $E_t$ ,  $S_t$ , and  $N_t$  will also double in value. That is, for this macroscopic system (the whole ensemble),  $E_t$  is a linear homogeneous function

<sup>2</sup> This step provides maximum simplicity but is more restrictive than necessary.<sup>1</sup> See Sec. III for an example of the necessary procedure in handling small systems, with translation, in a solvent.

of  $S_i$ ,  $N_i$ , and  $\mathcal{N}$ , if  $\mu$ ,  $V$ , and  $T$  are held constant. The volume  $V$  has the status here of a parameter necessary to characterize completely (with  $\mu$  and  $T$ ) a small system. Hence, from Eq. (1),

$$E_i = TS_i + \mu N_i + X\mathcal{N}. \quad (2)$$

Before proceeding, it may be helpful to make some further comments about Eq. (1). Our point of view so far is that the first four terms in Eq. (1) are typical terms in macroscopic thermodynamics and that the last term  $Xd\mathcal{N}$  associated with the addition of further systems to the ensemble, is a new kind of term required for completeness and whose inclusion represents the essential step in our argument. But there is an alternative point of view. This is that

$$dE_i = TdS_i + \mu dN_i + Xd\mathcal{N} \quad (V \text{ constant})$$

is a typical macroscopic equation for a two-component system with numbers of molecules  $N_i$  and  $\mathcal{N}$ . The new feature is, then, that the second kind of molecule can vary in size, the size parameter being  $V$ . We want to allow in the thermodynamics for variations in this parameter, so we add a term in  $dV(-p\mathcal{N} \equiv \partial E_i/\partial V)$  to again obtain Eq. (1).

Let us illustrate this with a particular model. Suppose that the small system consists of molecules from a reservoir at  $\mu$  and  $T$  adsorbed on  $B$  sites on the surface of a distinguishable, independent, spherical colloidal particle with fixed center of mass. The colloidal particle is assumed for simplicity to be unperturbed by adsorbed molecules—it merely furnishes an adsorbing surface. We shall therefore subtract out the thermodynamic properties of the colloidal particles themselves. The size of the colloidal particle can be varied, and hence  $B$  can be varied. For a fixed value of  $B$  we then have

$$dE = TdS + \mu dN_i + \mu' d\mathcal{N},$$

$$dE_0 = TdS_0 + \mu_0' d\mathcal{N},$$

$$dE_i = TdS_i + \mu dN_i + Xd\mathcal{N},$$

$$E_i = E - E_0, \quad S_i = S - S_0, \quad X = \mu' - \mu_0',$$

where the first equation refers to a macroscopic system of  $\mathcal{N}$  colloidal particles and  $N_i$  adsorbed molecules, the second equation refers to  $\mathcal{N}$  colloidal particles without any adsorbed molecules, and the third equation is obtained by subtraction and refers to  $N_i$  molecules adsorbed on  $\mathcal{N}$  spherical surfaces, each with  $B$  sites. If we now allow variations in  $B$ , we must add to the respective equations the terms  $x dB$  (where  $x \equiv \partial E/\partial B$ ),  $x_0 dB$  (where  $x_0 \equiv \partial E_0/\partial B$ ) and  $-p\mathcal{N} dB$ , where  $p$  is defined by  $-p\mathcal{N} = x - x_0$ . Thus we again obtain Eq. (1), with  $B$  in place of  $V$ .

The treatment in Secs. IIG and III should also be consulted in this connection.

We return now to the main argument and define  $\bar{E}$ ,  $\bar{N}$ , and  $\bar{S}$  by

$$E_i = \mathcal{N}\bar{E}, \quad N_i = \mathcal{N}\bar{N}, \quad S_i = \mathcal{N}\bar{S}. \quad (3)$$

Let us digress from pure thermodynamics to make some comments of a statistical mechanical nature on the significance of  $\bar{E}$ ,  $\bar{N}$ , and  $\bar{S}$ . These remarks are not essential to the thermodynamic discussion. The quantities  $\bar{E}$  and  $\bar{N}$  are average values per system of the ensemble; since all systems of the ensemble are equivalent,  $\bar{E}$  and  $\bar{N}$  are also time averages for a single system ( $E$  and  $N$  fluctuate in an environment characterized by  $\mu$ ,  $V$ ,  $T$ ). They are thus appropriately considered thermodynamic properties of a single small system. We do not put a bar over  $S$  because it is not an average value in the same sense. That is,  $S$  does not fluctuate in value but is a property of the complete probability distribution ( $p_i$  below) in  $E$  and  $N$  for a single system<sup>3</sup>; thus  $S$  has the same value for each system in the ensemble. To verify that  $S$ , defined by  $S_i/\mathcal{N}$ , has the usual meaning of an entropy in statistical mechanics, consider the following simple argument: Let  $p_{ijk\dots}$  be the probability of a quantum state  $ijk\dots$  of the ensemble, where  $i$  designates the state of the first system,  $j$  the second, etc. Since the systems are equivalent and independent,  $p_{ijk\dots} = p_i p_j p_k \dots$ , where  $p_i$  is the probability of state  $i$  for the first system, etc. Then

$$\begin{aligned} S_i &= -k \sum_{ijk\dots} p_{ijk\dots} \ln p_{ijk\dots} \\ &= -k \sum_{ijk\dots} p_i p_j p_k \dots (\ln p_i + \ln p_j + \dots) \\ &= \mathcal{N}(-k \sum_i p_i \ln p_i), \end{aligned} \quad (4)$$

where we have used  $\sum_i p_i = 1$ . Thus  $S = -k \sum_i p_i \ln p_i$ , which is the standard form.<sup>3</sup>

We now return to the definitions in (3). Putting these in Eq. (2), we have

$$X = \bar{E} - T\bar{S} - \mu\bar{N}. \quad (5)$$

Because of the form of this result, we define a quantity  $\bar{p}$  by  $-\bar{p}V \equiv X$ . Thus

$$\bar{E} = T\bar{S} - \bar{p}V + \mu\bar{N}. \quad (6)$$

From Eq. (1) it is clear that  $\bar{p}$  is a "differential" pressure while  $\bar{p}$  is an "integral" pressure (i.e., in the "work" term  $-\bar{p}Vd\mathcal{N}$ , the volume of the ensemble  $V_i = \mathcal{N}V$  is increased by adding  $d\mathcal{N}$  systems to the ensemble, holding  $S_i$ ,  $V$ , and  $N_i$  constant).

We substitute Eqs. (3) and (5) into Eq. (1) and find, after cancellation and division by  $\mathcal{N}$ ,

$$d\bar{E} = Td\bar{S} - \bar{p}dV + \mu d\bar{N}. \quad (7)$$

Note that  $\bar{p}$  and  $\bar{p}$  are different in Eqs. (6) and (7).

<sup>3</sup> See T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, New York, 1956), pp. 75-79.

Hence  $\bar{E}$  is not a linear homogeneous function of  $S$ ,  $V$ , and  $\bar{N}$

$$\bar{E} \neq TS - pV + \mu\bar{N}.$$

This is what we should expect for a small system: If we hold  $\mu$  and  $T$  constant and double the value of  $V$ , we will not double the values of other extensive properties; furthermore, intensive properties such as  $p$ ,  $\bar{p}$ ,  $\bar{N}/V$ , etc., will change in value (i.e., they are functions of  $\mu$ ,  $T$ , and  $V$ ). But in the macroscopic limit ( $V \rightarrow \infty$ )  $\bar{p} \rightarrow p$ ,  $\bar{E}$  becomes a linear homogeneous function of  $S$ ,  $V$ , and  $\bar{N}$ , and all intensive properties become functions of  $\mu$  and  $T$  only. Thus, for small systems, we have to abandon the conventional implications of "extensive" and "intensive" properties. We still refer to extensive and intensive variables, however, basing the classification on the macroscopic limit.

If we take the differential of both sides of Eq. (6) to obtain  $d(\bar{p}V)$ , and use Eq. (7), we find

$$d(\bar{p}V) = SdT + p dV + \bar{N}d\mu. \quad (8)$$

This equation is especially useful since the independent variables are the same as the "environmental variables." From Eq. (8) we have

$$\begin{aligned} (\partial \bar{p}V / \partial T)_{V, \mu} &= S, & (\partial \bar{p}V / \partial V)_{T, \mu} &= p, \\ (\partial \bar{p}V / \partial \mu)_{T, V} &= \bar{N}. \end{aligned} \quad (9)$$

For a macroscopic system  $(\partial \bar{p}V / \partial V)_{T, \mu} = \bar{p}V/V = \bar{p} = p$ .

We digress briefly to point out the connection here between thermodynamics and statistical mechanics. We will need this to discuss statistical mechanical models. The ensemble is an open macroscopic system ( $\mu$ ,  $V$ ,  $T$ ); we regard  $V$  as a parameter for which we can write conventional results. For example,

$$TS_i - E_i + \mu N_i = kT \ln \Xi_i,$$

where  $\Xi_i$  is the grand partition function of the ensemble. From Eq. (2),

$$-X\mathcal{H} = \bar{p}V\mathcal{H} = kT \ln \Xi_i.$$

But because of the independence, equivalence, and distinguishability of the systems of the ensemble,  $\Xi_i = \Xi^N$ , where  $\Xi$  is the grand partition function of a single (small) system. Hence

$$\bar{p}V = kT \ln \Xi, \quad (10)$$

where, in rather standard notation,

$$\begin{aligned} \Xi(\mu, V, T) &= \sum_{i, N} \exp[-E_i(N, V)/kT] \exp(N\mu/kT) \\ &= \sum_{N, E} \Omega(E, N, V) \exp(-E/kT) \exp(N\mu/kT) \\ &= \sum_N Q(N, V, T) \exp(N\mu/kT). \end{aligned}$$

Equation (10) is the required result.

Equation (8) can also be written as

$$d(\bar{p}V/kT) = \bar{E}d(-1/kT) + \bar{N}d(\mu/kT) + (p/kT)dV. \quad (11)$$

This form is used in Sec. V.

Other equations similar to Eqs. (7) and (8) are also useful. For example,

$$d(\bar{N}\mu - \bar{p}V) = -SdT - p dV + \mu d\bar{N}, \quad (12)$$

$$d(\bar{N}\mu - \bar{p}V + pV) = -SdT + Vd\mu + \mu d\bar{N}, \quad (13)$$

$$d[(\bar{p} - p)V] = SdT - Vd\mu + \bar{N}d\mu. \quad (14)$$

Also, we have

$$(\bar{p} - p)dV = SdT - Vd\mu + \bar{N}d\mu. \quad (15)$$

In a macroscopic system the left-hand sides of Eqs. (14) and (15) (they become the same equation) are zero. Equations (14) and (15) make it especially clear that intensive properties do not depend only on  $\mu$  and  $T$ . Thus,

$$\begin{aligned} \{\partial[(\bar{p} - p)V] / \partial p\}_{\mu, T} &= -V, \\ (\partial \bar{p} / \partial V)_{\mu, T} &= (p - \bar{p})/V. \end{aligned} \quad (16)$$

A great many equations involving derivatives can be deduced from Eqs. (7), (8), (11)–(15), and others of this type. We give only a few (isothermal) illustrations

$$\begin{aligned} (\partial \bar{p} / \partial \mu)_{T, V} &= \bar{N}/V, \\ (\partial \bar{p} / \partial \rho)_{T, V} &= \rho(\partial \mu / \partial \rho)_{T, V}; \end{aligned} \quad (17)$$

$$(\partial p / \partial \mu)_{T, V} = (\partial \bar{N} / \partial V)_{T, \mu} = \rho - [(\partial(\bar{p} - p) / \partial \mu)_{T, V}]; \quad (18)$$

$$(\partial \rho / \partial V)_{T, \mu} = -V^{-1}[(\partial(\bar{p} - p) / \partial \mu)_{T, V}]; \quad (19)$$

$$(\partial \bar{p} / \partial V)_{T, \mu} = [(p - \bar{p})/V] - (\partial \rho / \partial V)_{T, \mu}(\partial \bar{p} / \partial \rho)_{T, V}. \quad (20)$$

The derivatives  $(\partial \rho / \partial V)_{T, \mu}$  and  $(\partial \bar{p} / \partial V)_{T, \mu}$  emphasize small-system effects since they would both be zero for a macroscopic system.

In Eqs. (14) and (15), and in many others, some terms are of "macroscopic order" while others are of "small order" (negligible for a macroscopic system). Thus it is sometimes useful to introduce "excess" quantities as follows ( $x$  = excess):

$$\begin{aligned} S(\mu, V, T) &= V s^{(0)}(\mu, T) + s^{(x)}(\mu, V, T), \\ \bar{N}(\mu, V, T) &= V n^{(0)}(\mu, T) + n^{(x)}(\mu, V, T), \\ \bar{E} &= V e^{(0)} + e^{(x)}, & \bar{p}V &= p^{(0)}V + \hat{p}^{(x)}, \\ pV &= p^{(0)}V + p^{(x)}. \end{aligned} \quad (21)$$

The quantities  $s^{(0)}$ ,  $n^{(0)}$ ,  $e^{(0)}$ , and  $p^{(0)}$  are intensive properties of the macroscopic system. They are the values that  $S/V$ ,  $\bar{N}/V$ , etc., would have at the same  $\mu$  and  $T$  as the small system, if  $V \rightarrow \infty$ .



Various equations involving only excess quantities follow. For example,

$$\begin{aligned} e^{(s)} &= T s^{(s)} - \hat{p}^{(s)} + \mu n^{(s)}, \\ d e^{(s)} &= T d s^{(s)} - (\hat{p}^{(s)}/V) dV + \mu d n^{(s)}, \\ d \hat{p}^{(s)} &= s^{(s)} dT + (\hat{p}^{(s)}/V) dV + n^{(s)} d\mu. \end{aligned} \quad (22)$$

We do not pursue these further here.<sup>1</sup>

### Example: Bragg-Williams Lattice Gas

Consider the binding of molecules from a reservoir at  $\mu$  and  $T$  on the surface of a spherical protein molecule or colloidal particle, with  $B$  uniformly distributed binding sites. The bound molecules at  $\mu$ ,  $T$ , and  $B$ , which is proportional to the area, form the system of interest. Because we are concerned with a spherical surface, there are no "edge effects"—only the effects of small values of  $B$ . Another very similar system is the adsorption of a gas on a finely divided powder. We use the Bragg-Williams approximation for maximum simplicity. The canonical ensemble partition function is

$$Q(N, B, T) = [B! j^N / N! (B-N)!] \exp(-\alpha N^2/B), \quad (23)$$

where  $\alpha = zw/2kT$ ,  $z$  = nearest-neighbor number,  $w$  = nearest-neighbor pair interaction energy, and  $j$  = partition function at a site. We take  $j=1$  below for simplicity. The grand partition function is

$$\Xi = \sum_N Q(N, B, T) \exp(N\mu/kT). \quad (24)$$

We have previously had occasion<sup>4</sup> to calculate  $\mu(p)$  and  $\hat{p}(p)$  from this  $\Xi$  for finite values of  $B$ . These calculations serve as a good numerical illustration of some of the above thermodynamic discussion. For example, one can see the magnitude of  $(\partial p/\partial V)_{T,\mu}$  and  $(\partial \hat{p}/\partial V)_{T,\mu}$  in phase transition (see also the next example) and critical regions. Here our object is to examine an "ordinary point" (i.e., outside of phase transition and critical regions) analytically for first departures from macroscopic behavior.

For a macroscopic system we can use Stirling's approximation and replace  $\ln \Xi$  by  $\ln$  (maximum term in  $\Xi$ ). That is, there is essentially a  $\delta$  function at the maximum term when  $B \rightarrow \infty$ . When the system is not quite large enough for this procedure to be valid, we have to use

$$\ln N! = N \ln N - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi, \quad (25)$$

and replace the  $\delta$  function by a Gaussian distribution. This gives us the first-order departure from macroscopic behavior.

Define  $P = Q \exp(N\mu/kT)$ . Using Eqs. (23) and

(25), we have

$$\begin{aligned} \ln P &= B \ln B + \frac{1}{2} \ln B - N \ln N - \frac{1}{2} \ln N - \frac{1}{2} \ln 2\pi \\ &\quad - (B-N) \ln(B-N) - \frac{1}{2} \ln(B-N) \\ &\quad - (\alpha N^2/B) + (N\mu/kT), \end{aligned} \quad (26)$$

$$\begin{aligned} (\partial \ln P / \partial N)_{B,\mu,T} &= 0 = -\ln N^* - (2N^*)^{-1} + \ln(B-N^*) \\ &\quad + [2(B-N^*)]^{-1} + (\mu/kT) - (2\alpha N^*/B), \end{aligned} \quad (27)$$

$$\begin{aligned} (\partial^2 \ln P / \partial N^2)_{B,\mu,T} &= - (N^*)^{-1} + (2N^{*2})^{-1} - (B-N^*)^{-1} \\ &\quad + [2(B-N^*)^2]^{-1} - (2\alpha/B), \end{aligned} \quad (28)$$

where  $N^*$  is that value of  $N$  giving the maximum  $\ln P$ . Equation (27) provides us with  $N^*(B, \mu, T)$ . Then the desired Gaussian distribution is

$$P(N) = P(N^*) \exp[-\beta(N-N^*)^2],$$

where

$$\beta = -\frac{1}{2} (\partial^2 \ln P / \partial N^2)_{N=N^*}.$$

Equation (28) gives  $\beta$  as a function of  $N^*$ ,  $B$ ,  $T$ , and hence as a function of  $\mu$ ,  $B$ ,  $T$ , using  $N^*(B, \mu, T)$  from Eq. (27). It follows that

$$\begin{aligned} \Xi &= \int_{-\infty}^{+\infty} P(N^*) \exp[-\beta(N-N^*)^2] d(N-N^*) \\ &= P(N^*) \pi^{1/2} / \beta^{1/2}, \end{aligned}$$

or

$$\ln \Xi = \ln P(N^*) + \frac{1}{2} \ln \pi - \frac{1}{2} \ln \beta(N^*, B, T). \quad (29)$$

We can now use Eq. (10) and the thermodynamic equations of the present section to find any property of interest. For example, we obtain

$$\begin{aligned} \frac{\hat{p}}{kT} &= \ln \frac{B}{B-N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B-2N^*}{2B(B-N^*)} \\ &\quad - \frac{1}{2B} \ln \left[ \frac{B^2 + 2\alpha N^*(B-N^*)}{B^2} \right], \end{aligned} \quad (30)$$

$$\frac{p}{kT} = \ln \frac{B}{B-N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B-2N^*}{2B(B-N^*)}, \quad (31)$$

$$\frac{\bar{N}}{B} = \frac{N^*}{B} + \frac{B^2(B-2N^*)}{2[B^2 + 2\alpha N^*(B-N^*)]^2}. \quad (32)$$

Terms of order unity are placed first, followed by terms of order  $B^{-1}$ . The work here is not sufficient to obtain  $O(B^{-2})$ .

The macroscopic properties  $p^{(0)}$  and  $\bar{N}^{(0)}$  are given by

$$\frac{p^{(0)}}{kT} = \ln \frac{B}{B-N^0} + \frac{\alpha N^{02}}{B^2}, \quad \bar{N}^{(0)} = N^0, \quad (33)$$

where  $N^0(B, \mu, T)$  is determined by [see Eq. (27)]

$$0 = -\ln N^0 + \ln(B-N^0) + (\mu/kT) - (2\alpha N^0/B). \quad (34)$$

<sup>4</sup> T. L. Hill, J. Phys. Chem. **57**, 324 (1953); also reference 3, pp. 416-418. For a very recent statistical mechanical example, see J. L. Lebowitz and J. K. Percus, Phys. Rev. **124**, 1673 (1961).

One can then show that, contrary to the superficial appearance of Eq. (31),

$$p/kT = (p^{(0)}/kT) + O(B^{-2}), \quad (35)$$

whereas

$$\bar{p}/kT = (p^{(0)}/kT) + O(B^{-1}). \quad (36)$$

This is verified by Eq. (9b) which shows that if  $\bar{p}/kT$  has a term in  $B^{-1}$ , the  $B^{-1}$  term is missing in  $p/kT$ .

The above remarks suggest, incidentally, that in cases in which  $V$  can be varied continuously, and in which there are no "edge effects," excess functions [Eqs. (21)] may be expanded as follows:

$$\begin{aligned} S(\mu, V, T) &= V s^{(0)}(\mu, T) + s^{(1)}(\mu, T) \\ &\quad + (1/V) s^{(2)}(\mu, T) + \dots, \\ \bar{N} &= V n^{(0)} + n^{(1)} + (1/V) n^{(2)} + \dots, \\ \bar{E} &= V e^{(0)} + e^{(1)} + (1/V) e^{(2)} + \dots, \\ \bar{p} &= p^{(0)} + (1/V) \bar{p}^{(1)} + (1/V^2) \bar{p}^{(2)} + \dots, \\ p &= p^{(0)} - (1/V^2) \bar{p}^{(2)} + \dots. \end{aligned} \quad (37)$$

This leads to hierarchies of thermodynamic equations, one example of which is

$$\begin{aligned} e^{(0)} &= T s^{(0)} - p^{(0)} + \mu n^{(0)} \quad (\text{macroscopic}), \\ e^{(1)} &= T s^{(1)} - \bar{p}^{(1)} + \mu n^{(1)}, \\ e^{(2)} &= T s^{(2)} - \bar{p}^{(2)} + \mu n^{(2)} \\ &\vdots \\ &\vdots \end{aligned} \quad (38)$$

As a check on self-consistency we can calculate both sides of Eq. (19) for this model ( $V=B$ ) and obtain the result

$$B \left( \frac{\partial p}{\partial B} \right)_{T, \mu} = \frac{\alpha N^* (B - N^*) (B - 2N^*)}{[B^2 + 2\alpha N^* (B - N^*)]^2} = O(B^{-1}). \quad (39)$$

This order of magnitude is expected from Eqs. (37).

#### Example: Lattice Gas at a Phase Transition

We examine here first-order effects of "smallness" at a phase transition in an open system, using a lattice gas as a convenient model (the Bragg-Williams approximation is not introduced in this example).

For the macroscopic system ( $B \rightarrow \infty$ ) at  $T$ , suppose the densities ( $\bar{N}/B$ ) of the two phases in equilibrium are  $\rho_1$  and  $\rho_2$  ( $\rho_1 + \rho_2 = 1$  for a lattice gas). First-order effects will be exhibited in this case if  $P(N) = Q(N) \lambda^N$ , where  $\lambda = \exp(\mu/kT)$ , is taken as essentially two  $\delta$  functions at  $N = \rho_1 B$  and  $\rho_2 B$ . That is,

$$\Xi = Q(\rho_1 B, B, T) \lambda^{\rho_1 B} + Q(\rho_2 B, B, T) \lambda^{\rho_2 B}. \quad (40)$$

The next approximation would use two Gaussian distributions. Each phase associated with a  $\delta$  function should be treated "macroscopically," for self-con-

sistency. Thus we write

$$Q(\rho_1 B, B, T) = \exp(-A_1 B/kT),$$

$$Q(\rho_2 B, B, T) = \exp(-A_2 B/kT),$$

where  $A_1 = A_1$  (Helmholtz free energy)/ $B$ . Let  $\lambda_r = \exp(\mu_r/kT)$  ( $r$ =transition) be the value of  $\lambda$  at which  $\bar{N}/B = 1/2$  [the two terms in Eq. (40) are equal in this case]. Then

$$\exp(-A_1/kT) \lambda_r^{\rho_1} = \exp(-A_2/kT) \lambda_r^{\rho_2}.$$

Equation (40) can be rewritten as

$$\begin{aligned} \Xi &= [\exp(-A_1/kT) \lambda_r]^B (x^{\rho_1 B} + x^{\rho_2 B}) \\ &= \frac{1}{2} \exp(p_r B/kT) (x^{\rho_1 B} + x^{\rho_2 B}), \end{aligned} \quad (41)$$

where  $x = \lambda/\lambda_r$ , and  $p_r$  is defined by:  $\Xi = \exp(p_r B/kT)$  when  $\lambda = \lambda_r$ . Again for consistency, we regard all of the quantities  $\rho_1$ ,  $\rho_2$ ,  $A_1$ ,  $A_2$ ,  $\lambda_r$ , and  $p_r$  as functions of  $T$  only (two-phase equilibrium). We can now use Eq. (41) to obtain thermodynamic properties.

For example, we find

$$\bar{p}/kT = (p_r/kT) + B^{-1} \ln(x^{\rho_1 B} + x^{\rho_2 B}) - B^{-1} \ln 2, \quad (42)$$

$$\bar{N}/B = (\rho_1 x^{\rho_1 B} + \rho_2 x^{\rho_2 B}) / (x^{\rho_1 B} + x^{\rho_2 B}) \equiv \bar{p}, \quad (43)$$

$$x(\partial \bar{p} / \partial x)_{B, T} = [\langle \rho^2 \rangle_N - (\bar{p})^2] B, \quad (44)$$

$$p/kT = (p_r/kT) + \bar{p} \ln x. \quad (45)$$

Either Eq. (42) or (45) gives, for a macroscopic system near  $\mu = \mu_r$ ,

$$\begin{aligned} p^{(0)}/kT &= (p_r/kT) + \rho_2 \ln(\lambda/\lambda_r) \quad \lambda > \lambda_r, \\ &= (p_r/kT) + \rho_1 \ln(\lambda/\lambda_r) \quad \lambda < \lambda_r, \end{aligned} \quad (46)$$

which is what we should expect. At  $\bar{p} = 1/2$  ( $x=1$ ), Eq. (44) becomes

$$x \left( \frac{\partial \bar{p}}{\partial x} \right)_{B, T} = \left( \frac{\partial \bar{p}}{\partial \mu/kT} \right)_{B, T} = \left( \frac{\rho_1^2 + \rho_2^2}{2} - \frac{1}{4} \right) B = O(B). \quad (47)$$

Again, as a check, we can evaluate both sides of Eq. (19). We find

$$(\partial \bar{p} / \partial B)_{T, \mu} = [\langle \rho^2 \rangle_N - (\bar{p})^2] \ln x = O(1). \quad (48)$$

This is a much larger effect than in Eq. (39). Also,

$$\left( \frac{\partial \mu/kT}{\partial B} \right)_{p, T} = - \left( \frac{\partial \bar{p}}{\partial B} \right)_{T, \mu} \left( \frac{\partial \mu/kT}{\partial \bar{p}} \right)_{B, T} = - \frac{\ln x}{B} \left( \frac{\partial \ln x}{\partial B} \right)_{p, T}. \quad (49)$$

Integration of this equation simply leads to the conclusion that  $x^B$  is some function of  $\bar{p}$  and  $T$ , in agreement with Eq. (43).

Reference 4, which employs the Bragg-Williams approximation, serves as an illustration of these equations.

#### B. Small System with $p, N, T$

This is a closed one-component system in contact with a heat bath, and at pressure  $p$ . An example would



be a small colloidal particle or crystallite made up of  $N$  molecules. We consider a simple model of an incompressible crystallite in Sec. II D. Another example is a linear macromolecule made up of  $N$  monomers, each of which can exist in two or more states of different length (e.g., the helix-coil transition in natural and synthetic proteins and nucleic acids). Here  $V$  = length, which fluctuates, and  $p$  = force on chain = 0, since the chain has free ends in solution. As already mentioned in Sec. I, there is no experimental way to vary the force in this case. Alternatively, the different states may be regarded as different components, with an isomeric chemical equilibrium between them. If the macromolecule also binds<sup>1</sup> molecules or ions from a reservoir, we would have the set of environmental variables  $p$  (force),  $N$  (monomers),  $\mu'$  (bound ions),  $T$ . The effect of chain length ( $N$ ) on the helix-coil transition has been studied experimentally and theoretically.<sup>6</sup> The present paper, together with reference 1, provides the necessary machinery for a thermodynamic analysis of these results.

Solvent effects for a  $p, N, T$  system are discussed in Sec. III.

Formally this case is the same as that of Sec. II A because there are one extensive variable and two intensive variables (see Sec. V). We need only replace  $\mu$  by  $-\rho$ ,  $\bar{N}$  by  $\bar{V}$ ,  $-\rho$  by  $\mu$ ,  $-\bar{p}$  by  $\mu$ , and  $V$  by  $N$ . A few of the basic equations are

$$dE_i = TdS_i - pdV_i + \mu\bar{N}dN + Xd\bar{N}; \quad X = \rho N, \quad (50a)$$

$$E_i = TS_i - pV_i + \mu N\bar{N}, \quad (50b)$$

$$\bar{E} = TS - p\bar{V} + \mu N, \quad (51)$$

$$d(\bar{E} + p\bar{V}) = TdS + \bar{V}dp + \mu dN, \quad (52)$$

$$d(N\rho) = -SdT + \bar{V}dp + \mu dN, \quad (53)$$

$$d(N\rho - p\bar{V}) = -SdT - p d\bar{V} + \mu dN, \quad (54)$$

$$(\mu - \rho)dN = SdT - \bar{V}dp + Nd\mu, \quad (55)$$

$$d[(\mu - \rho)N] = SdT - \bar{V}dp + Nd\mu. \quad (56)$$

From the first of these equations we see that  $\mu$  is a chemical potential for a single molecule ( $\bar{N}$  constant) while  $\rho N$  is a chemical potential for a whole system ( $N$  constant). See also the discussion of Eq. (1) and Sec. III in this connection.

In the helix-coil type of system, one is interested in derivatives of the form  $(\partial\bar{V}/\partial N)_{T,p}$ , etc., where  $\bar{V}$  (length) is linearly related to helical content and approximately to optical rotation, etc. We find, for example,

$$\begin{aligned} (\partial\bar{V}/\partial N)_{T,p} &= (\partial\mu/\partial p)_{T,N}, \\ (\partial\bar{V}/\partial T)_{p,N} &= -(\partial S/\partial p)_{T,N}. \end{aligned} \quad (57)$$

<sup>6</sup> See, for example, P. Urnes and P. Doty, *Advances in Protein Chem.* **16**, 1961; R. F. Steiner and R. F. Beers, Jr., *Polynucleotides* (Elsevier Publishing Corporation, Amsterdam, 1961).

Combining these

$$(\partial T/\partial N)_{p,\bar{V}} = (\partial\mu/\partial S)_{T,N}. \quad (58)$$

Equations (57) are not useful (except with theoretical models) if  $p$  (force) cannot be varied (e.g.,  $p=0$  = constant).

A few further equations, of some interest for, say, a colloidal particle, are

$$(\partial\mu/\partial p)_{T,N} = \bar{V}/N, \quad (59)$$

$$(\partial\bar{V}/\partial N)_{T,p} = -(1/N)[\partial(\mu - \rho)/\partial p]_{T,N}, \quad (60)$$

$$[\partial(\bar{E} + p\bar{V})/\partial T]_{p,N} = T(\partial S/\partial T)_{p,N}. \quad (61)$$

See also Sec. II D.

Excess quantities may be defined by

$$S(p, N, T) = Ns^{(0)}(p, T) + s^{(r)}(p, N, T), \quad (62)$$

etc. Here  $s^{(0)}$  is the entropy per molecule and not per unit volume, as in Eq. (21). There is an example in Sec. II D.

The connection with statistical mechanics is

$$-\rho N = kT \ln \Delta, \quad (63)$$

where

$$\begin{aligned} \Delta(p, N, T) &= \sum_{E,V} \Omega(E, N, V) \exp(-E/kT) \\ &\times \exp(-pV/kT) \\ &= \sum_V Q(N, V, T) \exp(-pV/kT). \end{aligned}$$

### C. Small System with $N, V, T$

This is a closed system at constant volume (area, length, etc.), in contact with a heat bath at  $T$ . This case does not seem very important experimentally because of the difficulty of keeping  $N$  and  $V$  both constant. Hence we give only the basic equations.

The analog of Eq. (1) is

$$dE_i = TdS_i - p dV_i + \mu\bar{N}dN + Xd\bar{N}. \quad (64)$$

Then

$$E_i = TS_i + X\bar{N}, \quad X = \bar{E} - TS. \quad (65)$$

Because of this result, we use the symbol  $A$  for  $X$  below. We put  $\bar{E} - TS$  for  $X$  in Eq. (64) and get

$$d\bar{E} = TdS - p dV + \mu dN, \quad (66)$$

$$dA = -SdT - p dV + \mu dN. \quad (67)$$

Only for a macroscopic system does  $A = -pV + \mu N$ . The analog of Eqs. (14) and (56) is

$$d(\mu N - pV - A) = SdT - V dp + Nd\mu. \quad (68)$$

The connection with statistical mechanics is

$$-A = kT \ln Q. \quad (69)$$

D. Small System with  $N, T$ 

Here we consider a small colloidal particle (the system) which is incompressible. The system has  $N$  molecules and is in a heat bath at  $T$ . The volume  $V$  is not a separate variable:  $V$  is simply proportional to  $N$  with a constant proportionality factor. This is a degenerate form of cases  $B$  and  $C$  above.

Then

$$dE_t = TdS_t + \mu\mathfrak{N}dN + Xd\mathfrak{N}, \quad (70)$$

$$E_t = TS_t + X\mathfrak{N}, \quad (71)$$

$$A = \mu N = X = \bar{E} - TS_t, \quad (72)$$

$$d\bar{E} = TdS + \mu dN, \quad (73)$$

$$d(\mu N) = -SdT + \mu dN, \quad (74)$$

$$(\mu - \beta)dN = SdT + Nd\mu, \quad (75)$$

$$d[(\mu - \beta)N] = SdT + Nd\mu. \quad (76)$$

Thus, for example,

$$(\partial\mu/\partial T)_N = -(\partial S/\partial N)_T,$$

$$(\partial\mu/\partial T)_N = -S/N, \quad (77)$$

$$(\partial\mu/\partial N)_T = (\mu - \beta)/N, \quad \mu = [\partial(\mu N)/\partial N]_T, \quad (78)$$

$$-S = [\partial(\mu N)/\partial T]_N = \{\partial[(\mu - \beta)N]/\partial T\}_N. \quad (79)$$

Equation (69) relates statistical mechanics to thermodynamics.

*Example: Incompressible Einstein Crystallite*

This example is a very trivial one mathematically but it is a first approximation to an important class of applications (see, for example, Sec. IV).

Consider an "Einstein crystal" sufficiently small so that surface effects enter. For simplicity the crystal is assumed incompressible. The independent variables are  $N$  and  $T$  ( $V$  is proportional to  $N$ ; see above). The partition function  $Q$  is assumed to have the simple form

$$Q = j(T)^N \{\exp[-\epsilon(T)/kT]\}^N \exp[-a(T)N^{\frac{1}{2}}/kT]. \quad (80)$$

The factor  $j(T)$  is a vibrational partition function,  $\epsilon(T)$  is an average neighbor interaction free energy, and the term  $a(T)N^{\frac{1}{2}}$  is a surface free energy (with  $a > 0$ ;  $a$  has the order of magnitude of the surface tension multiplied by the square of the nearest-neighbor distance).

We find from Eqs. (69), (72), (74), and (80) that

$$\mu = -kT \ln j + \epsilon + aN^{-\frac{1}{2}}, \quad (81)$$

$$\mu = -kT \ln j + \epsilon + \frac{1}{2}aN^{-\frac{1}{2}}, \quad (82)$$

$$S = N[k \ln j + kT(d \ln j/dT) - d\epsilon/dT] - N^{\frac{1}{2}}(da/dT), \quad (83)$$

$$\bar{E} = N[kT^2(d \ln j/dT) + \epsilon - T(d\epsilon/dT)] + N^{\frac{1}{2}}[a - T(da/dT)]. \quad (84)$$

Equations (77)–(79) can all be verified with these functions.

Excess functions may be defined as follows:

$$S(N, T) = Ns^{(0)}(T) + s^{(s)}(N, T),$$

$$\bar{E} = Ne^{(0)} + e^{(s)},$$

$$N\mu = N\mu^{(0)} + \mu^{(s)},$$

$$N\mu = N\mu^{(0)} + \mu^{(s)} = N\mu^{(0)} + N(\partial\mu^{(s)}/\partial N)_T. \quad (85)$$

These functions in the present example are

$$s^{(s)} = -N^{\frac{1}{2}}(da/dT), \quad e^{(s)} = N^{\frac{1}{2}}[a - T(da/dT)],$$

$$\mu^{(s)} = aN^{\frac{1}{2}}, \quad \mu^{(s)} = \frac{1}{2}aN^{\frac{1}{2}}. \quad (86)$$

Examples of equations connecting the excess functions are

$$\mu^{(s)} = e^{(s)} - Ts^{(s)},$$

$$d\mu^{(s)} = -s^{(s)}dT + (\mu^{(s)}/N)dN. \quad (87)$$

We might digress at this point to summarize what the examples considered so far indicate concerning orders of magnitude of nonmacroscopic terms. First, consider a quantity such as  $E/kT$  or  $N\mu/kT$  (i.e., an energy or free-energy term divided by  $kT$ ). The macroscopic magnitude is  $O(N)$ . As to "edge effects": in three dimensions the magnitude is  $O(N^{\frac{1}{2}})$ ; in two dimensions,  $O(N^{\frac{1}{2}})$ ; and in one dimension,  $O(1)$ . The "pure" small-number effect (no edges) is  $O(1)$  [see Eq. (37), for example]. Translation and rotation give  $O(\ln N)$ . Second, consider a quantity such as  $\partial(\mu/kT)/\partial N$ , with intensive properties constant. The macroscopic value is zero. At a first-order phase transition we have  $O(N^{-1})$  [see Eq. (49)]. For edge effects: in three dimensions,  $O(N^{-\frac{1}{2}})$ ; in two dimensions,  $O(N^{-\frac{1}{2}})$ ; in one dimension,  $O(N^{-2})$ . The pure small-number effect is  $O(N^{-2})$ .

E. Small System with  $N, E, V$ 

Cases A to D above are all examples of systems which are partially "open" and partially "closed." That is, some of the environmental variables are extensive ("closed") and some are conjugate intensive ("open") variables. In E and F we consider the two extreme cases (for a one-component system): completely closed (i.e., "isolated," with environmental variables  $N, E, V$ ); and completely open (environmental variables  $\mu, T, p$ ).

The analog of Eq. (1) for an ensemble of isolated systems, each with  $N, E, V$ , is

$$\mathfrak{N}dE = TdS_t - p\mathfrak{N}dV + \mu\mathfrak{N}dN + Xd\mathfrak{N}. \quad (88)$$

Here,  $S_t$  is a linear homogeneous function of  $\mathfrak{N}$  when  $E, V$ , and  $N$  are held constant. Therefore,

$$0 = TS_t + X\mathfrak{N}, \quad X = -TS. \quad (89)$$

Equation (88) then becomes

$$dE = TdS - pdV + \mu dN, \quad (90)$$

$$dS = (1/T)dE + (p/T)dV - (\mu/T)dN. \quad (91)$$

The connection with statistical mechanics is  $S = k \ln \Omega(E, N, V)$ . In general,  $E \neq TS - pV + \mu N$ . Also,

$$d(TS - pV + \mu N - E) = SdT - Vdp + Nd\mu, \quad (92)$$

or

$$d\left(S - \frac{pV}{T} + \frac{\mu N}{T} - \frac{E}{T}\right) = -Ed\left(\frac{1}{T}\right) - Vd\left(\frac{p}{T}\right) + Nd\left(\frac{\mu}{T}\right). \quad (93)$$

Legendre transformations can be used to obtain other sets of independent variables

$$d\left(S - \frac{E}{T}\right) = -Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu}{T}dN, \quad (94)$$

$$d\left(S - \frac{E}{T} + \frac{\mu N}{T}\right) = -Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV + Nd\left(\frac{\mu}{T}\right), \quad (95)$$

and so forth. Many Maxwell relations follow from these equations. For example, from Eq. (91),

$$-\left[\partial(\mu/T)/\partial V\right]_{E,N} = \left[\partial(p/T)/\partial N\right]_{E,V}. \quad (96)$$

#### Example: Ideal Lattice Gas

Let us consider a very simple example of an isolated system: an ideal lattice gas with no internal degrees of freedom. This is the same as the model in Eq. (23), taking  $j=1$  and  $\alpha=0$ . The energy of this system is constant:  $E = \text{constant} = 0$ . The partition function is

$$\Omega(N, B) = B! / N! (B-N)!. \quad (97)$$

To find first-order "smallness" effects, we keep terms of order unity in  $\ln \Omega$

$$S/k = \ln \Omega = B \ln B - N \ln N - (B-N) \ln (B-N) - \frac{1}{2} \ln [2\pi N (B-N)/B]. \quad (98)$$

From Eq. (91),

$$-\frac{\mu}{kT} = \left(\frac{\partial S/k}{\partial N}\right)_B = \ln \frac{B-N}{N} + \frac{2N-B}{2N(B-N)}, \quad (99)$$

$$\frac{p}{kT} = \left(\frac{\partial S/k}{\partial B}\right)_N = \ln \frac{B}{B-N} - \frac{N}{2B(B-N)}, \quad (100)$$

and hence

$$\frac{S}{k} - \frac{pB}{kT} + \frac{\mu N}{kT} = \frac{1}{2} - \frac{1}{2} \ln \frac{2\pi N (B-N)}{B}. \quad (101)$$

Using these results we can verify for example, Eq. (96)

and

$$N = \left[ \frac{\partial [(S/k) - (pB/kT) + (\mu N/kT)]}{\partial (\mu/kT)} \right]_{p/kT} = \left[ \frac{\partial [(S/k) + (\mu N/kT)]}{\partial (\mu/kT)} \right]_B. \quad (102)$$

#### F. Small System with $\mu, T, p$

We consider a "completely open" one-component system. Examples are: a colloidal aggregate in a solvent at  $p$  and  $T$ ; the solvent containing molecules of the aggregate at  $\mu$ ; or a liquid-like cluster of molecules in a gas near the critical point.

Instead of Eq. (1), we have

$$dE_i = TdS_i - pdV_i + \mu dN_i + Xd\mathfrak{N}_i, \quad (103)$$

and hence,

$$E_i = TS_i - pV_i + \mu N_i + X\mathfrak{N}_i, \\ X = E - TS + pV - \mu N, \quad (104)$$

$$dE = TdS - pdV + \mu dN, \quad (105)$$

$$d(-X) = SdT - \bar{V}dp + \bar{N}d\mu, \quad (106)$$

$$d(-X/T) = -\bar{E}d(1/T) - \bar{V}d(p/T) + \bar{N}d(\mu/T). \quad (107)$$

Other independent variables can be introduced by Legendre transformations, as usual.

The relation to statistical mechanics is

$$-X = kT \ln \mathfrak{T}, \quad (108)$$

$$\mathfrak{T} = \sum_{E,N,V} \Omega(E, N, V) \exp(-E/kT) \exp(-pV/kT) \\ \times \exp(N\mu/kT), \quad (109)$$

$$= \sum_V \Xi(\mu, V, T) \exp(-pV/kT), \quad (110)$$

$$= \sum_N \Delta(p, N, T) \exp(N\mu/kT). \quad (111)$$

This partition function requires special care when used with a macroscopic system,<sup>6</sup> basically because of the fact that  $T, p$ , and  $\mu$  cannot all be independent. But we have already seen with other environments [Eqs. (14), (56), (68), and (92)] that  $T, p$ , and  $\mu$  can be independent in the thermodynamics of small systems. We might therefore anticipate that there is no special difficulty in applying  $\mathfrak{T}$  to a completely open small system, and this proves to be the case.

#### Example: Incompressible Einstein Crystallite

This is the same model as in Sec. II D. We have

$$\mathfrak{T}(\mu, T) = \sum_N Q(N, T) \exp(N\mu/kT), \\ = \sum_N \exp[-N(\bar{\mu} - \mu)/kT], \\ = \sum_N \exp\{-N[\mu^{(0)}(T) - \mu]/kT\} \\ \times \exp[-\bar{\mu}^{(2)}(N, T)/kT], \quad (112)$$

<sup>6</sup> See reference 3, pp. 71-75 and Appendixes 2 to 4.

where  $\mu^{(0)}$  and  $\mu^{(a)}$  are given by Eqs. (81), (85), and (86). It should be emphasized that  $\mu$  is an assigned constant here—this is not the  $\mu$  of Eq. (82). If we choose  $\mu > \mu^{(0)}(T)$  (the macroscopic chemical potential at  $T$ ), the first exponential dominates for large  $N$ , the sum diverges, and  $\bar{N} \rightarrow \infty$ . Hence it is not possible to have a stable "open" small crystallite with  $\mu > \mu^{(0)}$ . We must therefore take  $\mu \leq \mu^{(0)}$ . We define  $\delta$  and  $\alpha$  by

$$\delta(\mu, T) = [\mu^0(T) - \mu]/kT \geq 0, \quad \alpha(T) = a(T)/kT > 0.$$

In order to obtain crystallites of reasonable size we have to choose  $\delta$  very small. In fact, we confine ourselves to the case  $\delta \rightarrow 0+$ . This means we are examining "open" crystallites which are in equilibrium with the bulk phase. Such crystallites are analogous to clusters in the saturated vapor phase in equilibrium with a liquid. But even with a saturated vapor the clusters will be sizeable only near the critical temperature where the surface tension is very small. The metastable equilibrium of a supersaturated vapor and liquid drop is discussed in Sec. IV.

Equation (112) becomes

$$\begin{aligned} T(\mu, T) &= \int_0^\infty (1 - \delta N) \exp(-\alpha N^{\frac{1}{2}}) dN \\ &= (3\pi^{\frac{1}{2}}/4\alpha^{\frac{1}{2}}) - (3\delta/\alpha^{\frac{1}{2}}). \end{aligned} \quad (113)$$

Then, from Eq. (107),

$$\bar{N} = \left( \frac{\partial \ln T}{\partial \mu / kT} \right)_T = \left( \frac{\partial \ln T}{\partial \delta} \right)_\alpha \left( \frac{\partial \delta}{\partial \mu / kT} \right)_T = \frac{4}{\pi^{\frac{1}{2}} \alpha^{\frac{1}{2}}}. \quad (114)$$

Thus  $T = 3\pi\bar{N}/16$ . The same result for  $\bar{N}$  follows from

$$\bar{N} = \frac{\int_0^\infty N \exp(-\alpha N^{\frac{1}{2}}) dN}{\int_0^\infty \exp(-\alpha N^{\frac{1}{2}}) dN}. \quad (115)$$

According to Eq. (114),  $\bar{N} = O(kT/\gamma r^{\frac{1}{2}})^{\frac{1}{2}}$ , where  $\gamma$  is the surface tension and  $r^{\frac{1}{2}}$  is the nearest-neighbor distance. The mean crystallite size increases with decreasing  $\gamma$ , as expected. We also note for use below, that a calculation as in Eq. (115) gives

$$\langle N^{\frac{1}{2}} \rangle_m = 3/2\alpha. \quad (116)$$

In general for this model  $\bar{N}$  (and  $\langle N^{\frac{1}{2}} \rangle_m$ ) would be a function of  $\mu$  and  $T$ , but we have taken  $\mu \rightarrow \mu^{(0)}(T)$  so  $\bar{N}$  is a function of  $T$  only.

The above results illustrate the fact that a complete set of intensive variables (in this case  $\mu$  and  $T$ ) can determine the extensive variables (e.g.,  $\bar{N}$  above) of a small system. In the case of a macroscopic system, there is one less intensive variable in a complete set, and these cannot determine extensive variables (the system can have any size).

Equation (113) for  $T$  and

$$-E = \left( \frac{\partial \ln T}{\partial 1/kT} \right)_{\mu/kT} \quad (117)$$

lead to

$$\begin{aligned} E &= \bar{N} [kT^2(d \ln j/dT) + \epsilon - T(d\epsilon/dT)] \\ &\quad + \langle N^{\frac{1}{2}} \rangle_m [a - T(da/dT)]. \end{aligned} \quad (118)$$

This result also follows immediately from Eq. (84). For, if we denote the average energy in Eq. (84) by  $E^E$  (the superscript  $E$  means averaging has been carried out over  $E$ ), then

$$\begin{aligned} E(\mu, T) &\equiv E^{E, N} = T^{-1} \sum_N \exp(N\mu/kT) \sum_E E \Omega(N, E) \\ &\quad \times \exp(-E/kT) \\ &= \frac{\sum_N E^E(N, T) \exp[-N(\bar{\mu} - \mu)/kT]}{\sum_N \exp[-N(\bar{\mu} - \mu)/kT]}. \end{aligned} \quad (119)$$

Substitution of Eq. (84) for  $E^E$  in Eq. (119) gives Eq. (118).

Equations (84) and (118) for the energy illustrate the fact that thermodynamic properties of small systems are different in different environments. For if in Eq. (84) we choose the same  $T$  as here and choose  $\bar{N}$  there equal to the  $\bar{N}$  here, then the two energies differ because  $\langle \bar{N}^{\frac{1}{2}} \rangle_m \neq \langle N^{\frac{1}{2}} \rangle_m$ .

The entropy is, from Eq. (104),

$$\begin{aligned} S &= (E/T) - (\mu^{(0)}/\bar{N}T) + k \ln T \\ &= \bar{N} [k \ln j + kT(d \ln j/dT) - d\epsilon/dT] - \langle N^{\frac{1}{2}} \rangle_m (da/dT) \\ &\quad + k \ln(3\pi\bar{N}/16) + \langle N^{\frac{1}{2}} \rangle_m (a/T). \end{aligned} \quad (120)$$

This result also follows from  $S = (\partial kT \ln T / \partial T)_\mu$ , using Eq. (113) for  $T$ . If we take the same  $T$  and choose  $\bar{N}$  in Eq. (83) equal to the  $\bar{N}$  here, the entropy in Eq. (120) is larger than that of Eq. (83). This is always to be expected<sup>7</sup> when passing from a given environment to a more open environment. The effect is negligible for a macroscopic system, of course.

#### Example: Ideal Lattice Gas

This is the same model as in Sec. II E. We have

$$T = \sum_{B=0}^{\infty} \sum_{N=0}^B \frac{B!}{N!(B-N)!} \exp(mN) \exp(-\phi B),$$

where  $m = \mu/kT$  and  $\phi = p/kT$ . It is most convenient to sum first over  $N$

$$T = \sum_{B=0}^{\infty} (1 + e^m)^B \exp(-\phi B). \quad (121)$$

<sup>7</sup> See reference 3, pp. 75-76 and E. A. Guggenheim, *Research* 2, 450 (1949).

In this very special case

$$\Xi = \exp(\bar{p}B/kT) = (1 + \epsilon^*)^B = \exp(\bar{p}^{(0)}B/kT) \\ = \exp(\phi^{(0)}B) \quad (122)$$

has no "excess" factor as in Eq. (112);  $\bar{p}$  is the same (for any  $B$ ) as the macroscopic  $\bar{p}^{(0)}$ . This is because each site is independent (and contributes a factor  $1 + \epsilon^*$  to  $\Xi$ ). Then

$$\Upsilon(m, \phi) = \sum_{B=0}^{\infty} \exp[-(\phi - \phi^{(0)})B] \\ = \{1 - \exp[-(\phi - \phi^{(0)})]\}^{-1} \quad (123)$$

converges and will lead to a finite  $\bar{B}$  (small system) if  $\phi$  is chosen so that  $\phi > \phi^{(0)}$ . If  $\phi \leq \phi^{(0)}$ , a small system cannot exist ( $\bar{B} \rightarrow \infty$ ).

If we sum first over  $B$ , the second sum (over  $N$ ) converges if  $m$  is chosen less than  $m^{(0)}(\phi)$ , and Eq. (123) is again obtained. In this case  $N\bar{p}/kT$  contains an excess function:  $\bar{p}^{(ex)}/kT = \ln(1 - \epsilon^*)$ .

From Eq. (107) we find

$$\bar{B}(\phi, m) = -\left(\frac{\partial \ln \Upsilon}{\partial \phi}\right)_m = \frac{\exp[-(\phi - \phi^{(0)})]}{1 - \exp[-(\phi - \phi^{(0)})]} \quad (124)$$

and

$$\bar{N}(\phi, m) = \left(\frac{\partial \ln T}{\partial m}\right)_\phi = \frac{\bar{B}(\phi, m)\epsilon^*}{1 + \epsilon^*} = \bar{B}[1 - \exp(-\phi^{(0)})]. \quad (125)$$

Hence  $T = 1 + \bar{B}$ . This result for  $\bar{N}/\bar{B}$  is the same as for a macroscopic system (any ensemble). To obtain a sizeable  $\bar{B}$ , we need  $\phi - \phi^{(0)} \ll 1$ . Then  $\bar{B} = (\phi - \phi^{(0)})^{-1}$ . The entropy is

$$S/k = \phi \bar{B} - m \bar{N} + \ln T \\ = (1 + \bar{B}) \ln(1 + \bar{B}) - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln(\bar{B} - \bar{N}). \quad (126)$$

This is an exact expression (no Stirling approximation, etc.). It is of interest to compare this with the entropy from other environments. For the  $\mu, B$  case:

$$S/k = (\bar{p}B/kT) - (\mu \bar{N}/kT) = B \ln B - \bar{N} \ln \bar{N} \\ - (\bar{B} - \bar{N}) \ln(\bar{B} - \bar{N}), \quad (127)$$

also without approximation. Equation (98) gives  $S/k$  in the  $N, B$  case to  $O(1)$ . As expected,  $S/k$  increases in the order  $N, B; \mu, B; \mu, p$ .

One needs, in general, to use<sup>1</sup> difference as well as differential relations when applying thermodynamics to very small systems with environmental variables which include one or more extensive properties (e.g., in a  $\mu, B, T$  lattice gas system there is a discrete difference between, say,  $B=9$  and  $B=10$ ). One special feature which is associated only with a completely open system is that all the variables  $\mu, p, T, \bar{N}, \bar{V}, \bar{E}, S$  vary smoothly, even for systems which are very

small on the average. As an example of this, we consider the present model when  $\phi - \phi^{(0)} \gg 1$  so that  $B = \exp[-(\phi - \phi^{(0)})] \ll 1$ . Equation (125) is unchanged and Eq. (126) becomes

$$S/k = \bar{B} - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln(\bar{B} - \bar{N}). \quad (128)$$

Only the first few terms in  $T$  need be retained

$$T = 1 + \epsilon^* + \epsilon^* \epsilon^*. \quad (129)$$

The probabilities  $p_{NB}$  of the various states are

$$p_{00} = 1/T = 1 - \bar{B}, \quad p_{01} = \epsilon^*/T = \bar{B} - \bar{N}, \\ p_{11} = \epsilon^* \epsilon^*/T = \bar{N}. \quad (130)$$

We can then verify that [see Eq. (4)]

$$S/k = - (p_{00} \ln p_{00} + p_{01} \ln p_{01} + p_{11} \ln p_{11}) \quad (131)$$

also gives Eq. (128).

### Statistical Mechanical Summary

We supplement the two examples above with the following summary. In a  $\mu, p, T$  system, if the last sum is over, say,  $V$  as in Eq. (110), we have

$$T = \sum_V \exp\left\{\frac{[\bar{p}^{(0)}(\mu, T) - p]V}{kT}\right\} \exp\left(\frac{\bar{p}^{(ex)}(\mu, T, V)}{kT}\right). \quad (132)$$

The first factor dominates for large  $V$ . A stable small system is therefore possible ( $T$  converges) if  $p$  is chosen so that  $p > \bar{p}^{(0)}(\mu, T)$ . Such a system is not possible if  $p < \bar{p}^{(0)}(V \rightarrow \infty)$ . The behavior at  $p = \bar{p}^{(0)}$  depends on the particular case. The choice of the last variable over which to sum is obviously arbitrary. If the last sum is over  $N$ , the sufficient condition for convergence is  $\mu < \mu^{(0)}(p, T)$ . If the last sum is over  $E$ , it is  $T < T^{(0)}(\mu, p)$ . It is easy to show that if values of  $\mu, p$ , and  $T$  are chosen so that  $p > \bar{p}^{(0)}(\mu, T)$ , then it will also be true that  $\mu < \mu^{(0)}(p, T)$  and  $T < T^{(0)}(\mu, p)$ . If the surface  $\mu^{(0)}(p, T)$  is drawn in a  $p, T, \mu$  coordinate system ( $\mu$  increases in the upward direction), then  $T$  converges for points under this surface and possibly on it, but not above it.

### G. General Treatment

We have given a separate analysis for each environment in Secs. IIA through IIF. This is a natural and illuminating approach since: (a) The values of the thermodynamic functions are in general different for each environment; (b) a particular set of independent variables (i.e., the environmental variables) has unique importance operationally and theoretically; (c) a particular statistical mechanical partition function must be used (instead of having an option, as in macroscopic statistical mechanics); and (d) Secs. III through V require this type of treatment.

However, it is possible to give a single, alternative,



general development, applicable to all environments. This also has obvious advantages. We merely show the starting point here and leave details to another publication.<sup>1</sup>

In the basic Eqs. (1), (50a), (64), (70), and (88), we add systems to the ensemble, in defining  $X$ , holding the parameters (nonfluctuating extensive variables) constant. Here we add systems to the ensemble, for any environment, as in Eq. (103). We omit bars over  $E$ ,  $V$ , and  $N$  in order to have a single notation for all cases. With or without bars we have, of course,

$$E_i = E\mathfrak{N}_i, \quad V_i = V\mathfrak{N}_i, \quad N_i = N\mathfrak{N}_i, \quad S_i = S\mathfrak{N}_i.$$

Thus, we write

$$dS_i = (1/T)dE_i + (p/T)dV_i - (\mu/T)dN_i + \delta d\mathfrak{N}_i,$$

or

$$dE_i = TdS_i - pdV_i + \mu dN_i + \epsilon d\mathfrak{N}_i,$$

where

$$\begin{aligned} \delta &= (\partial S_i / \partial \mathfrak{N}_i)_{E_i, V_i, N_i}, & \epsilon &= (\partial E_i / \partial \mathfrak{N}_i)_{S_i, V_i, N_i}, \\ s &= -\epsilon / T. \end{aligned}$$

In defining  $\delta$ , systems are added to the ensemble holding  $E_i$ ,  $V_i$ , and  $N_i$  constant. Hence  $E$ ,  $V$ , and  $N$  are decreased as  $\mathfrak{N}$  increases. The ensemble is "divided into smaller pieces" keeping the total energy, volume, and number of molecules the same. On integration,

$$E_i = TS_i - pV_i + \mu N_i + \epsilon \mathfrak{N}_i,$$

$$E = TS - pV + \mu N + \epsilon,$$

$$S = (1/T)E + (p/T)V - (\mu/T)N + \delta.$$

Also,

$$dE = TdS - pdV + \mu dN,$$

$$d\epsilon = -SdT + Vdp - Nd\mu,$$

$$d\delta = -Ed(1/T) - Vd(p/T) + Nd(\mu/T).$$

The functions  $\epsilon$  and  $\delta$  vanish for a macroscopic system.

If the environmental variables are, say,  $\mu$ ,  $V$ , and  $T$ , then we would be especially interested in the equation

$$d(\epsilon - pV) = -SdT - pdV - Nd\mu.$$

Clearly  $\epsilon = (p - \bar{p})V$ . For an  $N$ ,  $p$ ,  $T$  system,  $\epsilon = (\bar{p} - \mu)N$ , etc.

### III. SOLVENT EFFECTS

If the thermodynamic equations of the preceding section are applied to experimental data on, say, a macromolecule or colloidal particle in a solvent, the question arises as to the exact meaning of the thermodynamic functions. We examine this point here. We give details for only one case to illustrate the procedure.

If the small system is immersed in a solvent, the system will have the pressure and temperature of the solvent. Therefore,  $p$  and  $T$  ordinarily will be two of

the environmental variables. By the same token,  $V$  and  $E$  are not possible as environmental variables. As an approximation, one might, however, completely omit the pair  $p$ ,  $V$  [see Eq. (73) for example] or even  $E$ ,  $T$  [see Eq. (121) for example].

The variables of most interest in simple cases are then  $p$ ,  $T$ ,  $N$  or  $p$ ,  $T$ ,  $\mu$ . If, in addition, there is binding of another species ( $N'$ ,  $\mu'$ ) on a macromolecule the variables would be  $p$ ,  $T$ ,  $N$  or  $\mu$ ,  $N'$  or  $\mu'$ . If the macromolecule is made up of monomers which can exist in states of, say, different length we would add  $f$  or  $l$  (force, length) to the above list. The choice of most interest would be  $f = \text{constant} = 0$ .

As an example we treat a  $p$ ,  $T$ ,  $N$  system in a one-component solvent. We consider a solution of  $\mathfrak{N}$  of these systems in a solvent characterized by  $p$ ,  $T$ ,  $N_1$ . The small systems are "infinitely dilute" in the solvent, but  $\mathfrak{N}$  is a very large number. The systems in the present "ensemble" have translational motion. From ordinary solution thermodynamics we then have

$$dE_T = TdS_T - pdV_T + \mu_1 dN_1 + \mu_s d\mathfrak{N} + \mu \mathfrak{N} dN. \quad (133)$$

In this equation,  $N$  is regarded as a parameter and  $\mu$  is defined by  $\mu \mathfrak{N} = \partial E_T / \partial N$ . The subscript  $T$  (total now including the solvent) refers to the whole solution  $T$ ,  $p$ ,  $N_1$ ,  $\mathfrak{N}$ ; the subscript  $s$  means "small system." Now consider the same solvent ( $p$ ,  $T$ ,  $N_1$ ) but with no "small systems" present ( $\mathfrak{N} = 0$ ):

$$dE_s = TdS_s - pdV_s + \mu_1 dN_1 \quad (s = \text{solvent}). \quad (134)$$

In Eqs. (133) and (134) we have (dilute solution)

$$E_T = N_1 E_1(p, T) + \mathfrak{N} \bar{E}^0(N, p, T),$$

$$S_T = N_1 S_1(p, T, \mathfrak{N}/N_1) + \mathfrak{N} \bar{S}^0(N, p, T, \mathfrak{N}/N_1),$$

$$V_T = N_1 V_1(p, T) + \mathfrak{N} \bar{V}^0(N, p, T),$$

$$E_s = N_1 E_1, \quad S_s = N_1 S_1, \quad V_s = N_1 V_1. \quad (135)$$

The quantities  $E_1$ ,  $S_1$ , and  $V_1$  are properties of the pure solvent;  $\bar{E}^0$ , etc., are partial molal quantities at infinite dilution. Further, we have (dilute solution)

$$\mu_1 = \mu_1(p, T) - (\mathfrak{N} k T / N_1),$$

$$\bar{S}_1 = S_1(p, T) + (\mathfrak{N} k / N_1),$$

$$\bar{S}^0 = S(N, p, T) - k \ln(\mathfrak{N}/N_1),$$

$$\mu_s = \bar{E}^0 = N \bar{\mu}(N, p, T) + k T \ln(\mathfrak{N}/N_1), \quad (136)$$

where  $S$  and  $\bar{\mu}$  are defined by these equations. This is the essential step, which separates out the divergent terms in  $\ln(\mathfrak{N}/N_1)$  from  $\bar{S}^0$  and  $\mu_s$ . The remaining quantities,  $S$  and  $N\bar{\mu}$ , are functions of  $N$ ,  $p$ , and  $T$  only (they also depend on the choice of solvent), and may be regarded as "intrinsic" properties of a small system. These are the properties of interest to us. Also, at this point we introduce the symbol  $\bar{E}$  for  $\bar{E}^0$  and  $\bar{V}$  for  $\bar{V}^0$ . We now subtract Eq. (134) from Eq. (133)

and obtain

$$d(\mathcal{H}\tilde{E}) = Td[\mathcal{H}S - \mathcal{H}k \ln(\mathcal{H}/N_1) + \mathcal{H}k] - p d(\mathcal{H}\tilde{V}) \\ - (\mathcal{H}kT/N_1)dN_1 + [\mu N + kT \ln(\mathcal{H}/N_1)]d\mathcal{H} + \mu dN.$$

After cancellation of terms, this gives

$$d(\mathcal{H}\tilde{E}) = Td(\mathcal{H}S) - p d(\mathcal{H}\tilde{V}) + \mu dN + \mu \mathcal{H} dN. \quad (137)$$

From Eqs. (133) and (134) we also have

$$E_T = TS_T - pV_T + \mu_1 N_1 + \mu_2 \mathcal{H},$$

$$E_s = TS_s - pV_s + \mu_1(s)N_1,$$

and then, after subtraction and cancellation,

$$\tilde{E} = TS - p\tilde{V} + \mu N. \quad (138)$$

This result also follows directly from Eq. (137). Substitution of this expression for  $\mu N$  in Eq. (137) gives

$$d\tilde{E} = TdS - p d\tilde{V} + \mu dN. \quad (139)$$

Thus we have arrived at equations which are formally identical with (50) and (51), even though solvent is present. The above discussion is necessary to establish the significance of  $E$ ,  $S$ ,  $\tilde{V}$ ,  $\mu$ , and  $\rho$  in the presence of solvent.

We emphasize that there are two distinct thermodynamic levels here: Eq. (133) refers to a macroscopic dilute binary solution of "small systems" (macromolecules, colloidal particles, etc.) in a solvent; Eqs. (138) and (139) refer to a single small system (including interaction with solvent). The latter equations themselves go over into macroscopic thermodynamic equations if the small system becomes indefinitely large.

#### IV. SPHERICAL DROPS OR BUBBLES

This is a rather special topic which has some features in common with both Secs. II and III. Also, this discussion provides a link between the general approach to small system thermodynamics which we have outlined here and earlier work, beginning with Gibbs, on the thermodynamics of curved interfaces.<sup>8-10</sup>

To be specific, we use the language of "drop in vapor" but the equations apply as well to "bubble in liquid."

Consider a spherical drop in a spherical container of volume  $V$ . The center of mass of the drop is imagined restrained to the origin ( $r=0$ ). The drop is in contact with a supersaturated (metastable) vapor characterized by  $T$ ,  $\mu_1$ ,  $\mu_2$ , ... These variables completely determine the nature of the drop. There is a continuous transition, at the interface, from drop to vapor. There is no restriction on the size of the drop; it may

be so small that properties of bulk liquid (at  $T$ ,  $\mu_1$ ,  $\mu_2$ , ...) do not obtain even at  $r=0$ . The volume  $V$  is taken as macroscopic and large enough so that properties of bulk metastable vapor (at  $T$ ,  $\mu_1$ ,  $\mu_2$ , ...) are reached at least at the periphery of  $V$ ; otherwise  $V$  is arbitrary. The pressure at the periphery is  $p$  (determined by  $T$ ,  $\mu_1$ ,  $\mu_2$ , ...).

Now consider, as in Sec. II, an ensemble of  $\mathcal{H}$  of these open systems [compare Eq. (1)]:

$$dE_i = TdS_i - p dV_i + \sum \mu_i dN_{i,i} + W d\mathcal{H}, \quad (140)$$

where  $W = (\partial E_i / \partial \mathcal{H})_{S_i, V_i, N_{i,i}}$ . Integration at constant  $T$ ,  $\mu_i$ ,  $V$  gives

$$E_i = TS_i + \sum \mu_i N_{i,i} + W\mathcal{H},$$

or

$$W = \tilde{E} - TS - \sum \mu_i \tilde{N}_i. \quad (141)$$

We can define  $\tilde{p}$  by  $W = -\tilde{p}V$ . Substitution of Eq. (141) in Eq. (140) yields

$$d\tilde{E} = TdS - p dV + \sum \mu_i d\tilde{N}_i. \quad (142)$$

Now consider, for reference,  $\mathcal{H}$  systems containing the same vapor at  $T$ ,  $\mu_i$  but with no drop in the center. (Actually, since such a system is macroscopic and homogeneous, it would suffice to treat only one system.) Then, with obvious notation,

$$dE_i^0 = TdS_i^0 - p dV_i^0 + \sum \mu_i dN_{i,i}^0 + W^0 d\mathcal{H},$$

$$W^0 = -pV = E^0 - TS^0 - \sum \mu_i \tilde{N}_i^0, \quad (143)$$

$$dE^0 = TdS^0 - p dV + \sum \mu_i d\tilde{N}_i^0. \quad (144)$$

If we subtract Eqs. (143) and (144) from Eqs. (141) and (142), we obtain

$$W' = W - W^0 = (p - \tilde{p})V = \tilde{E}' - TS' - \sum \mu_i \tilde{N}_i', \quad (145)$$

$$d\tilde{E}' = TdS' + \sum \mu_i d\tilde{N}_i', \quad (146)$$

in obvious notation. These primed functions are characteristic of the drop (with the vapor subtracted out) and are independent of the arbitrary choice of  $V$ . They are determined (experimentally or from molecular theory) by the variables  $T$ ,  $\mu_i$ . Also, they do not depend on the choice of a Gibbs "dividing surface." If  $T$ ,  $\mu_i$  are chosen so as to make the drop become vanishingly small, then all of the primed functions approach zero.

The drop, with properties  $W'$ ,  $\tilde{E}'$ ,  $S'$ , etc., may be regarded as a completely open, small system with independent environmental variables  $T$ ,  $\mu_i$  (the pressure  $p$  is not independent; in the notation of Sec. II F we would denote it by  $p^{(0)}(T, \mu_i)$  for the macroscopic metastable vapor).

<sup>8</sup> The Scientific Papers of J. Willard Gibbs (Dover Publications Inc., New York, 1961).

<sup>9</sup> For recent summaries, with references, see the chapters by S. Ono and S. Kondo and by F. P. Buff in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1960), Vol. 10.

<sup>10</sup> T. L. Hill, J. Phys. Chem. **56**, 526 (1952).

From quite different considerations, Gibbs<sup>11</sup> introduced a quantity  $W$ , the work required to form a drop in the vapor, which is in fact the same as  $W'$  here. This work property of  $W'$  is obvious from our definition:

$$W' = (\partial E_i / \partial \bar{N}_i)_{S_i, V, N_i} - (\partial E_i / \partial \bar{N}_i)_{S_i, V, N_i}^0. \quad (147)$$

From Eqs. (145) and (146) we find the basic equation (with environmental independent variables)

$$dW' = -S'dT - \sum_i \bar{N}_i' d\mu_i. \quad (148)$$

This may be compared with the Gibbs equation

$$d\gamma = -S'dT - \sum_i \bar{N}_i' d\mu_i, \quad (149)$$

where  $\mathcal{A}$ =area,  $\gamma$ =surface tension, and  $S'$ ,  $\bar{N}_i'$ =Gibbs surface excesses. All of these listed quantities refer to a particular choice of dividing surface, namely, the surface of tension. Equation (148) seems more fundamental than Eq. (149) in that the dividing surface concept is not involved. The relation between  $W'$  and  $\gamma$ , as shown by Gibbs, is  $W' = \frac{1}{2}\gamma\mathcal{A}$ . Although the left-hand sides of Eqs. (148) and (149) have the same order of magnitude,  $S'$  and  $S'$ , etc., on the right, do not. In this respect, the relationship between these two equations rather resembles that between Eq. (14) and

$$d[(\bar{p} - p)V] = s^{(s)}dT - Vd(p - p^{(0)}) + n^{(s)}d\mu,$$

which follows from Eqs. (21) and (22), or between Eqs. (14) and (22c).

We also have, for example,

$$d(W' + TS') = TdS' - \sum_i \bar{N}_i' d\mu_i, \quad (150)$$

$$d(W' + \sum_i \mu_i \bar{N}_i') = -S'dT + \sum_i \mu_i d\bar{N}_i'. \quad (151)$$

From Eqs. (148), (150), and (151), we can obtain many relations such as

$$(\partial S' / \partial \mu)_T = (\partial \bar{N}' / \partial T)_\mu, \quad (\partial W' / \partial \mu)_T = -\bar{N}' \quad (152)$$

(one-component system).

We can find some illuminating relationships if we imagine  $V$  filled with bulk liquid at  $T$ ,  $\mu_i$ , denote the corresponding properties by  $E^0$ ,  $S^0$ , etc., then form the differences  $E - E^0$ , etc., and finally compare the behavior of these differences with that of  $E'$ , etc. This procedure is especially useful in isolating "edge effects" and defining excess quantities of the type  $e^{(s)}$ , etc. It is closely related to Gibbs' introduction of surface excesses. We shall discuss this subject elsewhere.<sup>1</sup>

## V. HIGHER MOMENT THERMODYNAMIC EQUATIONS

Up to this point we have been concerned only with mean values of fluctuating extensive variables ( $E$ ,  $N$ ,  $V$ , etc.). In macroscopic thermodynamics fluctua-

tions are unimportant in general, but they become more significant in smaller systems. One is therefore led to seek, for small systems, analogs of the equations of Sec. II involving higher moments of the probability distribution, since mean values now no longer suffice to give a complete picture. We again give only a single example here.

Consider a system with environmental variables  $g_1$ ,  $g_2$  (small  $g$ =intensive), and  $G_3$  (large  $G$ =extensive), chosen so that

$$[(S/k) + \hat{g}_3 G_3] + g_1 \bar{G}_1 + g_2 \bar{G}_2 = 0 \quad (I)$$

(the reason for the brackets will be apparent later). For example:

$$g_1 = -1/kT, \quad G_1 = E; \quad g_2 = \mu/kT, \quad G_2 = N; \quad g_3 = -p/kT, \quad G_3 = V, \quad (153)$$

or

$$g_1 = -1/kT, \quad G_1 = E; \quad g_2 = -p/kT, \quad G_2 = V; \quad g_3 = \mu/kT, \quad G_3 = N, \quad (154)$$

or

$$g_1 = -p/kT, \quad G_1 = V; \quad g_2 = \mu/kT, \quad G_2 = N; \quad g_3 = -1/kT, \quad G_3 = E. \quad (155)$$

That is,  $G_1$  and  $G_2$  fluctuate, but  $G_3$  does not. Equation (153) corresponds to Sec. II A and Eq. (154) to Sec. II B. Besides Eq. (I), other important mean-value equations are

$$d[(S/k) + g_1 d\bar{G}_1 + g_2 d\bar{G}_2 + g_3 dG_3] = 0, \quad (II)$$

$$d[(\hat{g}_3 G_3) + \bar{G}_1 dg_1 + \bar{G}_2 dg_2 - g_3 dG_3] = 0, \quad (III)$$

$$d[(\bar{g}_3 - g_3) G_3] + \bar{G}_1 dg_1 + \bar{G}_2 dg_2 + G_3 dg_3 = 0. \quad (IV)$$

These correspond, for example, to Eqs. (7), (8), and (14), respectively.

We have now to appeal to statistical mechanics to relate probability distribution moments to thermodynamics. The partition function here is

$$\exp(-\hat{g}_3 G_3) = \sum_{G_1, G_2} \Omega(G_1, G_2, G_3) \exp(g_1 G_1) \exp(g_2 G_2), \quad (156)$$

and the probability of observing a  $g_1, g_2, G_3$  system with particular values of  $G_1, G_2$  is

$$\Omega(G_1, G_2, G_3) \exp(g_1 G_1) \exp(g_2 G_2) / \exp(-\hat{g}_3 G_3).$$

Then, as is well known,

$$(\partial^{n+m} \bar{G}_1 / \partial g_1^n \partial g_2^m)_{G_3} = \langle (G_1 - \bar{G}_1)^{n+1} (G_2 - \bar{G}_2)^m \rangle_n, \quad (157)$$

or we can exchange 1 and 2 in this equation. Hence the central moments of the  $G_1, G_2$  distribution are related to derivatives of  $\bar{G}_1$  and  $\bar{G}_2$  with respect to  $g_1$  and  $g_2$ . Therefore, if  $\bar{G}_1(g_1, g_2, G_3)$  and  $\bar{G}_2(g_1, g_2, G_3)$  are known, all higher central moments follow by differentiation. Thus, in a sense, the mean-value thermodynamic equations tell the whole story after all. But we still

<sup>11</sup> Reference 8, p. 254.



look for equations explicitly involving the higher moments [actually, we use the equivalent derivatives from Eq. (157)]. There does not appear to be a unique set of such equations, incidentally. We derive the simplest set we have so far encountered.

If  $Y$  is a function of  $g_1, g_2$ , and  $G_3$ , we define  $Y'$  by

$$Y' = g_1(\partial Y / \partial g_1)_{g_2, G_3} + g_2(\partial Y / \partial g_2)_{g_1, G_3}, \quad (158)$$

and  $Y''$  by  $(Y')'$ , etc. We also define

$$Y^{(1)} = g_1(\partial Y / \partial g_1) + g_2(\partial Y / \partial g_2) = Y' \quad (159)$$

$$Y^{(2)} = g_1^2(\partial^2 Y / \partial g_1^2) + 2g_1g_2(\partial^2 Y / \partial g_1 \partial g_2) + g_2^2(\partial^2 Y / \partial g_2^2) \\ = Y'' - Y', \quad (160)$$

and so forth (using binomial coefficients). Thus

$$Y^{(3)} = Y''' - 3Y'' + 2Y', \quad (161)$$

$$Y^{(4)} = Y'''' - 6Y''' + 11Y'' - 6Y', \quad (162)$$

and so forth.

We start with Eq. (I) and apply to each term the "prime" operation defined in Eq. (158). We use the fact that

$$(-\hat{g}_3 G_3)' = g_1 \bar{G}_1 + g_2 \bar{G}_2 = -[(S/k) + \hat{g}_3 G_3],$$

and find

$$(S^{(1)}/k) + g_1 \bar{G}_1^{(1)} + g_2 \bar{G}_2^{(1)} = 0. \quad (I^{(1)})$$

By repeating the "prime" operation we also find

$$[(S^{(2)} - 2S^{(1)})/k] + g_1 \bar{G}_1^{(2)} + g_2 \bar{G}_2^{(2)} = 0, \quad (I^{(2)})$$

$$[(S^{(3)} - 2S^{(2)} + 2S^{(1)})/k] + g_1 \bar{G}_1^{(3)} + g_2 \bar{G}_2^{(3)} = 0, \quad (I^{(3)})$$

$$[(S^{(4)} - 3S^{(3)} + 6S^{(2)} - 6S^{(1)})/k] + g_1 \bar{G}_1^{(4)} + g_2 \bar{G}_2^{(4)} = 0. \quad (I^{(4)})$$

These equations are the higher moment analogs of Eq. (I). The coefficients in the first terms are simply related to binomial coefficients.

From Eq. (I<sup>(1)</sup>) we have

$$-(S'/k) = g_1 \bar{G}_1' + g_2 \bar{G}_2' = g_1 [\partial(-S/k) / \partial g_1] \\ + g_2 [\partial(-S/k) / \partial g_2].$$

Therefore

$$\partial(-S/k) / \partial g_1 = \bar{G}_1', \quad \partial(-S/k) / \partial g_2 = \bar{G}_2'$$

and

$$\partial(-S/k) = \bar{G}_1' d g_1 + \bar{G}_2' d g_2 + [\partial(-S/k) / \partial G_3] d G_3.$$

This is similar to Eq. (III) above. If we use Eq. (I) for  $S/k$ , we find

$$\frac{\partial(-S/k)}{\partial G_3} = g_1 \frac{\partial \bar{G}_1}{\partial G_3} + g_2 \frac{\partial \bar{G}_2}{\partial G_3} + \frac{\partial(\hat{g}_3 G_3)}{\partial G_3} \\ = -g_1 \frac{\partial g_3}{\partial g_1} - g_2 \frac{\partial g_3}{\partial g_2} + g_3 = -g_3' + g_3.$$

Therefore,

$$d(S/k) + \bar{G}_1^{(1)} d g_1 + \bar{G}_2^{(1)} d g_2 + (-g_3^{(1)} + g_3) d G_3 = 0 \quad (III^{(1)})$$

is the next higher analog of Eq. (III).

Similarly, if we start with Eqs. (I<sup>(2)</sup>), (I<sup>(3)</sup>), etc., we can derive

$$d[(S^{(1)} - 2S)/k] + \bar{G}_1^{(2)} d g_1 + \bar{G}_2^{(2)} d g_2 \\ + (-g_3^{(2)} + 2g_3^{(1)} - 2g_3) d G_3 = 0 \quad (III^{(2)}) \\ d[(S^{(2)} - 4S^{(1)} + 6S)/k] + \bar{G}_1^{(3)} d g_1 + \bar{G}_2^{(3)} d g_2 \\ + (-g_3^{(3)} + 3g_3^{(2)} - 6g_3^{(1)} + 6g_3) d G_3 = 0. \quad (III^{(3)})$$

The coefficients in (III<sup>(4)</sup>) are 1, -6, +18, -24 and -1, +4, -12, +24, -24, respectively.

If we differentiate Eq. (I<sup>(1)</sup>) and combine it with Eq. (III<sup>(1)</sup>), we get

$$d[(S^{(1)} - S)/k] + g_1 d \bar{G}_1^{(1)} + g_2 d \bar{G}_2^{(1)} \\ + (g_3^{(1)} - g_3) d G_3 = 0. \quad (II^{(1)})$$

Similarly, from (I<sup>(2)</sup>) and (III<sup>(2)</sup>), etc.,

$$d[(S^{(2)} - 2S^{(1)} + 2S)/k] + g_1 d \bar{G}_1^{(2)} + g_2 d \bar{G}_2^{(2)} \\ + (g_3^{(2)} - 2g_3^{(1)} + 2g_3) d G_3 = 0 \quad (II^{(2)}) \\ d[(S^{(3)} - 3S^{(2)} + 6S^{(1)} - 6S)/k] + g_1 d \bar{G}_1^{(3)} + g_2 d \bar{G}_2^{(3)} \\ + (g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3) d G_3 = 0. \quad (II^{(3)})$$

The coefficients in (II<sup>(4)</sup>) are 1, -4, +12, -24, +24.

Finally, from (III<sup>(1)</sup>), (III<sup>(2)</sup>), etc., we have

$$d\{[-g_3^{(1)} + g_3 + (S/G_3 k)] G_3\} + \bar{G}_1^{(1)} d g_1 + \bar{G}_2^{(1)} d g_2 \\ + G_3 d(g_3^{(1)} - g_3) = 0, \quad (IV^{(1)})$$

$$d\{(-g_3^{(2)} + 2g_3^{(1)} - 2g_3 + [(S^{(1)} - 2S)/G_3 k]) G_3\} \\ + \bar{G}_1^{(2)} d g_1 + \bar{G}_2^{(2)} d g_2 + G_3 d(g_3^{(2)} - 2g_3^{(1)} + 2g_3) = 0, \quad (IV^{(2)})$$

and so forth.

On comparing the functions playing equivalent roles in the above hierarchy of equations we note the sequences

$$\bar{G}_1, \bar{G}_1^{(1)}, \bar{G}_1^{(2)}, \dots, \\ \bar{G}_2, \bar{G}_2^{(1)}, \bar{G}_2^{(2)}, \dots,$$

$$\hat{g}_3 G_3, S/k, (S^{(1)} - 2S)/k, (S^{(2)} - 4S^{(1)} + 6S)/k, \dots, \\ g_3, g_3^{(1)} - g_3, g_3^{(2)} - 2g_3^{(1)} + 2g_3, \dots,$$

from which the other sequences can be constructed.

There is some simplification in these equations in the case of macroscopic systems. In Eqs. (I), (III), and (IV),  $\hat{g}_3$  is replaced by  $g_3$ . In the sequences of equations beginning with (III<sup>(1)</sup>), (II<sup>(1)</sup>) and (IV<sup>(1)</sup>), we replace

$$g_3^{(1)} - g_3, \quad g_3^{(2)} - 2g_3^{(1)} + 2g_3, \\ g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3, \quad \dots$$

by

$$\frac{S}{G_3 k}, \quad \frac{S^{(1)} - 2S}{G_3 k}, \quad \frac{S^{(2)} - 4S^{(1)} + 6S}{G_3 k}, \quad \dots,$$

as is apparent from the sequence (III<sup>(1)</sup>), (III<sup>(2)</sup>), ..., Thus the leading term in each of the equations (IV), (IV<sup>(1)</sup>), ... vanishes.

Many further equations now follow from the above by Maxwell relations, Legendre transformations, etc.

## VI. SUMMARY

Because of the length of this paper, it may be helpful to outline the contents of the various sections. *Section I* points out that ordinary thermodynamics applies only to macroscopic systems and that a generalization is required in order to extend thermodynamic equations to small systems. In treating small systems we have to expect that the macroscopic thermodynamic principle of equivalence of "environments" will break down.

*Section IIA* gives a fairly detailed treatment of an open one-component small system (environmental variables  $\mu, V, T$ ). The starting point is an ensemble of independent small systems—to which we can apply macroscopic thermodynamics. The number of systems in the ensemble is varied and the equivalence of ensemble and time averages is assumed. This suffices to obtain the desired mean value thermodynamic equations for a single small  $\mu, V, T$  system. These equations go over into the usual macroscopic equations in the limit  $V \rightarrow \infty$ . Two statistical mechanical models are treated as examples: the Bragg-Williams lattice gas outside of phase transition and critical regions; and a general lattice gas at a phase transition.

In *Secs. IIB, C, and D* the environments  $p, N, T$ ;  $N, V, T$ ; and  $N, T$  are treated briefly. The case  $p, N, T$  is especially important since it represents a macromolecule or colloidal particle ( $N$ =degree of polymerization or aggregation) in a surrounding medium at  $p$  and  $T$ . It also represents an incompressible but extensible macromolecule in solution (e.g., the helix-coil transition), with  $p$ =force on ends of chain=0. An incompressible Einstein crystallite with surface terms is considered as a simple example.

*Sections IIE and F* treat the two extreme cases of completely closed ( $N, E, V$ ) and completely open ( $\mu, T, p$ ) small systems. The ideal lattice gas and incompressible Einstein crystallite are used as examples. It is found for all environments that  $\mu, T, p$  can all be independent for a small system (unlike the macroscopic situation). This is especially important when  $\mu, T$ ,

and  $p$  are the environmental variables because the corresponding statistical mechanical partition function  $T(\mu, T, p)$  is then no longer especially troublesome as it is for a macroscopic system. The variables  $\mu, T, p$  suffice to determine all the (mean) extensive properties of the small system—again quite unlike the macroscopic situation. There is thus a certain loss of distinction between intensive and extensive properties in a small system. For a system with  $c$  components, there are  $c+2$  degrees of freedom for any set of environmental variables. The  $c+2$  variables may be intensive or extensive.

*Section IIG* shows that, although thermodynamic functions have different values in different environments, it is still possible to derive, as in macroscopic thermodynamics, a single set of equations which apply to all environments.

Interactions between a small system and a surrounding medium or solvent cannot be ignored as with a macroscopic system. This problem is analyzed in *Sec. III* for a  $p, T, N$  system, as an example. It is found that, by an appropriate redefinition of thermodynamic functions, solvent interactions can be taken into account rigorously without altering the form of the equations for a  $p, T, N$  system where the solvent is absent or ignored (*Sec. IIB*). This is somewhat reminiscent, in statistical mechanics, of the formal identity between Mayer's imperfect gas theory (no solvent) and the McMillan-Mayer solution theory (solvent).

*Section IV* treats a spherical drop (or bubble) from the present point of view. This results in thermodynamic functions and equations, referring to a single drop, which do not involve any choice of a dividing surface (as in Gibbs' method).

In *Sec. V* it is pointed out that higher moments of the probability distribution of fluctuating extensive quantities are of interest, as well as mean values, in the case of small systems. The thermodynamics of the previous sections is "mean value" thermodynamics. We therefore develop in this section, for a system with two intensive and one extensive environmental variables as an example, a hierarchy of thermodynamic equations concerned with higher moments. However, since higher moments are all related to derivatives of mean values, nothing fundamentally new comes out of the analysis. But the explicit higher moment thermodynamic equations may still prove useful.

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# THERMODYNAMICS OF SMALL SYSTEMS

## PART II



*To my early and best teachers:*

E. J. Albrecht  
*(High School Mathematics)*

J. H. Hildebrand  
*(Freshman Chemistry)*

E. A. Guggenheim  
*(through his books)*





## PREFACE

This volume continues and completes the subject introduced in Part I of *Thermodynamics of Small Systems*, which appeared in 1963.

It was planned originally to publish, at this time, a combined volume containing Part II and a revised version of Part I. However, the necessary changes in Part I have proved to be minor. Therefore the author and publisher have decided to issue Part II as a separate work. But a list of corrections to be made in Part I is included here.

There are three areas covered in the present volume. First, Chapters 7 and 10 treat binding on macromolecules and aggregation (soap micelles, etc.) in such a way as to be applicable to both experimental and theoretical work in these fields. Second, Chapters 8, 9, and 10 complete the discussion of certain choices of environmental variables important in the analysis of statistical mechanical models of finite systems. Finally, Chapters 11 through 15 contain very brief summaries of certain special topics.

Chapter 10 includes a discussion of the partition function for completely open systems. It is believed that use of a finite system avoids the complications usually met with this partition function and provides the method of choice in applications of the partition function (to finite or macroscopic systems).

It is assumed in Part II that the reader is familiar with the notation and basic ideas introduced in Part I.

T.L.H.

*Eugene, Oregon*  
*March 1964*



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# CORRECTIONS AND COMMENTS

## ON PART I

*p. 10, Part I.* The word "vanishes," following Eq. (1-11), should be replaced by "becomes negligible." See the discussion of  $\mathcal{E}$  on p. 101.

*p. 14, Part I.* This is an addendum to Section 1-2, suggested by Eq. (10-35). The probability that any system of the ensemble contains exactly  $N$  molecules is

$$P(N) = \frac{Q(N, V, T)e^{N\mu/kT}}{\Xi}$$

If  $Q(0, V, T) = 1$  (as will usually be the case), the probability that any system is empty is  $P(0) = 1/\Xi$ . Therefore,

$$\hat{p}V = kT \ln \Xi = -kT \ln P(0).$$

Consider a *closed* ensemble ( $N_t = \text{constant}$ ) of  $\mu, V, T$  systems. Equation (1-4) becomes

$$\begin{aligned} dE_t &= T dS_t - \hat{p} \mathcal{N} dV - \hat{p} V d\mathcal{N} \\ &= DQ' + DW' \end{aligned}$$

where  $DQ' = T dS_t$  and  $DW'$  is work done *on* the ensemble:

$$DW' = -\hat{p} \mathcal{N} dV - \hat{p} V d\mathcal{N}.$$

In the special case in which  $V = \text{constant}$  and  $d\mathcal{N} = -1$  (i.e., the molecules are forced out of one system of the ensemble and into the remaining  $\mathcal{N} - 1$  systems), the work done on the system is

$$DW' = \hat{p}V = -kT \ln P(0).$$

This is analogous to the work required to create a cavity in a fluid.\* But in our case the molecules of the system being evacuated have no intermolecular interaction with the surroundings.

*p. 40, Part I.* The second sentence should read: But, for a discrete variable such as  $N$ , the equations of Chapter 15 have to be used as a starting point.

\* E. Helfand, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, **34**, 1037 (1961).

*p. 43, Part I.* See p. 195 in connection with the differentiation with respect to  $N$ .

*p. 57, Part I.* The second equation on this page is the same as Eq. (7-71). The footnote on this page is proved in Eq. (7-75).

*p. 69, Part I.* See p. 195 in connection with the differentiation with respect to  $N$ .

*p. 69, Part I.* Incompressible linear aggregate in an inert solvent: see Eq. (10-312)ff.

*p. 70, Part I.* An intrinsic partition function  $j(T)^N$  may be included as a factor in Eq. (3-55) [see Eqs. (3-61) and (10-21)].

*p. 70, Part I.* Spherical crystallite in an inert solvent: see Eq. (10-312)ff.

*p. 79, Part I.* The superscript  $S$  has been changed to  $s$  in Part II.

*p. 87, Part I.* The treatment of an ideal binary mixture is corrected for discreteness of variables on p. 205.

*p. 117, Part I.* A real, macroscopic  $N, p, T$  system at a phase transition (e.g., ice + water in a heat bath) would not always be observed as all ice or all water because of the length of time required to switch from one state to the other. This time would be relatively short for small systems.

*p. 142, Part I.* See p. 196 in connection with the treatment of  $B$  as a continuous variable.

*p. 143, Part I.* The statistical mechanics of a finite lattice gas in the grand ensemble has been studied by a Monte Carlo procedure by Chesnut and Salsburg.\*

*p. 145, Part I.* See p. 196 in connection with treatment of  $B$  and  $N$  as continuous variables.

*p. 152, Part I.* The reference to Section 8-1 should be changed to p. 198.

*p. 166, Part I.* Equation (157) is corrected in Eq. (14-5)ff.

\* D. A. Chesnut and Z. W. Salsburg, *J. Chem. Phys.*, **38**, 2861 (1963).

# ENVIRONMENTAL VARIABLES $N_1, \mu_2, p, T$

A polymer molecule in solution which binds small molecules or ions from the solution is representative of a class of small systems that is especially important in physical biochemistry. There are two components in this example. The system is closed with respect to component 1 (the polymer contains  $N_1$  monomers) but open with respect to component 2 (the molecules being bound by the polymer have chemical potential  $\mu_2$  on the polymer and in the solution). The variables  $N_2, V$ , and  $E$  fluctuate about mean values.

A similar example is the binding or adsorption of molecules from solution or from the gas phase onto the surface of a colloidal particle.

If charged species are involved in these systems, the two components must be chosen in neutral combinations, as is usual in macroscopic thermodynamics. For example: component 1 = polyelectrolyte monomer + counterion; and component 2 = bound ion + counterion.

It should be recognized that the classification of molecules of component 2 into molecules in solution and "bound" molecules is an extrathermodynamic and, in principle at least, somewhat arbitrary procedure.<sup>1</sup> But in practice, if the binding forces are reasonably strong, this arbitrariness is unimportant.

The environment variables  $N_1, \mu_2, p, T$  resemble  $N, p, T$  (Chapter 2) and  $\mu, V, T$  (Chapter 6) in that each set has only one extensive variable. The analogy is still closer with  $N, p, T, \psi$  (Chapter 5),  $N, p, f, T$ , or  $\mu_1, \mu_2, V, T$ . If the pressure is dropped from the list of variables because of assumed incompressibility or other reasons, then a formal correspondence can easily be established between the variables  $N_1, \mu_2, T$  on the one hand, and  $N, p, T$  or  $\mu, V, T$  on the other. Thus the equations in Chapter 2 or, especially, those in Chapter 6 (including the discussion of phase transitions) can easily be transcribed<sup>2</sup> to the case  $N_1, \mu_2, T$ .

<sup>1</sup> See T. L. Hill, *J. Chem. Phys.*, **23**, 623 (1955), Sec. III.

<sup>2</sup> The details are left to the interested reader. Equations (6-1) to (6-5) should be noted in this connection. See also Eq. (7-131), below.



In an  $N_1, \mu_2, p, T$  system, the number of binding sites  $B$  (or, say, the area if the binding is not confined to definite sites) is not a further independent thermodynamic variable. In most cases  $B$  will be determined primarily by  $N_1$ . For example: binding on a linear polyelectrolyte,  $B \propto N_1$ ; absorption in a spherical crystallite,  $B \propto N_1$ ; adsorption on the surface of a spherical crystallite,  $B \propto N_1^{2/3}$ ; hydrogen ion binding by the normal dicarboxylic acids or diamines,  $B = 2 = \text{constant}$  ( $N_1 = \text{number of CH}_2 \text{ groups in chain}$ ).

Binding on, say, a naturally occurring protein molecule, which is not composed of a variable number of identical units or monomers, must be treated as a  $\mu_2, p, T$  system (Chapter 10). That is,  $N_1$  is, in effect, always constant and hence drops out as a variable.

The elasticity of a polymer with binding is of some interest. The environmental variables are  $N_1, \mu_2, p, f, T$ , or, if incompressibility is assumed,  $N_1, \mu_2, f, T$ . In the latter case,  $f$  simply replaces  $p$  in the basic set  $N_1, \mu_2, p, T$ .

Closely related to the elasticity problem, at least formally, and important experimentally, is the case of binding of molecules on a small system with an isomeric chemical equilibrium. An example is the hydrogen ion titration of synthetic polypeptides or polynucleotides, both of which have the possibility of a helix  $\rightleftharpoons$  coil isomeric equilibrium (see Section 5-3). The environmental variables are  $N_1$  (total number of monomers or units),  $\mu_2, p, T, \psi$ , or  $N_1, \mu_2, T, \psi$  (incompressibility).

Section 7-1 is concerned with the basic equations for an ensemble of  $N_1, \mu_2, p, T$  systems. Small systems in solvent or gas are considered in Section 7-2. Isomeric equilibrium with binding is treated in Section 7-3.

## 7-1. BASIC EQUATIONS

The fundamental macroscopic equation, analogous to Eqs. (1-4) and (1-24), for an ensemble of  $\mathcal{N}$  distinguishable and independent  $N_1, \mu_2, p, T$  systems is

$$dE_t = T dS_t - p dV_t + \mu_1 \mathcal{N} dN_1 + \mu_2 dN_{t2} + X d\mathcal{N}. \quad (7-1)$$

Integration gives

$$E_t = TS_t - pV_t + \mu_2 N_{t2} + X\mathcal{N},$$

or

$$X \equiv \hat{\mu}_1 N_1 = \bar{E} - TS + p\bar{V} - \mu_2 \bar{N}_2. \quad (7-2)$$

Then

$$\mathcal{E} \equiv \bar{E} - TS + p\bar{V} - \mu_1 N_1 - \mu_2 \bar{N}_2 = (\hat{\mu}_1 - \mu_1)N_1. \quad (7-3)$$

We substitute Eq. (7-2) for  $X$  in Eq. (7-1) and obtain

$$d\bar{E} = T dS - p d\bar{V} + \mu_1 dN_1 + \mu_2 d\bar{N}_2. \quad (7-4)$$

Also,

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1 dN_1 - \bar{N}_2 d\mu_2 \quad (7-5)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - N_1 d\mu_1 - \bar{N}_2 d\mu_2. \quad (7-6)$$

The relation to statistical mechanics is<sup>1</sup>

$$\Gamma(N_1, \mu_2, p, T) = \sum_{N_2, V} Q(N_1, N_2, V, T) e^{-pV/kT} e^{N_2 \mu_2 / kT} \quad (7-7)$$

$$N_1 \hat{\mu}_1 = X = -kT \ln \Gamma. \quad (7-8)$$

This is a "semigrand" partition function appropriate to a semiopen system.

Several Legendre transformations will prove useful:

$$d(\hat{\mu}_1 N_1 + \mu_2 \bar{N}_2) = dF = -S dT + \bar{V} dp + \mu_1 dN_1 + \mu_2 d\bar{N}_2 \quad (7-9)$$

$$d(\hat{\mu}_1 N_1 - p\bar{V}) = -S dT - p d\bar{V} + \mu_1 dN_1 - \bar{N}_2 d\mu_2 \quad (7-10)$$

$$d(\hat{\mu}_1 N_1 + \mu_2 \bar{N}_2 - p\bar{V}) = dA = -S dT - p d\bar{V} + \mu_1 dN_1 + \mu_2 d\bar{N}_2. \quad (7-11)$$

One can write six Maxwell relations for each of Eqs. (7-4) to (7-6) and (7-9) to (7-11), and these, of course, by no means exhaust the possibilities. For example, from Eq. (7-5),

$$\left( \frac{\partial \mu_1}{\partial T} \right)_{p, N_1, \mu_2} = - \left( \frac{\partial S}{\partial N_1} \right)_{T, p, \mu_2}, \quad \left( \frac{\partial \mu_1}{\partial p} \right)_{T, N_1, \mu_2} = \left( \frac{\partial \bar{V}}{\partial N_1} \right)_{T, p, \mu_2},$$

$$\left( \frac{\partial \mu_1}{\partial \mu_2} \right)_{T, p, N_1} = - \left( \frac{\partial \bar{N}_2}{\partial N_1} \right)_{T, p, \mu_2}. \quad (7-12)$$

<sup>1</sup> See S.T., p. 363.

We find, from Eqs. (7-5), (7-6), and (7-12),

$$d\hat{\mu}_1 = -\frac{S}{N_1} dT + \frac{\bar{V}}{N_1} dp - \frac{\bar{N}_2}{N_1} d\mu_2 - \frac{\mathcal{E}}{N_1^2} dN_1 \quad (7-13)$$

$$d\mu_1 = -\left(\frac{\partial S}{\partial N_1}\right)_{T, p, \mu_2} dT + \left(\frac{\partial \bar{V}}{\partial N_1}\right)_{T, p, \mu_2} dp - \left(\frac{\partial \bar{N}_2}{\partial N_1}\right)_{T, p, \mu_2} d\mu_2 \\ - \frac{1}{N_1} \left(\frac{\partial \mathcal{E}}{\partial N_1}\right)_{T, p, \mu_2} dN_1. \quad (7-14)$$

If we substitute Eq. (7-14) for  $d\mu_1$  in Eq. (7-6), we have

$$d\mathcal{E} = -[S]_1 dT + [\bar{V}]_1 dp - [\bar{N}_2]_1 d\mu_2 + \left(\frac{\partial \mathcal{E}}{\partial N_1}\right)_{T, p, \mu_2} dN_1, \quad (7-15)$$

where

$$[G]_1 \equiv G - N_1 \left(\frac{\partial G}{\partial N_1}\right)_{T, p, \mu_2}. \quad (7-16)$$

Then we find, from Eq. (7-15),

$$\left(\frac{\partial S/N_1}{\partial N_1}\right)_{T, p, \mu_2} = \frac{1}{N_1^2} \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p, \mu_2, N_1} \quad (7-17)$$

$$\left(\frac{\partial \bar{V}/N_1}{\partial N_1}\right)_{T, p, \mu_2} = -\frac{1}{N_1^2} \left(\frac{\partial \mathcal{E}}{\partial p}\right)_{T, \mu_2, N_1} \quad (7-18)$$

$$\left(\frac{\partial \bar{N}_2/N_1}{\partial N_1}\right)_{T, p, \mu_2} = \frac{1}{N_1^2} \left(\frac{\partial \mathcal{E}}{\partial \mu_2}\right)_{T, p, N_1}. \quad (7-19)$$

These also follow directly from Eq. (7-13). The last equation is concerned with the effect of the size of the small system on the amount of binding per unit. It is of interest especially when the number of binding sites is proportional to  $N_1$ .

**EQUATION-OF-STATE RELATIONS.** We are interested here in derivatives involving the observable<sup>1</sup> quantities  $p$ ,  $\bar{V}$ ,  $T$ ,  $N_1$ ,  $\bar{N}_2$ , and

<sup>1</sup> Changes in  $\mu_2$  at constant  $p$  and  $T$  can be measured by means of a change in concentration, partial pressure, activity, etc., in the reservoir. However, when the temperature is not constant, the choice of the arbitrary zero of entropy in  $\mu_2$  becomes involved. Nonisothermal equations in the present section are correct but are not useful experimentally if  $\mu_2$  is concerned explicitly. See Eqs. (6-38) to (6-41) et seq. and Section 7-2.

$\mu_2$ , and the thermodynamic information that can be derived therefrom. There are a great many of these derivatives (in fact, 60). Equations (7-12b) and (7-12c) are examples. A few others are given below.

The effect of the environmental variables  $\mu_2, p$ , and  $T$  on  $\bar{N}_2$  and  $\bar{V}$  is as follows:

$$\left(\frac{\partial \bar{N}_2}{\partial T}\right)_{p, N_1, \mu_2} = \left(\frac{\partial S}{\partial \mu_2}\right)_{T, p, N_1}, \quad \left(\frac{\partial \bar{V}}{\partial T}\right)_{p, N_1, \mu_2} = -\left(\frac{\partial S}{\partial p}\right)_{T, N_1, \mu_2} \quad (7-20)$$

$$\left(\frac{\partial \bar{N}_2}{\partial p}\right)_{T, N_1, \mu_2} = -\left(\frac{\partial \bar{V}}{\partial \mu_2}\right)_{T, p, N_1} \quad (7-21)$$

$$\left(\frac{\partial \bar{N}_2}{\partial \mu_2}\right)_{T, p, N_1} = -\frac{(\partial \bar{N}_2 / \partial N_1)_{T, p, \mu_2}}{(\partial \mu_2 / \partial N_1)_{T, p, \bar{N}_2}} \quad (7-22)$$

$$\left(\frac{\partial \bar{V}}{\partial p}\right)_{T, N_1, \mu_2} = -\frac{(\partial \bar{V} / \partial N_1)_{T, \mu_2, p}}{(\partial p / \partial N_1)_{T, \mu_2, \bar{V}}} \quad (7-23)$$

Two other quotients can be written on the right-hand side of each of Eqs. (7-22) and (7-23), replacing  $N_1$  by  $T$  or  $p$  in the former case or by  $T$  or  $\mu_2$  in the latter [see, for example, Eq. (2-46)].

Four derivatives at constant temperature, which are of some interest in connection with phase transitions (see below) and otherwise, are

$$\left(\frac{\partial p}{\partial N_1}\right)_{T, \bar{V}, \mu_2} = -\left(\frac{\partial \mu_1}{\partial \bar{V}}\right)_{T, N_1, \mu_2}, \quad \left(\frac{\partial \mu_2}{\partial p}\right)_{T, \bar{V}, N_1} = \left(\frac{\partial \bar{V}}{\partial \bar{N}_2}\right)_{T, N_1, \mu_2} \quad (7-24)$$

$$\left(\frac{\partial \mu_2}{\partial N_1}\right)_{T, p, \bar{N}_2} = \left(\frac{\partial \mu_1}{\partial \bar{N}_2}\right)_{T, p, N_1}, \quad \left(\frac{\partial \mu_2}{\partial p}\right)_{T, N_1, \bar{N}_2} = \left(\frac{\partial \bar{V}}{\partial \bar{N}_2}\right)_{T, p, N_1} \quad (7-25)$$

Four nonisothermal derivatives of the same type are

$$\left(\frac{\partial p}{\partial T}\right)_{\bar{V}, N_1, \mu_2} = \left(\frac{\partial S}{\partial \bar{V}}\right)_{T, N_1, \mu_2}, \quad \left(\frac{\partial \mu_2}{\partial T}\right)_{p, N_1, \bar{N}_2} = -\left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, p, N_1} \quad (7-26)$$

$$\left(\frac{\partial T}{\partial N_1}\right)_{p, \bar{V}, \mu_2} = \left(\frac{\partial \mu_1}{\partial S}\right)_{T, N_1, \mu_2}, \quad \left(\frac{\partial T}{\partial N_1}\right)_{p, \mu_2, \bar{N}_2} = \left(\frac{\partial \mu_1}{\partial S}\right)_{T, p, N_1} \quad (7-27)$$

A few other, possibly useful, relations are

$$\left(\frac{\partial \mu_2}{\partial N_1}\right)_{T, p, \bar{V}} = \left(\frac{\partial \mu_1}{\partial \bar{N}_2}\right)_{T, N_1, \mu_2}, \quad \left(\frac{\partial \mu_2}{\partial T}\right)_{p, \bar{V}, N_1} = -\left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, N_1, \mu_2} \quad (7-28)$$

$$\left(\frac{\partial p}{\partial N_1}\right)_{T, \mu_2, \bar{N}_2} = -\left(\frac{\partial \mu_1}{\partial \bar{V}}\right)_{T, p, N_1}, \quad \left(\frac{\partial p}{\partial T}\right)_{N_1, \mu_2, \bar{N}_2} = \left(\frac{\partial S}{\partial \bar{V}}\right)_{T, p, N_1} \quad (7-29)$$

Equations (7-20), (7-21), and (7-24) to (7-26) are Maxwell relations obtained from the appropriate independent variables. Equations (7-27) to (7-29) were deduced using, in addition, quotients of the type in Eqs. (7-22) and (7-23).

As an example of an application, suppose the amount bound,  $\bar{N}_2$ , is measured as a function of the reservoir concentration  $c^s$ , of this same component, from  $c^s = 0$  to  $c^s = c'$ , for two values of  $N_1$  not too far apart. Let  $\bar{N}_2 = \bar{N}'_2$  (for the mean value of  $N_1$ ) when  $c^s = c'$ . Pressure and temperature are constant and we assume  $d\mu_2 = kT d \ln c^s$ . Then for each value of  $\bar{N}_2$  we can approximate the left-hand side of Eq. (7-25a) by (see Fig. 7-1)

$$\frac{(\Delta \mu_2)_{\bar{N}_2}}{\Delta N_1} = \frac{kT \Delta c^s}{c^s(\text{mean}) \Delta N_1}.$$

This quantity is a function of  $\bar{N}_2$ , with  $p$ ,  $T$ , and (the mean value of)  $N_1$  constant. Hence integration of Eq. (7-25a) gives

$$\mu_1(\bar{N}'_2) - \mu_1(0) = kT \int_0^{\bar{N}'_2} \frac{1}{c^s} \frac{\Delta c^s}{\Delta N_1} d\bar{N}_2 \quad (T, p, N_1 \text{ constant}). \quad (7-30)$$

Also, using  $\bar{N}_2(c^s)$  corresponding to the mean value of  $N_1$ ,

$$N_1[\hat{\mu}_1(\bar{N}'_2) - \hat{\mu}_1(0)] = -kT \int_0^{c'} \frac{\bar{N}_2(c^s)}{c^s} dc^s \quad (T, p, N_1 \text{ constant}). \quad (7-31)$$

This follows from Eq. (7-5). We can combine Eqs. (7-30) and (7-31) to obtain  $\mathcal{E}(\bar{N}'_2) - \mathcal{E}(0)$ . Integration of  $-[\bar{N}_2]_1 d\mu_2$  in Eq. (7-15) provides a check.

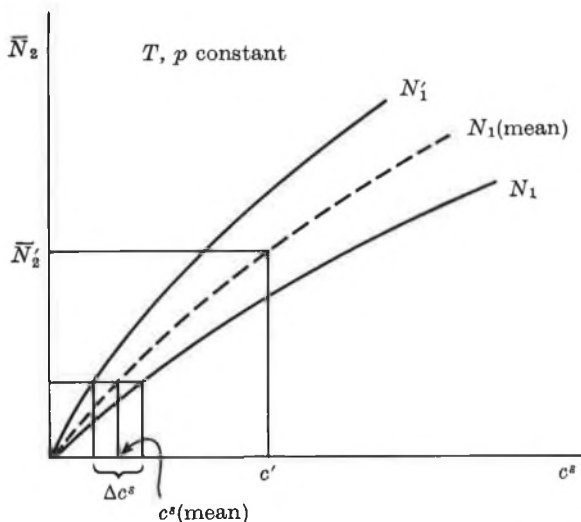


FIGURE 7-1. Schematic plot of amount bound  $\bar{N}_2$  versus reservoir concentration  $c^s$  at two different values of  $N_1$  for use in Eq. (7-30).

*Example. Crystallite with Adsorption.* For the crystallite, we use the model in Eqs. (2-68) to (2-71) but keep the surface term only. We assume that the partition function  $\Delta(N_1, N_2, p, T)$  for a crystallite of  $N_1$  molecules with  $N_2$  molecules adsorbed has the simple form

$$\Delta(N_1, N_2, p, T) = \Delta(N_1, 0, p, T) \left[ \frac{B!q^{N_2}}{N_2!(B - N_2)!} \right], \quad (7-32)$$

where  $q(p, T)$  is the partition function of a bound molecule (including the energy of adsorption) and  $B$  is the number of independent and equivalent sites for adsorption ("Langmuir model"). We take  $B = \alpha(p, T)N_1^{2/3}$ , where  $\alpha$  is a proportionality factor. That is, the sites are assumed to be on the surface of the crystallite. According to Eq. (2-68),

$$-kT \ln \Delta(N_1, 0, p, T) = N_1 f(p, T) + a(p, T)N_1^{2/3}. \quad (7-33)$$

From Eq. (7-7),

$$\begin{aligned} \Gamma &= \sum_{N_2=0}^M \Delta(N_1, N_2, p, T) \lambda_2^{N_2} \\ &= \Delta(N_1, 0, p, T) (1 + q\lambda_2)^B, \end{aligned} \quad (7-34)$$

where  $\lambda_2 = e^{\mu_2/kT}$ . Then

$$N_1\hat{\mu}_1 = -kT \ln \Gamma = N_1 f(p, T) + a(p, T)N_1^{2/3} - kT\alpha(p, T)N_1^{2/3} \ln[1 + q(p, T)\lambda_2]. \quad (7-35)$$

The first term on the right, which has nothing to do with adsorption, is the only macroscopic term. This comes about because the adsorption is confined to the surface and the surface becomes relatively unimportant as  $N_1 \rightarrow \infty$ .

Equations (7-5) and (7-35) then lead, for example, to

$$\frac{\bar{N}_2}{B} = \frac{q\lambda_2}{1 + q\lambda_2} \quad (7-36)$$

$$\mu_1 = f + \frac{2}{3}aN_1^{-1/3} - \frac{2}{3}kT\alpha N_1^{-1/3} \ln(1 + q\lambda_2) \quad (7-37)$$

$$\bar{V} = N_1 \frac{\partial f}{\partial p} + N_1^{2/3} \frac{\partial a}{\partial p} - kT \bar{N}_2 \frac{\partial \ln q}{\partial p} - kT \frac{\partial \alpha}{\partial p} N_1^{2/3} \ln(1 + q\lambda_2). \quad (7-38)$$

The reader may wish to use this model to verify some of the thermodynamic equations given earlier in this section.

**TWO-STATE APPROXIMATION FOR PHASE TRANSITIONS.** There are two obvious possibilities for first-order phase transitions in  $N_1, \mu_2, p, T$  systems. First, a small system of  $N_1$  molecules may undergo a transition irrespective of the value of  $\mu_2$  or  $\bar{N}_2$  (see Section 5-4). For example, a crystallite may melt irrespective of adsorption or binding on its surface, although of course the adsorption would be expected to perturb the melting somewhat. Second, the molecules being adsorbed or absorbed may themselves show a phase transition,<sup>1</sup> for example, from a dilute to a concentrated adsorbed layer (see Section 6-2). An absorption example would be expected in a colloidal  $H_2$ -Pt or  $H_2$ -Pd system.

Neither of the above types of phase transition would be anticipated in experimental linear (one-dimensional) polymer systems.

A two-state approximation should again often be useful here. With reference to Eq. (7-7), we define the function

$$P(N_2, V) = \frac{Q(N_1, N_2, V, T)e^{-pV/kT}e^{N_2\mu_2/kT}}{\Gamma}. \quad (7-39)$$

<sup>1</sup> See, for example, J. R. Colvin, *Can. J. Chem.*, **30**, 320 (1952).

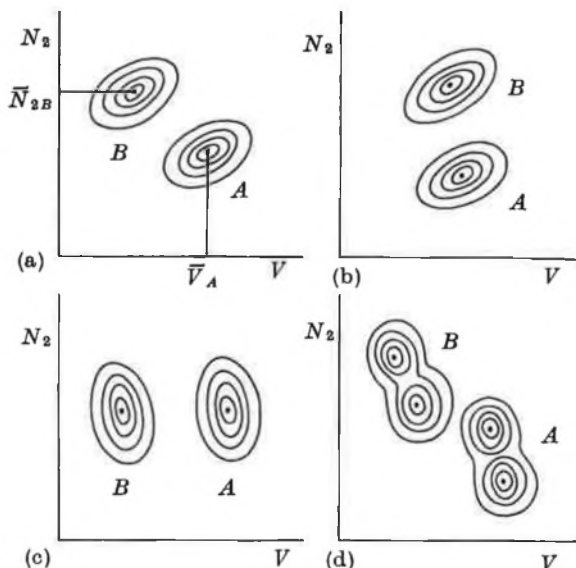


FIGURE 7-2. Schematic contour diagrams of the probability  $P(N_2, V)$  of observing a small system with  $N_2$  and  $V$ . The contour centers correspond to maximum probability. The two-state approximation is appropriate in all cases. In cases (a), (c), and (d), we have  $\bar{V}_A > \bar{V}_B$ . In cases (a), (b), and (d),  $\bar{N}_{2B} > \bar{N}_{2A}$ .

This is the probability of observing a small system with  $N_2$  and  $V$ , for given values of  $N_1, \mu_2, p$ , and  $T$ . In Fig. 7-2a, a two-state situation is illustrated by a schematic plot of  $P(N_2, V)$  in the form of a contour diagram. There are two separated and more or less Gaussian peaks labeled states  $A$  and  $B$ . This figure is the analogue of Fig. 5-1c for an  $N, p, T$  system.

Incidentally, if we had defined [compare Eq. (5-113)]

$$P(E, V) = \frac{\Omega(N, V, E) e^{-E/kT} e^{-pV/kT}}{\Delta}$$

for an  $N, p, T$  system, a contour diagram of  $P(E, V)$  in the  $E, V$  plane would also appear as in Fig. 7-2a. Figure 5-1c is a summation-projection of the  $E, V$  contour diagram onto the  $V$  axis:

$$P(V) = \sum_E P(E, V).$$



This projection is natural in the  $N, p, T$  case because  $E$  is not a readily observable variable.

Figure 7-2*b* shows a "pure" adsorption phase transition whereas Fig. 7-2*c* shows the opposite case. Figure 7-2*a* is intermediate. Figure 7-2*d* illustrates a double phase transition which could occur for certain choices of the parameters  $N_1$ ,  $\mu_2$ ,  $p$ , and  $T$ . The two-state approximation is still applicable.

We adopt the two-state approximation at this point and deduce, by the same method<sup>1</sup> as in Sections 5-4 and 6-1,

$$\frac{\mathcal{N}_A}{\mathcal{N}_B} = \left( \frac{e^{-\hat{\mu}_{1A}/kT}}{e^{-\hat{\mu}_{1B}/kT}} \right)^{N_1} \quad (7-40)$$

$$\hat{\mu}_1 = P_A \hat{\mu}_{1A} + P_B \hat{\mu}_{1B} + \frac{kT}{N_1} (P_A \ln P_A + P_B \ln P_B) \quad (7-41)$$

$$\bar{V} = P_A \bar{V}_A + P_B \bar{V}_B \quad (7-42)$$

$$\bar{E} = P_A \bar{E}_A + P_B \bar{E}_B \quad (7-43)$$

$$\bar{N}_2 = P_A \bar{N}_{2A} + P_B \bar{N}_{2B} \quad (7-44)$$

$$\mu_1 = P_A \mu_{1A} + P_B \mu_{1B} \quad (7-45)$$

$$S = P_A S_A + P_B S_B - k(P_A \ln P_A + P_B \ln P_B). \quad (7-46)$$

Section 5-4 should be used as a guide to fill in some of the details that we are omitting here.

From the above results and Eq. (7-5) we arrive at the following conclusions: (1) an equal-area theorem and an equal-distance theorem both apply to a  $\bar{V}$  versus  $p$  diagram ( $N_1, \mu_2, T$  constant); and (2) both also apply to an  $\bar{N}_2$  versus  $\mu_2$  diagram ( $N_1, p, T$  constant).

The  $\bar{V}$  "fluctuation" equation (5-126) is unchanged here except that  $N_1$ ,  $\mu_2$ , and  $T$  are held constant in the derivatives. The corresponding  $\bar{N}_2$  equation is

$$\begin{aligned} \left( \frac{\partial \bar{N}_2}{\partial \mu_2} \right)_{N_1, p, T} &= P_A \left( \frac{\partial \bar{N}_{2A}}{\partial \mu_2} \right)_{N_1, p, T} + P_B \left( \frac{\partial \bar{N}_{2B}}{\partial \mu_2} \right)_{N_1, p, T} \\ &+ \frac{P_A P_B}{kT} (\bar{N}_{2A} - \bar{N}_{2B})^2. \end{aligned} \quad (7-47)$$

<sup>1</sup> See also the footnote on p. 149 of Part I concerning a derivation from statistical mechanics.

There are also cross relations:

$$\begin{aligned} \left( \frac{\partial \bar{V}}{\partial \mu_2} \right)_{N_1, p, T} &= P_A \left( \frac{\partial \bar{V}_A}{\partial \mu_2} \right)_{N_1, p, T} + P_B \left( \frac{\partial \bar{V}_B}{\partial \mu_2} \right)_{N_1, p, T} \\ &+ \frac{P_A P_B}{kT} (\bar{N}_{2A} - \bar{N}_{2B}) (\bar{V}_A - \bar{V}_B), \end{aligned} \quad (7-48)$$

or  $\partial \bar{V} / \partial \mu_2$  can be replaced by  $-(\partial \bar{N}_2 / \partial p)_{N_1, \mu_2, T}$ . These follow by differentiation of Eqs. (7-24) and (7-44), or on making use of

$$\overline{VN_2} - \bar{V} \bar{N}_2 = kT \left( \frac{\partial \bar{V}}{\partial \mu_2} \right)_{N_1, p, T} = -kT \left( \frac{\partial \bar{N}_2}{\partial p} \right)_{N_1, \mu_2, T}. \quad (7-49)$$

EQUATIONS OF THE CLAUSIUS-CLAPEYRON TYPE. The two metastable states  $A$  and  $B$ , in equilibrium,<sup>1</sup> have the same values of  $N_1, \mu_2, p, T$ , and  $\hat{\mu}_1$ . They have different values of  $\mu_1, \bar{N}_2, \bar{V}, S, \bar{E}$ , and  $\bar{\mathcal{E}}$ . If we regard  $\hat{\mu}_1$  as a function of  $N_1, \mu_2, p$ , and  $T$ , and shift the equilibrium state by variations in these variables, then from  $d\hat{\mu}_{1A} = d\hat{\mu}_{1B}$  and Eq. (7-13),

$$\left( \frac{\partial p}{\partial T} \right)_{N_1, \mu_2} = \frac{\Delta S}{\Delta \bar{V}}, \quad \left( \frac{\partial \mu_2}{\partial T} \right)_{p, N_1} = -\frac{\Delta S}{\Delta \bar{N}_2} \quad (7-50)$$

$$\left( \frac{\partial T}{\partial N_1} \right)_{p, \mu_2} = \frac{\Delta \mu_1}{\Delta S}, \quad \left( \frac{\partial p}{\partial \mu_2} \right)_{T, N_1} = \frac{\Delta \bar{N}_2}{\Delta \bar{V}} \quad (7-51)$$

$$\left( \frac{\partial p}{\partial N_1} \right)_{T, \mu_2} = -\frac{\Delta \mu_1}{\Delta \bar{V}}, \quad \left( \frac{\partial \mu_2}{\partial N_1} \right)_{T, p} = \frac{\Delta \mu_1}{\Delta \bar{N}_2}, \quad (7-52)$$

where  $\Delta$  refers to the difference between the two metastable states  $A$  and  $B$  mentioned above. Only three of Eqs. (7-50) to (7-52) are independent. There are  $4 \times 6$  other equations of this type which follow from  $dN_{1A}(\mu_2, p, T, \hat{\mu}_1) = dN_{1B}(\mu_2, p, T, \hat{\mu}_1)$ , etc. The relation between Eqs. (7-24) to (7-27) and (7-50) to (7-52) should be noted.

Of the above equations, only (7-52b) is ordinarily very practical to use. In fact, both sides of the first three of these equations depend

<sup>1</sup> We remind the reader that states  $A$  and  $B$  here are "metastable" in the sense that *all* small systems are in state  $A$  or *all* are in state  $B$ , whereas the stable equilibrium state of the ensemble is a mixture of small systems in states  $A$  and  $B$ , as determined by Eq. (7-40). Also, "in equilibrium" means simply that conditions are chosen so that the two metastable states have  $\hat{\mu}_{1A} = \hat{\mu}_{1B}$ . But we can take the alternative and equivalent point of view that Eqs. (7-50) to (7-54) refer to the single point  $\mathcal{N}_A = \mathcal{N}_B$  on the stable equilibrium path.

on the choice of the zero of entropy for component 2 [compare Eqs. (6-38) and (6-39)].

The following relations are of interest:

$$\Delta(N_1\hat{\mu}_1) = 0 = \Delta\bar{E} - T \Delta S + p \Delta\bar{V} - \mu_2 \Delta\bar{N}_2 \quad (7-53)$$

$$\Delta\mathcal{E} = -N_1 \Delta\mu_1. \quad (7-54)$$

We cannot set  $T \Delta S$  equal to a heat of transition  $Q$  because the process does not occur in a closed system ( $\Delta\bar{N}_2 \neq 0$ ).

*Example. Crystallite Melting with Adsorption.* This is the example at the end of Chapter 5, but with adsorption on the surface of the small system from a solvent reservoir now included. Let us use Eq. (7-35) as the basic equation for both liquid and solid states, but we simplify matters by considering only the Henry's law adsorption region ( $\lambda_2 \rightarrow 0$ ). Then we write

$$\hat{\mu}_1 = f + aN_1^{-1/3} - \chi N_1^{-1/3}\lambda_2 \quad (7-55)$$

where  $\chi = kT\alpha q$  and

$$\lambda_2 = m^s \exp\left[\frac{\mu^\Delta(p, T)}{kT}\right].$$

Here,  $m^s$  is the molality and  $\mu^\Delta$  the standard chemical potential of the adsorbate in the solvent.

As in Chapter 5, we take  $p_\infty$  and  $T_\infty$  as values of  $p$  and  $T$  at which the two macroscopic phases are in equilibrium. Our object is to find the first-order effect of finite  $N_1$  [as in Eq. (5-152)] and of adsorption on the equilibrium pressure  $p$  and temperature  $T$ .

To find the effect on  $p$ , we start with

$$\begin{aligned} \Delta\hat{\mu}_1 = 0 = \Delta f(p, T_\infty) + N_1^{-1/3} \\ \times \left\{ \Delta a(p, T_\infty) - m^s \exp\left[\frac{\mu^\Delta(p, T_\infty)}{kT_\infty}\right] \Delta\chi(p, T_\infty) \right\}. \end{aligned}$$

On introduction of the expansions (about  $p = p_\infty$ )

$$\Delta f(p, T_\infty) = \Delta v_\infty(p - p_\infty) + \cdots$$

$$\Delta a(p, T_\infty) = \Delta a(p_\infty, T_\infty) + \cdots$$

$$\Delta\chi(p, T_\infty) = \Delta\chi(p_\infty, T_\infty) + \cdots$$

$$\mu^\Delta(p, T_\infty) = \mu^\Delta(p_\infty, T_\infty) + \cdots,$$

we obtain the desired result:

$$p = p_\infty - \frac{N_1^{-1/3} [\Delta a(\infty) - m^s e^{\mu \Delta(\infty)/kT_\infty} \Delta \chi(\infty)]}{\Delta v_\infty}. \quad (7-56)$$

Thus, if there is more adsorption on the solid than on the liquid particles,  $\Delta \chi = \chi_L - \chi_S$  is negative and an increase in  $m^s$  decreases the equilibrium pressure (assuming  $\Delta v_\infty$  is positive). This is confirmed by Eq. (7-51b), which states that  $\partial p / \partial \mu_2$  has the same sign as  $\Delta \bar{N}_2 / \Delta \bar{V}$ . In this example, according to Eq. (7-56),

$$\frac{\lambda_2}{kT} \left( \frac{\partial p}{\partial \lambda_2} \right)_{T, N} = \frac{N_1^{-1/3} \Delta \chi(\infty) \lambda_2}{kT \Delta v_\infty} = \frac{\Delta \bar{N}_2}{\Delta \bar{V}},$$

where

$$\begin{aligned} \Delta \bar{N}_2 &= N_1^{2/3} \Delta \chi(\infty) \lambda_2 / kT \\ \Delta \bar{V} &= N_1 \Delta v_\infty. \end{aligned}$$

Equations (7-52a) and (7-56) give

$$\Delta \mu_1 = -\frac{1}{3} N_1^{-1/3} [\Delta a(\infty) - \lambda_2 \Delta \chi(\infty)]. \quad (7-57)$$

By the same methods as above we also find

$$T = T_\infty + \frac{N_1^{-1/3} [\Delta a(\infty) - m^s e^{\mu \Delta(\infty)/kT_\infty} \Delta \chi(\infty)]}{\Delta s_\infty}. \quad (7-58)$$

## 7-2. SMALL SYSTEMS IN SOLVENT OR GAS

The starting point in Section 7-1 was, as usual, an ensemble of distinguishable and independent small systems. We now have to investigate whether the equations deduced there apply as well to infinitely dilute experimental small systems in a liquid or gas.

Real small systems with environmental variables  $N_1, \mu_2, p, T$  will always exist in the presence of at least one other component, namely, molecules of the species being bound or adsorbed. The two most important cases are molecules being adsorbed from a gas onto small systems also in the gas phase, and molecules of a solute species in a liquid solution being bound on small systems suspended in the liquid.

We make use of the approach in Eqs. (2-121) to (2-123) for a mixed solvent, with the notational change for the solvent which is indicated at the end of Section 4-2.

The solvent may be liquid or gaseous and contains  $c$  components. For definiteness, suppose solvent component  $1^s$  ( $s$  for solvent) is the species being bound—i.e., it is the same as component 2 in the small system. Thus  $c \geq 1$ . In the gas case mentioned above, usually  $c = 1$ ; in the liquid case, usually  $c \geq 2$ .

The basic equation for the macroscopic solution containing solvent and (infinitely dilute) small systems is

$$dE_T = T dS_T - p dV_T + \sum_{i=1}^c \mu_i^s dN_i^s + \mu_2 d(\mathcal{N}\bar{N}_2) \\ + \mu^{\square\dagger} d\mathcal{N} + \mu_1 \mathcal{N} dN_1, \quad (7-59)$$

or

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu_2 d(\mathcal{N}\bar{N}_2) \\ + \mu^{\square\dagger} d\mathcal{N} + \mu_1 \mathcal{N} dN_1. \quad (7-60)$$

Equation (7-59) should be compared with Eq. (2-117) for an  $N, p, T$  system in a mixed solvent. The terms

$$\mu_1^s dN_1^s + \mu_2 d(\mathcal{N}\bar{N}_2)$$

refer to the same component. The separation of this component into “free” ( $N_1^s$ ) and “bound” ( $\mathcal{N}\bar{N}_2$ ) molecules is, strictly speaking, a nonthermodynamic procedure, as already mentioned in the introduction to this chapter. The rigorous but uninformative “black-box” attitude would be that a total of  $N_1^s + \mathcal{N}\bar{N}_2$  molecules of species  $1^s$  has been introduced into the solution and there is no *thermodynamic* information concerning a division of the molecules into two classes. But it is implicit in our entire discussion of  $N_1, \mu_2, p, T$  systems that some reliable, basically nonthermodynamic experimental technique is available to measure either  $\mathcal{N}\bar{N}_2$  or  $N_1^s$  separately.

Consider the transfer of an infinitesimal amount of component  $1^s$  from solvent to small systems, with the macroscopic solution closed, at equilibrium with respect to the transfer, and at constant  $T$  and  $p$ . Then  $N_1, \mathcal{N}, N_2^s, \dots, N_c^s$ , and  $N_1^s + \mathcal{N}\bar{N}_2$  are all constant, and

$$dF_T = 0 = \mu_1^s dN_1^s + \mu_2 d(\mathcal{N}\bar{N}_2) = (\mu_1^s - \mu_2) dN_1^s.$$

Therefore  $\mu_1^s = \mu_2$  at equilibrium as might have been expected. This equilibrium condition will not be introduced explicitly until we reach Eq. (7-80).

The chemical potential  $\mu^{\square\dagger}$  is defined formally as a differential coefficient, in terms of  $E_T$  by Eq. (7-59), or, from Eq. (7-60), by

$$\mu^{\square\dagger} = \left( \frac{\partial F_T}{\partial \mathcal{N}} \right)_{T, p, N_i^s, \mathcal{N} \bar{N}_2, N_1} \quad (7-61)$$

In the process implicit here,  $d\mathcal{N}$  "bare" small systems (i.e., with no adsorbed molecules) are added to the macroscopic solution, and the total  $\mathcal{N} \bar{N}_2$  adsorbed molecules are redistributed over the  $\mathcal{N} + d\mathcal{N}$  small systems. The double dagger on  $\mu^{\square\dagger}$  means "bare."

Let us rewrite Eq. (7-60) in a more convenient form:

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu^{\square} d\mathcal{N} + \mu_1 \mathcal{N} dN_1 + \mu_2 \mathcal{N} d\bar{N}_2, \quad (7-62)$$

where

$$\mu^{\square} \equiv \mu^{\square\dagger} + \mu_2 \bar{N}_2$$

or

$$\mu^{\square} = \left( \frac{\partial F_T}{\partial \mathcal{N}} \right)_{T, p, N_i^s, N_1, \bar{N}_2} \quad (7-63)$$

In this process the  $d\mathcal{N}$  added small systems are not "bare": each has  $\bar{N}_2$  adsorbed molecules.

**SOLVENT CONTAINS TWO OR MORE COMPONENTS.** In this case the composition of the macroscopic solution can be specified by  $x' = \mathcal{N} / \sum_i N_i^s$  and  $c-1$  solvent composition variables (denoted by  $sc$ ). We choose, as one of these, the molality  $m_1^s$  of component  $1^s$ , defined by  $m_1^s = 1000 N_1^s / (N_2^s + \cdots + N_c^s) M$ , where  $M$  is the mean molecular weight of the  $N_2^s + \cdots + N_c^s$  molecules. The molality is used instead of the concentration to avoid taking into account the dependence of solvent density on pressure and temperature. We denote the remaining  $c-2$  solvent composition variables, collectively, by  $sc'$ . These variables specify the composition of components  $2^s, 3^s, \dots, c^s$  relative to each other. In a typical case,  $1^s$  would be the molecular species bound on the small systems,  $2^s$  might be water, and  $3^s$  might be, say, added salt. We shall hold  $sc'$  constant in all the equations below, but of course different sets of experiments can be done with different choices of  $sc'$ .

Corresponding to Eqs. (2-121) and (2-122), we now have

$$\mu^\square = \tilde{E}^\square - T\tilde{S}^\square + p\tilde{V}^\square \quad (7-64)$$

and<sup>1</sup>

$$\begin{aligned} d\mu^\square = & -\tilde{S}^\square dT + \tilde{V}^\square dp + \frac{\partial\mu^\square}{\partial x'} dx' + \frac{\partial\mu^\square}{\partial m_1^s} dm_1^s \\ & + \frac{\partial\mu^\square}{\partial N_1} dN_1 + \frac{\partial\mu^\square}{\partial \bar{N}_2} d\bar{N}_2 \quad (sc') \end{aligned} \quad (7-65)$$

for the chemical potential of the small systems. We define  $F$ ,  $\hat{\mu}_1$ , and  $\mathcal{E}$  by the equations

$$\mu^\square = F(N_1, \bar{N}_2, p, T, sc) + kT \ln x' \quad (7-66)$$

$$F = N_1 \hat{\mu}_1(N_1, \bar{N}_2, p, T, sc) + \bar{N}_2 \mu_2 = \mathcal{E} + N_1 \mu_1 + \bar{N}_2 \mu_2, \quad (7-67)$$

and  $S$  by

$$\tilde{S}^\square = S - k \ln x'. \quad (7-68)$$

Of course, at equilibrium,  $\bar{N}_2$  is itself a function of  $N_1$ ,  $p$ ,  $T$ , and  $sc$ . If we write  $\tilde{E}^\square = \bar{E}$  and  $\tilde{V}^\square = \bar{V}$ , Eq. (7-64) becomes

$$F = N_1 \hat{\mu}_1 + \bar{N}_2 \mu_2 = \bar{E} - TS + p\bar{V}. \quad (7-69)$$

This is formally identical with Eq. (7-2).

Equation (7-65) requires a more detailed discussion. We show first that the coefficient  $\partial\mu^\square/\partial N_1$  in this equation is equal to  $\mu_1$  in Eq. (7-62). From Eqs. (7-62) and (7-66), we have

$$\begin{aligned} \left( \frac{\partial\mu_k^s}{\partial \mathcal{N}} \right)_{T, p, N_i^s, N_1, \bar{N}_2} &= \left( \frac{\partial\mu^\square}{\partial N_k^s} \right)_{T, p, N_j^s, \mathcal{N}, N_1, \bar{N}_2} \\ &= \left( \frac{\partial F}{\partial N_k^s} \right)_{T, p, N_j^s, N_1, \bar{N}_2} - \frac{kT}{N_1^s + \cdots + N_c^s}. \end{aligned} \quad (7-70)$$

Integration of Eq. (7-70) from  $\mathcal{N} = 0$  to  $\mathcal{N}$  gives

$$\mu_k^s = \mu_k^*(p, T, sc) + \left[ (N_1^s + \cdots + N_c^s) \frac{\partial F}{\partial N_k^s} - kT \right] x', \quad (7-71)$$

where  $\mu_k^*$  refers to the pure solvent ( $x' \rightarrow 0$ ). The Gibbs–Duhem equation for the macroscopic solution is

$$\sum_{k=1}^c N_k^s d\mu_k^s + \mathcal{N} d\mu^\square = 0 \quad (T, p, N_1, \bar{N}_2 \text{ constant}).$$

<sup>1</sup> The notation ( $sc'$ ) following an equation is shorthand for ( $sc'$  constant).

Then

$$\begin{aligned} 0 &= \sum_k N_k^s \left( \frac{\partial \mu_k^s}{\partial \mathcal{N}} \right)_{T, p, N_1^s, N_2, \bar{N}_2} + \mathcal{N} \left( \frac{\partial \mu^\square}{\partial \mathcal{N}} \right)_{T, p, N_1^s, \bar{N}_1, \bar{N}_2} \\ &= \sum_k N_k^s \left( \frac{\partial F}{\partial N_k^s} - \frac{kT}{N_1^s + \dots + N_c^s} \right) + kT = \sum_k N_k^s \frac{\partial F}{\partial N_k^s}. \end{aligned} \quad (7-72)$$

We now multiply Eq. (7-71) by  $N_k^s$  and sum, using Eq. (7-72):

$$\sum_k N_k^s \mu_k^s = \sum_k N_k^s \mu_k^* - \mathcal{N} kT. \quad (7-73)$$

Finally, from Eqs. (7-62), (7-73), and

$$F_T = \sum_k N_k^s \mu_k^s + \mathcal{N} \mu^\square, \quad (7-74)$$

we obtain

$$\begin{aligned} \mu_1 &= \frac{1}{\mathcal{N}} \left( \frac{\partial F_T}{\partial N_1} \right)_{T, p, N_1^s, \mathcal{N}, \bar{N}_2} = \left( \frac{\partial \mu^\square}{\partial N_1} \right)_{T, p, N_1^s, \mathcal{N}, \bar{N}_2} \\ &= \left( \frac{\partial \mu^\square}{\partial N_1} \right)_{T, p, \bar{N}_2, x', sc}. \end{aligned} \quad (7-75)$$

A completely analogous argument shows that  $\mu_2 = \partial \mu^\square / \partial \bar{N}_2$ . Hence Eq. (7-65) becomes

$$\begin{aligned} d\mu^\square &= -\bar{s}^\square dT + \bar{v}^\square dp + kT d \ln x' \\ &\quad + \beta dm_1^s + \mu_1 dN_1 + \mu_2 d\bar{N}_2 \quad (sc'), \end{aligned} \quad (7-76)$$

where  $\beta = (\partial F / \partial m_1^s)_{T, p, N_1, \bar{N}_2, sc}$ . We now substitute Eqs. (7-66) to (7-68) and  $\bar{v}^\square = \bar{V}$  into the above relation and find

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1 dN_1 - \bar{N}_2 d\mu_2 + \beta dm_1^s \quad (sc') \quad (7-77)$$

$$dF = -S dT + \bar{V} dp + \mu_1 dN_1 + \mu_2 d\bar{N}_2 + \beta dm_1^s \quad (sc'). \quad (7-78)$$

These equations should be compared with Eqs. (7-5) and (2-123), respectively. We see that the term in  $\beta$  is a new feature, not encountered before, and a complication. It arises essentially because we cannot change  $\mu_2$  and hence  $\bar{N}_2$ , the amount of binding, by an alteration in  $m_1^s$  without simultaneously changing the solvent environment of each small system. This will influence the small system thermodynamic functions, for example  $F$ , quite aside from binding effects (note that  $\bar{N}_2$  is held constant in  $\beta = \partial F / \partial m_1^s$ ).



An equivalent observation is that  $sc$  is constant in Eq. (2-123) but not in Eqs. (7-77) and (7-78): in these latter equations  $sc'$  is constant but  $m_1^s$  varies.

If the interaction between small systems and solvent is at the surface of the small system only, then in the macroscopic limit,  $N_1 \rightarrow \infty$ , the small system becomes a bulk phase and  $\beta$  (a surface effect) becomes negligible. But if, for example, the small system is a rodlike macromolecule,  $\beta$  becomes proportional to  $N_1$  (i.e.,  $\beta$  becomes an extensive property) as  $N_1$  becomes large. In the former case we may drop  $\beta dm_1^s$  in Eq. (7-78) in the macroscopic limit, but not in the latter case. In both cases  $F = \mu_1 N_1 + \mu_2 \bar{N}_2$ .

Thus we do not have an exact, formal correspondence between Eqs. (7-5) and (7-77) as we might have expected from our previous treatments of small systems in a solvent. Furthermore, this type of complication may be anticipated with any *experimental* open or semiopen small system. We encounter it again, for example, in Chapter 10.

Actually, in many experimental cases of interest, the binding of the species  $1^s$  on the small systems is strong, so that  $m_1^s$  is quite small over the whole range of values of interest. In this case, as we shall see below, the term in  $\beta$  may be dropped, and Eq. (7-77) becomes

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1 dN_1 - \bar{N}_2 d\mu_2 \quad (m_1^s \rightarrow 0, sc'). \quad (7-79)$$

This equation is identical with Eq. (7-5).

We return now to Eq. (7-77). Since  $\mu_2 = \mu_1^s$  at equilibrium and  $\mu_1^s$  is a function of  $m_1^s$ , we want to eliminate  $d\mu_2$  from this equation in favor of the more directly measurable quantity  $dm_1^s$ . At the same time this will avoid any arbitrariness, in later equations, associated with the choice of the zeros of energy and entropy in  $\mu_2$ . Such arbitrariness would otherwise arise, for example, in equations in which the temperature is varied holding  $\mu_2$  constant.<sup>1</sup>

We are always interested in the limit  $x' \rightarrow 0$  (isolated small systems) and retain the lowest-order term in  $x'$  possible. For this reason,  $\mu_2 = \mu_1^s$  in Eq. (7-77) should be taken as  $\mu_1^s(p, T, m_1^s, sc')$ , the chemical potential of  $1^s$  in the solvent ( $x' = 0$ ). Thus

$$d\mu_2 = d\mu_1^s = -\bar{s}_1^* dT + \bar{v}_1^* dp + \left( \frac{\partial \mu_1^s}{\partial m_1^s} \right)_{T, p, sc'} dm_1^s \quad (sc'). \quad (7-80)$$

<sup>1</sup> See the footnote on p. 4.

If we substitute Eq. (7-80) in Eq. (7-77), we obtain

$$d(\hat{\mu}_1 N_1) = - (S - \bar{N}_2 \bar{s}_1^*) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^*) dp \\ + \mu_1 dN_1 + \left[ \beta - \bar{N}_2 \left( \frac{\partial \mu_1^*}{\partial m_1^s} \right)_{T, p, sc'} \right] dm_1^s \quad (sc'). \quad (7-81)$$

The independent variables in Eq. (7-81) are the "equilibrium" set  $T, p, N_1, m_1^s$ , and  $sc'$ , which recognize explicitly the existence of the binding equilibrium. That is, the redundancies (at equilibrium) in independent variables ( $\mu_2$  and  $\bar{N}_2$ , respectively) which occur in Eqs. (7-77) and (7-78) do not appear here. For  $\mu_2 (= \mu_1^*)$  is determined by  $T, p, m_1^s$ , and  $sc'$ , and  $\bar{N}_2$  is determined by these variables and  $N_1$  in addition. Equations (7-77) and (7-78), as they stand (without the equilibrium condition  $\mu_2 = \mu_1^*$ ), apply to a binary small system in a solvent, with variations in solvent composition ( $m_1^s$ ) included.

From the list of independent variables in Eq. (7-81) it is apparent that an alternative expression for the coefficient of  $dm_1^s$  must be

$$\beta - \bar{N}_2 \left( \frac{\partial \mu_1^*}{\partial m_1^s} \right)_{T, p, sc'} = \left( \frac{\partial \hat{\mu}_1 N_1}{\partial m_1^s} \right)_{T, p, N_1, sc'}. \quad (7-82)$$

Still another form is

$$\left( \frac{\partial \hat{\mu}_1 N_1}{\partial m_1^s} \right)_{T, p, N_1, sc'} = \left( \frac{\partial \hat{\mu}_1 N_1}{\partial m_1^s} \right)_{T, p, N_1, \bar{N}_2, sc'} \\ + \left( \frac{\partial \hat{\mu}_1 N_1}{\partial \bar{N}_2} \right)_{T, p, N_1, sc} \left( \frac{\partial \bar{N}_2}{\partial m_1^s} \right)_{T, p, N_1, sc'}. \quad (7-83)$$

The first derivative on the right can be written (from  $N_1 \hat{\mu}_1 = F - \bar{N}_2 \mu_2$ ) as

$$\left( \frac{\partial \hat{\mu}_1 N_1}{\partial m_1^s} \right)_{T, p, N_1, \bar{N}_2, sc'} = \beta - \bar{N}_2 \left( \frac{\partial \mu_2}{\partial m_1^s} \right)_{T, p, N_1, \bar{N}_2, sc'}. \quad (7-84)$$

We also have, from Eqs. (7-77) and (7-78), respectively,

$$\left( \frac{\partial \hat{\mu}_1 N_1}{\partial \bar{N}_2} \right)_{T, p, N_1, sc} = - \bar{N}_2 \left( \frac{\partial \mu_2}{\partial \bar{N}_2} \right)_{T, p, N_1, sc} \\ \left( \frac{\partial \mu_2}{\partial m_1^s} \right)_{T, p, N_1, \bar{N}_2, sc'} = \left( \frac{\partial \beta}{\partial \bar{N}_2} \right)_{T, p, N_1, sc}. \quad (7-85)$$

If we use Eqs. (7-84) and (7-85) in Eq. (7-83), we obtain

$$\left(\frac{\partial \hat{\mu}_1 N_1}{\partial m_1^s}\right)_{T, p, N_1, sc'} = \beta - \bar{N}_2 \left(\frac{\partial \beta}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} - \bar{N}_2 \left(\frac{\partial \bar{N}_2}{\partial m_1^s}\right)_{T, p, N_1, sc'} \left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, sc}. \quad (7-86)$$

An expression for the dependence of the equilibrium amount of binding  $\bar{N}_2$  on  $m_1^s$  follows on combining Eqs. (7-82) and (7-86):

$$\begin{aligned} \left(\frac{\partial \bar{N}_2}{\partial m_1^s}\right)_{T, p, N_1, sc'} &= \left[ \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} - \left(\frac{\partial \beta}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} \right] / \left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, sc}. \end{aligned} \quad (7-87)$$

A more direct derivation of this relation will be given below.

When the solvent is very dilute in  $1^s$ , as will often either be the case or be assumed for simplicity [see Eq. (7-79)],

$$\mu_1^* = \mu_1^\Delta(p, T, sc') + kT \ln m_1^s \quad (m_1^s \rightarrow 0) \quad (7-88)$$

$$\left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} = \frac{kT}{m_1^s} \quad (m_1^s \rightarrow 0), \quad (7-89)$$

where  $\mu^\Delta$  is a "standard" chemical potential for component  $1^s$  in the solvent. Now  $\beta$  can be expressed as a power series in  $m_1^s$  and it becomes a function of  $N_1$ ,  $\bar{N}_2$ ,  $p$ ,  $T$ , and  $sc'$  in the limit  $m_1^s \rightarrow 0$ . Statistical mechanical considerations show that, for small  $m_1^s$ , the ratio of  $\beta$  to  $kT/m_1^s$  in the last term of Eq. (7-81) has the order of magnitude of the ratio of the "van der Waals volume" of a small system to the volume per molecule ( $V_T/N_1^s$ ) of species  $1^s$ . This ratio becomes small as  $m_1^s \rightarrow 0$ . The ratio of  $\beta$  to  $\bar{N}_2 kT/m_1^s$  is of course even smaller (we are assuming strong binding so that ordinarily  $\bar{N}_2 > 1$  or  $\bar{N}_2 \gg 1$  even though  $m_1^s$  is small). Hence we drop  $\beta$  in Eq. (7-81) with the result

$$\begin{aligned} d(\hat{\mu}_1 N_1) &= -(S - \bar{N}_2 \bar{s}_1^\square) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^\square) dp + \mu_1 dN_1 \\ &\quad - \bar{N}_2 kT d \ln m_1^s \quad (m_1^s \rightarrow 0, \quad sc'), \end{aligned} \quad (7-90)$$

where  $\bar{s}_1^\square$  and  $\bar{v}_1^\square$  are partial molal quantities for  $1^s$  in the solvent

in the limit  $m_1^s \rightarrow 0$  (that is,  $\bar{s}_1^* \rightarrow \bar{s}_1^\square$ , etc.). This equation is completely equivalent to but is a more practical form of Eq. (7-79). It is therefore also identical with Eq. (7-5).

Similarly, when  $m_1^s \rightarrow 0$ , Eq. (7-87) becomes

$$\left( \frac{\partial \bar{N}_2}{\partial m_1^s} \right)_{T, p, N_1, sc'} = \frac{kT}{m_1^s} / \left( \frac{\partial \mu_2}{\partial \bar{N}_2} \right)_{T, p, N_1, sc'} \quad (m_1^s \rightarrow 0). \quad (7-91)$$

Measurement of  $\partial \bar{N}_2 / \partial m_1^s$  and  $m_1^s$  allows evaluation of  $\partial \mu_2 / \partial \bar{N}_2$ . If  $m_1^s$  is so small that the amount of binding is also small ( $\bar{N}_2 \rightarrow 0$ ), then, according to Eq. (4-68),  $\partial \mu_2 / \partial \bar{N}_2 = kT / \bar{N}_2$ . Therefore

$$\bar{N}_2 = k_1^s(T, p, N_1, sc') m_1^s, \quad (7-92)$$

where  $k_1^s$  is an integration constant. This is Henry's law.

Equation (7-78) can obviously be rewritten with the same independent variables as in Eq. (7-81):

$$\begin{aligned} dF = & \left[ -S + \mu_1^* \left( \frac{\partial \bar{N}_2}{\partial T} \right)_{p, N_1, sc'} \right] dT + \left[ \bar{V} + \mu_1^* \left( \frac{\partial \bar{N}_2}{\partial p} \right)_{T, N_1, sc'} \right] dp \\ & + \left[ \mu_1 + \mu_1^* \left( \frac{\partial \bar{N}_2}{\partial N_1} \right)_{T, p, sc'} \right] dN_1 + \left[ \beta + \mu_1^* \left( \frac{\partial \bar{N}_2}{\partial m_1^s} \right)_{T, p, N_1, sc'} \right] dm_1^s \quad (sc') \end{aligned} \quad (7-93)$$

where

$$\beta + \mu_1^* \left( \frac{\partial \bar{N}_2}{\partial m_1^s} \right)_{T, p, N_1, sc'} = \left( \frac{\partial F}{\partial m_1^s} \right)_{T, p, N_1, sc'}. \quad (7-94)$$

An explicit expression for  $\partial \bar{N}_2 / \partial m_1^s$  is given in Eq. (7-87). Similar relations for  $\partial \bar{N}_2 / \partial T$ , etc., will be derived below.

Equation (7-81) results from Eq. (7-77) on elimination of  $\mu_2$  as an independent variable. If, instead, we eliminate  $m_1^s$  using Eq. (7-80), we find

$$\begin{aligned} d(\hat{\mu}_1 N_1) = & \left[ -S + \bar{s}_1^* \left( \frac{\partial F}{\partial \mu_1^*} \right)_{T, p, N_1, \bar{N}_2, sc'} \right] dT \\ & + \left[ \bar{V} - \bar{v}_1^* \left( \frac{\partial F}{\partial \mu_1^*} \right)_{T, p, N_1, \bar{N}_2, sc'} \right] dp + \mu_1 dN_1 \\ & + \left[ \left( \frac{\partial F}{\partial \mu_1^*} \right)_{T, p, N_1, \bar{N}_2, sc'} - \bar{N}_2 \right] d\mu_1^* \quad (sc'), \end{aligned} \quad (7-95)$$

where

$$\left(\frac{\partial F}{\partial \mu_1^*}\right)_{T, p, N_1, \bar{N}_2, sc'} - \bar{N}_2 = \left(\frac{\partial \hat{\mu}_1 N_1}{\partial \mu_1^*}\right)_{T, p, N_1, sc'}. \quad (7-96)$$

In the special case  $m_1^s \rightarrow 0$ ,  $\partial F / \partial \mu_1^*$  becomes negligible and

$$\frac{\partial \hat{\mu}_1 N_1}{\partial \mu_1^*} \rightarrow -\bar{N}_2. \quad (7-97)$$

Hence Eq. (7-79) is again recovered.

So far in this subsection we have been concerned primarily with analogues of the fundamental Eq. (7-5). We can summarize the work thus far as follows.

If we use the same definitions of thermodynamic functions for a two-component small system in a solvent as in Section 4-2, we find that in the present problem Eq. (7-2) is satisfied by these functions but Eq. (7-5) is satisfied only in the limit  $m_1^s \rightarrow 0$  [see Eq. (7-90)]. However, this limit is a common special case and even otherwise is a useful approximation. Extensions of Eq. (7-5) [for example, Eq. (7-81)] must be employed when the limit  $m_1^s \rightarrow 0$  is not appropriate.

Finally, in this subsection, we deduce a number of other relations that follow directly from the condition  $d\mu_2 = d\mu_1^*$ . Equation (7-80) contains an explicit expression for  $d\mu_1^*$ . We now consider  $d\mu_2$  and related topics. Section 4-1 is applicable here, with the added complication that  $m_1^s$  may vary ( $sc = \text{constant}$  is understood in Section 4-1; see Section 4-2). Thus

$$\begin{aligned} d\mu_2 = & -\bar{s}_2 dT + \bar{v}_2 dp + \left(\frac{\partial \mu_2}{\partial N_1}\right)_{T, p, \bar{N}_2, sc} dN_1 \\ & + \left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} d\bar{N}_2 + \left(\frac{\partial \mu_2}{\partial m_1^s}\right)_{T, p, N_1, \bar{N}_2, sc'} dm_1^s \quad (sc'), \end{aligned} \quad (7-98)$$

where  $\bar{s}_2 = (\partial S / \partial \bar{N}_2)_{T, p, N_1, sc}$ , etc. These are partial molal quantities for the small system, not the solvent. In view of Eq. (7-85b) and the cross relation  $\partial \mu_2 / \partial N_1 = \partial \mu_1 / \partial \bar{N}_2$ , we can also write

$$\begin{aligned} d\mu_2 = & -\bar{s}_2 dT + \bar{v}_2 dp + \left(\frac{\partial \mu_1}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} d\bar{N}_2 \\ & + \left(\frac{\partial \mu_2}{\partial N_1}\right)_{T, p, \bar{N}_2, sc} dN_1 + \tilde{\beta}_2 dm_1^s \quad (sc'). \end{aligned} \quad (7-99)$$

The Gibbs-Duhem relation is

$$d\mathcal{E} = -S dT + \bar{V} dp - N_1 d\mu_1 - \bar{N}_2 d\mu_2 + \beta dm_1^s \quad (sc'). \quad (7-100)$$

A special case is

$$\left(\frac{\partial \mathcal{E}}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} = -N_1 \left(\frac{\partial \mu_1}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} - \bar{N}_2 \left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} \quad (7-101)$$

If we put this in Eq. (7-99), we have

$$d\mu_2 = -\tilde{s}_2 dT + \tilde{v}_2 dp - \frac{1}{N_1} \left(\frac{\partial \mathcal{E}}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} dN_1 \\ + \left(\frac{\partial \mu_2}{\partial \bar{N}_2/N_1}\right)_{T, p, N_1, sc} d\left(\frac{\bar{N}_2}{N_1}\right) + \tilde{\beta}_2 dm_1^s \quad (sc'). \quad (7-102)$$

If we now set  $d\mu_1^*$  in Eq. (7-80) equal to  $d\mu_2$  in Eq. (7-102), five variables ( $T, p, N_1, \bar{N}_2/N_1, m_1^s$ ) appear in the resulting equation. Ten different pairs may be chosen out of the five variables and hence there are ten equations of the "Clausius-Clapeyron" type that can be derived (only four are independent). Equation (7-87) is one of these. A few others are

$$\left(\frac{\partial \bar{N}_2/N_1}{\partial N_1}\right)_{T, p, sc} = \frac{1}{N_1} \left(\frac{\partial \mathcal{E}}{\partial \bar{N}_2}\right)_{T, p, N_1, sc} / \left(\frac{\partial \mu_2}{\partial \bar{N}_2/N_1}\right)_{T, p, N_1, sc} \\ = \frac{1}{N_1^2} \left(\frac{\partial \mathcal{E}}{\partial \mu_2}\right)_{T, p, N_1, sc} \quad (7-103)$$

$$\left(\frac{\partial \bar{N}_2}{\partial T}\right)_{p, N_1, sc} = \frac{\tilde{s}_2 - \tilde{s}_1^*}{\left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, sc}} \quad (7-104)$$

$$\left(\frac{\partial m_1^s}{\partial T}\right)_{p, N_1, \bar{N}_2, sc'} = \frac{\tilde{s}_1^* - \tilde{s}_2}{\left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} - \tilde{\beta}_2} \quad (7-105)$$

$$\left(\frac{\partial p}{\partial T}\right)_{N_1, \bar{N}_2, sc} = \frac{\tilde{s}_1^* - \tilde{s}_2}{\tilde{v}_1^* - \tilde{v}_2} \quad (7-106)$$

where  $\bar{S}_1^* - \bar{S}_2$  can also be written as  $(\bar{H}_1^* - \bar{H}_2)/T$  [see Eq. (4-17)]. We see from Eqs. (7-91) and (7-103) that measurement of  $\partial \bar{N}_2 / \partial m_1^s$  and  $\partial \bar{N}_2 / \partial N_1$  (or  $\partial m_1^s / \partial N_1$ ) will give  $\partial \mathcal{E} / \partial \bar{N}_2$ . When the solvent is dilute in  $1^s$ , Eq. (7-105) becomes

$$\left( \frac{\partial \ln m_1^s}{\partial T} \right)_{p, N_1, \bar{N}_2, sc'} = \frac{\bar{S}_1^\square - \bar{S}_2}{kT} = \frac{\bar{H}_1^\square - \bar{H}_2}{kT^2} \quad (m_1^s \rightarrow 0). \quad (7-107)$$

Thus, measurement of  $\partial \ln m_1 / \partial T$  makes  $\bar{S}_1^\square - \bar{S}_2$  and  $\bar{H}_1^\square - \bar{H}_2$  accessible. Equation (7-107) is the analogue of the "isosteric heat equation" familiar in gas adsorption work. It is easy to show that  $(\bar{H}_1^\square - \bar{H}_2) dN_1^s$  is the heat absorbed by the closed macroscopic solution in the transfer of  $dN_1^s$  molecules of component  $1^s$  from the bound state to the solvent, at equilibrium and at constant pressure and temperature.

There is an alternative form of Eqs. (7-105) and (7-107) that is of some interest. In Eq. (7-77), we use the notation  $\hat{\mu}_{10}$ ,  $S_0$ , etc., to indicate values of these functions when<sup>1</sup>  $\bar{N}_2 = 0$ . Then, on subtracting  $d(\hat{\mu}_{10}N_1)$  from  $d(\hat{\mu}_1N_1)$  and solving for  $d\mu_2$ ,

$$d\mu_2 = - \frac{S - S_0}{\bar{N}_2} dT + \frac{\beta - \beta_0}{\bar{N}_2} dm_1^s - \frac{N_1}{\bar{N}_2} d(\hat{\mu}_1 - \hat{\mu}_{10})$$

( $p, N_1, sc'$  constant). (7-108)

We set this equal to  $d\mu_1^*$  in Eq. (7-80) and find

$$\left( \frac{\partial m_1^s}{\partial T} \right)_{p, N_1, sc', \hat{\mu}_1 - \hat{\mu}_{10}} = \frac{\bar{S}_1^* - \frac{S - S_0}{\bar{N}_2}}{\left( \frac{\partial m_1^s}{\partial T} \right)_{T, p, sc'} - \frac{\beta - \beta_0}{\bar{N}_2}} \quad (7-109)$$

When  $m_1^s$  is small,

$$\left( \frac{\partial \ln m_1^s}{\partial T} \right)_{p, N_1, sc', \hat{\mu}_1 - \hat{\mu}_{10}} = \frac{1}{kT} \left( \bar{S}_1^\square - \frac{S - S_0}{\bar{N}_2} \right) \quad (m_1^s \rightarrow 0). \quad (7-110)$$

These equations give the entropy  $S - S_0$  rather than  $\partial S / \partial \bar{N}_2$ , as in Eq. (7-105). There is an analogous equation, useful in gas adsorption work, in which the surface pressure (the analogue of  $\hat{\mu}_{10} - \hat{\mu}_1$ ) is held constant.

<sup>1</sup> These functions refer to "bare" small systems in the presence of solvent with  $m_1^s \neq 0$ . See p. 15.

In order to find  $\hat{\mu}_1 - \hat{\mu}_{10}$  from experimental data, we put Eq. (7-108) in the form

$$d(\hat{\mu}_1 - \hat{\mu}_{10}) = \left[ -\frac{\bar{N}_2}{N_1} \left( \frac{\partial \mu_1^*}{\partial m_1^s} \right)_{T, p, sc'} + \frac{\beta - \beta_0}{N_1} \right] dm_1^s \quad (T, p, N_1, sc' \text{ constant}). \quad (7-111)$$

This equation is not very practical to use as it stands, but when the solvent is dilute in 1<sup>s</sup>,

$$d(\hat{\mu}_1 - \hat{\mu}_{10}) = -\frac{\bar{N}_2 kT}{N_1 m_1^s} dm_1^s \quad (m_1^s \rightarrow 0; T, p, N_1, sc' \text{ constant}). \quad (7-112)$$

Then, if  $\bar{N}_2(m_1^s)$  is measured experimentally between  $\bar{N}_2 = 0$  at  $m_1^s = 0$  and  $\bar{N}_2 = N'$  at  $m_1^s = m'$ ,

$$\hat{\mu}_1(N') - \hat{\mu}_{10} = -\frac{kT}{N_1} \int_0^{m'} \frac{\bar{N}_2(m_1^s)}{m_1^s} dm_1^s \quad (m_1^s \rightarrow 0; T, p, N_1, sc' \text{ constant}). \quad (7-113)$$

This is the analogue of the "Gibbs adsorption isotherm." One can calculate  $\hat{\mu}_1 - \hat{\mu}_{10}$  from Eq. (7-113) for use<sup>1</sup> in Eq. (7-110). In the Henry's law region,  $\bar{N}_2 = k_1^s m_1^s$ , as in Eq. (7-92), and

$$-[\hat{\mu}_1(\bar{N}_2) - \hat{\mu}_{10}] = \frac{kT \bar{N}_2}{N_1} \quad (\bar{N}_2 \rightarrow 0). \quad (7-114)$$

This is the analogue of an ideal equation of state.<sup>2</sup>

"BLACK-BOX" POINT OF VIEW. Here we consider exactly the same system as above but adopt the alternative point of view that we are unaware of the fact that binding is taking place. That is, the binding will now be included implicitly but not explicitly. The fundamental equations are [see Eq. 7-60]:

$$dF_T = -S_T dT + V_T dp + \mu_1^s d(N_1^s + \mathcal{N} \bar{N}_2) + \sum_{j=2}^c \mu_j^s dN_j^s + \mu^{\square \dagger} d\mathcal{N} + \mu_1 \mathcal{N} dN_1 \quad (7-115)$$

<sup>1</sup> Compare T. L. Hill, P. H. Emmett, and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5102 (1951), for the gas adsorption case.

<sup>2</sup> Compare T. L. Hill, *J. Am. Chem. Soc.*, **79**, 4885 (1957), Eq. (15), for the macroscopic solution case.



and

$$d\mu^{\square\dagger} = -\tilde{s}^{\square\dagger} dT + \tilde{v}^{\square\dagger} dp + kT d \ln x' + \mu_1 dN_1 \quad (sc) \quad (7-116)$$

where

$$x' = \frac{\mathcal{N}}{N_1^s + \mathcal{N} \bar{N}_2 + \sum_j N_j^s}.$$

This is the same as the earlier definition,  $x' = \mathcal{N}/\sum_i N_i^s$ , in the limit  $\mathcal{N} \rightarrow 0$ . Equations (7-115) and (7-116) are essentially the same as Eqs. (2-117) and (2-122), respectively. The partial molal quantities,  $\mu^{\square\dagger}$ ,  $\tilde{s}^{\square\dagger}$ , etc., refer to the addition of "bare" small systems to the macroscopic solution [that is  $\partial F_T/\partial \mathcal{N}$ ,  $\partial S_T/\partial \mathcal{N}$ , etc., as in Eq. (7-61)]. From Eqs. (7-66), (7-67), and the equation following (7-62), we have

$$\mu^{\square\dagger} = N_1 \hat{\mu}_1 + kT \ln x'.$$

Also, we define (as in Section 2-3 for a one-component small system)

$$S^{\dagger} = \tilde{s}^{\square\dagger} + k \ln x', \quad \bar{E}^{\dagger} = \tilde{E}^{\square\dagger}, \quad \bar{V}^{\dagger} = \tilde{v}^{\square\dagger}.$$

With these definitions, Eq. (7-116) becomes

$$d(\hat{\mu}_1 N_1) = -S^{\dagger} dT + \bar{V}^{\dagger} dp + \mu_1 dN_1 \quad (sc). \quad (7-117)$$

This is equivalent to Eq. (2-123) and identical with Eq. (7-81) when  $m_1^s$  and  $sc'$  (that is,  $sc$ ) are both constant. Thus the physical significance of the coefficients of  $dT$  and  $dp$  in Eq. (7-81) is seen to be

$$\begin{aligned} S - \bar{N}_2 \tilde{s}_1^* &= S^{\dagger} = \tilde{s}^{\square\dagger} + k \ln x' \\ \bar{V} - \bar{N}_2 \tilde{v}_1^* &= \bar{V}^{\dagger} = \tilde{v}^{\square\dagger}. \end{aligned} \quad (7-118)$$

These are the ("bare") small system thermodynamic functions which would be obtained if the binding were ignored in the thermodynamics, even though it is known, on extrathermodynamic grounds, to exist. This result should be expected since the introduction of the concept of binding adds a degree of freedom ( $\mu_2$  or  $\bar{N}_2$ ), but this degree of freedom is taken away again when the binding equilibrium condition ( $\mu_2 = \mu_1^*$ ) is introduced explicitly as in Eq. (7-81). Of course, the complete Eq. (7-81) is more general than Eq. (7-117) in that the former equation allows variations in  $m_1^s$ . Such variations are essential in an explicit study of a binding equilibrium.

Naturally, the discussion of the relation  $d\mu_2 = d\mu_1^*$ , beginning with Eq. (7-98), has no parallel from the "black-box" point of view since binding is included explicitly in  $d\mu_2$ .

Note that Eqs. (7-118) are consistent with

$$\begin{aligned}\mu^\square - \mu^{\square\dagger} &= (\bar{E}^\square - \bar{E}^{\square\dagger}) - T(\bar{S}^\square - \bar{S}^{\square\dagger}) + p(\bar{V}^\square - \bar{V}^{\square\dagger}) \\ &= \bar{N}_2\mu_1^* = \bar{N}_2(\bar{E}_1^* - T\bar{S}_1^* + p\bar{V}_1^*).\end{aligned}\quad (7-119)$$

If  $S^\dagger$ ,  $\bar{V}^\dagger$ , and  $\bar{E}^\dagger$  are measured, ignoring binding, then

$$\begin{aligned}S &= S^\dagger + \bar{N}_2\bar{S}_1^* \\ \bar{V} &= \bar{V}^\dagger + \bar{N}_2\bar{V}_1^* \\ \bar{E} &= \bar{E}^\dagger + \bar{N}_2\bar{E}_1^*.\end{aligned}\quad (7-120)$$

ONE-COMPONENT SOLVENT. If the solvent consists of only one component ( $1^s$ ) and this component is bound to some extent on the small systems, then Eq. (7-65) simplifies somewhat to

$$d\mu^\square = -\bar{S}^\square dT + \bar{V}^\square dp + \frac{\partial\mu^\square}{\partial x'} dx' + \mu_1 dN_1 + \mu_2 d\bar{N}_2, \quad (7-121)$$

where  $x' = \mathcal{N}/N_1^s$ . Examples are the hydration of a macromolecule and the adsorption of a gas onto gaseous colloidal particles. We use the same definitions as in Eqs. (7-66) to (7-68), although now there is no dependence of  $F$ , etc., on solvent composition. Then

$$F = N_1\hat{\mu}_1 + \bar{N}_2\mu_2 = \bar{E} - TS + p\bar{V} \quad (7-122)$$

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1 dN_1 - \bar{N}_2 d\mu_2. \quad (7-123)$$

These are the same as Eqs. (7-2) and (7-5). However, because of the binding equilibrium, there is redundancy in the independent variables in Eq. (7-123), since  $\mu_2 = \mu_1^*$  and  $\mu_1^*$  is a function of  $p$  and  $T$ . We substitute

$$d\mu_1^* = -s_1^* dT + v_1^* dp$$

for  $d\mu_2$  in Eq. (7-123) and obtain

$$d(\hat{\mu}_1 N_1) = -(S - \bar{N}_2 s_1^*) dT + (\bar{V} - \bar{N}_2 v_1^*) dp + \mu_1 dN_1. \quad (7-124)$$

The quantities  $\mu_1^*$ ,  $s_1^*$ , etc., are properties per molecule of the pure solvent at  $p$  and  $T$ . The independent "equilibrium" variables are in this case  $T$ ,  $p$ , and  $N_1$ .

If the binding is ignored ("black-box" point of view),

$$d(\hat{\mu}_1 N_1) = - S^\dagger dT + \bar{V}^\dagger dp + \mu_1 dN_1, \quad (7-125)$$

as in Eq. (7-117). Thus  $S = S^\dagger + \bar{N}_2 s_1^*$ , etc. Equation (7-125) is equivalent to Eq. (2-114).

If the solvent is a liquid or dense gas,<sup>1</sup> the pressure effect on the small system in Eq. (7-124) is hydrostatic in nature. But if the solvent is a very dilute gas ( $p \rightarrow 0$ ),  $\bar{V} = v_1^* = kT/p$  and

$$d(\hat{\mu}_1 N_1) = - (S - \bar{N}_2 s_1^\square) dT - (\bar{N}_2 - 1)kT d \ln p + \mu_1 dN_1 \quad (p \rightarrow 0). \quad (7-126)$$

In this case the hydrostatic pressure on the small system is negligible but  $p$  serves as a measure of the chemical potential of the species,  $1^s$ , being adsorbed. The entropy per molecule  $s_1^\square$  is that of  $1^s$  in the ideal-gas state at  $T$  and  $p$ .

In the very dilute gas case just mentioned, there is a close relation to Section 3-3, as might be expected. Let us denote small system thermodynamic functions defined as in Section 3-3 by the superscript<sup>(3)</sup>. Then

$$\begin{aligned} \mu^\square &= N_1 \hat{\mu}_1^{(3)} + \bar{N}_2 \mu_2 + kT \ln \frac{\mathcal{N}}{\mathcal{N}^\dagger} \\ \bar{s}^\square &= S^{(3)} + k - k \ln \frac{\mathcal{N}}{\mathcal{N}^\dagger}, \end{aligned} \quad (7-127)$$

so that

$$\begin{aligned} N_1 \hat{\mu}_1 &= N_1 \hat{\mu}_1^{(3)} + kT \ln \frac{N_1^s}{\mathcal{N}^\dagger} \\ S &= S^{(3)} + k + k \ln \frac{\mathcal{N}^\dagger}{N_1^s}. \end{aligned} \quad (7-128)$$

If we put Eqs. (7-128) and  $\bar{V} = kT/p$  in Eqs. (7-69) and (7-126), we find

$$d(\hat{\mu}_1^{(3)} N_1) = - (S^{(3)} - \bar{N}_2 s_1^\square) dT - \bar{N}_2 kT d \ln p + \mu_1 dN_1 \quad (p \rightarrow 0) \quad (7-129)$$

$$N_1 \hat{\mu}_1^{(3)} + \bar{N}_2 \mu_2 = \bar{E} - TS^{(3)}. \quad (7-130)$$

<sup>1</sup> See the footnote on p. 55 of Part I.

Equation (7-129) can be written as

$$d(\mu_1^{(3)} N_1) = -S^{(3)} dT - \bar{N}_2 d\mu_2 + \mu_1 dN_1. \quad (7-131)$$

Equations (7-130) and (7-131) are two-component equivalents of Eqs. (3-29) and (3-31).

Equations (7-129) to (7-131) are unaltered if the very dilute gas contains other (very dilute) species 2<sup>s</sup>, 3<sup>s</sup>, ... . But the pressure  $p$  in  $d \ln p$  and  $s_1^\square(p)$  is then the partial pressure of 1<sup>s</sup>.

As a final topic in this subsection, we note, as we did beginning with Eq. (7-98), various deductions which can be made from the relation  $d\mu_2 = d\mu_1^*$ . We have first

$$\begin{aligned} -\tilde{s}_2 dT + \tilde{v}_2 dp - \frac{1}{N_1} \left( \frac{\partial \mathcal{E}}{\partial \bar{N}_2} \right)_{T, p, N_1} dN_1 \\ + \left( \frac{\partial \mu_2}{\partial \bar{N}_2 / N_1} \right)_{T, p, N_1} d \left( \frac{\bar{N}_2}{N_1} \right) = -s_1^* dT + v_1^* dp. \end{aligned}$$

There are six equations of the Clausius–Clapeyron type that now follow, three of which are independent. Thus

$$\left( \frac{\partial p}{\partial T} \right)_{N_1, \bar{N}_2} = \frac{s_1^* - \tilde{s}_2}{v_1^* - \tilde{v}_2}, \quad \left( \frac{\partial \bar{N}_2}{\partial T} \right)_{p, N_1} = \frac{\tilde{s}_2 - s_1^*}{\left( \frac{\partial \mu_2}{\partial \bar{N}_2} \right)_{T, p, N_1}} \quad (7-132)$$

$$\left( \frac{\partial \bar{N}_2}{\partial p} \right)_{T, N_1} = \frac{v_1^* - \tilde{v}_2}{\left( \frac{\partial \mu_2}{\partial \bar{N}_2} \right)_{T, p, N_1}} \quad (7-133)$$

$$\begin{aligned} \left( \frac{\partial \bar{N}_2 / N_1}{\partial N_1} \right)_{T, p} &= \frac{1}{N_1} \left( \frac{\partial \mathcal{E}}{\partial \bar{N}_2} \right)_{T, p, N_1} / \left( \frac{\partial \mu_2}{\partial \bar{N}_2 / N_1} \right)_{T, p, N_1} \\ &= \frac{1}{N_1^2} \left( \frac{\partial \mathcal{E}}{\partial \mu_2} \right)_{T, p, N_1}. \end{aligned} \quad (7-134)$$

In the very dilute gas case,  $\tilde{v}_2 = 0$  and  $v_1^* = kT/p$ , so that

$$\left( \frac{\partial \ln p}{\partial T} \right)_{N_1, \bar{N}_2} = \frac{s_1^\square - \tilde{s}_2}{kT} = \frac{H_1^\square - \tilde{E}_2}{kT^2} \quad (p \rightarrow 0) \quad (7-135)$$

$$\left( \frac{\partial \bar{N}_2}{\partial \ln p} \right)_{T, N_1} = \frac{kT}{\left( \frac{\partial \mu_2}{\partial \bar{N}_2} \right)_{T, N_1}} \quad (p \rightarrow 0) \quad (7-136)$$

$$\begin{aligned} \left( \frac{\partial \bar{N}_2 / N_1}{\partial N_1} \right)_{T, p} &= \frac{1}{N_1} \left( \frac{\partial \mathcal{E}}{\partial \bar{N}_2} \right)_{T, N_1} \left( \frac{\partial \mu_2}{\partial \bar{N}_2 / N_1} \right)_{T, N_1} \\ &= \frac{1}{N_1^2} \left( \frac{\partial \mathcal{E}}{\partial \mu_2} \right)_{T, N_1}. \end{aligned} \quad (7-137)$$

The analogue of Eq. (7-108) is most conveniently written in the notation

$$d\mu_2 = - \frac{S^{(3)} - S_0^{(3)}}{\bar{N}_2} dT - \frac{N_1}{\bar{N}_2} d(\hat{\mu}_1^{(3)} - \hat{\mu}_{10}^{(3)}) \quad (N_1 \text{ constant}).$$

Then, from  $d\mu_2 = d\mu_1^*$ ,

$$\left( \frac{\partial \ln p}{\partial T} \right)_{N_1, \Delta \hat{\mu}_1^{(3)}} = \frac{1}{kT} \left( s_1^\square - \frac{S^{(3)} - S_0^{(3)}}{\bar{N}_2} \right) \quad (p \rightarrow 0). \quad (7-138)$$

To find  $\Delta \hat{\mu}_1^{(3)}$ , we use

$$\hat{\mu}_1^{(3)}(N') - \hat{\mu}_{10}^{(3)} = - \frac{kT}{N_1} \int_0^{p'} \frac{\bar{N}_2(p)}{p} dp \quad (p \rightarrow 0; T, N_1 \text{ constant}), \quad (7-139)$$

where  $\bar{N}_2 = N'$  when  $p = p'$ . Measurement of  $\bar{N}_2$  as a function of  $p$ , starting from  $p = 0$  (with the aid of extrapolation), at several temperatures and values of  $N_1$ , will yield  $s_1^\square - \bar{s}_2$ ,  $h_1^\square - \bar{e}_2$ ,  $\partial \mu_2 / \partial \bar{N}_2$ ,  $\Delta \hat{\mu}_1^{(3)}(\bar{N}_2)$ ,  $s_1^\square - [(S^{(3)} - S_0^{(3)}) / \bar{N}_2]$ , and  $\partial \mathcal{E} / \partial \bar{N}_2$ . Incidentally, it is easy to see that  $\bar{s}_2 = \bar{s}_2^{(3)}$ .

ANALOGUES OF SECTION 7-1. Much of Section 7-1 is concerned with deductions from the fundamental equation

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1 dN_1 - \bar{N}_2 d\mu_2, \quad (7-140)$$

which has the environmental variables as independent variables. We have derived several corresponding expressions for  $d(\hat{\mu}_1 N_1)$  in the present section, applicable to experimental small systems in solvent or gas. We now want to indicate a few consequences of two of these expressions that parallel some of the deductions from Eq. (7-140) referred to above.

The two basic equations with which we begin are

$$(7-90): \quad d(\hat{\mu}_1 N_1) = - (S - \bar{N}_2 \bar{s}_1^\square) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^\square) dp \\ + \mu_1 dN_1 - \bar{N}_2 kT d \ln m_1^s \quad (m_1^s \rightarrow 0; sc') \quad (7-141)$$

$$(7-129): \quad d(\hat{\mu}_1^{(3)} N_1) = - (S^{(3)} - \bar{N}_2 \bar{s}_1^\square) dT + \mu_1 dN_1 \\ - \bar{N}_2 kT d \ln p \quad (p \rightarrow 0). \quad (7-142)$$

Both of these are equivalent in form to Eq. (7-140), whereas the more general but less practical Eq. (7-81), for example, is not equivalent because of the term in  $\beta$ . Equations (7-141) and (7-142) have the advantage over Eq. (7-140) of being expressed in terms of "operational" independent variables. One consequence of this is that arbitrariness associated with the choice of the zero of entropy is avoided.

We can replace  $d \ln m_1^s$  in Eq. (7-141) by  $d \ln c_1^s$  (concentration) if we make the approximation that the density of the 2<sup>s</sup>, 3<sup>s</sup>, ...,  $c^s$  solvent is independent of  $p$  and  $T$ .

To avoid separate discussion of the two cases above, we shall write both Eqs. (7-141) and (7-142) in the notation

$$d(\hat{\mu}_1 N_1) = - S' dT + V' dp + \mu_1 dN_1 - \bar{N}_2 kT d \ln a_1^s, \quad (7-143)$$

with the following interpretations:

*Liquid solvent, dilute component 1<sup>s</sup>, Eq. (7-141):*

$$S' = S - \bar{N}_2 \bar{s}_1^\square, \quad V' = \bar{V} - \bar{N}_2 \bar{v}_1^\square, \quad a_1^s = m_1^s \quad \text{or} \quad c_1^s. \quad (7-144)$$

*Dilute gaseous solvent, Eq. (7-142):*

$$\hat{\mu}_1 = \hat{\mu}_1^{(3)}, \quad S' = S^{(3)} - \bar{N}_2 \bar{s}_1^\square, \quad V' = 0, \quad a_1^s = p. \quad (7-145)$$

A few Legendre transformations on Eq. (7-143) are useful:

$$d\mathcal{E} = d[(\hat{\mu}_1 - \mu_1)N_1] = - S' dT + V' dp - N_1 d\mu_1 - \bar{N}_2 kT d \ln a_1^s \quad (7-146)$$

$$d(\hat{\mu}_1 N_1 - pV') = - S' dT - p dV' + \mu_1 dN_1 - \bar{N}_2 kT d \ln a_1^s \quad (7-147)$$

$$d(\hat{\mu}_1 N_1 + \bar{N}_2 kT \ln a_1^s) = - S'' dT + V' dp + \mu_1 dN_1 \\ + (kT \ln a_1^s) d\bar{N}_2, \quad (7-148)$$

where

$$S'' = S' - \bar{N}_2 k \ln a_1^s. \quad (7-149)$$

We now follow Section 7-1, more or less, and rewrite in "operational" form some of the equations to be found there.

The six Maxwell relations from Eq. (7-143) are

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{p, N_1, a_1^s} = - \left(\frac{\partial S'}{\partial N_1}\right)_{T, p, a_1^s}, \quad \left(\frac{\partial \mu_1}{\partial p}\right)_{T, N_1, a_1^s} = \left(\frac{\partial V'}{\partial N_1}\right)_{T, p, a_1^s},$$

$$\left(\frac{\partial \mu_1}{\partial \ln a_1^s}\right)_{T, p, N_1} = - kT \left(\frac{\partial \bar{N}_2}{\partial N_1}\right)_{T, p, a_1^s} \quad (7-150)$$

$$\left(\frac{\partial V'}{\partial T}\right)_{p, N_1, a_1^s} = - \left(\frac{\partial S'}{\partial p}\right)_{T, N_1, a_1^s},$$

$$\left(\frac{\partial V'}{\partial \ln a_1^s}\right)_{T, p, N_1} = - kT \left(\frac{\partial \bar{N}_2}{\partial p}\right)_{T, N_1, a_1^s} \quad (7-151)$$

$$\left(\frac{\partial S'}{\partial \ln a_1^s}\right)_{T, p, N_1} = \bar{N}_2 k + kT \left(\frac{\partial \bar{N}_2}{\partial T}\right)_{p, N_1, a_1^s}. \quad (7-152)$$

Equation (7-150c) is essentially unchanged from Section 7-1. This is because both  $T$  and  $p$  are held constant in both derivatives. Equation (7-152) is a good example of an "operational" equation; it should be contrasted with Eq. (7-20a), both sides of which depend on the arbitrary choice of the zero of entropy.

For a solvent dilute in component 1<sup>s</sup>: Eq. (7-150c) is equivalent to Eq. (7-103); Eq. (7-152) is equivalent to Eq. (7-104); and Eq. (7-151b) is equivalent to Eq. (7-104) divided by Eq. (7-106).

Equations (7-143), (7-146), and (7-150) give

$$d\hat{\mu}_1 = - \frac{S'}{N_1} dT + \frac{V'}{N_1} dp - \frac{\bar{N}_2 kT}{N_1} d \ln a_1^s - \frac{\mathcal{E}}{N_1^2} dN_1 \quad (7-153)$$

$$d\mu_1 = - \left(\frac{\partial S'}{\partial N_1}\right)_{T, p, a_1^s} dT + \left(\frac{\partial V'}{\partial N_1}\right)_{T, p, a_1^s} dp$$

$$- kT \left(\frac{\partial \bar{N}_2}{\partial N_1}\right)_{T, p, a_1^s} d \ln a_1^s - \frac{1}{N_1} \left(\frac{\partial \mathcal{E}}{\partial N_1}\right)_{T, p, a_1^s} dN_1 \quad (7-154)$$

$$d\mathcal{E} = - \left[ S' - N_1 \left(\frac{\partial S'}{\partial N_1}\right)_{T, p, a_1^s} \right] dT + \left[ V' - N_1 \left(\frac{\partial V'}{\partial N_1}\right)_{T, p, a_1^s} \right] dp$$

$$- kT \left[ \bar{N}_2 - N_1 \left(\frac{\partial \bar{N}_2}{\partial N_1}\right)_{T, p, a_1^s} \right] d \ln a_1^s + \left(\frac{\partial \mathcal{E}}{\partial N_1}\right)_{T, p, a_1^s} dN_1. \quad (7-155)$$

Equations analogous to (7-24) and (7-26a) follow from Eq. (7-147). Similarly, analogues of Eqs. (7-25) and (7-26b) are consequences of Eq. (7-148).

Equations (7-27) are modified here to

$$\left(\frac{\partial T}{\partial N_1}\right)_{p, V', a_1^s} = \left(\frac{\partial \mu_1}{\partial S'}\right)_{T, N_1, a_1^s} \quad (7-156)$$

$$\left(\frac{\partial N_1}{\partial T}\right)_{p, a_1^s, \bar{N}_2} = \left(\frac{\partial S'}{\partial \mu_1}\right)_{T, p, N_1} - \bar{N}_2 k \left(\frac{\partial \ln a_1^s}{\partial \mu_1}\right)_{T, p, N_1} \quad (7-157)$$

Also, Eqs. (7-28b) and (7-29) become

$$\left(\frac{\partial \ln a_1^s}{\partial T}\right)_{p, V', N_1} = -\frac{1}{kT} \left(\frac{\partial S'}{\partial \bar{N}_2}\right)_{T, N_1, a_1^s} \quad (7-158)$$

$$\left(\frac{\partial p}{\partial N_1}\right)_{T, a_1^s, \bar{N}_2} = -\left(\frac{\partial \mu_1}{\partial V'}\right)_{T, p, N_1} \quad (7-159)$$

$$\left(\frac{\partial p}{\partial T}\right)_{N_1, a_1^s, \bar{N}_2} = \left(\frac{\partial S'}{\partial V'}\right)_{T, p, N_1} - \bar{N}_2 k \left(\frac{\partial \ln a_1^s}{\partial V'}\right)_{T, p, N_1} \quad (7-160)$$

In Eqs. (7-150) to (7-152) and (7-156) to (7-160), and in the many others of this sort that can be written, the "equation-of-state" variables which are easiest to measure are  $p$ ,  $T$ ,  $N_1$ ,  $\bar{N}_2$ , and  $a_1^s$  ( $V'$  is accessible, but not so directly). In these equations one will therefore generally evaluate experimentally those derivatives involving only the variables mentioned, and thus obtain information about the less accessible or inaccessible derivatives. Furthermore, the variables listed above are just those which occur on the left-hand sides of Eqs. (7-103) to (7-107), etc. Hence equations involving derivatives with these variables may be derived in either of two ways [i.e., from  $d\mu_2 = d\mu_1^*$ , or from Eq. (7-143)ff.]. We have already mentioned three examples of this [Eq. (7-150c), etc.]. In addition, for a solvent dilute in component 1: Eq. (7-160) is equivalent to Eq. (7-106); Eq. (7-157) is equivalent to Eq. (7-104) divided by Eq. (7-103); and Eq. (7-159) is equivalent to

$$\left(\frac{\partial p}{\partial N_1}\right)_{T, \bar{N}_2, sc} = \frac{(\partial \mu_1 / \partial \bar{N}_2)_{T, p, N_1, sc}}{\bar{v}_1^* - \bar{v}_2}, \quad (7-161)$$

which follows from Eqs. (7-80) and (7-99).



TWO-STATE APPROXIMATION. We consider here the two-state approximation for small systems in a solvent. We have, as in Eqs. (5-130) and (7-62),

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu_A^\square d\mathcal{N}_A + \mu_B^\square d\mathcal{N}_B \\ + (\mu_{1A}\mathcal{N}_A + \mu_{1B}\mathcal{N}_B) dN_1 + \mu_{2A}\mathcal{N}_A d\bar{N}_{2A} + \mu_{2B}\mathcal{N}_B d\bar{N}_{2B}. \quad (7-162)$$

Both types of small systems,  $A$  and  $B$ , are infinitely dilute in the macroscopic solution. If the macroscopic solution is closed, the following quantities are constant:

$$N_1, \quad \mathcal{N}_A + \mathcal{N}_B, \quad N_2^s, \dots, N_c^s, \\ \text{and} \quad N_1^s + \mathcal{N}_A \bar{N}_{2A} + \mathcal{N}_B \bar{N}_{2B}. \quad (7-163)$$

At equilibrium, at constant  $T$  and  $p$ ,  $dF_T = 0$ . Equation (7-162), together with Eq. (7-163), then gives, for the conditions of equilibrium,

$$\mu_1^s = \mu_{2A} = \mu_{2B} \quad (\equiv \mu_2) \\ \mu_A^\square - \mu_{2A} \bar{N}_{2A} = \mu_B^\square - \mu_{2B} \bar{N}_{2B}. \quad (7-164)$$

We define  $\hat{\mu}_{1A}$  and  $\hat{\mu}_{1B}$  by

$$\mu_A^\square = N_1 \hat{\mu}_{1A} + \bar{N}_{2A} \mu_{2A} + kT \ln \frac{\mathcal{N}_A}{\sum_i N_i^s} \\ \mu_B^\square = N_1 \hat{\mu}_{1B} + \bar{N}_{2B} \mu_{2B} + kT \ln \frac{\mathcal{N}_B}{\sum_i N_i^s}, \quad (7-165)$$

as in Eqs. (7-66) and (7-67). According to Eqs. (7-164) and (7-165), the equilibrium ratio of  $A$  systems to  $B$  systems is

$$\frac{\mathcal{N}_A}{\mathcal{N}_B} = \left( \frac{e^{-\hat{\mu}_{1A}/kT}}{e^{-\hat{\mu}_{1B}/kT}} \right)^{N_1}, \quad (7-166)$$

just as in Eq. (7-40). Equations (7-41) to (7-46) also follow.

The metastable states  $A$  and  $B$ , at equilibrium, have the same values of  $T$ ,  $p$ ,  $N_1$ ,  $m_1^s$ ,  $\hat{\mu}_1$ , and  $sc'$ . We could therefore set  $d(\hat{\mu}_{1A}N_1) = d(\hat{\mu}_{1B}N_1)$ , using Eq. (7-81), in order to obtain equations of the Clausius-Clapeyron type for the transition  $B \rightarrow A$ . But for simplicity we assume in the remainder of this subsection that  $m_1^s$

is small, use Eq. (7-143) or (7-153), and obtain, instead of Eqs. (7-50) to (7-52),

$$\left(\frac{\partial p}{\partial T}\right)_{N_1, sc} = \frac{\Delta S'}{\Delta V'}, \quad \left(\frac{\partial \ln m_1^s}{\partial T}\right)_{p, N_1, sc'} = -\frac{\Delta S'}{kT \Delta \bar{N}_2} \quad (7-167)$$

$$\left(\frac{\partial T}{\partial N_1}\right)_{p, sc} = \frac{\Delta \mu_1}{\Delta S'}, \quad \left(\frac{\partial p}{\partial \ln m_1^s}\right)_{T, N_1, sc'} = \frac{kT \Delta \bar{N}_2}{\Delta V'} \quad (7-168)$$

$$\left(\frac{\partial p}{\partial N_1}\right)_{T, sc} = -\frac{\Delta \mu_1}{\Delta V'}, \quad \left(\frac{\partial \ln m_1^s}{\partial N_1}\right)_{T, p, sc'} = \frac{\Delta \mu_1}{kT \Delta \bar{N}_2}. \quad (7-169)$$

We can replace  $m_1^s$  by  $c_1^s$  in the approximation already referred to above. All derivatives (only three are independent), as well as  $\Delta \bar{N}_2$  and  $\Delta V'$ , can be measured. Then  $\Delta S'$  and  $\Delta \mu_1$  may be calculated. From Eqs. (7-144),

$$\Delta S' = \Delta S - \bar{s}_1^\square \Delta \bar{N}_2, \quad \Delta V' = \Delta \bar{V} - \bar{v}_1^\square \Delta \bar{N}_2. \quad (7-170)$$

If we define  $E'$  by  $\bar{E} - \bar{N}_2 \bar{e}_1^\square$ , in analogy with  $S'$  and  $V'$ , Eq. (7-53) becomes

$$0 = \Delta E' + p \Delta V' - T \Delta S' \quad (7-171)$$

or

$$\Delta H' = T \Delta S'. \quad (7-172)$$

As pointed out on pages 126 of Part I and 11 of Part II, the above equations also refer to the single point  $\mathcal{N}_A = \mathcal{N}_B$  on the stable equilibrium path. That is, we consider only those variations in  $T, p, N_1$ , and  $m_1^s$  consistent with the maintenance of  $\mathcal{N}_A = \mathcal{N}_B$ .

If the phase transition between the metastable states  $A$  and  $B$  occurs at equilibrium between these states,<sup>1</sup> and if we include the macroscopic solvent as well as the small systems in our reckoning, then the macroscopic solution is closed and is at constant pressure and temperature. The heat of the over-all process (i.e., phase transition plus transfer of component 1<sup>s</sup> from or to the solvent), per small system, is

$$Q_T = \Delta H_T = T \Delta S_T = T(\Delta S - \bar{s}_1^\square \Delta \bar{N}_2) = T \Delta S' = \Delta H'. \quad (7-173)$$

<sup>1</sup> In other words, in a solution with  $T, p, N_1$ , and  $m_1^s$  chosen so that  $\hat{\mu}_{1A} = \hat{\mu}_{1B}$ , the initial state in the process under consideration has all small systems in state  $B$  and the final state has all of them in state  $A$ .

The heat  $Q_T$  refers to a metastable process and hence would ordinarily not be measurable. Expressions can be derived for the heat of the over-all process, *along* the *stable* equilibrium path, where the process takes place by virtue of a variation in  $p$  or  $T$  in a closed macroscopic solution (see page 127 of Part I). There are three contributions to  $DQ_T$  in this case, and these cannot be disentangled experimentally: (a) heat absorbed by small systems undergoing the transition; (b) heat absorbed by adsorption (or desorption) of  $1^s$  molecules on small systems of the two types (transition frozen); and (c) heat absorbed at constant solution composition (transition and adsorption frozen). We shall not set down these rather complicated expressions. A simpler situation is the one in which the small systems adsorb  $1^s$  molecules, but there is no  $B \rightarrow A$  transition. Then if the pressure or temperature is varied and the closed macroscopic solution absorbs heat,

$$DQ_T = T dS_T \quad (N_2^s, \dots, N_c^s, \mathcal{N}, N_1, N_1^s + \mathcal{N}\bar{N}_2 \text{ constant}).$$

One finds

$$\begin{aligned} \left(\frac{DQ_T}{\partial p}\right)_{T, \text{closed}} &= T \left(\frac{\partial S_T}{\partial p}\right)_{T, N_1^s, \bar{N}_2, \mathcal{N}, N_1} \\ &\quad + T\mathcal{N}(\bar{s}_2 - \bar{s}_1^\square) \left(\frac{\partial \bar{N}_2}{\partial p}\right)_{T, \text{closed}}, \end{aligned} \quad (7-174)$$

or

$$\begin{aligned} \left(\frac{DQ_T}{\partial T}\right)_{p, \text{closed}} &= T \left(\frac{\partial S_T}{\partial T}\right)_{p, N_1^s, \bar{N}_2, \mathcal{N}, N_1} \\ &\quad + T\mathcal{N}(\bar{s}_2 - \bar{s}_1^\square) \left(\frac{\partial \bar{N}_2}{\partial T}\right)_{p, \text{closed}}, \end{aligned} \quad (7-175)$$

where

$$T(\bar{s}_2 - \bar{s}_1^\square) = \bar{H}_2 - \bar{H}_1^\square.$$

In the above equations for  $DQ_T/\partial p$  and  $DQ_T/\partial T$ , the first term is a constant composition term (adsorption frozen) whereas the second term arises from a shift in the adsorption equilibrium.

It is easy to see from Eqs. (7-42), (7-44), (7-46), and (7-143) that: (1) an equal-area theorem and an equal-distance theorem both apply to a  $V'$  versus  $p$  diagram ( $T, N_1, m_1^s$  constant) and to an  $\bar{N}_2$  versus  $\ln m_1^s$  diagram ( $T, p, N_1$  constant); (2) on an  $S'$  versus  $T$  diagram ( $p, N_1, m_1^s$  constant), there is an equal-area theorem but

not an exact equal-distance theorem [the same usually negligible term  $k \ln 2$  appears which was mentioned following Eq. (5-129)]; and (3) on  $\bar{V}$  versus  $T$ ,  $V'$  versus  $T$ , or  $\bar{N}_2$  versus  $T$  diagrams ( $p, N_1, m_1^s$  constant), or on a  $\bar{V}$  versus  $p$  diagram ( $T, N_1, m_1^s$  constant), there are equal-distance but not equal-area theorems.

A convenient way to derive some important relations that pertain to the stable equilibrium situation [as determined by Eq. (7-166)] is to make explicit use of the condition

$$d(\mu_A^\square - \mu_1^* \bar{N}_{2A}) = d(\mu_B^\square - \mu_1^* \bar{N}_{2B}), \quad (7-176)$$

which follows from Eqs. (7-164). Equations (7-76) and (7-80) give, for small  $m_1^s$ ,

$$\begin{aligned} d(\mu_A^\square - \mu_1^* \bar{N}_{2A}) = & (-\bar{s}_A^\square + \bar{N}_{2A} \bar{s}_1^\square) dT + (\bar{v}_A^\square - \bar{N}_{2A} \bar{v}_1^\square) dp \\ & + kT d \ln x_A' + \mu_{1A} dN_1 - \bar{N}_{2A} kT d \ln m_1^s \quad (sc'), \end{aligned} \quad (7-177)$$

and there is an analogous equation for  $B$ . Then, from Eq. (7-176),

$$\frac{dP_A}{P_A P_B} = \frac{\Delta H'}{kT^2} dT - \frac{\Delta V'}{kT} dp - \frac{\Delta \mu_1}{kT} dN_1 + \Delta \bar{N}_2 d \ln m^s \quad (sc'), \quad (7-178)$$

where  $P_A = \mathcal{N}_A/\mathcal{N}$  and  $P_B = 1 - P_A$ . It should be emphasized that  $\Delta H'$ ,  $\Delta V'$ , etc., in this equation refer to differences between  $A$  and  $B$  properties in an arbitrary ( $P_A$ ) stable equilibrium mixture of  $A$  and  $B$  systems. This is not the case in Eqs. (7-167) to (7-173), which pertain to the metastable transition or to  $\mathcal{N}_A = \mathcal{N}_B$  (that is,  $P_A = \frac{1}{2} = \text{constant}$ ). Thus we have here, for example,

$$N_1 \Delta \hat{\mu}_1 = \Delta H' - T \Delta S' = -kT \ln \frac{\mathcal{N}_A}{\mathcal{N}_B} = -kT \ln \frac{P_A}{P_B}. \quad (7-179)$$

These relations follow from Eqs. (7-69) and (7-166). They should be contrasted with Eq. (7-172). We also note that there is one more degree of freedom in the present case. We may consider each of  $T, p, N_1$ , and  $m_1^s$  as independent variables here, but the metastable equilibrium condition (or  $\mathcal{N}_A = \mathcal{N}_B$ ) is more restrictive and only three of these variables can be independent in Eqs. (7-167) to (7-169). In fact, if we put  $P_A = \frac{1}{2} = \text{constant}$  and therefore  $dP_A = 0$  in Eq. (7-178), we recover Eqs. (7-167) to (7-169).

Equation (7-178) gives us the following explicit relations showing how the equilibrium between  $A$  and  $B$  systems depends on the

independent variables:

$$\left(\frac{\partial P_A}{\partial T}\right)_{p, N_1, sc} = \frac{P_A P_B \Delta H'}{kT^2}, \quad \left(\frac{\partial P_A}{\partial p}\right)_{T, N_1, sc} = -\frac{P_A P_B \Delta V'}{kT} \quad (7-180)$$

$$\left(\frac{\partial P_A}{\partial N_1}\right)_{T, p, sc} = -\frac{P_A P_B \Delta \mu_1}{kT}, \quad \left(\frac{\partial P_A}{\partial \ln m_1'}\right)_{T, p, N_1, sc} = P_A P_B \Delta \bar{N}_2. \quad (7-181)$$

If desired, one can substitute in these equations

$$\frac{dP_A}{P_A P_B} = d \ln \frac{P_A}{1 - P_A} = d \ln \frac{\mathcal{N}_A}{\mathcal{N}_B}.$$

The last quotient has the form of an equilibrium constant. Analogues of Eqs. (7-180) and (7-181a) were encountered in Section 5-4, derived by a different method.

Six equations with the appearance of Eqs. (7-167) to (7-169) also follow from Eq. (7-178), if we take  $P_A = \text{constant}$  (we have already mentioned the special case  $P_A = \frac{1}{2}$ ).

*Simple Example. Dibasic Long-Chain Acid.* This is an example of simple binding, not of a phase transition. Consider a linear polymer molecule in solution, made up of  $N_1$  monomers and containing one site for binding  $H^+$  at each end of the chain. Examples are  $NH_2(CH_2)_{N_1}COO^-$ ,  $NH_2(CH_2)_{N_1}NH_2$ , etc. The solution is assumed dilute in both polymer molecule and  $H^+$ . Then the titration curve may be expressed in the familiar form

$$\bar{N}_2 = \frac{\frac{c_1^s}{K_{(2)}} + \frac{2(c_1^s)^2}{K_{(1)}K_{(2)}}}{1 + \frac{c_1^s}{K_{(2)}} + \frac{(c_1^s)^2}{K_{(1)}K_{(2)}}}, \quad (7-182)$$

where  $K_{(1)}$  and  $K_{(2)}$  are the successive thermodynamic dissociation constants,  $c_1^s$  is the  $H^+$  concentration in solution, and  $\bar{N}_2$  is the average number of bound hydrogen ions per polymer:  $0 \leq \bar{N}_2 \leq 2$ . If  $K_{(1)}$  and  $K_{(2)}$  are measured as functions of  $N_1$  and  $T$  (ignoring pressure effects), we then have  $\bar{N}_2$  as a function of the environmental variables  $c_1^s$ ,  $N_1$ , and  $T$ . Hence, for example, from Eqs. (7-91), (7-103), (7-104), and (7-110), we can obtain information about the dependence of  $\mu_2$ ,  $S$ , and  $\mathcal{E}$  on  $\bar{N}_2$ .

In the limit  $N_1 \rightarrow \infty$  (assuming that the polymer is still soluble enough to measure  $K_{(1)}$  and  $K_{(2)}$ ): (a) the hydrogen ion binding becomes relatively insignificant ( $\bar{N}_2 \ll N_1$ ) and the system, in effect, approaches an  $N_1, T$  system; and (b)

$$K_{(1)} \rightarrow K_1 + K_2$$

and

$$\frac{1}{K_{(2)}} \rightarrow \frac{1}{K_1} + \frac{1}{K_2},$$

where  $K_1$  and  $K_2$  are "intrinsic" dissociation constants for the two end groups, which dissociate independently of each other in this limit. If the end groups are the same,  $K_1 = K_2$  and  $K_{(1)}/K_{(2)} = 4$ .

### 7-3. ISOMERIC EQUILIBRIUM WITH BINDING

In this section we consider the thermodynamics of binding or adsorption on a small system with an isomeric equilibrium. The most obvious example is hydrogen ion binding on a macromolecule with a helix-coil transition.

As usual, we shall begin by writing the basic equations for an ensemble of distinguishable systems. Because of the fact that we merely have to combine the treatments in Sections 5-3 and 7-1, we shall proceed directly to small system equations, without explicit discussion of the ensemble.

The small system consists of  $N_1$  molecules, monomers, or units of component 1 and  $\bar{N}_2$  bound or adsorbed molecules of component 2 at chemical potential  $\mu_2$ . The units of component 1 are of two types which are in an isomeric equilibrium with each other:  $A_1^{(1)} \rightleftharpoons A_1^{(2)}$ . The numbers of these units are designated  $N_1^{(1)}$  and  $N_1^{(2)}$ , with  $N_1^{(1)} + N_1^{(2)} = N_1$ . For convenience, we write  $N_1^{(1)} = n$  and  $N_1^{(2)} = N_1 - n$ . Also, we define  $\psi = \mu_1^{(2)} - \mu_1^{(1)}$ , where the latter quantities are chemical potentials. The environmental variables are then  $N_1, \mu_2, p, T$ , and  $\psi$ . It is easy to show that the equilibrium value of  $\psi$  is  $\psi = 0$ , but we permit arbitrary values of  $\psi$  in many equations. There are fluctuations in  $N_2, V, E$ , and  $n$ .

We now have five independent variables. This means that there will be an extremely large number of possible thermodynamic relations. We shall derive only a few of these in this section and leave it to the interested reader to pursue this case further.

The fundamental equations for a small system are

$$\begin{aligned} d\bar{E} &= T dS - p d\bar{V} + \mu_1^{(1)} d\bar{N}_1^{(1)} + \mu_1^{(2)} d\bar{N}_1^{(2)} + \mu_2 d\bar{N}_2 \\ &= T dS - p d\bar{V} - \psi d\bar{n} + \mu_1^{(2)} dN_1 + \mu_2 d\bar{N}_2 \end{aligned} \quad (7-183)$$

$$\bar{E} = TS - p\bar{V} - \psi\bar{n} + \mu_1^{(2)}N_1 + \mu_2\bar{N}_2 + \mathcal{E} \quad (7-184)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - N_1 d\mu_1^{(2)} - \bar{N}_2 d\mu_2 + \bar{n} d\psi \quad (7-185)$$

$$\begin{aligned} d(\mu_1^{(2)}N_1 + \mathcal{E}) &= d(\hat{\mu}_1N_1) = -S dT + \bar{V} dp \\ &\quad + \mu_1^{(2)} dN_1 - \bar{N}_2 d\mu_2 + \bar{n} d\psi \end{aligned} \quad (7-186)$$

$$d\hat{\mu}_1 = -\frac{S}{N_1} dT + \frac{\bar{V}}{N_1} dp - \frac{\mathcal{E}}{N_1^2} dN_1 - \frac{\bar{N}_2}{N_1} d\mu_2 + \frac{\bar{n}}{N_1} d\psi.$$

The last equations have the environmental variables as independent variables. We have introduced here the notation  $\hat{\mu}_1N_1 \equiv \mu_1^{(2)}N_1 + \mathcal{E}$ .

As usual we define

$$F = \bar{E} - TS + p\bar{V}, \quad H = \bar{E} + p\bar{V}, \quad F = H - TS, \quad (7-187)$$

so that

$$F = -\psi\bar{n} + \hat{\mu}_1N_1 + \mu_2\bar{N}_2 \quad (7-188)$$

and

$$dF = -S dT + \bar{V} dp + \mu_1^{(2)} dN_1 + \mu_2 d\bar{N}_2 - \psi d\bar{n}. \quad (7-189)$$

The appropriate statistical mechanical partition function is

$$Z(N_1, \mu_2, p, T, \psi) = \sum_{n, N_2} \Delta(N_1^{(1)}, N_1^{(2)}, N_2, p, T) e^{-n\psi/kT} e^{N_2\mu_2/kT}, \quad (7-190)$$

where  $N_1^{(1)} = n$  and  $N_1^{(2)} = N_1 - n$ . Then

$$\hat{\mu}_1N_1 = -kT \ln Z. \quad (7-191)$$

From Eqs. (7-186) and (7-190),

$$\bar{n} = -kT \left( \frac{\partial \ln Z}{\partial \psi} \right)_{T, p, N_1, \mu_2} \quad (7-192)$$

and

$$\bar{n}^2 - \bar{n}^2 = -kT \left( \frac{\partial \bar{n}}{\partial \psi} \right)_{T, p, N_1, \mu_2}. \quad (7-193)$$

When a solvent is present,  $\Delta$  in Eq. (7-190) will be more complicated [see Eqs. (1-32) and (2-124), for example] but the factor  $e^{-n\psi/kT}$  will still be present and hence Eqs. (7-192) and (7-193) will still obtain.

**SMALL SYSTEMS IN SOLVENT.** Let us turn at this point to the practical case of interest: the small systems are in a solvent. Our task is to superimpose on Section 7-2 the complication of an isomeric equilibrium.

We start with an obvious generalization of Eq. (7-62):

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu^\square d\mathcal{N} + \mu_1^{(1)} \mathcal{N} d\bar{N}_1^{(1)} + \mu_1^{(2)} \mathcal{N} d\bar{N}_1^{(2)} + \mu_2 \mathcal{N} d\bar{N}_2. \quad (7-194)$$

If the macroscopic system is closed, is held at constant  $T$  and  $p$ , and is at equilibrium, then

$$N_1^s + \mathcal{N} \bar{N}_2, \quad N_2^s, \dots, N_c^s, \quad \mathcal{N}, \quad \text{and} \quad \bar{N}_1^{(1)} + \bar{N}_1^{(2)}$$

are constant and

$$dF_T = 0 = (\mu_1^s - \mu_2) dN_1^s + \mathcal{N}(\mu_1^{(1)} - \mu_1^{(2)}) d\bar{N}_1^{(1)}.$$

Thus, at equilibrium,  $\mu_1^s = \mu_2$  and  $\mu_1^{(1)} = \mu_1^{(2)}$ .

As above, we introduce the notation

$$\psi = \mu_1^{(2)} - \mu_1^{(1)}, \quad n = N_1^{(1)}, \quad N_1 - n = N_1^{(2)}.$$

Thus Eq. (7-194) becomes

$$dF_T = -S_T dT + V_T dp + \sum_i \mu_i^s dN_i^s + \mu^\square d\mathcal{N} + \mu_1^{(2)} \mathcal{N} dN_1 + \mu_2 \mathcal{N} d\bar{N}_2 - \psi \mathcal{N} d\bar{n}. \quad (7-195)$$

Integration of this equation, holding intensive properties and  $N_1, \bar{N}_2$ , and  $\bar{n}$  (parameters characterizing the small systems) constant, gives

$$F_T = \sum_i \mu_i^s N_i^s + \mu^\square \mathcal{N} = E_T - TS_T + pV_T. \quad (7-196)$$

Also,

$$\mu^\square = \left( \frac{\partial F_T}{\partial \mathcal{N}} \right)_{T, p, N_i^s, N_1, \bar{N}_2, \bar{n}} = \tilde{E}^\square - T\tilde{S}^\square + p\tilde{V}^\square, \quad (7-197)$$

where  $\tilde{E}^\square$ , etc., are defined by similar derivatives.



We define  $F$  by

$$\mu^\square = F(N_1, \bar{N}_2, \bar{n}, p, T, sc) + kT \ln x' \quad (7-198)$$

and then  $\mathcal{E}$  and  $\hat{\mu}_1$  by

$$F = N_1 \mu_1^{(2)} + \bar{N}_2 \mu_2 - \psi \bar{n} + \mathcal{E} = N_1 \hat{\mu}_1 + \bar{N}_2 \mu_2 - \psi \bar{n}. \quad (7-199)$$

Further definitions are

$$S = \bar{S}^\square + k \ln x', \quad E = \bar{E}^\square, \quad \text{and} \quad \bar{V} = \bar{V}^\square. \quad (7-200)$$

Then Eq. (7-197) becomes

$$F = E - TS + p\bar{V}. \quad (7-201)$$

As in Eq. (7-65), we have from Eq. (7-195),

$$\begin{aligned} d\mu^\square = & -\bar{s}^\square dT + \bar{v}^\square dp + \frac{\partial \mu^\square}{\partial x'} dx' + \frac{\partial \mu^\square}{\partial m_1^s} dm_1^s \\ & + \frac{\partial \mu^\square}{\partial N_1} dN_1 + \frac{\partial \mu^\square}{\partial \bar{N}_2} d\bar{N}_2 + \frac{\partial \mu^\square}{\partial \bar{n}} d\bar{n} \quad (sc'). \end{aligned} \quad (7-202)$$

From Eq. (7-198), we know that  $\partial \mu^\square / \partial x' = kT/x'$ . Also, we define  $\beta$  by

$$\beta = \left( \frac{\partial \mu^\square}{\partial m_1^s} \right)_{T, p, x', N_1, \bar{N}_2, \bar{n}, sc'} = \left( \frac{\partial F}{\partial m_1^s} \right)_{T, p, N_1, \bar{N}_2, \bar{n}, sc'}. \quad (7-203)$$

The next coefficient,  $\partial \mu^\square / \partial N_1$ , can be shown to be equal to  $\mu_1^{(2)}$  in Eq. (7-195). The argument is unchanged from that in Eqs. (7-70) to (7-75) except that  $\bar{n}$  must be held constant in all the derivatives. Similarly,  $\partial \mu^\square / \partial \bar{N}_2$  is equal to  $\mu_2$ . Finally, using Eqs. (7-73) and (7-74),

$$-\psi = \frac{1}{\mathcal{N}} \left( \frac{\partial F}{\partial \bar{n}} \right)_{T, p, N_1^s, \mathcal{N}, N_1, \bar{N}_2} = \left( \frac{\partial \mu^\square}{\partial \bar{n}} \right)_{T, p, x', N_1, \bar{N}_2, sc'}.$$

Thus, in summary,

$$\begin{aligned} d\mu^\square = & -\bar{s}^\square dT + \bar{v}^\square dp + kT d \ln x' + \beta dm_1^s \\ & + \mu_1^{(2)} dN_1 + \mu_2 d\bar{N}_2 - \psi d\bar{n} \quad (sc'). \end{aligned} \quad (7-204)$$

If we now introduce the definitions of  $F$ ,  $S$ , and  $\bar{V}$  into this relation, we find

$$\begin{aligned} dF = & -S dT + \bar{V} dp + \mu_1^{(2)} dN_1 + \mu_2 d\bar{N}_2 \\ & - \psi d\bar{n} + \beta dm_1^s \quad (sc'). \end{aligned} \quad (7-205)$$

Legendre transformations give

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp + \mu_1^{(2)} dN_1 - \bar{N}_2 d\mu_2 + \bar{n} d\psi + \beta dm_1^s \quad (sc') \quad (7-206)$$

$$d(\hat{\mu}_1 N_1 + \mu_2 \bar{N}_2) = d(F + \bar{n}\psi) = -S dT + \bar{V} dp + \mu_1^{(2)} dN_1 + \mu_2 d\bar{N}_2 + \bar{n} d\psi + \beta dm_1^s \quad (sc') \quad (7-207)$$

$$d(\hat{\mu}_1 N_1 - \bar{n}\psi) = d(F - \mu_2 \bar{N}_2) = -S dT + \bar{V} dp + \mu_1^{(2)} dN_1 - \bar{N}_2 d\mu_2 - \psi d\bar{n} + \beta dm_1^s \quad (sc'). \quad (7-208)$$

Equation (7-206) is the most important of these. It differs from Eq. (7-186) in that there is an extra term,  $\beta dm_1^s$ , here. The discussion of this type of term on page 17 should be referred to. Equation (7-206) becomes the same as Eq. (7-186) in the special case  $m_1^s \rightarrow 0$ .

Up to this point in this subsection, we have not made use of the fact that we have a binding equilibrium ( $\mu_1^s = \mu_2$ ). To take this into account, we substitute Eq. (7-80) for  $d\mu_2$  in Eq. (7-206) and obtain

$$d(\hat{\mu}_1 N_1) = -(S - \bar{N}_2 \bar{s}_1^*) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^*) dp + \mu_1^{(2)} dN_1 + \bar{n} d\psi + \left[ \beta - \bar{N}_2 \left( \frac{\partial \mu_1^s}{\partial m_1^s} \right)_{T, p, sc'} \right] dm_1^s \quad (\delta, sc'). \quad (7-209)$$

This simplifies as in Eq. (7-90) when  $m_1^s$  is small.

Actually, we have used  $d(\mu_2 - \mu_1^s) = 0$  to deduce Eq. (7-209); that is,  $\mu_2 - \mu_1^s = \text{constant}$ . Hence Eq. (7-209) is a little more general than indicated above ( $\mu_1^s = \mu_2$ ), although of course the experimentally significant value of  $\mu_2 - \mu_1^s = \text{constant}$  is zero. This is obviously analogous to considering, for generality,  $\psi = \text{constant}$ , not necessarily zero. To emphasize this analogy, we define  $\delta = \mu_2 - \mu_1^s$  and we shall indicate explicitly that  $\delta = \text{constant}$  in some of the deductions we make from Eq. (7-209). We did not do this in Section 7-2; it was simply understood there that  $\delta = 0$ .

By taking cross-derivatives in Eq. (7-209) we can obtain expressions for the variation of the extent of reaction  $\bar{n}$  with  $T, p, N_1$ ,

and  $m_1^s$ . For example,

$$\left(\frac{\partial \bar{n}}{\partial T}\right)_{p, N_1, \psi, \delta, sc} = -\left(\frac{\partial S}{\partial \psi}\right)_{T, p, N_1, \delta, sc} + \bar{s}_1^* \left(\frac{\partial \bar{N}_2}{\partial \psi}\right)_{T, p, N_1, \delta, sc} \quad (7-210)$$

$$\begin{aligned} \left(\frac{\partial \bar{n}}{\partial m_1^s}\right)_{T, p, N_1, \psi, \delta, sc'} &= \left(\frac{\partial \beta}{\partial \psi}\right)_{T, p, N_1, \delta, sc} \\ &- \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} \left(\frac{\partial \bar{N}_2}{\partial \psi}\right)_{T, p, N_1, \delta, sc} \end{aligned} \quad (7-211)$$

$$\left(\frac{\partial \bar{n}}{\partial N_1}\right)_{T, p, \psi, \delta, sc} = \left(\frac{\partial \mu_1^{(2)}}{\partial \psi}\right)_{T, p, N_1, \delta, sc}. \quad (7-212)$$

All of these derivatives are of course to be evaluated at  $\psi = 0$ ,  $\delta = 0$ . Where  $T$ ,  $p$ , and  $sc$  are all held constant in a derivative,  $\mu_1^s$  is constant. With  $\delta$  also constant,  $\mu_2$  is then constant. Hence the set of constant variables  $T$ ,  $p$ ,  $sc$ ,  $\delta$  could be replaced by  $T$ ,  $p$ ,  $sc$ ,  $\mu_2$ .

The derivatives on the left, above, are measurable. The derivatives with respect to  $\psi$ , on the right, can all be rewritten as

$$\left(\frac{\partial}{\partial \psi}\right)_{T, p, N_1, \delta, sc} = \left(\frac{\partial \bar{n}}{\partial \psi}\right)_{T, p, N_1, \delta, sc} \left(\frac{\partial}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc},$$

where

$$\left(\frac{\partial \bar{n}}{\partial \psi}\right)_{T, p, N_1, \delta, sc} = -\frac{\bar{n}^2 - \bar{n}^2}{kT}, \quad (7-213)$$

as in Eq. (7-193).

If the solution is dilute with respect to  $1^s$ , we put  $\bar{s}_1^* = \bar{s}_1^\square$ ,  $\partial \beta / \partial \psi = 0$ , and  $\partial \mu_1^* / \partial m_1^s = kT / m_1^s$  in Eqs. (7-210) and (7-211).

Next, we find expressions for the dependence of  $\bar{N}_2$ , the amount of binding, on several variables of interest. We shall do this by setting  $d\mu_2 = d\mu_1^*$ , where  $\mu_2$  is regarded as a function of  $T$ ,  $p$ ,  $N_1$ ,  $\bar{N}_2$ ,  $\psi$ , and  $sc$ . This choice of variables is convenient because it contains  $\bar{N}_2$  and we can easily put  $d\psi = 0$ . We start with

$$\begin{aligned} d\mu_2 &= \frac{\partial \mu_2}{\partial T} dT + \frac{\partial \mu_2}{\partial p} dp + \frac{\partial \mu_2}{\partial N_1} dN_1 + \frac{\partial \mu_2}{\partial \bar{N}_2} d\bar{N}_2 \\ &+ \frac{\partial \mu_2}{\partial \psi} d\psi + \frac{\partial \mu_2}{\partial m_1^s} dm_1^s \quad (sc'). \end{aligned} \quad (7-214)$$

Using Eq. (7-207), this becomes

$$d\mu_2 = -\frac{\partial S}{\partial \bar{N}_2} dT + \frac{\partial \bar{V}}{\partial \bar{N}_2} dp + \frac{\partial \mu_1^{(2)}}{\partial \bar{N}_2} dN_1 + \frac{\partial \mu_2}{\partial \bar{N}_2} d\bar{N}_2 \\ + \frac{\partial \mu_2}{\partial \psi} d\psi + \frac{\partial \beta}{\partial \bar{N}_2} dm_1^s \quad (sc'), \quad (7-215)$$

where all derivatives with respect to  $\bar{N}_2$  are with  $T, p, N_1, \psi$ , and  $sc$  held constant. These are not quite small system partial molal quantities, as previously defined, because  $\psi$  is constant rather than  $\bar{n}$ . But it should be pointed out that if we were unaware of the isomeric equilibrium, or chose to ignore its existence (the "black-box" attitude), Eq. (7-215) with  $\psi = 0$  would be identical with Eq. (7-98), and the derivatives with respect to  $\bar{N}_2$  would then be partial molal quantities [for a small system of two components ( $N_1, \bar{N}_2$ ) instead of three ( $N_1^{(1)}, N_1^{(2)}, \bar{N}_2$ )].

In this connection, one can state quite generally that any deductions made here concerning the amount of binding and other properties at  $\psi = 0$  (equilibrium with respect to the isomeric reaction) must be formally identical with corresponding results in Section 7-2 where an isomeric reaction is not taken into account.

We now set  $d\mu_2$  in Eq. (7-215) equal to  $d\mu_1^*$  in Eq. (7-80), take  $d\psi = 0$ , and find

$$\left(-\frac{\partial S}{\partial \bar{N}_2} + \bar{s}_1^*\right) dT + \left(\frac{\partial \bar{V}}{\partial \bar{N}_2} - \bar{v}_1^*\right) dp + \frac{\partial \mu_1^{(2)}}{\partial \bar{N}_2} dN_1 + \frac{\partial \mu_2}{\partial \bar{N}_2} d\bar{N}_2 \\ + \left(\frac{\partial \beta}{\partial \bar{N}_2} - \frac{\partial \mu_1^*}{\partial m_1^s}\right) dm_1^s = 0 \quad (\psi, \delta, sc'). \quad (7-216)$$

We can deduce ten equations of the Clausius-Clapeyron type from Eq. (7-216) [just as in Eqs. (7-103) to (7-106)]. Four of these are expressions for derivatives of  $\bar{N}_2$  with respect to  $T, p, N_1$ , and  $m_1^s$ . For example,

$$\left(\frac{\partial \bar{N}_2}{\partial m_1^s}\right)_{T, p, N_1, \psi, \delta, sc'} \\ = \left[\left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} - \left(\frac{\partial \beta}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc'}\right] / \left(\frac{\partial \mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc'} \quad (7-217)$$

When  $m_1^s$  is small, this equation simplifies as in Eq. (7-91).

Another deduction from Eq. (7-216) is

$$\left(\frac{\partial m_1^s}{\partial T}\right)_{p, N_1, \bar{N}_2, \psi, \delta, sc'} = \frac{\left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} - \tilde{s}_1^*}{\left(\frac{\partial \beta}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} - \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'}}.$$

When  $m_1^s$  is small,

$$kT \left(\frac{\partial \ln m_1^s}{\partial T}\right)_{p, N_1, \bar{N}_2, \psi, \delta, sc'} = \tilde{s}_1^\square - \left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} \quad (m_1^s \rightarrow 0). \quad (7-218)$$

These equations are the generalizations of Eqs. (7-105) and (7-107).

The quantity  $\tilde{s}_1^* - (\partial S / \partial \bar{N}_2)$ , which occurs, for example, in the equations for  $\partial m_1^s / \partial T$ ,  $\partial \bar{N}_2 / \partial T$ , and  $\partial p / \partial T$ , is equal to  $[\tilde{H}_1^* - (\partial H / \partial \bar{N}_2)] / T$  when  $\psi = 0$  and  $\delta = 0$ . This follows from

$$\begin{aligned} \mu_1^* &= \tilde{H}_1^* - T\tilde{s}_1^* \\ &= \mu_2 = \left[ \frac{\partial(F + \bar{n}\psi)}{\partial \bar{N}_2} \right]_{T, p, N_1, \psi, sc} \quad (\delta = 0) \\ &= \left(\frac{\partial H}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} - T \left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} + \psi \left(\frac{\partial \bar{n}}{\partial \bar{N}_2}\right)_{T, p, N_1, \psi, sc} \\ &= \frac{\partial H}{\partial \bar{N}_2} - T \frac{\partial S}{\partial \bar{N}_2} \quad (\psi = 0, \delta = 0). \end{aligned}$$

An alternative, more complicated, but equivalent way of deducing the derivatives with respect to  $\bar{n}$  and  $\bar{N}_2$  found above, as well as other relations, is to use the two simultaneous equations

$$d\mu_2(T, p, N_1, \bar{N}_2, \bar{n}, sc) = d\mu_1^*(T, p, sc), \quad d\psi(T, p, N_1, \bar{N}_2, \bar{n}, sc) = 0, \quad (7-219)$$

with the independent variables indicated. On employing cross-derivatives in Eq. (7-205), we find for  $d\mu_2$ ,

$$d\mu_2 = -\tilde{s}_2 dT + \tilde{v}_2 dp + \left(\frac{\partial\mu_2}{\partial N_1}\right)_{T, p, \bar{N}_2, \bar{n}, sc} dN_1 \\ + \left(\frac{\partial\mu_2}{\partial \bar{N}_2}\right)_{T, p, N_1, \bar{n}, sc} d\bar{N}_2 - \tilde{\psi}_2 d\bar{n} + \tilde{\beta}_2 dm_1^s \quad (sc'), \quad (7-220)$$

where

$$\tilde{s}_2 = \left(\frac{\partial S}{\partial \bar{N}_2}\right)_{T, p, N_1, \bar{n}, sc}, \text{ etc.}$$

These are small system partial molal quantities. For  $d\psi$  we have

$$d\psi = \frac{\partial\psi}{\partial T} dT + \frac{\partial\psi}{\partial p} dp + \frac{\partial\psi}{\partial N_1} dN_1 + \frac{\partial\psi}{\partial \bar{N}_2} d\bar{N}_2 \\ + \frac{\partial\psi}{\partial \bar{n}} d\bar{n} + \frac{\partial\psi}{\partial m_1^s} dm_1^s \quad (sc') \\ = \frac{\partial S}{\partial \bar{n}} dT - \frac{\partial \bar{V}}{\partial \bar{n}} dp - \frac{\partial \mu_1^{(2)}}{\partial \bar{n}} dN_1 - \frac{\partial \mu_2}{\partial \bar{n}} d\bar{N}_2 \\ + \frac{\partial\psi}{\partial \bar{n}} d\bar{n} - \frac{\partial\beta}{\partial \bar{n}} dm_1^s \quad (sc'), \quad (7-221)$$

where all the derivatives with respect to  $\bar{n}$  are at constant  $T, p, N_1, \bar{N}_2$ , and  $sc$ . If we now put Eqs. (7-80), (7-220), and (7-221) into Eqs. (7-219), we obtain two linear simultaneous equations in the quantities  $dT, dp, dN_1, d\bar{N}_2, d\bar{n}$ , and  $dm_1^s$ , with  $\delta, \psi$ , and  $sc'$  constant. Hence four of the six variables listed can be independent, just as in Eq. (7-217) where  $T, p, N_1$ , and  $m_1^s$  are independent variables and  $\bar{N}_2$  is a dependent variable. For example, one might solve  $d\psi = 0$  for  $d\bar{N}_2$ , use this expression to eliminate  $d\bar{N}_2$  from Eq. (7-219a), and then obtain, say, an expression for the derivative  $\partial\bar{n}/\partial T$ :

$$\tilde{s}_2 - \tilde{s}_1^* - (\partial\mu_2/\partial\bar{N}_2)_{T, p, N_1, \bar{n}, sc} \\ \left(\frac{\partial\bar{n}}{\partial T}\right)_{p, N_1, \psi, \delta, sc} = \frac{\times (\partial\bar{n}/\partial\mu_2)_{T, p, N_1, \bar{N}_2, sc} (\partial S/\partial\bar{n})_{T, p, N_1, \bar{N}_2, sc}}{(\partial\mu_2/\partial\bar{N}_2)_{T, p, N_1, \bar{n}, sc} (\partial\bar{n}/\partial\mu_2)_{T, p, N_1, \bar{N}_2, sc}} \\ \times (\partial\psi/\partial\bar{n})_{T, p, N_1, \bar{N}_2, sc} - \tilde{\psi}_2$$

This can be shown to reduce to Eq. (7-210). Alternatively,  $d\psi = 0$  may be used to eliminate  $d\bar{n}$  rather than  $d\bar{N}_2$  from Eq. (7-219a).

We define the equilibrium constant  $K'$  by

$$K' = \frac{\bar{N}_1^{(2)}}{\bar{N}_1^{(1)}} = \frac{N_1 - \bar{n}}{\bar{n}} \quad \text{at} \quad \psi = 0, \quad \delta = 0. \quad (7-222)$$

In general,  $\bar{n}$  is a function of  $T$ ,  $p$ ,  $N_1$ ,  $\psi$ , and  $m_1^s$  ( $\delta$ ,  $sc'$  constant), as in Eqs. (7-210) to (7-212), and hence  $K'$  is also. But the operationally significant value of  $K'$  is its value at  $\psi = 0$  and  $\delta = 0$ , and this quantity is a function of  $T$ ,  $p$ ,  $N_1$ , and  $m_1^s$  ( $sc'$  constant). In a macroscopic system, it would be a function of  $T$ ,  $p$ , and  $m_1^s$  ( $sc'$  constant).

The equilibrium constant defined above is not a "constant" in the conventional sense, for the value of the ratio  $\bar{N}_1^{(2)}/\bar{N}_1^{(1)}$ , at equilibrium, is influenced by the amount ( $\bar{N}_2$ ) of component 2 present. But we take the more practical point of view that  $m_1^s$ , like  $p$  and  $T$ , is an externally controllable, intensive parameter on which  $K'$  at  $\psi = 0$ ,  $\delta = 0$  depends, and hence  $K'$  is a useful "constant."

The temperature derivative of  $\ln K'$  is

$$\left( \frac{\partial \ln K'}{\partial T} \right)_{p, N_1, \psi, \delta, sc} = - \frac{N_1}{\bar{n}(N_1 - \bar{n})} \left( \frac{\partial \bar{n}}{\partial T} \right)_{p, N_1, \psi, \delta, sc}, \quad (7-223)$$

where  $\partial \bar{n} / \partial T$  is given by Eq. (7-210). According to Eq. (7-208),

$$\frac{\partial(F - \mu_2 \bar{N}_2)}{\partial \bar{n}} = -\psi = \frac{\partial H}{\partial \bar{n}} - T \frac{\partial S}{\partial \bar{n}} - \mu_2 \frac{\partial \bar{N}_2}{\partial \bar{n}}, \quad (7-224)$$

with all derivatives at constant  $T$ ,  $p$ ,  $N_1$ ,  $\mu_2$ , and  $sc$ . At equilibrium,  $\psi = 0$  and  $\mu_2 = \mu_1^* = \bar{H}_1^* - T\bar{S}_1^*$ . Then

$$\frac{\partial H}{\partial \bar{n}} - \bar{H}_1^* \frac{\partial \bar{N}_2}{\partial \bar{n}} = T \left( \frac{\partial S}{\partial \bar{n}} - \bar{S}_1^* \frac{\partial \bar{N}_2}{\partial \bar{n}} \right) \quad (\psi = 0), \quad (7-225)$$

with all derivatives<sup>1</sup> at constant  $T$ ,  $p$ ,  $N_1$ , and  $sc$ , and with  $\delta = 0$ . Let us call this quantity  $-\Delta H$ . We now combine Eqs. (7-210),

<sup>1</sup> As in Eq. (5-26), for example, the change  $d\pi$  may be regarded as having been brought about by a variation  $d\psi$  at  $\psi = 0$  as the system approaches equilibrium with respect to the isomeric reaction.

(7-213), (7-223), and (7-225) to find

$$\left(\frac{\partial \ln K'}{\partial T}\right)_{p, N_1, \psi, \delta, sc} = \frac{\Delta H}{kT^2} \left[ \frac{N_1(\bar{x}^2 - \bar{x}^2)}{\bar{x}(1 - \bar{x})} \right] \quad (\psi = 0, \delta = 0), \quad (7-226)$$

where

$$x = \frac{n}{N_1} = \frac{N_1^{(1)}}{N_1^{(1)} + N_1^{(2)}}.$$

The heat of reaction and binding, and its relation to  $\Delta H$ , will be discussed in the next subsection because some digression is required.

For the pressure derivative of  $\ln K'$ , we find

$$\begin{aligned} \left(\frac{\partial \ln K'}{\partial p}\right)_{T, N_1, \psi, \delta, sc} &= \frac{1}{kT} \left[ \left(\frac{\partial \bar{V}}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} - \bar{v}_1^* \left(\frac{\partial \bar{N}_2}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \right] \left[ \frac{N_1(\bar{x}^2 - \bar{x}^2)}{\bar{x}(1 - \bar{x})} \right]. \end{aligned} \quad (7-227)$$

To find the effect of the size ( $N_1$ ) of the small system on  $K'$ , we need the Gibbs-Duhem equation

$$\begin{aligned} d\mathcal{E} &= d[(\hat{\mu}_1 - \mu_1^{(2)})N_1] \\ &= -(S - \bar{N}_2 \bar{s}_1^*) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^*) dp - N_1 d\mu_1^{(2)} + \bar{n} d\psi \\ &\quad + \left[ \beta - \bar{N}_2 \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} \right] dm_1^s \quad (\delta, sc'), \end{aligned} \quad (7-228)$$

which follows from Eq. (7-209). Using this and Eq. (7-212), we deduce

$$\left(\frac{\partial \ln K'}{\partial N_1}\right)_{T, p, \psi, \delta, sc} = -\frac{1}{N_1 kT} \left(\frac{\partial \mathcal{E}}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \left[ \frac{N_1(\bar{x}^2 - \bar{x}^2)}{\bar{x}(1 - \bar{x})} \right]. \quad (7-229)$$

Also, from Eq. (7-211),

$$\begin{aligned} \left(\frac{\partial \ln K'}{\partial m_1^s}\right)_{T, p, N_1, \psi, \delta, sc'} &= \frac{1}{kT} \left[ \left(\frac{\partial \beta}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} - \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} \left(\frac{\partial \bar{N}_2}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \right] \\ &\quad \times \left[ \frac{N_1(\bar{x}^2 - \bar{x}^2)}{\bar{x}(1 - \bar{x})} \right]. \end{aligned} \quad (7-230)$$



When  $m_1^s$  is small,

$$\left(\frac{\partial \ln K'}{\partial \ln m_1^s}\right)_{T, p, N_1, \psi, \delta, sc'} = - \left(\frac{\partial \bar{N}_2}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \left[ \frac{N_1(\bar{x}^2 - \bar{x})}{\bar{x}(1 - \bar{x})} \right]. \quad (7-231)$$

Finally, there is the somewhat less practical relation

$$\left(\frac{\partial \ln K'}{\partial \psi}\right)_{T, p, N_1, \delta, sc} = \frac{1}{kT} \left[ \frac{N_1(\bar{x}^2 - \bar{x})}{\bar{x}(1 - \bar{x})} \right]. \quad (7-232)$$

If in Eq. (7-227) we measure (at  $\psi = 0$ )  $\partial \ln K' / \partial p$ ,  $\partial \bar{V} / \partial \bar{n}$ , and  $\bar{v}_1^*(\partial \bar{N}_2 / \partial \bar{n})$ , or if in Eq. (7-231) we measure  $\partial \ln K' / \partial \ln m_1^s$  and  $\partial \bar{N}_2 / \partial \bar{n}$ , [ ] may be calculated. From [ ] we can then find  $\partial \ln K' / \partial \psi$ , from [ ] and  $\partial \ln K' / \partial N_1$  we get  $\partial \mathcal{E} / \partial \bar{n}$ , and from [ ] and  $\partial \ln K' / \partial T$  we obtain  $\Delta H$ .

We can combine Eqs. (7-226) [or (7-223)], (7-227), (7-229), and (7-231), in pairs, to obtain derivatives at constant  $K'$  (or  $\bar{n}/N_1$ ). For example,

$$\begin{aligned} \left(\frac{\partial N_1}{\partial T}\right)_{p, \psi, \delta, K', sc} \\ = - N_1 \left[ \left(\frac{\partial S}{\partial \mathcal{E}}\right)_{T, p, N_1, \delta, sc} - \bar{s}_1^* \left(\frac{\partial \bar{N}_2}{\partial \mathcal{E}}\right)_{T, p, N_1, \delta, sc} \right]. \end{aligned} \quad (7-233)$$

Another Legendre transformation of Eq. (7-209) is

$$\begin{aligned} d(\hat{\mu}_1 N_1 - \bar{n} \psi) = - (S - \bar{N}_2 \bar{s}_1^*) dT + (\bar{V} - \bar{N}_2 \bar{v}_1^*) dp + \mu_1^{(2)} dN_1 \\ - \psi d\bar{n} + \left[ \beta - \bar{N}_2 \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} \right] dm_1^s \quad (\delta, sc'). \end{aligned} \quad (7-234)$$

From this we can deduce, for example,

$$\left(\frac{\partial \psi}{\partial T}\right)_{p, N_1, \bar{n}, \delta, sc} = \left(\frac{\partial S}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} - \bar{s}_1^* \left(\frac{\partial \bar{N}_2}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \quad (7-235)$$

$$\left(\frac{\partial \psi}{\partial p}\right)_{T, N_1, \bar{n}, \delta, sc} = - \left(\frac{\partial \bar{V}}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} + \bar{v}_1^* \left(\frac{\partial \bar{N}_2}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc} \quad (7-236)$$

$$\left(\frac{\partial \psi}{\partial N_1}\right)_{T, p, \bar{n}, \delta, sc} = - \left(\frac{\partial \mu_1^{(2)}}{\partial \bar{n}}\right)_{T, p, N_1, \delta, sc}. \quad (7-237)$$

Equation (7-235) also follows from Eq. (7-210). On combining Eqs. (7-235) and (7-237), we get

$$\left(\frac{\partial N_1}{\partial T}\right)_{p, \bar{n}, \psi, \delta, sc} = \left(\frac{\partial S}{\partial \mu_1^{(2)}}\right)_{T, p, N_1, \delta, sc} - \tilde{S}_1^* \left(\frac{\partial \bar{N}_2}{\partial \mu_1^{(2)}}\right)_{T, p, N_1, \delta, sc} \quad (7-238)$$

This differs from Eq. (7-233) in that  $\bar{n}$  rather than  $\bar{n}/N_1$  is constant here.

There are, of course, a vast number of other relations which can be derived. We have presented what we hope is a reasonable sample.

**HEAT OF REACTION AND BINDING.** Because of the binding of component 2 from solution, the small systems are not closed. We therefore consider the whole macroscopic solution in discussing the heat of reaction and binding. For the macroscopic solution [compare Eq. (7-195)],

$$dE_T = T dS_T - p dV_T + \sum_i \mu_i^s dN_i^s + \mu^\square d\mathcal{N} + \mu_1^{(2)} \mathcal{N} dN_1 + \mu_2 \mathcal{N} d\bar{N}_2 - \psi \mathcal{N} d\bar{n}. \quad (7-239)$$

For an infinitesimal, reversible process occurring in the closed macroscopic system, the following quantities are constant:

$$N_2^s, \dots, N_c^s, \quad N_1^s + \mathcal{N} \bar{N}_2, \quad \mathcal{N}, \quad N_1. \quad (7-240)$$

In such a process,  $DQ_T = T dS_T$ .

A general expression for  $dS_T$ , which we shall use below, is

$$dS_T = \frac{\partial S_T}{\partial T} dT + \frac{\partial S_T}{\partial p} dp + \sum_i \frac{\partial S_T}{\partial N_i^s} dN_i^s + \frac{\partial S_T}{\partial \bar{N}_2} d\bar{N}_2 + \frac{\partial S_T}{\partial \bar{N}_1^{(1)}} d\bar{N}_1^{(1)} + \frac{\partial S_T}{\partial \bar{N}_1^{(2)}} d\bar{N}_1^{(2)} + \frac{\partial S_T}{\partial \mathcal{N}} d\mathcal{N}. \quad (7-241)$$

From this point on we consider specifically the heat of the process in which the reaction proceeds to an extent  $d\bar{n}$  (at  $\psi = 0$ ,  $\delta = 0$ ) with the macroscopic system closed and with  $p$  and  $T$  constant. This process could be realized experimentally by following the closed macroscopic system at constant  $p$  and  $T$  in its approach to isomeric equilibrium ( $\psi \rightarrow 0$ ) and noting the heat absorbed by the

macroscopic system at the last stage  $d\bar{n}$  of this approach. For the process just described,

$$DQ_T = T dS_T = T \left( -\mathcal{N} \frac{\partial S_T}{\partial N_1^s} + \frac{\partial S_T}{\partial \bar{N}_2} \right) d\bar{N}_2 + T \left( \frac{\partial S_T}{\partial \bar{N}_1^{(1)}} - \frac{\partial S_T}{\partial \bar{N}_1^{(2)}} \right) d\bar{n}, \quad (7-242)$$

where we have used Eqs. (7-240) and (7-241). From

$$S_T = \mathcal{N}(S - k \ln x') + \sum_i N_i^s \tilde{s}_i^s$$

we find

$$DQ_T = T dS_T = \mathcal{N}T \left[ \left( \frac{\partial S}{\partial \bar{N}_2} \right)_{T, p, N_1, \bar{n}, sc} - \tilde{s}_1^* \right] d\bar{N}_2 + \mathcal{N}T \left( \frac{\partial S}{\partial \bar{n}} \right)_{T, p, N_1, \bar{N}_2, sc} d\bar{n}. \quad (7-243)$$

The term in  $d\bar{N}_2$  is the heat of binding, whereas the term in  $d\bar{n}$  is the heat of reaction.

In the above process, although an average of  $d\bar{N}_2$  molecules of component 1<sup>s</sup> are removed from the solution and bound on each small system, the chemical potential  $\mu_1^*$  in the solution remains effectively constant. This follows because the number of small systems is so small ( $\mathcal{N} \rightarrow 0$ ) relative to the amount of solvent that  $N_1^s$  is virtually constant. Since  $\delta = 0$  and  $\mu_1^* = \text{constant}$ ,  $\mu_2 = \text{constant}$ .

Thus Eq. (7-243) can be written

$$\left( \frac{DQ_T}{d\bar{n}} \right)_{p, T, \text{closed}} = \mathcal{N}T \left[ \left( \frac{\partial S}{\partial \bar{N}_2} \right)_{T, p, N_1, \bar{n}, sc} - \tilde{s}_1^* \right] \times \left( \frac{\partial \bar{N}_2}{\partial \bar{n}} \right)_{T, p, N_1, \mu_2, sc} + \mathcal{N}T \left( \frac{\partial S}{\partial \bar{n}} \right)_{T, p, N_1, \bar{N}_2, sc} \quad (\psi = 0, \delta = 0). \quad (7-244)$$

If we employ

$$\left( \frac{\partial S}{\partial \bar{n}} \right)_{T, p, N_1, \mu_2, sc} = \left( \frac{\partial S}{\partial \bar{n}} \right)_{T, p, N_1, \bar{N}_2, sc} + \left( \frac{\partial S}{\partial \bar{N}_2} \right)_{T, p, N_1, \bar{n}, sc} \left( \frac{\partial \bar{N}_2}{\partial \bar{n}} \right)_{T, p, N_1, \mu_2, sc},$$

Eq. (7-244) becomes

$$\begin{aligned} & \left( \frac{DQ_T}{\partial \bar{n}} \right)_{p, T, \text{closed}} \\ &= \mathcal{N} T \left[ \left( \frac{\partial S}{\partial \bar{n}} \right)_{T, p, N_1, \delta, sc} - \bar{s}_1^* \left( \frac{\partial \bar{N}_2}{\partial \bar{n}} \right)_{T, p, N_1, \delta, sc} \right] \quad (\psi = 0, \delta = 0). \end{aligned} \quad (7-245)$$

Finally, from Eq. (7-226),

$$\begin{aligned} & \left( \frac{\partial \ln K'}{\partial T} \right)_{p, N_1, \psi, \delta, sc} = - \left[ \frac{N_1(\bar{x}^2 - \bar{x})}{\bar{x}(1 - \bar{x})} \right] \\ & \quad \times \frac{1}{\mathcal{N} k T^2} \left( \frac{DQ_T}{\partial \bar{n}} \right)_{p, T, \text{closed}} \quad (\psi = 0, \delta = 0). \end{aligned} \quad (7-246)$$

*Example. Helix-Coil Transition. Independent Helix and Coil Units.*

We assume here, as in Eqs. (2-99) and (5-107), that any one of the  $N_1$  units in the chain can be of helix or coil type, independently. When there are  $n$  helix units and no binding of component 2 on the chain, the canonical ensemble partition function is

$$Q = \frac{q_H^n q_C^{N_1 - n} N_1!}{n! (N_1 - n)!}, \quad (7-247)$$

where  $q_H(T)$  and  $q_C(T)$  are individual unit partition functions.

Now let us assume further that each unit has one site for binding one molecule of component 2. All sites are independent; all  $H$  sites are equivalent, as are all  $C$  sites. The partition function for a bound molecule is  $j_H(T)$  on an  $H$  site and  $j_C(T)$  on a  $C$  site. Then for a chain with  $n$  helix units,  $N_{2H}$  component 2 molecules bound on  $H$  sites, and  $N_{2C}$  component 2 molecules bound on  $C$  sites,

$$\begin{aligned} Q(n, N_1, N_{2H}, N_{2C}, T) &= \frac{q_H^n q_C^{N_1 - n} N_1!}{n! (N_1 - n)!} \frac{j_H^{N_{2H}} n!}{N_{2H}! (n - N_{2H})!} \\ &\quad \times \frac{j_C^{N_{2C}} (N_1 - n)!}{N_{2C}! (N_1 - n - N_{2C})!}. \end{aligned} \quad (7-248)$$

The partition function  $Z$  of Eq. (7-190) is in this case

$$\begin{aligned} Z(N_1, \mu_2, T, \psi) &= \sum_{n=0}^{N_1} \sum_{N_{2H}=0}^n \sum_{N_{2C}=0}^{N_1-n} Q(n, N_1, N_{2H}, N_{2C}, T) \\ &\quad \times e^{-n\psi/kT} e^{(N_{2H}+N_{2C})\mu_2/kT} \\ &= [q_C(1 + j_C\lambda_2) + q_H e^{-\psi/kT}(1 + j_H\lambda_2)]^{N_1}, \end{aligned} \quad (7-249)$$

where  $\lambda_2 = e^{\mu_2/kT}$ . This is a special case of Eqs. (7-64) and (7-68) in S.T. From Eq. (7-191),

$$\hat{\mu}_1 N_1 = -N_1 kT \ln [ ] \quad (7-250)$$

where  $[ ]$  is the expression in brackets in Eq. (7-249).

Equation (7-186) then gives the thermodynamic functions. Thus we find

$$\mathcal{E} = 0 \quad (7-251)$$

$$\frac{\bar{n}}{N_1} = \frac{q_H e^{-\psi/kT}(1 + j_H\lambda_2)}{[ ]} \quad (7-252)$$

$$K' = \frac{N_1 - \bar{n}}{\bar{n}} = \frac{q_C(1 + j_C\lambda_2)}{q_H(1 + j_H\lambda_2)} \quad \text{at } \psi = 0 \quad (7-253)$$

$$\begin{aligned} \frac{\bar{N}_2}{N_1} &= \frac{\bar{N}_{2C}}{N_1} + \frac{\bar{N}_{2H}}{N_1} \\ &= \frac{q_C j_C \lambda_2}{[ ]} + \frac{q_H e^{-\psi/kT} j_H \lambda_2}{[ ]} \\ &= \frac{N_1 - \bar{n}}{N_1} \frac{j_C \lambda_2}{1 + j_C \lambda_2} + \frac{\bar{n}}{N_1} \frac{j_H \lambda_2}{1 + j_H \lambda_2}. \end{aligned} \quad (7-254)$$

These results are simple and their interpretation self-evident. Also, from Eq. (7-193),

$$\frac{\overline{n^2} - \bar{n}^2}{\bar{n}^2} = \frac{N_1 - \bar{n}}{N_1 \bar{n}} = O\left(\frac{1}{N_1}\right). \quad (7-255)$$

This is the same as Eq. (5-111).

*All-or-None Model.* This is essentially the model in Eq. (2-95), but here we introduce binding of component 2 on  $H$  and  $C$  units as in Eq. (7-248) above. Without binding,

$$Q = q_C^{N_1} + q_H^{N_1}. \quad (7-256)$$

With binding,

$$\begin{aligned} Q(n, N_1, N_{2H}, N_{2C}, T) &= Q_C + Q_H \\ &= \frac{q_C^N j_C^{N_{2C}} N_1!}{N_{2C}!(N_1 - N_{2C})!} + \frac{q_H^N j_H^{N_{2H}} N_1!}{N_{2H}!(N_1 - N_{2H})!} \end{aligned} \quad (7-257)$$

and

$$\begin{aligned} Z(N_1, \mu_2, T, \psi) &= \sum_{N_{2C}=0}^{N_1} Q_C \lambda_2^{N_{2C}} + \sum_{N_{2H}=0}^{N_1} Q_H \lambda_2^{N_{2H}} e^{-N_1 \psi / kT} \\ &= [q_C(1 + j_C \lambda_2)]^{N_1} + [q_H e^{-\psi / kT} (1 + j_H \lambda_2)]^{N_1}. \end{aligned} \quad (7-258)$$

Then we deduce

$$\hat{\mu}_1 N_1 = -kT \ln Z \quad (7-259)$$

$$\begin{aligned} -\frac{\mu_1^{(2)}}{kT} &= \frac{1}{Z} \{ [q_C(1 + j_C \lambda_2)]^{N_1} \ln [q_C(1 + j_C \lambda_2)] \\ &\quad + [q_H e^{-\psi / kT} (1 + j_H \lambda_2)]^{N_1} \ln [q_H e^{-\psi / kT} (1 + j_H \lambda_2)] \} \end{aligned} \quad (7-260)$$

$$\frac{\bar{n}}{N_1} = \frac{[q_H e^{-\psi / kT} (1 + j_H \lambda_2)]^{N_1}}{Z} \quad (7-261)$$

$$K' = \left[ \frac{q_C(1 + j_C \lambda_2)}{q_H(1 + j_H \lambda_2)} \right]^{N_1} \quad \text{at } \psi = 0. \quad (7-262)$$

The helix-coil transition may be said to occur at  $K' = 1$ , that is, when

$$q_C(1 + j_C \lambda_2) = q_H(1 + j_H \lambda_2). \quad (7-263)$$

This equation gives, for example, the molality  $m_1^s$  at which the transition takes place as a function of temperature. The transition becomes sharper, of course, as  $N_1 \rightarrow \infty$  (Fig. 2-4).

Equation (7-254) for  $\bar{N}_2/N_1$  is again found, but with  $\bar{n}/N_1$  given by Eq. (7-261). Finally,

$$\frac{\overline{n^2} - \bar{n}^2}{\bar{n}^2} = \frac{N_1 - \bar{n}}{\bar{n}} = O(1). \quad (7-264)$$

This should be contrasted with Eq. (7-255). Fluctuations are larger here because the system is forced by the model to be all helix or all coil. The order of magnitude of the fluctuations is the same as in a first-order phase transition, as expected.

*More Detailed Model.* The helix-coil transition with binding (for an infinite system) is discussed in a much more detailed way than above by R. F. Steiner.<sup>1</sup>

*Experimental.* The only experimental small system effect of this sort known to the author is the work of A. Wada,<sup>2</sup> which shows a dependence of the titration curve of poly-L-glutamic acid on molecular weight. The observed effect is small because both molecular weights used are large.

<sup>1</sup> See R. F. Steiner and R. F. Beers, Jr., "Polynucleotides," pp. 277-289, Elsevier, Amsterdam, 1961.

<sup>2</sup> A. Wada, *Mol. Phys.*, **3**, 409 (1960).

# ENVIRONMENTAL VARIABLES $N, V, T$

The small system under consideration in this chapter is closed, has an assigned volume  $V$ , and is in a heat bath at temperature  $T$ . This case is unimportant experimentally. However, on the theoretical side, the pertinent partition function is the canonical ensemble partition function  $Q(N, V, T)$ , probably the most widely used in statistical mechanics. Hence our point of view in this chapter will be primarily theoretical.

It will be recalled that Section 3-1 was concerned with an incompressible  $N, T$  system. Such a system is a degenerate case of an  $N, p, T$  system, as was pointed out in Chapter 3. But an  $N, T$  system may of course also be regarded as a degenerate form of an  $N, V, T$  system, to be studied in the present chapter.

## 8-1. THERMODYNAMIC RELATIONS

An introduction to this subject is provided by Eqs. (1-43) to (1-48) and Section 1-4. The fundamental equations for a small system are

$$d\bar{E} = T dS - p dV + \mu dN \quad (8-1)$$

$$A = \bar{E} - TS \quad (8-2)$$

$$\mathcal{E} = \bar{E} - TS + pV - \mu N \quad (8-3)$$

$$dA = -S dT - p dV + \mu dN \quad (8-4)$$

$$d\mathcal{E} = -S dT + V dp - N d\mu \quad (8-5)$$

$$A = -kT \ln Q(N, V, T). \quad (8-6)$$

Because there are two extensive environmental variables,  $N$  and  $V$ , it is not generally advantageous to introduce either  $\hat{\mu}$  or  $\hat{p}$ . However, there are exceptions, as will be noted below.

The reader will recall that, with the environmental variables  $N, p, T$ , the important quantity  $\hat{\mu}$  is equal to the "characteristic function" [see Eq. (1-81)] divided by  $N$ . If we consider the environmental variables here to be  $N, V/N, T$  (one extensive variable), then an analogue of  $\hat{\mu}$  would be  $A/N$ . Similarly, if the environmental



variables are regarded as  $N/V$ ,  $V$ ,  $T$ , then an analogue of  $-\hat{p}$  is  $A/V$ .

With these facts in mind, we rewrite Eq. (8-4) in the forms

$$d\left(\frac{A}{N}\right) = -\frac{S}{N}dT - \frac{pN}{N}d\left(\frac{V}{N}\right) - \frac{\mathcal{E}}{N^2}dN \quad (8-7)$$

and

$$d\left(\frac{A}{V}\right) = -\frac{S}{V}dT + \frac{\mu V}{V}d\left(\frac{N}{V}\right) - \frac{\mathcal{E}}{V^2}dV, \quad (8-8)$$

which resemble Eqs. (2-13) and (6-10), respectively.

Similarly, the analogue here of  $\mu = (\hat{\mu}N - \mathcal{E})/N$  in an  $N, p, T$  system is  $(A - \mathcal{E})/N$ . Using Maxwell relations from

$$dA = -SdT - pNd\left(\frac{V}{N}\right) + \left(\frac{A - \mathcal{E}}{N}\right)dN, \quad (8-9)$$

we obtain

$$\begin{aligned} d\left(\frac{A - \mathcal{E}}{N}\right) &= -\left(\frac{\partial S}{\partial N}\right)_{T, V/N}dT - \left(\frac{\partial pN}{\partial N}\right)_{T, V/N}d\left(\frac{V}{N}\right) \\ &\quad - \frac{1}{N}\left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, V/N}dN. \end{aligned} \quad (8-10)$$

This corresponds to Eq. (2-17). The expression with  $V$  is

$$\begin{aligned} d\left(\frac{A - \mathcal{E}}{V}\right) &= -\left(\frac{\partial S}{\partial V}\right)_{T, N/V}dT + \left(\frac{\partial \mu V}{\partial V}\right)_{T, N/V}d\left(\frac{N}{V}\right) \\ &\quad - \frac{1}{V}\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, N/V}dV, \end{aligned} \quad (8-11)$$

which should be compared with Eq. (6-11).

We also have

$$\frac{A}{N} = \frac{\bar{E}}{N} - \frac{TS}{N}, \quad \frac{A}{V} = \frac{\bar{E}}{V} - \frac{TS}{V} \quad (8-12)$$

$$\frac{A - \mathcal{E}}{N} = \left(\frac{\partial A}{\partial N}\right)_{T, V/N} = \left(\frac{\partial \bar{E}}{\partial N}\right)_{T, V/N} - T\left(\frac{\partial S}{\partial N}\right)_{T, V/N} \quad (8-13)$$

$$\frac{A - \mathcal{E}}{V} = \left(\frac{\partial A}{\partial V}\right)_{T, N/V} = \left(\frac{\partial \bar{E}}{\partial V}\right)_{T, N/V} - T\left(\frac{\partial S}{\partial V}\right)_{T, N/V}. \quad (8-14)$$

A few relations showing the effect of the size of the system on intensive properties are:

$$\left(\frac{\partial p}{\partial N}\right)_{T, V/N} = \frac{1}{N} \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, N} \quad (8-15)$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{T, N/V} = -\frac{1}{V} \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, V} \quad (8-16)$$

$$N^2 \left(\frac{\partial S/N}{\partial N}\right)_{T, V/N} = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{N, V} = V^2 \left(\frac{\partial S/V}{\partial V}\right)_{T, N/V} \quad (8-17)$$

$$N^2 \left(\frac{\partial A/N}{\partial N}\right)_{T, V/N} = -\mathcal{E} = V^2 \left(\frac{\partial A/V}{\partial V}\right)_{T, N/V}. \quad (8-18)$$

Excess functions may be defined in terms of either  $N$  or  $V$ . For example, for  $N$  [compare Eq. (2-54) et seq.]:

$$G(N, V/N, T) = N G^{(0)}(V/N, T) + G^{(x)}(N, V/N, T) \quad (8-19)$$

$$\mu(N, V/N, T) = \mu^{(0)}(V/N, T) + \mu^{(x)}(N, V/N, T) \quad (8-20)$$

$$p(N, V/N, T) = p^{(0)}(V/N, T) + p^{(x)}(N, V/N, T). \quad (8-21)$$

Then

$$\mathcal{E} = A^{(x)} + p^{(x)} V - \mu^{(x)} N \quad (8-22)$$

$$dA^{(x)} = -S^{(x)} dT - p^{(x)} dV + \mu^{(x)} dN \quad (8-23)$$

$$d\mathcal{E} = -S^{(x)} dT + V dp^{(x)} - N d\mu^{(x)}. \quad (8-24)$$

The calorimetric equations for a small  $N, V, T$  system are uncomplicated [compare Eq. (2-29) et seq.]:

$$d\bar{E} = T dS = DQ \quad (N, V \text{ constant}) \quad (8-25)$$

$$C_V = \left(\frac{DQ}{dT}\right)_{N, V} = \left(\frac{\partial \bar{E}}{\partial T}\right)_{N, V} = T \left(\frac{\partial S}{\partial T}\right)_{N, V}. \quad (8-26)$$

As a final topic, we derive the analogue of the well-known macroscopic equation

$$\left(\frac{N}{V}\right)^2 \left(\frac{\partial \mu}{\partial N}\right)_{T, V} = -\left(\frac{\partial p}{\partial V}\right)_{T, N} \quad (\text{macroscopic}).$$

This equation is useful in relating  $\mu$  versus  $N/V$  and  $p$  versus  $V/N$  curves, for example, in connection with phase transitions. From

Eq. (8-5),

$$\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, N} = V \left(\frac{\partial p}{\partial V}\right)_{T, N} - N \left(\frac{\partial \mu}{\partial V}\right)_{T, N} \quad (8-27)$$

and

$$\left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, V} = V \left(\frac{\partial p}{\partial N}\right)_{T, V} - N \left(\frac{\partial \mu}{\partial N}\right)_{T, V}. \quad (8-28)$$

A Maxwell relation which follows from Eq. (8-4) is

$$\left(\frac{\partial \mu}{\partial V}\right)_{T, N} = - \left(\frac{\partial p}{\partial N}\right)_{T, V}. \quad (8-29)$$

Using this in Eqs. (8-27) and (8-28), we have

$$\frac{N^2}{V^2} \left(\frac{\partial \mu}{\partial N}\right)_{T, V} + \frac{N}{V^2} \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T, V} = - \left(\frac{\partial p}{\partial V}\right)_{T, N} + \frac{1}{V} \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{T, N}. \quad (8-30)$$

This is the desired result. A more compact form of this equation is

$$\frac{N^2}{V^2} \left(\frac{\partial \hat{\mu}}{\partial N}\right)_{T, V} = - \left(\frac{\partial \hat{p}}{\partial V}\right)_{T, N}, \quad (8-31)$$

where, as usual,

$$\hat{\mu} = \mu + \frac{\mathcal{E}}{N}, \quad \hat{p} = p - \frac{\mathcal{E}}{V}. \quad (8-32)$$

Equations (10-132) and (10-135) should also be noted in this connection.

## 8-2. PHASE TRANSITIONS

A rather detailed discussion of first-order phase transitions in finite  $N, V, T$  systems has already been given elsewhere.<sup>1</sup> There seems little point in repeating this material here. Instead, we shall give below a brief summary of the general situation and supplement this with a consideration of three examples.

Because of interfacial effects, an *exact* theory of a first-order phase transition in a finite system will give: (a) two peaks in the probability curve  $P(V)$  for an  $N, p, T$  system (Section 5-4); (b) two peaks in the probability curve  $P(N)$  for a  $\mu, V, T$  system (Section 6-1); and

<sup>1</sup> S.M., Appendix 9; and T. L. Hill, *J. Chem. Phys.*, **23**, 812 (1955).

(c) a "loop" in the  $p$  versus  $V/N$  ( $N$  constant) and  $\mu$  versus  $N/V$  ( $V$  constant) curves for an  $N, V, T$  system. These loops are *not* of the van der Waals type. They are "small" loops which disappear (leaving horizontal lines) as  $N \rightarrow \infty$ , whereas loops of the van der Waals type, which arise through the imposition of a restraint of uniform density, do not so disappear.

It is possible for  $N, p, T$  and  $\mu, V, T$  systems at a phase transition to "avoid" an interface by existing solely as one phase or the other. But an  $N, V, T$  system cannot do this; it must have an interface.

The small loops referred to above arise in exact theories, so there is no question here (as with van der Waals loops in macroscopic systems) of finding a horizontal line which is "more exact" than a given small loop. However, if a horizontal line is drawn in a  $p$ - $V/N$  ( $N$  constant) or  $\mu$ - $N/V$  ( $V$  constant) diagram, based on equal areas in the conventional way, the two ends of the line *do* correspond to the same value of  $\hat{\mu}$  in the former case and of  $\hat{p}$  in the latter. Otherwise, however, the horizontal line has no particular interest.

The proof of the above statement about  $\hat{\mu}$  and  $\hat{p}$  follows. From Eq. (8-5),

$$d(\mathcal{E} + \mu N) = d(\hat{\mu} N) = -S dT + V dp + \mu dN \quad (8-33)$$

$$d(\mathcal{E} - pV) = -d(\hat{p} V) = -S dT - p dV - N d\mu. \quad (8-34)$$

Then

$$d\hat{\mu} = \frac{V}{N} dp \quad (T, N \text{ constant}) \quad (8-35)$$

$$d\hat{p} = \frac{N}{V} d\mu \quad (T, V \text{ constant}). \quad (8-36)$$

Integration of these equations gives the desired results.

A finite system with the restraint of uniform density imposed will exhibit  $p$ - $V/N$  and  $\mu$ - $N/V$  loops of the van der Waals type which will differ from the macroscopic van der Waals loops for the same system by "small" amounts only. Presumably there is no general thermodynamic theorem (such as exists in the macroscopic case, i.e., the equal-area theorem) that will tell us how to pass from the van der Waals loops to the small loops when the restraint of uniform density is removed.

Consider *any*  $Q(N, V, T)$ , exact or approximate, which gives a loop in, say, a  $p$  versus  $V/N$  ( $N$  constant) diagram. That is,

$(\partial p/\partial V)_{T, N}$  is positive in the "middle" of the curve. Then, since the first and third terms in Eq. (8-30) are larger than the other two by a factor of order  $N$ ,  $(\partial \mu/\partial N)_{T, V}$  will be negative in the middle of a  $\mu$  versus  $N/V$  ( $V$  constant) curve for the same  $N, V, T$  system. That is, this latter diagram will also show a loop. Furthermore, the existence of a  $p$ - $V$  loop for an  $N, V, T$  system implies<sup>1</sup> two peaks in the  $P(V)$  probability curve for an  $N, p, T$  system (with the same  $Q$ ), and the existence of a  $\mu$ - $N$  loop for an  $N, V, T$  system implies two peaks in the  $P(N)$  probability curve for a  $\mu, V, T$  system (with the same  $Q$ ). Thus the four properties mentioned above are all tied together and all follow from the given  $Q(N, V, T)$ .

*Example. Twelve-Site Lattice Gas on a Sphere.* Consider a lattice gas of twelve sites ( $B = 12$ ) arranged on the surface of a sphere (cubic close packing). Each site has four nearest-neighbor sites. Let  $w$  be the nearest-neighbor pair interaction energy. Then the exact canonical ensemble partition function is

$$Q(N, T) = \sum_M \Omega(N, M) y^M, \quad (8-37)$$

where  $y = e^{-w/kT}$  and  $\Omega(N, M)$  is the number of ways in which  $N$  sites can be occupied so that there are  $M$  nearest-neighbor occupied pairs of sites. Of course

$$\sum_M \Omega(N, M) = \frac{12!}{N!(12 - N)!}$$

and

$$\sum_{N, M} \Omega(N, M) = 2^{12} = 4096.$$

Then one finds<sup>2</sup> by actual count (first done by R. Peierls for another purpose)

$$Q(0, T) = 1, \quad Q(1, T) = 12, \quad Q(2, T) = 42 + 24y,$$

$$Q(3, T) = 44 + 120y + 48y^2 + 8y^3,$$

$$Q(4, T) = 9 + 96y + 240y^2 + 96y^3 + 54y^4,$$

$$Q(5, T) = 108y^2 + 264y^3 + 264y^4 + 120y^5 + 36y^6,$$

$$Q(6, T) = 216y^4 + 240y^5 + 336y^6 + 96y^7 + 36y^8,$$

$$Q(N, T) = Q(12 - N, T)y^{4(N-6)} \quad (7 \leq N \leq 12).$$

<sup>1</sup> See S.M., pp. 415-416.

<sup>2</sup> T. L. Hill, *J. Chem. Phys.*, **23**, 812 (1955). The function  $P(N)$  for an open system is discussed for this example in this reference, in Appendix 9 of S.M., and following Eq. (10-182).

We cannot vary  $B$  in this example to find  $p$  but we can vary  $N$  to find  $\mu$ . However,  $N$  is a small number so we have to use differences rather than differentials. We therefore define<sup>1</sup>

$$\mu_N \equiv A_{N+1} - A_N = -kT \ln \frac{Q_{N+1}}{Q_N}. \quad (8-38)$$

Then

$$\frac{\mu_0}{kT} = -\ln 12, \quad \frac{\mu_1}{kT} = -\ln\left(\frac{7+4y}{2}\right), \quad \text{etc.}$$

The symmetry relation

$$\frac{\mu_N}{kT} + \frac{\mu_{11-N}}{kT} = -\ln y^4$$

is useful here. It is now easy to compute  $\mu_N$  as a function of  $N$  and  $y$ .

Figure 8-1 shows  $\mu_N/kT$  plotted against  $N$  for various values of  $y = e^{-w/kT}$ . The curves are not smooth because  $N$  is small. But it is clear that  $y = 3$  is approximately the critical curve,<sup>2</sup> and for  $y > 3$  one finds the equivalent of loops. That is, in the middle of the  $\mu_N$ - $N$  curves, for  $y > 3$ , the slope is negative, whereas at the edges the loops are not completed only because of discreteness in  $N$ . This is indicated schematically by the dashed additions to the  $y = 4$  curve.

These curves<sup>3</sup> leave no doubt that an exact theory of a first-order phase transition in the canonical ensemble will give loops. The loops here appear "large" rather than "small" only because  $B$  is so small. The extent of the "loop" along the  $\mu_N/kT$  axis in Fig. 8-1 is

$$\Delta\left(\frac{\mu_N}{kT}\right) = O(1),$$

which is consistent with the expected range<sup>4</sup>

$$\Delta\left(\frac{\mu_N}{kT}\right) = O(B^{-1/2}).$$

<sup>1</sup> See Chapter 15.

<sup>2</sup> The value  $y = 3.1$  was guessed (loc. cit.) from the  $P(N)$  curves.

<sup>3</sup> My colleague, Professor S. Katsura, has verified these results by the same kind of calculation for sites on a finite torus ( $3 \times 3, 4 \times 4, 6 \times 6, 8 \times 8$ ). See also Z. W. Salsburg, J. D. Jacobson, W. Fickett, and W. W. Wood, *J. Chem. Phys.*, **30**, 65 (1959).

<sup>4</sup> T. L. Hill, loc. cit.

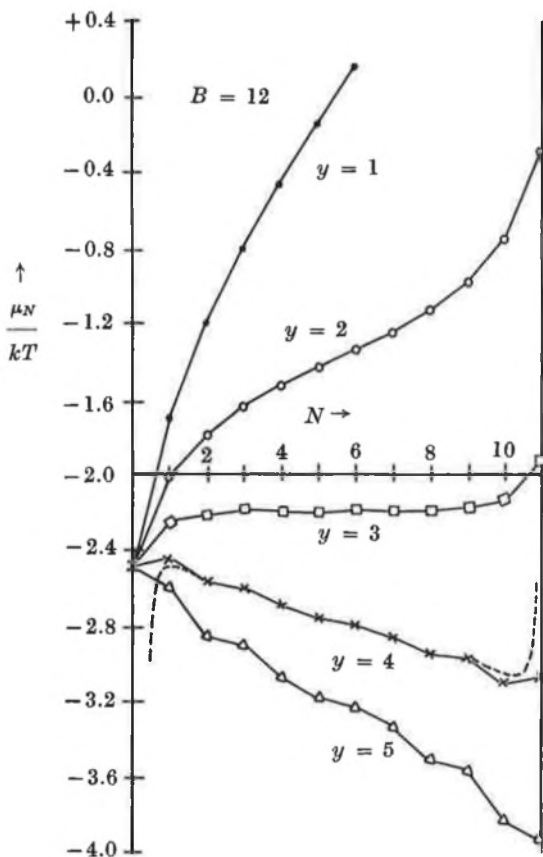


FIGURE 8-1. Exact calculation of  $\mu_N/kT$  versus  $N$  for twelve-site spherical lattice gas in canonical ensemble.  $\gamma = e^{-w/kT}$  is essentially a measure of temperature. "Loops" are obtained.

*Example. Incompressible Phases.* This is the same simple model as in Eqs. (5-144) and (5-145), but here we must put in an explicit interfacial term.

We consider a first-order transition between two condensed phases  $A$  and  $B$ . When only phase  $A$  is present (i.e., at one end of the transition), the number density ( $\equiv N/V$ ) is  $\rho_A$ , assumed a function of  $T$  only. When only  $B$  is present,  $\rho = \rho_B(T)$ . We take

$\rho_B > \rho_A$ , as before. The phase transition occurs at  $p = p_0$  and  $\mu = \mu_0$ , both assumed functions of  $T$  only.

For values of  $\rho$  between  $\rho_A$  and  $\rho_B$ , an interface must be present and there is an interfacial contribution,  $A_{\text{int}}$ , to the Helmholtz free energy  $A$ . To a first approximation,  $A_{\text{int}}$  is simply proportional to the interfacial area. This area, in turn, is a function of  $\rho$  which is determined by the geometry of the system. The case we consider here is very simple: we assume that the interfacial area varies linearly with  $\rho$ , with a maximum area at  $\rho = (\rho_A + \rho_B)/2$ . We take  $A_{\text{int}}$  at this maximum to be  $c(T)V^{2/3}$ , where  $c > 0$ . Thus

$$\begin{aligned} A_{\text{int}} &= \frac{2cV^{2/3}(\rho - \rho_A)}{\rho_B - \rho_A} & \left( \rho_A \leq \rho \leq \frac{\rho_A + \rho_B}{2} \right) \\ &= \frac{2cV^{2/3}(\rho_B - \rho)}{\rho_B - \rho_A} & \left( \frac{\rho_A + \rho_B}{2} \leq \rho \leq \rho_B \right). \end{aligned} \quad (8-39)$$

Then, for the complete free energy,

$$A = N\mu_0 - p_0V + A_{\text{int}} \quad (\rho_A \leq \rho \leq \rho_B). \quad (8-40)$$

We can now derive thermodynamic properties of interest in the two-phase region. For the chemical potential, we find

$$\begin{aligned} \mu &= \left( \frac{\partial A}{\partial N} \right)_{T, V} = \mu_0 + \frac{2cV^{-1/3}}{\rho_B - \rho_A} & (A) \\ &= \mu_0 - \frac{2cV^{-1/3}}{\rho_B - \rho_A} & (B), \end{aligned} \quad (8-41)$$

where (A) and (B) refer to the respective intervals in Eq. (8-39). Figure 8-2a shows  $\mu$  as a function of  $\rho$ , with the simplified loop that is a consequence of Eq. (8-39).

The pressure is

$$\begin{aligned} p &= - \left( \frac{\partial A}{\partial V} \right)_{T, N} = p_0 + \frac{2cV^{-1/3}(\rho + 2\rho_A)}{3(\rho_B - \rho_A)} & (A) \\ &= p_0 - \frac{2cV^{-1/3}(2\rho_B + \rho)}{3(\rho_B - \rho_A)} & (B). \end{aligned} \quad (8-42)$$

This is shown schematically in Fig. 8-2b.



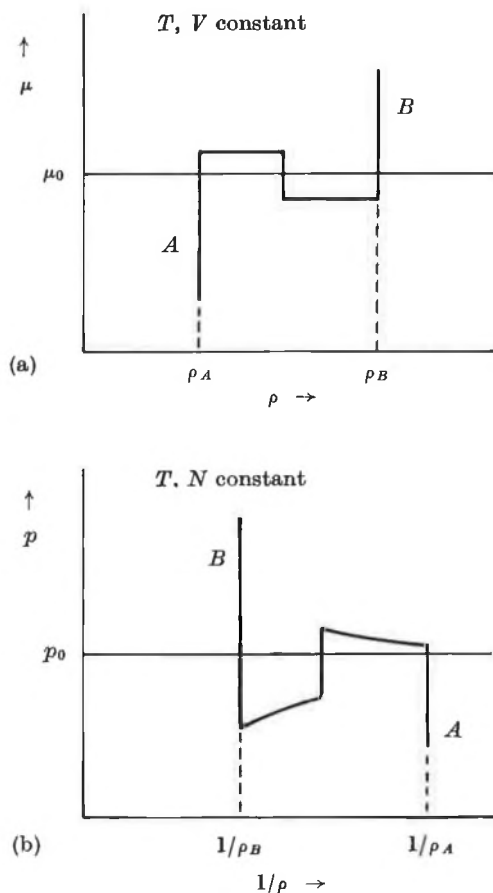


FIGURE 8-2. (a)  $\mu$  as a function of  $\rho$  for simple phase transition model. (b)  $p$  as a function of  $1/\rho$  for simple phase transition model.

From  $A$ ,  $p$ , and  $\mu$  we can easily deduce  $\mathcal{E}$ :

$$\begin{aligned} \mathcal{E} &= \frac{2cV^{2/3}(\rho - \rho_A)}{3(\rho_B - \rho_A)} \quad (A) \\ &= \frac{2cV^{2/3}(\rho_B - \rho)}{3(\rho_B - \rho_A)} \quad (B). \end{aligned} \quad (8-43)$$

Thus  $\mathcal{E} = A_{\text{int}}/3$ . Using  $\mathcal{E}$ , we then have

$$\hat{\mu} = \mu_0 + \frac{2cV^{-1/3}(4\rho - \rho_A)}{3(\rho_B - \rho_A)\rho} \quad (A)$$

$$= \mu_0 - \frac{2cV^{-1/3}(4\rho - \rho_B)}{3(\rho_B - \rho_A)\rho} \quad (B)$$

and

$$\hat{p} = p_0 + \frac{2cV^{-1/3}\rho_A}{\rho_B - \rho_A} \quad (A)$$

$$= p_0 - \frac{2cV^{-1/3}\rho_B}{\rho_B - \rho_A} \quad (B).$$

Equations (8-30) and (8-31) may be used as a check on Eqs. (8-41) to (8-45).

*Example. Bragg-Williams Lattice Gas.* This model was discussed in Section 6-2 for an open system. The canonical ensemble partition function [Eq. (6-58)] is

$$Q(N, B, T) = \frac{B!e^{-\alpha N^2/B}}{N!(B - N)!}. \quad (8-46)$$

As is well known, this partition function gives a loop of the van der Waals type in a  $\mu$  versus  $N/B$  plot for a macroscopic system when  $-\alpha > 2$ . Our object here is merely to confirm the expected: that the loop still exists for a finite system but is modified by small terms.

To obtain the first-order nonmacroscopic effect, we write

$$\begin{aligned} \ln Q &= B \ln B - N \ln N - (B - N) \ln (B - N) \\ &\quad - \frac{1}{2} \ln \frac{2\pi N(B - N)}{B} - \frac{\alpha N^2}{B} + \dots \end{aligned} \quad (8-47)$$

Then, from

$$-\frac{\mu}{kT} = \left( \frac{\partial \ln Q}{\partial N} \right)_{V, T},$$

we find

$$\lambda = e^{\mu/kT} = \frac{\rho e^{2\alpha\rho}}{1 - \rho} \left[ 1 + \frac{1}{B} \frac{(1 - 2\rho)}{2\rho(1 - \rho)} + \dots \right], \quad (8-48)$$

where  $\rho = N/B$ . The leading factor on the right-hand side is the macroscopic ( $B \rightarrow \infty$ ) expression which exhibits the van der Waals loop referred to above. The quantity in brackets will obviously modify the loop quantitatively but not qualitatively for  $B$  large but finite.

## ENVIRONMENTAL VARIABLES $N, V, E$

An isolated small system with environmental variables  $N, V, E$  is of no interest experimentally. It is also usually a difficult case to handle in statistical mechanics, because of the restraints of constant  $N$  and  $E$ . But an isolated system occupies an important position in the development of the principles of statistical mechanics and represents one extreme in the classification of environmental variables (all variables are extensive, or "closed"), hence it deserves at least passing mention for the sake of completeness.

The basic equations are [see Eqs. (1-49) to (1-54)]:

$$dE = T dS - p dV + \mu dN \quad (9-1)$$

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \quad (9-2)$$

$$\mathcal{S} = -\frac{\mathcal{E}}{T} = S - \frac{E}{T} - \frac{pV}{T} + \frac{\mu N}{T} \quad (9-3)$$

$$\begin{aligned} d\mathcal{S} &= d\left(-\frac{\mathcal{E}}{T}\right) = d\left(S - \frac{E}{T} - \frac{pV}{T} + \frac{\mu N}{T}\right) \\ &= -E d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + N d\left(\frac{\mu}{T}\right). \end{aligned} \quad (9-4)$$

The relation to statistical mechanics is

$$S = k \ln \Omega(N, V, E). \quad (9-5)$$

Legendre transformations give equations "intermediate" between (9-2) and (9-4). For example,

$$d\left(S - \frac{E}{T}\right) = d\left(-\frac{\mathcal{A}}{T}\right) = -E d\left(\frac{1}{T}\right) + \frac{p}{T} dV - \frac{\mu}{T} dN \quad (9-6)$$

$$d\left(S - \frac{E}{T} - \frac{pV}{T}\right) = d\left(-\frac{\mathcal{F}}{T}\right) = -E d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) - \frac{\mu}{T} dN \quad (9-7)$$

$$d\left(S - \frac{E}{T} + \frac{\mu N}{T}\right) = -E d\left(\frac{1}{T}\right) + \frac{p}{T} dV + N d\left(\frac{\mu}{T}\right). \quad (9-8)$$

Three Maxwell relations follow from each of the six differential equations above.

ENVIRONMENTAL VARIABLES  $N$ ,  $p = 0$ ,  $E$ . In a sense, a more realistic small, isolated system is one with given  $N$  and  $E$  and fluctuating  $V$  at  $p = 0$ . An example would be a nonvolatile colloidal particle in a vacuum. An  $N, p/T, E$  system is formally identical with an  $N, V, T$  system (one intensive environmental variable). Hence, a transcription of the equations of Chapter 8 could be made to treat this case. The differential equation with environmental variables independent is

$$d\left(S - \frac{p\bar{V}}{T}\right) = \frac{1}{T} dE - \bar{V} d\left(\frac{p}{T}\right) - \frac{\mu}{T} dN, \quad (9-9)$$

whereas the connection with statistical mechanics is

$$S - \frac{p\bar{V}}{T} = k \ln \sum_V \Omega(N, V, E) e^{-pV/kT}. \quad (9-10)$$

*Example. Twelve-Site Spherical Lattice Gas.* An exact treatment of a twelve-site lattice gas on the surface of a sphere, using the canonical ensemble, was presented in Section 8-2. The microcanonical partition function  $\Omega(N, M)$  ( $M$  is a measure of  $E$  since  $E = Mw$ ) was included in that discussion and can now be used for comparative purposes.

Thus, for example, let us compare the dependence of the energy on temperature in the canonical ( $N, T$ ) and microcanonical ( $N, E$ ) ensembles. In both cases, of course,  $B$  is fixed at  $B = 12$ . In the canonical ensemble,

$$\bar{E} = - \left[ \frac{\partial \ln Q}{\partial (1/kT)} \right]_N$$

or

$$\bar{M} = \frac{y}{Q} \left( \frac{\partial Q}{\partial y} \right)_N. \quad (9-11)$$

Thus  $\bar{M}$  is a quotient of two polynomials in  $y$ , and hence is a smooth function of  $y$ . The parameter  $y$  is related to the temperature by  $y = e^{-w/kT}$ . Figures 9-1a and 9-1b show  $\bar{M}$  versus  $y$  for  $N = 5$

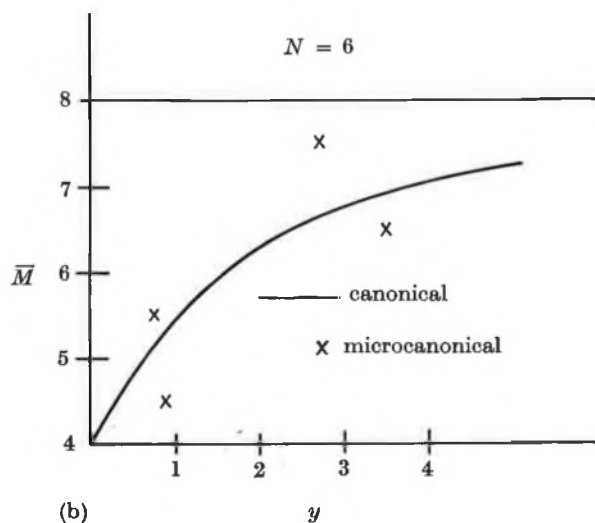
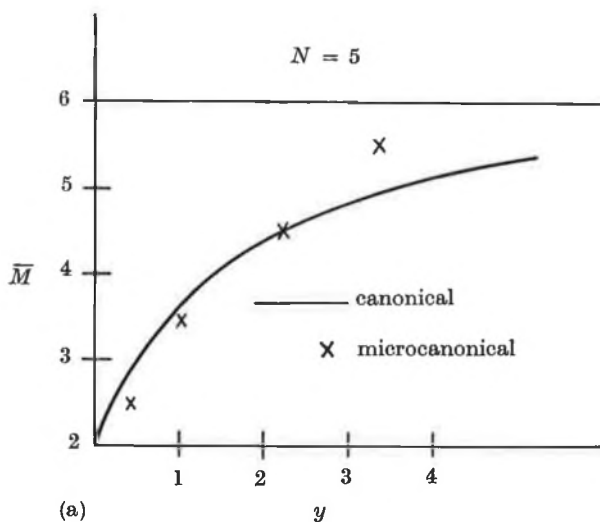


FIGURE 9-1.  $\bar{M}$  (energy) against  $y$  (related to temperature) in canonical and microcanonical ensembles for twelve-site spherical lattice gas.

and  $N = 6$ . The interval  $0 \leq y < 1$  corresponds to  $w > 0$  (repulsion between nearest neighbors) whereas the interval  $1 < y \leq \infty$  corresponds to  $w < 0$  (attraction). At  $y = 1$ , either  $w = 0$  or  $T = \infty$ .

For an  $N, E$  system,

$$\frac{1}{kT} = \left( \frac{\partial \ln \Omega}{\partial E} \right)_N \quad \text{or} \quad \frac{w}{kT} = \left( \frac{\partial \ln \Omega}{\partial M} \right)_N.$$

This gives  $T$  as a function of  $E$ , instead of vice versa as in Eq. (9-11). But  $M$  is discrete and a small number. Hence, differences must be used and irregular points anticipated. Ordinarily<sup>1</sup> we would define  $\ln [\Omega(M+1)/\Omega(M)]$  as  $w/kT_M$ , but here, since our only object is a comparison with Eq. (9-11), we use

$$\frac{w}{kT_{M+1/2}} = \ln \frac{\Omega(N, M+1)}{\Omega(N, M)}$$

or

$$y_{M+1/2} = \frac{\Omega(N, M)}{\Omega(N, M+1)} \quad (9-12)$$

The four points which can be calculated in this way for each of  $N = 5$  and  $N = 6$  are shown in Figs. 9-1a and 9-1b, respectively. The order-of-magnitude agreement is as expected.

<sup>1</sup> See Chapter 15.

# ENVIRONMENTAL VARIABLES $\mu$ , $p$ , $T$

As a convenience to the reader, we begin by repeating here a few of the comments made in the introduction to Chapter 2.

Consider an experimental one-component small system at  $p$  and  $T$ . The pressure on the system (colloidal particle, macromolecule, etc.) is that exerted on the solvent in which it is immersed. Also, the temperature of the small system is that of the solvent. The remaining environmental variable may be  $N$  or  $\mu$ . If the small system is closed, we use  $N$ . A clear-cut example is a polymer molecule consisting of  $N$  monomers held together by chemical bonds. But an aggregate of molecules bound by relatively weak van der Waals forces would be open rather than closed. That is,  $N$  fluctuates. In this case, the third environmental variable is  $\mu$ . The criterion distinguishing the two cases is whether the system maintains  $N = \text{constant}$ , within experimental error, during the time required to make the thermodynamic measurements of interest.

The closed-system ( $N, p, T$ ) case was discussed in Chapter 2. Here we consider an open ( $\mu, p, T$ ) system. This encompasses an important class of colloidal particles: crystallite embryos in a liquid near the freezing point; precipitation crystallites in a dilute solution; micelles in a dilute soap solution; any kind of aggregate in solution which is in dynamic equilibrium with respect to the size of the aggregate; molecular clusters in a one-component gas; viruses which are aggregates of spherical particles; etc. In all cases, the macroscopic system must be dilute in small systems.

The equilibrium ensemble of  $\mu, p, T$  systems will include small systems with various values of  $N$ . Such an ensemble is, however, not to be confused with a collection of small, closed systems with different values of  $N$ . In the latter case, which we refer to as "poly-disperse," there is *not* a dynamic aggregation equilibrium. Poly-disperse systems are treated in Chapter 13.

In macroscopic statistical mechanics, completely open ( $\mu, p, T$ ) systems are rather troublesome and require special treatment (see Section 14 of S.M., for example). Basically, this is because only two of  $\mu, p$ , and  $T$  can be independent variables for a one-component



macroscopic system. But we have seen throughout this book that for a *small* system, any intensive property in a one-component system may be regarded as a function of two intensive variables *and* a size variable. The dependence on the size variable vanishes as the system gets larger. There is thus one extra degree of freedom for a small system, although this extra degree is, so to speak, not so "free" as the usual degrees of freedom. That is, the dependence of thermodynamic properties on the extra variable, whatever it is, involves "small" terms only. In a  $\mu, p, T$  system, the extra degree of freedom manifests itself in the independence of all three of  $\mu, p$ , and  $T$ , although again, as we shall see, one of the three variables is not so "free" as the other two.<sup>1</sup>

As one might expect, because of the independence of  $\mu, p$ , and  $T$ , there is no special difficulty in using the appropriate partition function  $\Upsilon$  [see Eq. (1-61)] for a small, completely open system. Hence the method of choice in applying  $\Upsilon$  to a macroscopic system would appear to be as follows: Set up  $\Upsilon$  using values of  $\mu, p$ , and  $T$  corresponding to a finite system; calculate  $\Upsilon$  and thermodynamic functions using small system thermodynamics; finally, note the asymptotic expressions for the thermodynamic functions of interest as the size of the system approaches infinity (i.e., as the chosen values of  $\mu, p$ , and  $T$  approach their macroscopic relationship). This will be illustrated in Section 10-2.

There are some completely open small systems which do not have a macroscopic limit—i.e., they are always small systems. An example is the system of bound ions or molecules on a naturally occurring protein molecule in solution. The size of the protein molecule cannot be varied. Hence the number of binding sites is constant and finite. The environmental variables are  $\mu$  (chemical potential of bound species),  $p$  (pressure on solvent), and  $T$ . This is closely related to an  $N_1, \mu_2, p, T$  system (Chapter 7) in which  $N_1$  is held constant. This type of system is considered in Section 10-5.

If component 1 is in a dynamic aggregation equilibrium and component 2 is bound on the aggregating units, the environmental variables are  $\mu_1, \mu_2, p$ , and  $T$ . Ion binding on a soap micelle is an example. This case is treated beginning on page 135. It involves a generalization of a  $\mu, p, T$  system to two components.

<sup>1</sup> See, for example, the discussion of Eq. (10-27).

## 10-1. BASIC EQUATIONS FOR ENSEMBLE OF DISTINGUISHABLE SYSTEMS

The reader should review the end of Section 1-3 and Section 1-4 as an introduction to the present section. We shall be concerned here (and in the following four sections) with an ensemble of equivalent, distinguishable, independent  $\mu, p, T$  systems, each with fixed center of mass. Such an ensemble is of interest primarily in connection with theoretical models in statistical mechanics. Experimental  $\mu, p, T$  systems, that is, those in solvent or gas, will be discussed in Section 10-6.

The fundamental thermodynamic equations, which we repeat here, are

$$d\bar{E} = T dS - p d\bar{V} + \mu d\bar{N} \quad (10-1)$$

$$dS = \frac{1}{T} d\bar{E} + \frac{p}{T} d\bar{V} - \frac{\mu}{T} d\bar{N} \quad (10-2)$$

$$\mathcal{E} = \bar{E} - TS + p\bar{V} - \mu\bar{N} \quad (10-3)$$

$$\mathcal{S} = -\frac{\mathcal{E}}{T} = S - \frac{1}{T}\bar{E} - \frac{p}{T}\bar{V} + \frac{\mu}{T}\bar{N} \quad (10-4)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - \bar{N} d\mu \quad (10-5)$$

$$d\mathcal{S} = -\bar{E} d\left(\frac{1}{T}\right) - \bar{V} d\left(\frac{p}{T}\right) + \bar{N} d\left(\frac{\mu}{T}\right). \quad (10-6)$$

The basic statistical mechanical equations are

$$\mathcal{E} = -kT \ln \Upsilon \quad (10-7)$$

$$\Upsilon = e^{-\mathcal{E}/kT} = \sum_{N, V} Q(N, V, T) e^{-pV/kT} e^{N\mu/kT} \quad (10-8)$$

$$= \sum_V \Xi(\mu, V, T) e^{-pV/kT} = \sum_V e^{\hat{p}V/kT} e^{-pV/kT} = \sum_V e^{-\mathcal{E}_V/kT} \quad (10-9)$$

$$= \sum_N \Delta(N, p, T) e^{N\mu/kT} = \sum_N e^{-N\hat{\mu}/kT} e^{N\mu/kT} = \sum_N e^{-\mathcal{E}_N/kT}, \quad (10-10)$$

where the definitions of  $\mathcal{E}_V$  and  $\mathcal{E}_N$  are obvious from the equations.

From Eq. (10-5),

$$-S = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p, \mu}, \quad \bar{V} = \left(\frac{\partial \mathcal{E}}{\partial p}\right)_{T, \mu}, \quad -\bar{N} = \left(\frac{\partial \mathcal{E}}{\partial \mu}\right)_{T, p} \quad (10-11)$$

Three similar equations follow from Eq. (10-6). Since  $\mathcal{E}$  is a function of  $\mu$ ,  $p$ , and  $T$ , Eqs. (10-11) show that these three intensive variables suffice to determine the extensive properties of the one-component small system. This is quite unlike the situation in macroscopic thermodynamics where only two intensive variables can be independent and their specification does not fix the size of the system. A completely open small system with  $c$  components will have  $c + 2$  independent intensive variables, and there will be  $c + 2$  relations of the type shown in Eq. (10-11).

An important special characteristic of a completely open system is that none of the thermodynamic functions occurring in Eqs. (10-1) to (10-6) is discrete because  $E$ ,  $V$ , and  $N$  are all averaged. Hence, very small systems can be included in the discussion.

There are, of course, various Maxwell relations. Examples are

$$\begin{aligned} - \left( \frac{\partial S}{\partial p} \right)_{T, \mu} &= \left( \frac{\partial \bar{V}}{\partial T} \right)_{p, \mu}, & \left( \frac{\partial S}{\partial \mu} \right)_{p, T} &= \left( \frac{\partial \bar{N}}{\partial T} \right)_{p, \mu}, \\ \left( \frac{\partial \bar{V}}{\partial \mu} \right)_{T, p} &= - \left( \frac{\partial \bar{N}}{\partial p} \right)_{\mu, T}. \end{aligned} \quad (10-12)$$

All these derivatives are infinite in macroscopic thermodynamics, since their reciprocals are equal to zero.

The independent variables in Eqs. (10-5) and (10-6) may be changed by Legendre transformations. An example is

$$d(\mathcal{E} + \mu \bar{N}) = -S dT + \bar{V} dp + \mu d\bar{N}, \quad (10-13)$$

an equation much used in Chapter 2.

Two rather unusual equations which have no counterparts in macroscopic thermodynamics are

$$d \left( \ln \mathcal{S} + \frac{S}{\mathcal{S}} \right) = \frac{1}{T} d \left( \frac{\bar{E}}{\mathcal{S}} \right) + \frac{p}{T} d \left( \frac{\bar{V}}{\mathcal{S}} \right) - \frac{\mu}{T} d \left( \frac{\bar{N}}{\mathcal{S}} \right) \quad (10-14)$$

and

$$d \left( \ln \mathcal{E} + \frac{\bar{E}}{\mathcal{E}} \right) = T d \left( \frac{S}{\mathcal{E}} \right) - p d \left( \frac{\bar{V}}{\mathcal{E}} \right) + \mu d \left( \frac{\bar{N}}{\mathcal{E}} \right). \quad (10-15)$$

Excess functions may be defined in several ways. For example, let us arbitrarily select  $p$  and  $T$  as the "basic" intensive variables. Let  $\mu^{(0)}(p, T)$  be the macroscopic chemical potential at  $p$  and  $T$ . For given values of the environmental variables  $\mu$ ,  $p$ , and  $T$ , the

small system will have some definite value of  $\bar{N}$ . For any extensive variable  $G$ , let  $G^{(0)}$  be the value of  $G$  for  $\bar{N}$  molecules of a macroscopic sample at the same  $p$  and  $T$  as the small system. Then the excess quantity  $G^{(x)}$  is defined by the equation

$$G(\mu, p, T) = G^{(0)}[\bar{N}(\mu, p, T), p, T] + G^{(x)}(\mu, p, T). \quad (10-16)$$

The excess quantity  $\mu^{(x)}$  is defined in terms of the assigned value of the environmental variable  $\mu$  and of  $\mu^{(0)}(p, T)$  by the equation

$$\mu = \mu^{(0)}(p, T) + \mu^{(x)}(\mu, p, T). \quad (10-17)$$

In Eq. (10-1), we now use Eq. (10-16) for  $\bar{E}$ ,  $S$ , and  $\bar{V}$ , and Eq. (10-17) for  $\mu$ , with the result

$$d\bar{E}^{(x)} = T dS^{(x)} - p d\bar{V}^{(x)} + \mu^{(x)} d\bar{N}. \quad (10-18)$$

Also, Eq. (10-3) becomes

$$\mathcal{E} = \bar{E}^{(x)} - TS^{(x)} + p\bar{V}^{(x)} - \mu^{(x)}\bar{N}. \quad (10-19)$$

Then

$$d\mathcal{E} = -S^{(x)}dT + \bar{V}^{(x)}dp - \bar{N}d\mu^{(x)}. \quad (10-20)$$

These relations are formally identical with those on page 39 of Part I for an  $N, p, T$  system (because of our arbitrary choice, at the outset, of  $p$  and  $T$  as basic intensive variables).

The next section is devoted to a discussion of four simple theoretical models of completely open systems. In all these examples we consider an ensemble of distinguishable systems without rotation or translation.

## 10-2. APPLICATIONS TO THEORETICAL MODELS

**LINEAR AGGREGATE.** This is the model on page 69 of Part I, but without rotation or translation.

In the *canonical ensemble* (environmental variables  $N, T$ ), a system consists of  $N$  units in a linear sequence. Each unit has an intrinsic partition function  $j(T)$ . The energy of interaction between neighboring units is  $\epsilon$ , a constant. The system is assumed incompressible. This model corresponds to a one-dimensional Einstein crystal. Thus  $Q(N, T)$  is simply

$$Q(N, T) = j(T)^N e^{-(N-1)\epsilon/kT} \quad (10-21)$$

for  $N \geq 1$ . But we note for future use that  $Q(0, T) = 1$ . Then (see page 61 of Part I)

$$N\hat{\mu} = -kT \ln Q = -NkT \ln j + (N-1)\epsilon \quad (N \geq 1). \quad (10-22)$$

The chemical potential  $\mu^{(0)}(T)$  of the macroscopic system (i.e., an infinitely long linear aggregate of units) at  $T$  is thus

$$\mu^{(0)}(T) = -kT \ln j + \epsilon \quad (10-23)$$

and (page 39 of part I)

$$\hat{\mu}^{(x)} = \hat{\mu} - \mu^{(0)} = -\frac{\epsilon}{N}. \quad (10-24)$$

Equation (10-23) is of course valid for *any* ensemble, as it refers to a macroscopic system. The entropy is

$$S = -\left(\frac{\partial N\hat{\mu}}{\partial T}\right)_N = Nk \ln j + NkT \frac{d \ln j}{dT} \quad (10-25)$$

and the energy

$$\bar{E} = TS + N\hat{\mu} = NkT^2 \frac{d \ln j}{dT} + (N-1)\epsilon. \quad (10-26)$$

The entropy above is just the “intrinsic” entropy per unit multiplied by the number of units.

We turn now to a *completely open system*. This is a linear aggregate of units at  $T$  and  $\mu$ . The number of units  $N$  in the system fluctuates. The aggregate may be thought of as being in equilibrium with a reservoir containing units (monomers) at  $\mu$ . The partition function [see Eq. (10-8)] is

$$\begin{aligned} \Upsilon &= \sum_{N=0}^{\infty} Q(N, T) e^{N\mu/kT} \\ &= 1 + e^{\epsilon/kT} \sum_{N=1}^{\infty} (je^{-\epsilon/kT} \lambda)^N \\ &= \frac{1 - x + cx}{1 - x} \quad (x < 1), \end{aligned} \quad (10-27)$$

where we have introduced the notation

$$\lambda = e^{\mu/kT}, \quad c = e^{\epsilon/kT}, \quad x = je^{-\epsilon/kT} \lambda, \quad cx = j\lambda. \quad (10-28)$$

The series above converges for  $x < 1$  but not for  $x \geq 1$ . In view of Eqs. (10-17) and (10-23), we also have

$$x = \exp\left[-\frac{\mu^{(0)}(T) - \mu}{kT}\right] = \exp\left[\frac{\mu^{(x)}(\mu, T)}{kT}\right]. \quad (10-29)$$

Thus  $\Upsilon$  converges and a small system can exist if, for given  $T$ ,  $\mu$  is chosen so that  $\mu < \mu^{(0)}(T)$ . Because of this restriction, we do not have a completely free choice of  $\mu$  (once  $T$  is assigned). Furthermore, as will be seen below, in order for the small system to be at all sizeable,  $\mu$  must be rather close to  $\mu^{(0)}$ . On the other hand, as has already been pointed out in Section 10-1, there is no difficulty (arising from discreteness in extensive environmental variables) in treating a very small, completely open system, since *all* variables are continuous ( $\mu, T, \bar{N}, S, \bar{E}, \mathcal{E}$ , etc., in the present example).

From Eq. (10-7),

$$\mathcal{E} = -kT \ln \frac{1 - x + cx}{1 - x}. \quad (10-30)$$

Then, using Eq. (10-11c), we find for the mean number of units in an aggregate

$$\bar{N} = \frac{cx}{(1 - x)(1 - x + cx)}. \quad (10-31)$$

Note that  $\bar{N} \rightarrow \infty$  (macroscopic system) as  $x \rightarrow 1$ . Equation (10-31) is identical in form with the well-known Brunauer-Emmett-Teller adsorption isotherm. The reason for this is that the B.E.T. equation can be derived<sup>1</sup> from statistical mechanics using as a model an independent linear pile of adsorbed molecules on each adsorption site of the surface. Thus a B.E.T. "pile" corresponds to an open linear aggregate here, and the whole adsorbed phase ( $\mathcal{N}$  sites) corresponds to the ensemble here ( $\mathcal{N}$  systems). In the B.E.T. model, the first molecule on a site is "different" because of interaction with the surface. Here, the first molecule in a system is "different" because it lacks an interaction energy  $\epsilon$  with a neighbor. In the B.E.T. theory, generally  $c > 1$ . In a typical aggregate, on the other hand,  $\epsilon < 0$  and  $c < 1$ . Figure 10-1 shows  $\bar{N}$  as a function of  $x$  for  $c = 10, 1$ , and  $\frac{1}{10}$ .

<sup>1</sup> See S.T., p. 134. It is because of the connection with B.E.T. theory that we have adopted the  $c, x$  notation, which otherwise would be a poor choice here.

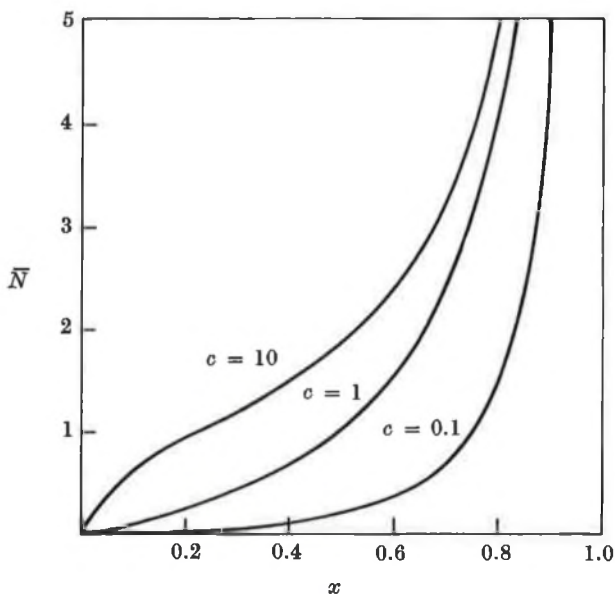


FIGURE 10-1. Size of open linear aggregate as function of normalized absolute activity.

It can be seen from the bottom of page 25, Part I, that  $-\mathcal{E}$  is the equivalent of the surface pressure in the B.E.T. theory.

When  $x \rightarrow 1$ ,

$$\begin{aligned} \bar{N} &\rightarrow \frac{1}{1-x}, & x &\rightarrow 1 - \frac{1}{\bar{N}} \\ \Upsilon &\rightarrow \frac{c}{1-x} = c\bar{N}, & \mathcal{E} &\rightarrow -kT \ln \bar{N}. \end{aligned} \quad (x \rightarrow 1) \quad (10-32)$$

When  $x \rightarrow 0$ ,

$$\bar{N} \rightarrow cx, \quad \Upsilon \rightarrow 1 + cx = 1 + \bar{N}, \quad \mathcal{E} \rightarrow -\bar{N}kT \quad (x \rightarrow 0). \quad (10-33)$$

The probability that a system (aggregate) contains  $N$  units is

$$P(N) = \frac{Q(N, T)e^{N\mu/kT}}{\Upsilon}. \quad (10-34)$$

Since  $Q(0, T) = 1$ , the probability that a system contains no units at all is  $P(0) = 1/\Upsilon$ . Hence

$$\mathcal{E} = kT \ln P(0), \quad (10-35)$$

where

$$P(0) = \frac{1 - x}{1 - x + cx}. \quad (10-36)$$

The relation (10-35) is valid for any  $\mu, T$  system for which  $Q(0, T) = 1$  [see p. xi].

We also have

$$P(N) = \frac{x^N c(1 - x)}{1 - x + cx} \quad (N \geq 1). \quad (10-37)$$

Thus, since  $x < 1$ ,  $P(N)$  falls off exponentially with  $N$ , and this decrease becomes more gradual as  $x \rightarrow 1$ . In particular,  $P(N)$  does *not* have a peak at or near  $N = \bar{N}$  which becomes sharper as  $\bar{N} \rightarrow \infty$ , as would be the case in a *partially* open system in the absence of a phase transition (e.g., in a  $\mu, V, T$  system; see page 145, Part I). The flatness of  $P(N)$  exhibited in Eq. (10-37) resembles the behavior of  $P(N)$  at a critical point (see Fig. 6-7). Fluctuations in  $N$  will be large, as we now verify.

From  $\Upsilon = \sum_N Q \lambda^N$  we easily find the usual type of expression for the fluctuation in  $N$ :

$$\overline{N^2} - \bar{N}^2 = kT \left( \frac{\partial \bar{N}}{\partial \mu} \right)_T. \quad (10-38)$$

Then, with the aid of Eq. (10-31), we obtain

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{1 - x^2 + cx^2}{cx}, \quad (10-39)$$

which is of order unity unless  $x$  is very small. For a partially open system, on the other hand, this quantity would ordinarily be of order  $1/\bar{N}$ .

The entropy of an aggregate is

$$\begin{aligned} S &= - \left( \frac{\partial \mathcal{E}}{\partial T} \right)_\mu \\ &= \bar{N}k \ln j + \bar{N}kT \frac{d \ln j}{dT} - \bar{N}k \ln x - k \ln P(0) - [1 - P(0)] \frac{\epsilon}{T}, \end{aligned} \quad (10-40)$$



and the energy is

$$\begin{aligned}\bar{E} &= \bar{\mathcal{E}} + TS + \bar{N}\mu \\ &= \bar{N}kT^2 \frac{d \ln j}{dT} + [\bar{N} - 1 + P(0)]\epsilon.\end{aligned}\quad (10-41)$$

The entropy contains the intrinsic entropy of  $\bar{N}$  units, as in Eq. (10-25), and in addition the excess entropy [see Eq. (10-16)]

$$S^{(x)} = -\bar{N}k \ln x - k \ln P(0) - [1 - P(0)]\frac{\epsilon}{T}. \quad (10-42)$$

It is easy to verify that

$$S^{(x)} = -k \sum_{N=0}^{\infty} P(N) \ln P(N), \quad (10-43)$$

as might have been expected. Thus  $S^{(x)}$  is the entropy associated with the fluctuations in  $N$ . This entropy is necessarily positive, and does not exist for a closed system [Eq. (10-25); environmental variables  $N, T$ ]. Therefore, if we choose  $\bar{N}$  in Eq. (10-25) equal to  $\bar{N}$  in Eq. (10-40),

$$S(\mu, T \text{ system}) > S(N, T \text{ system}) \quad (10-44)$$

because of the fact that the  $\mu, T$  system is open with respect to  $N$ . In a comparison of this sort, the more open system will always have the larger entropy.<sup>1</sup> For large  $\bar{N}$ ,

$$S^{(x)} \rightarrow k \ln \bar{N} \quad (x \rightarrow 1). \quad (10-45)$$

Despite the abnormally large fluctuations in  $N$ , this term becomes negligible compared to the first two terms ( $S^{(0)}$ ) in Eq. (10-40) when  $\bar{N}$  is very large.

The first term in  $\bar{E}$ , Eq. (10-41), is the "intrinsic energy." The second term is the mean potential energy:

$$\sum_{N=2}^{\infty} (N-1)\epsilon P(N) = [\bar{N} - 1 + P(0)]\epsilon. \quad (10-46)$$

The excess energy is

$$\bar{E}^{(x)} = -[1 - P(0)]\epsilon. \quad (10-47)$$

<sup>1</sup> See S.M., pp. 75-76, and E. A. Guggenheim, *Research*, **2**, 450 (1949).

It is easy to verify that the various excess quantities satisfy

$$\mathcal{E} = \bar{E}^{(x)} - TS^{(x)} - \mu^{(x)}\bar{N} \quad (10-48)$$

and also Eq. (10-20).

It should be noted that  $\Upsilon$  can be expressed in terms of excess quantities:

$$\begin{aligned} \Upsilon &= 1 + \sum_{N=1}^{\infty} \exp\left(\frac{-N\hat{\mu}}{kT}\right) \exp\left(\frac{N\mu}{kT}\right) \\ &= 1 + \sum_{N=1}^{\infty} \exp\left[\frac{N\mu^{(x)}(\mu, T)}{kT}\right] \exp\left[\frac{-N\hat{\mu}^{(x)}(N, T)}{kT}\right], \end{aligned} \quad (10-49)$$

where  $\mu^{(x)} = \mu - \mu^{(0)}(T)$  must be negative for convergence and  $\hat{\mu}^{(x)}$  is the excess chemical potential for the closed system with  $N$  and  $T$ . In the present example,  $\hat{\mu}^{(x)} = -\epsilon/N$ . Of course  $\mu^{(x)}$  and  $\hat{\mu}^{(x)}$  refer to two different environments ( $\mu, T$  and  $N, T$ , respectively).

This example illustrates a point made previously: The thermodynamic properties of a completely open macroscopic system can be obtained without difficulty and without the use of special techniques if we first deduce the properties of a finite system (as we have done above) and then take the macroscopic limit of these properties. Thus, in the present problem,

$$\mu^{(0)} = -kT \ln j + \epsilon \quad (\text{from } x = 1) \quad (10-50)$$

$$S^{(0)} = \bar{N}k \ln j + \bar{N}kT \frac{d \ln j}{dT} \quad (10-51)$$

$$\bar{E}^{(0)} = \bar{N}kT^2 \frac{d \ln j}{dT} + \bar{N}\epsilon. \quad (10-52)$$

**SPHERICAL AGGREGATE.** Various versions of this model have been mentioned on pages 41, 70, and 129 of Part I. Here we consider a spherical, incompressible liquid (or solid) aggregate without rotation or translation and take  $Q(N, T)$  for an  $N, T$  system to be

$$Q(N, T) = j(T)^N \exp\left[-\frac{a(T)N^{2/3}}{kT}\right], \quad (10-53)$$

where  $N$  is the number of molecules or monomers,  $aN^{2/3}$  is the surface free energy, and  $j(T)$  is the macroscopic partition function per molecule ("Einstein model"). The function  $j(T)$  includes the intermolecular potential energy per molecule, a partition function for vibration of a molecule about an equilibrium point, communal entropy (if any), and internal degrees of freedom (if any). The quantity  $a(T)$  is positive. Its physical significance is discussed on page 132 of Part I. The main point is that  $a$  is proportional to the surface tension.

For a *closed system* (environmental variables  $N, T$ ),

$$N\hat{\mu} = -kT \ln Q = -NkT \ln j + aN^{2/3}. \quad (10-54)$$

The first term is the macroscopic term:

$$\mu^{(0)} = -kT \ln j, \quad \hat{\mu}^{(x)} = aN^{-1/3}. \quad (10-55)$$

Also,

$$S = - \left( \frac{\partial N\hat{\mu}}{\partial T} \right)_N = Nk \ln j + NkT \frac{d \ln j}{dT} - \frac{da}{dT} N^{2/3} \quad (10-56)$$

$$E = TS + N\hat{\mu} = NkT^2 \frac{d \ln j}{dT} + \left( a - T \frac{da}{dT} \right) N^{2/3}. \quad (10-57)$$

We now turn to an *open system* (environmental variables  $\mu, T$ ). The surface free energy  $aN^{2/3}$  is realistic only for fairly large  $N$  ( $N > 20$ , e.g.). Hence we should restrict ourselves to values of  $\mu$  (for given  $T$ ) that lead to sizeable  $\bar{N}$ . The partition function  $\Upsilon$  is [see Eq. (10-49)]

$$\Upsilon = \sum_N \exp\left(\frac{N\mu^{(x)}}{kT}\right) \exp\left(-\frac{N\hat{\mu}^{(x)}}{kT}\right), \quad (10-58)$$

where  $\hat{\mu}^{(x)}$  is given in Eq. (10-55) and  $\mu^{(x)} = \mu - \mu^{(0)}(T)$ . If  $\mu^{(x)}$  is positive, the first exponential dominates for large  $N$ , and the sum diverges. A finite system is then not possible. If  $\mu^{(x)} \leq 0$ , the sum converges, since  $a(T)$  is positive.

For convenience, we introduce the notation

$$\delta(\mu, T) = \frac{\mu^{(0)}(T) - \mu}{kT} = -\frac{\mu^{(x)}}{kT} \geq 0$$

$$\alpha(T) = \frac{a(T)}{kT} > 0.$$

In order to obtain aggregates of reasonable size we must choose  $\delta$  very small. In fact, we confine ourselves below to the case  $\delta \rightarrow 0+$ . This means we are examining "open" aggregates which are in equilibrium with the bulk phase. In other words, these are clusters in the saturated vapor phase in equilibrium with a liquid. But even with a saturated vapor the clusters will be sizeable only near the critical temperature where the surface tension is very small, that is, where  $\alpha(T)$  is small. This requirement ( $T \rightarrow T_c$ ) can easily be verified by numerical substitution in the expression for  $\bar{N}$  below.

Because we are interested only in  $\bar{N}$  fairly large, we replace the sum in Eq. (10-58) by an integral and extend the integration to  $N = 0$ . Even though the model is inadequate for small  $N$ , the error introduced in this region of the integration (say  $0 \leq N \leq 20$ ) will not be serious when  $\bar{N}$  is large enough. Equation (10-58) becomes, for  $\delta \rightarrow 0+$ ,

$$\begin{aligned} \Upsilon(\mu, T) &= \int_0^{\infty} (1 - \delta N) e^{-\alpha N^{3/3}} dN \\ &= \frac{3\pi^{1/2}}{4\alpha^{3/2}} - \frac{3\delta}{\alpha^3}. \end{aligned} \quad (10-59)$$

Then, from Eq. (10-11c),

$$\bar{N} = \left( \frac{\partial \ln \Upsilon}{\partial \mu / kT} \right)_T = \left( \frac{\partial \ln \Upsilon}{\partial \delta} \right)_\alpha \left( \frac{\partial \delta}{\partial \mu / kT} \right)_T = \frac{4}{\pi^{1/2} \alpha^{3/2}}. \quad (10-60)$$

Thus,  $\Upsilon = 3\pi\bar{N}/16$ .

The probability that an aggregate contains between  $N$  and  $N + dN$  molecules is

$$P(N) dN = \frac{e^{-\alpha N^{3/3}} dN}{\Upsilon} = \frac{16e^{-\alpha N^{3/3}} dN}{3\pi\bar{N}} \quad (\delta \rightarrow 0+). \quad (10-61)$$

Since  $\alpha$  is small, this is again (as in the previous example) a slowly decreasing function of  $N$ , with no sign of the conventional peak at or near  $N = \bar{N}$ .

We can use

$$\bar{N} = \int_0^{\infty} NP(N) dN \quad (10-62)$$

to verify Eq. (10-60). From Eq. (5-153),

$$\bar{N} = \frac{2}{3\pi v} \left( \frac{kT}{\gamma} \right)^{3/2}. \quad (10-63)$$

Hence  $\bar{N} \rightarrow \infty$  as  $\gamma \rightarrow 0$ , as expected. We also find, in the same way,

$$\overline{N^{2/3}} = \frac{3}{2\alpha} \quad (10-64)$$

and

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{105\pi}{128} - 1 = O(1). \quad (10-65)$$

This result also follows from Eq. (10-38) if we calculate one more term  $(315\pi^{1/2}\delta^2/64\alpha^{9/2})$  in Eq. (10-59).

In general for this model,  $\bar{N}$  would be a function of  $\mu$  and  $T$ , but we have taken  $\mu \rightarrow \mu^{(0)}(T)$  so  $\bar{N}$  is a function of  $T$  only. The calculation of  $\bar{N}$  illustrates again (see the previous example) the fact that a complete set of intensive variables (in this case  $\mu$  and  $T$ ) can determine the extensive properties of a small system. In the case of a macroscopic system, there is one less intensive variable in a complete set, and these cannot determine extensive variables (the system can have any size).

Equation (10-59) for  $\Upsilon$  and

$$- \bar{E} = \left[ \frac{\partial \ln \Upsilon}{\partial (1/kT)} \right]_{\mu/kT} \quad (10-66)$$

lead to

$$\bar{E} = \bar{N} k T^2 \frac{d \ln j}{dT} + \left( \alpha - T \frac{d\alpha}{dT} \right) \overline{N^{2/3}}. \quad (10-67)$$

This result also follows immediately from Eq. (10-57). For, if we denote the average energy in Eq. (10-57) by  $\bar{E}^E$  (the super  $E$  means that averaging has been carried out over  $E$ ), then

$$\begin{aligned} \bar{E}(\mu, T) &\equiv \bar{E}^{E, N} = \frac{1}{\Upsilon} \sum_N e^{N\mu/kT} \sum_E E \Omega(N, E) e^{-E/kT} \\ &= \frac{\sum_N \bar{E}^E(N, T) Q(N, T) e^{N\mu/kT}}{\Upsilon}. \end{aligned} \quad (10-68)$$

Substitution of Eq. (10-57) for  $\bar{E}^E$  in Eq. (10-68) gives Eq. (10-67). In this example the energy is different for closed ( $N, T$ ) and open ( $\mu, T$ ) systems. For if in Eq. (10-57) we choose the same  $T$  as here and choose  $N$  there equal to the  $\bar{N}$  here, then the two energies differ because  $\bar{N}^{2/3} \neq \bar{N}^{2/3}$ .

The entropy is, from Eq. (10-3),

$$\begin{aligned} S &= \frac{\bar{E}}{T} - \frac{\mu^{(0)}\bar{N}}{T} + k \ln \Upsilon \\ &= \bar{N}k \ln j + \bar{N}kT \frac{d \ln j}{dT} - \frac{da}{dT} \frac{\bar{N}^{2/3}}{T} + k \ln \frac{3\pi\bar{N}}{16} + \frac{a}{T} \frac{\bar{N}^{2/3}}{T}. \end{aligned} \quad (10-69)$$

This result also follows from  $S = (\partial kT \ln \Upsilon / \partial T)_\mu$ , using Eq. (10-59) for  $\Upsilon$ . Comparison with Eq. (10-56) for  $S$  in an  $N, T$  system shows that the last two terms above are the additional positive terms associated with fluctuations in  $N$ . This is verified by

$$-k \int_0^\infty P(N) \ln P(N) dN = k \ln \frac{3\pi\bar{N}}{16} + \frac{a}{T} \frac{\bar{N}^{2/3}}{T}. \quad (10-70)$$

This expression approaches  $k \ln \bar{N}$  for large  $\bar{N}$  (the term in  $a$  is equal to  $3k/2$ ).

In the preceding example  $\Upsilon$  diverges at  $\mu = \mu^{(0)}(T)$  because  $N\hat{\mu}^{(x)}$  in Eq. (10-49) is a constant ( $-\epsilon$ ). As a consequence, a small system of any size ( $\bar{N}$ ) can be generated by choosing  $\mu$  as close as one pleases to  $\mu^{(0)}(T)$ . In the present example,  $\Upsilon$  converges at  $\mu = \mu^{(0)}(T)$  because  $N\hat{\mu}^{(x)}$  is a positive function of  $N$  which increases sufficiently rapidly with  $N$ . Consequently, for given  $T$  and  $a$ ,  $\bar{N}$  cannot be made arbitrarily large but has a maximum possible value at  $\mu = \mu^{(0)}(T)$ . This is the value in Eq. (10-60) or (10-63). But even in this case the macroscopic properties (i.e.,  $\bar{E}^{(0)}$  and  $S^{(0)}$ ) can easily be ascertained by inspection of the expressions for  $\bar{E}$  and  $S$  [Eqs. (10-67) and (10-69)] at  $\mu = \mu^{(0)}(T)$ . Of course  $\Upsilon$  diverges and  $\bar{N} = \infty$  for  $\mu > \mu^{(0)}(T)$ .

**IDEAL LATTICE GAS.** This is the same model as on pages 42 and 142 of Part I and 203 of Part II. The partition function is

$$\Upsilon = \sum_{B=0}^{\infty} \sum_{N=0}^B \frac{B!}{N!(B-N)!} e^{mN} e^{-\varphi B},$$

where for convenience we write  $m = \mu/kT$  and  $\varphi = p/kT$ . It might be noted that this may be thought of as the partition function for an open two-component system. One component ( $B, -p$ ) forms an aggregate of sites [as in Eq. (10-27), but with  $\epsilon = 0, j = 1$ ], whereas the other component ( $N, \mu$ ) can be bound on these sites, at most one per site. Note that  $P(N = 0, B = 0) = 1/Y$ .

It is most convenient to sum first over  $N$ :

$$Y = \sum_{B=0}^{\infty} (1 + e^m)^B e^{-\varphi B}. \quad (10-71)$$

We note that [see Eq. (6-51)ff.]

$$\Xi = e^{\hat{p}B/kT} = (1 + e^m)^B = e^{p^{(0)}B/kT} = e^{\varphi^{(0)}B} \quad (10-72)$$

and  $\hat{p}^{(x)} = 0$ . Therefore

$$\begin{aligned} Y(m, \varphi) &= \sum_{B=0}^{\infty} e^{-(\varphi - \varphi^{(0)})B} \\ &= \frac{1}{1 - e^{-(\varphi - \varphi^{(0)})}} \quad [\varphi > \varphi^{(0)}(m)]. \end{aligned} \quad (10-73)$$

That is,  $Y$  converges and will lead to a finite  $\bar{B}$  (small system) if  $\varphi$  is chosen so that  $\varphi > \varphi^{(0)}(m)$ . If  $\varphi \leq \varphi^{(0)}$ , a small system cannot exist ( $\bar{B} \rightarrow \infty$ ).

If we sum first over  $B$ , the second sum (over  $N$ ) converges if  $m$  is chosen less than  $m^{(0)}(\varphi)$ , and Eq. (10-73) is again obtained. In this case [see Eq. (2-79)],  $\hat{\mu}/kT$  contains an excess function:  $\hat{\mu}^{(x)}/kT = N^{-1} \ln(1 - e^{-\varphi})$ .

From Eq. (10-6) we find

$$\bar{B}(m, \varphi) = - \left( \frac{\partial \ln Y}{\partial \varphi} \right)_m = \frac{e^{-(\varphi - \varphi^{(0)})}}{1 - e^{-(\varphi - \varphi^{(0)})}} \quad (10-74)$$

and

$$\bar{N}(m, \varphi) = \left( \frac{\partial \ln Y}{\partial m} \right)_{\varphi} = \frac{\bar{B}(m, \varphi) e^m}{1 + e^m} = \bar{B}(1 - e^{-\varphi^{(0)}}). \quad (10-75)$$

Hence  $Y = 1 + \bar{B}$ . This result for  $\bar{N}/\bar{B}$  is the same as for a macroscopic system (any ensemble). To obtain a sizeable  $\bar{B}$ , we need  $\varphi - \varphi^{(0)} \ll 1$ . Then  $\bar{B} = (\varphi - \varphi^{(0)})^{-1}$ .

The entropy is

$$\begin{aligned}\frac{S}{k} &= \varphi \bar{B} - m \bar{N} + \ln \Upsilon \\ &= (1 + \bar{B}) \ln (1 + \bar{B}) - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln (\bar{B} - \bar{N}).\end{aligned}\quad (10-76)$$

This is an exact expression (no Stirling approximation, etc.). It is of interest to compare this with the entropy from other environments, all for the same  $N$  and  $B$ . Equation (2-84) gives  $S/k$  for the  $N, p/T$  case; Eq. (6-57) pertains to the  $\mu/T, B$  case; and Eq. (15-97) gives  $S/k$  to  $O(1)$  for the variables  $N, B$ . The order of increasing entropy is:  $N, B$ ;  $\mu/T, B$ ;  $N, p/T$ ; and  $\mu/T, p/T$ . This is just the expected sequence: completely closed; semiopen; semiopen; completely open.

One needs in general to use difference as well as differential relations when applying thermodynamics to very small systems with environmental variables which include one or more extensive properties (e.g., in a  $\mu, B, T$  lattice gas system there is a discrete difference between, say,  $B = 9$  and  $B = 10$ ). As we have already pointed out, a special feature associated only with a completely open system is that *all* thermodynamic functions vary smoothly, even for systems which are very small on the average. As an example of this, we consider the present model when  $\varphi - \varphi^{(0)} \gg 1$  so that  $\bar{B} = \exp[-(\varphi - \varphi^{(0)})] \ll 1$ . Equation (10-75) is unchanged and Eq. (10-76) becomes

$$\frac{S}{k} = \bar{B} - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln (\bar{B} - \bar{N}).\quad (10-77)$$

Only the first few terms in  $\Upsilon$  need be retained:

$$\Upsilon = 1 + e^{-\varphi} + e^{m e^{-\varphi}}.\quad (10-78)$$

The probabilities  $P_{NB}$  of the various states are

$$P_{00} = \frac{1}{\Upsilon} = 1 - \bar{B}, \quad P_{01} = \frac{e^{-\varphi}}{\Upsilon} = \bar{B} - \bar{N}, \quad P_{11} = \frac{e^{m e^{-\varphi}}}{\Upsilon} = \bar{N}.\quad (10-79)$$

We can then verify that (see page 13 of Part I)

$$\frac{S}{k} = - (P_{00} \ln P_{00} + P_{01} \ln P_{01} + P_{11} \ln P_{11})\quad (10-80)$$

also gives Eq. (10-77).



Fluctuations in both  $N$  and  $B$  are large, but we leave details to the reader.

**CLASSICAL IDEAL GAS.** This is a hypothetical gas of noninteracting point particles which obey classical statistics for all values of  $N$  and  $V$ . Or, alternatively, this is a very dilute, real, monatomic gas for which we ignore the small errors made on using a dilute-gas model over the whole range of  $N$  and  $V$ . That is, there are negligible contributions to integrals from  $N$  and  $V$  values which do not correspond to a dilute gas if  $\mu$ ,  $p$ , and  $T$  are chosen so that the gas is, in fact, dilute.

For an  $N, V, T$  system [see Eq. (15-59)],

$$Q(N, V, T) = \frac{V^N}{N! \Lambda^{3N}} \quad (10-81)$$

where

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}}.$$

For a  $\mu, V, T$  system,

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} Q \lambda^N = \exp\left(\frac{V\lambda}{\Lambda^3}\right) = e^{\hat{p}V/kT}, \quad (10-82)$$

where  $\lambda = e^{\mu/kT}$ . Note that  $\hat{p}^{(x)} = 0$ .

For an  $N, p, T$  system,

$$\Delta(N, p, T) = \int_0^{\infty} Q e^{-pV/kT} d\left(\frac{pV}{kT}\right). \quad (10-83)$$

Integration instead of summation over  $V$  must be used because  $V$  can be varied continuously. The choice of  $pV/kT$  as the dimensionless variable of integration is simple and natural but somewhat arbitrary.<sup>1</sup> We find

$$\Delta = \left(\frac{kT}{p\Lambda^3}\right)^N = e^{-N\hat{\mu}/kT}. \quad (10-84)$$

Note that  $\hat{\mu}^{(x)} = 0$ .

<sup>1</sup> See S.M., p. 63.

For a  $\mu, p, T$  system,

$$\Upsilon(\mu, p, T) = \sum_{N=0}^{\infty} \Delta\lambda^N = \frac{1}{1 - \frac{kT\lambda}{p\Lambda^3}} \quad \left( \frac{kT\lambda}{p\Lambda^3} < 1 \right). \quad (10-85)$$

The same result follows from

$$\Upsilon = \int_0^{\infty} \Xi e^{-pV/kT} d\left(\frac{pV}{kT}\right). \quad (10-86)$$

The macroscopic relationship between  $p, T$ , and  $\mu^{(0)}(p, T)$  is seen from Eq. (10-84) to be  $kT\lambda^{(0)}/p\Lambda^3 = 1$ . Hence  $\Upsilon$  can be written in the form

$$\Upsilon = \frac{1}{1 - e^{-(\mu^{(0)} - \mu)/kT}}. \quad (10-87)$$

Thus  $\Upsilon$  converges for  $\mu < \mu^{(0)}$  and diverges for  $\mu \geq \mu^{(0)}$ .

From

$$\mathcal{E} = kT \ln \left( 1 - \frac{kT\lambda}{p\Lambda^3} \right) \quad (10-88)$$

we deduce

$$\bar{N} = - \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{p, T} = \frac{(kT\lambda/p\Lambda^3)}{1 - (kT\lambda/p\Lambda^3)} \quad (10-89)$$

$$\bar{V} = \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{\mu, T} = \frac{\bar{N}kT}{p} \quad (10-90)$$

$$S = - \left( \frac{\partial \mathcal{E}}{\partial T} \right)_{\mu, p} = - \frac{\mathcal{E}}{T} + \frac{p\bar{V}}{T} - \frac{\mu\bar{N}}{T} + \frac{3}{2}\bar{N}k. \quad (10-91)$$

Therefore, from Eq. (10-3),

$$\bar{E} = \frac{3}{2}\bar{N}kT. \quad (10-92)$$

We note that  $\bar{N}$  and  $\bar{V}$  become infinitely large as  $\mu \rightarrow \mu^{(0)}$ .

For given  $\mu, p$ , and  $T$ , the probability that a system contains  $N$  molecules and has a volume such that  $pV/kT$  lies between  $pV/kT$

and  $(pV/kT) + d(pV/kT)$  is

$$P(N, V) d\left(\frac{pV}{kT}\right) = \frac{V^N e^{-pV/kT} \lambda^N}{\Upsilon N! \Lambda^{3N}} d\left(\frac{pV}{kT}\right). \quad (10-93)$$

The probability that a system contains  $N$  molecules, irrespective of  $V$ , is

$$\begin{aligned} P(N) &= \int_0^\infty P(N, V) d\left(\frac{pV}{kT}\right) = \frac{\Delta(N, p, T) \lambda^N}{\Upsilon} \\ &= \frac{1}{\Upsilon} \left(\frac{kT\lambda}{p\Lambda^3}\right)^N = \frac{1}{\Upsilon} [e^{-(\mu^{(0)} - \mu)/kT}]^N. \end{aligned} \quad (10-94)$$

This is the same dependence on  $N$  as in Eq. (10-37) (linear aggregate). Note that  $P(0) = 1/\Upsilon$  again. Similarly,

$$\begin{aligned} P(V) &= \sum_{N=0}^\infty P(N, V) = \frac{\Xi(\mu, V, T) e^{-pV/kT}}{\Upsilon} \\ &= \frac{1}{\Upsilon} \left[ \exp\left(\frac{\lambda}{\Lambda^3} - \frac{p}{kT}\right) \right]^V = \frac{1}{\Upsilon} [e^{(p^{(0)} - p)/kT}]^V, \end{aligned} \quad (10-95)$$

where  $p^{(0)}(\mu, T)$  is defined by  $kT\lambda/p^{(0)}\Lambda^3 = 1$ . This is the same dependence as that which follows from the expression preceding Eq. (10-73) (ideal lattice gas).

The function  $P(N, V)$ , for large  $N$  and  $V$ , has the form of a "Gaussian mountain range" (Fig. 10-2). This can be seen as follows. For large  $N$ ,

$$\begin{aligned} \ln P &= N \ln V - \frac{pV}{kT} + \frac{N\mu}{kT} - N \ln \Lambda^3 \\ &\quad - N \ln N + N - \frac{1}{2} \ln 2\pi N - \ln \Upsilon. \end{aligned} \quad (10-96)$$

Now we take  $N = \text{constant} = N'$  and investigate the dependence of  $\ln P$  on  $V$ . We find

$$\frac{\partial \ln P}{\partial V} = \frac{N'}{V} - \frac{p}{kT}, \quad \frac{\partial^2 \ln P}{\partial V^2} = -\frac{N'}{V^2},$$

Thus the maximum with respect to  $V$  occurs at  $V_m = N'kT/p$  and

$$P(N', V) \cong P(N', V_m) \exp\left[-\frac{1}{2}N' \left(\frac{V - V_m}{V_m}\right)^2\right]. \quad (10-97)$$

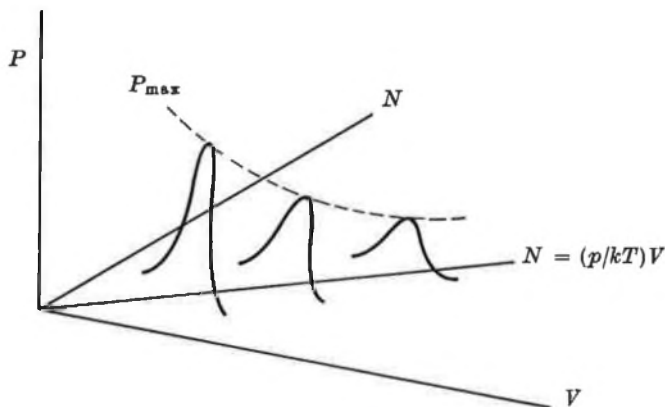


FIGURE 10-2. The probability function  $P(N, V)$  for a classical ideal gas (schematic).  $\mu, p$ , and  $T$  are constant.

The relative standard deviation in  $V$  is the usual  $(N')^{-1/2}$ . Equation (10-97) is of course also essentially the probability distribution in  $V$  for an  $N, p, T$  system.

Next, we take  $V = \text{constant} = V'$  and consider  $\ln P$  as a function of  $N$ :

$$\frac{\partial \ln P}{\partial N} = \ln \left( \frac{V'}{N\Lambda^3} \right) + \frac{\mu}{kT} - \frac{1}{2N}, \quad \frac{\partial^2 \ln P}{\partial N^2} = -\frac{1}{N} + \frac{1}{2N^2}.$$

If we denote by  $N_m$  the value of  $N$  at the maximum with respect to  $N$ , we find

$$P(N, V') \cong P(N_m, V') \exp \left[ -\frac{1}{2} \left( N_m - \frac{1}{2} \right) \left( \frac{N - N_m}{N_m} \right)^2 \right], \quad (10-98)$$

where

$$N_m + \frac{1}{2} = \frac{pV'}{kT} \exp \left[ -\frac{(\mu^{(0)} - \mu)}{kT} \right]. \quad (10-99)$$

As  $\mu \rightarrow \mu^{(0)}$ ,  $N_m \rightarrow pV'/kT$ . The relative standard deviation in  $N$  in Eq. (10-98) is  $N_m^{-1/2}$ . Equation (10-98) is also applicable to a  $\mu, V, T$  system.

Thus a vertical section taken parallel to either the ordinate or the abscissa in Fig. 10-2 produces a Gaussian curve. The axis of

this "Gaussian mountain range" is essentially along the line  $N = (p/kT)V$ . The function  $P(N)$  in Eq. (10-94) is the integrated projection of  $P(N, V)$  onto the  $N$  axis in Fig. 10-2. A similar remark applies to  $P(V)$ . For large  $N$  and  $V$ , the height of the mountain range is easily shown to be

$$P_{\max} \cong \frac{1}{(2\pi N)^{1/2} \Upsilon}. \quad (10-100)$$

Thus the range becomes somewhat lower and broader for large  $N$  and  $V$ .

**STATISTICAL MECHANICAL SUMMARY.** We supplement the examples above with the following summary. In a  $\mu, p, T$  system, if the last sum is over, say,  $V$ , we have

$$\Upsilon = \sum_V \exp\left\{\frac{[p^{(0)}(\mu, T) - p]V}{kT}\right\} \exp\left[\frac{\hat{p}^{(x)}(\mu, V, T)V}{kT}\right]. \quad (10-101)$$

The first factor dominates for large  $V$ . A small system is therefore possible ( $\Upsilon$  converges) if  $p$  is chosen so that  $p > p^{(0)}(\mu, T)$ . Such a system is not possible if  $p < p^{(0)}(\bar{V} \rightarrow \infty)$ . The behavior at  $p = p^{(0)}$  depends on the particular case.

The choice of the last variable over which to sum is obviously arbitrary. If the last sum is over  $N$  [compare Eq. (10-49)],

$$\Upsilon = \sum_N \exp\left\{\frac{[\mu - \mu^{(0)}(p, T)]N}{kT}\right\} \exp\left[-\frac{N\hat{\mu}^{(x)}(N, p, T)}{kT}\right]. \quad (10-102)$$

The sufficient condition for convergence here is  $\mu < \mu^{(0)}(p, T)$ . If the last sum is over  $E$ , this condition is  $T < T^{(0)}(\mu, p)$ . It is easy to show that if values of  $\mu, p$ , and  $T$  are chosen such that  $p > p^{(0)}(\mu, T)$ , then it will also be true that  $\mu < \mu^{(0)}(p, T)$  and  $T < T^{(0)}(\mu, p)$ . If the surface  $\mu^{(0)}(p, T)$  is drawn in a  $p, T, \mu$  coordinate system ( $\mu$  increases in the upward direction), then  $\Upsilon$  converges for points under this surface and possibly on it, but not above it.

### 10-3. SUBDIVISION POTENTIAL AND STABILITY CONDITIONS

The discussion here is not confined to  $\mu, p, T$  systems. As in the preceding two sections, we shall be referring specifically to ensembles of distinguishable systems.

For convenience, we reproduce a few of the relations from pages 23 to 25 of Part I. The fundamental equation (for any environment) for an ensemble of  $\mathcal{N}$  systems is (omitting bars)

$$dE_t = T dS_t - p dV_t + \sum_i \mu_i dN_{ti} + \mathcal{E} d\mathcal{N}, \quad (10-103)$$

where

$$E_t = \mathcal{N}E, \quad V_t = \mathcal{N}V, \quad N_{ti} = \mathcal{N}N_i, \quad S_t = \mathcal{N}S.$$

We also have

$$dA_t = -S_t dT - p dV_t + \sum_i \mu_i dN_{ti} + \mathcal{E} d\mathcal{N} \quad (10-104)$$

$$dF_t = -S_t dT + V_t dp + \sum_i \mu_i dN_{ti} + \mathcal{E} d\mathcal{N} \quad (10-105)$$

$$d(F_t - \sum_i \mu_i N_{ti}) = -S_t dT + V_t dp - \sum_i N_{ti} d\mu_i + \mathcal{E} d\mathcal{N}, \quad (10-106)$$

where

$$A_t = E_t - TS_t, \quad F_t = E_t - TS_t + pV_t.$$

Thus the subdivision potential  $\mathcal{E}$  has the alternative definitions (among others):

$$\mathcal{E} = \left( \frac{\partial E_t}{\partial \mathcal{N}} \right)_{S_t, V_t, N_{ti}} = \left( \frac{\partial A_t}{\partial \mathcal{N}} \right)_{T, V_t, N_{ti}} = \left( \frac{\partial F_t}{\partial \mathcal{N}} \right)_{T, p, N_{ti}} \quad (10-107)$$

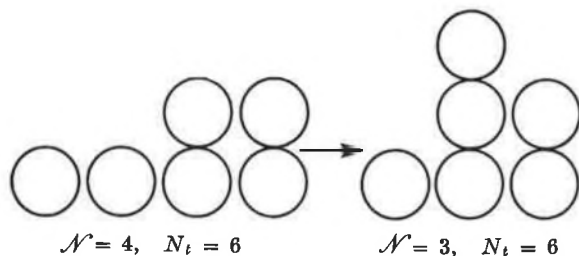
$$= \left[ \frac{\partial (F_t - \sum_i \mu_i N_{ti})}{\partial \mathcal{N}} \right]_{T, p, \mu_i} = \frac{F_t - \sum_i \mu_i N_{ti}}{\mathcal{N}} \quad (10-108)$$

$$= E - TS + pV - \sum_i \mu_i N_i. \quad (10-109)$$

These are reminiscent of the alternative definitions possible for the chemical potentials  $\mu_i$ . The subdivision potential is a measure of the increase in the appropriate energy or free energy function accompanying an increase in  $\mathcal{N}$  (i.e., accompanying further subdivision of the ensemble). From the first definition in Eq. (10-107) it is clear that  $\mathcal{E}$  is the work that must be done on the ensemble to create one more small system (since  $S_t$ ,  $V_t$ , and  $N_{ti}$  are held constant).

It is apparent from Eqs. (10-107) to (10-109) that  $\mathcal{E}$  is independent of any arbitrary choices of the zeros of energy or entropy.

**SPONTANEOUS CHANGE IN  $\mathcal{N}$ .** The subdivision potential has a deeper physical significance in the special case of a closed ensemble ( $N_t$  constant) of systems in which it is conceivable that  $\mathcal{N}$  could change spontaneously (i.e., without the intervention of any outside agency). Let us see what kind of ensemble this must be. In the first place, the ensemble must consist of open systems, each of which contains at least one molecule (monomer, etc.). That is, an empty "system" (all  $N_i = 0$ ) is *not* counted as a system of the ensemble.<sup>1</sup> The point is that in this case and only this case,  $\mathcal{N}$  *can* change *spontaneously*. For example (linear aggregates,  $N_t$  constant):



In the second place, if  $\mathcal{N}$  changes spontaneously, it is not possible, without outside intervention, to hold constant the total volume of the ensemble,  $V_t$ , for this would require precise distribution of the volumes of systems that become empty (through fluctuations in the  $N_i$ ) among those that are not empty. Therefore we must choose  $p$  rather than  $V_t$  as a variable to be kept constant during any spontaneous change in  $\mathcal{N}$ . Finally, since we cannot maintain  $S_t$  constant (in the spontaneous process under consideration,  $T dS_t > DQ_t$ ), we choose  $T = \text{constant}$ .

The conclusion we reach is therefore the following. A spontaneous process in which  $\mathcal{N}$  changes is possible in an ensemble of open systems (each of which contains at least one molecule) held at

<sup>1</sup> This is the natural, realistic, and necessary point of view which we will take in discussing experimental  $\mu, p, T$  systems (aggregates) in a solvent or gas. See Section 10-6.

constant  $N_{it}$ ,  $p$ , and  $T$ . The ensemble is as usual assumed to be very large ( $\mathcal{N} \rightarrow \infty$ ). The environmental variables for each system of the ensemble are  $\mu_i, p, T$ .

If the spontaneous process occurs, it takes place in a closed ensemble at constant  $p$  and  $T$ . Therefore, in the process,  $dF_t < 0$ . From Eq. (10-105), it then follows that  $\mathcal{E} d\bar{\mathcal{N}} < 0$ , where  $\bar{\mathcal{N}}$  is the average number of systems in the ensemble (this is a time average for one ensemble, or an ensemble average if we consider an ensemble of ensembles). Consequently, in such a spontaneous change,  $\bar{\mathcal{N}}$  will decrease (larger systems are formed) if  $\mathcal{E}$  is positive, and  $\bar{\mathcal{N}}$  will increase (smaller systems are formed) if  $\mathcal{E}$  is negative.

We also have, for the above ensemble, the stability condition

$$\left( \frac{\partial^2 F_t}{\partial \bar{\mathcal{N}}^2} \right)_{T, p, N_{it}} = \left( \frac{\partial \mathcal{E}}{\partial \bar{\mathcal{N}}} \right)_{T, p, N_{it}} > 0. \quad (10-110)$$

This follows immediately from statistical mechanics, as we now show. The ensemble partition function appropriate to the independent variables in Eq. (10-105) is

$$e^{-F_t/kT} = \Delta_t(N_{it}, \mathcal{N}, p, T). \quad (10-111)$$

Similarly, associated with the thermodynamic equation

$$d(F_t - \mathcal{E}\bar{\mathcal{N}}) = -S_t dT + V_t dp + \sum_i \mu_i dN_{it} - \bar{\mathcal{N}} d\mathcal{E}, \quad (10-112)$$

we have the partition function

$$\exp \left[ - \left( \frac{F_t - \mathcal{E}\bar{\mathcal{N}}}{kT} \right) \right] = \sum_{\mathcal{N}} \Delta_t(N_{it}, \mathcal{N}, p, T) e^{\mathcal{N}\mathcal{E}/kT}. \quad (10-113)$$

On differentiating twice with respect to  $\mathcal{E}$ , we find the usual kind of result,

$$\bar{\mathcal{N}}^2 - \bar{\mathcal{N}}^2 = kT \left( \frac{\partial \bar{\mathcal{N}}}{\partial \mathcal{E}} \right)_{p, T, N_{it}} > 0. \quad (10-114)$$

This is a quite general situation in statistical thermodynamics: Whenever the mean value of an extensive, mechanical<sup>1</sup> quantity ( $\mathcal{N}$  in this case) is free to vary in a spontaneous process, the quantity

<sup>1</sup> See p. 13 of Part I.



will also be free to fluctuate, and there will consequently be an inequality (stability condition) of the type (10-114).

The resemblance between the above paragraph and Eqs. (5-76) to (5-78), which pertain to a chemical reaction, should be noted. This similarity is not surprising because we are concerned here with a change in the degree of subdivision of small systems which, in a very general sense, is itself a special case of a "chemical reaction" (on the system rather than molecular level).

Thus we have

$$\mathcal{E} d\bar{\mathcal{N}} < 0 \quad \text{and} \quad \frac{\partial \mathcal{E}}{\partial \bar{\mathcal{N}}} > 0$$

in the spontaneous process under consideration. Since  $\mathcal{E}$  and  $d\bar{\mathcal{N}}$  have opposite signs, whereas  $d\bar{\mathcal{N}}$  and  $d\mathcal{E}$  have the same sign, it follows that  $\mathcal{E}$  and  $d\mathcal{E}$  have opposite signs:

$$\mathcal{E} d\mathcal{E} < 0, \quad d(\mathcal{E}^2) < 0, \quad d|\mathcal{E}| < 0. \quad (10-115)$$

That is, regardless of its sign,  $\mathcal{E}$  changes spontaneously in the direction of its final equilibrium value,

$$\left( \frac{\partial F_t}{\partial \bar{\mathcal{N}}} \right)_{T, p, N_{it}} = \mathcal{E} = 0. \quad (10-116)$$

Just as  $\Delta T$  determines the direction of heat transfer,  $\Delta p$  the direction of volume transfer, and  $\Delta \mu$  the direction of transfer of matter, so  $\mathcal{E}$  determines the tendency toward more or less subdivision in an ensemble of nonempty, small  $\mu_i, p, T$  systems.

A complete set of independent variables for the ensemble is  $N_{it}, p, T, \mathcal{E}$ , when  $\mathcal{E}$  has an arbitrary value [see Eq. (10-112)]. In the special case of subdivision equilibrium ( $\mathcal{E} = 0$ ), a complete set is  $N_{it}, p, T$ . For a single system, a complete set is ordinarily  $\mu_i, p, T$  (or  $\bar{N}_i, p, T$ ). In the special case of subdivision equilibrium, the condition

$$\mathcal{E}(\mu_i, p, T) = 0 \quad \text{or} \quad \mathcal{E}(\bar{N}_i, p, T) = 0 \quad (10-117)$$

furnishes one relation between independent variables which reduces their number by one.

In a closed ensemble of  $\mathcal{N}$  one-component  $\mu, p, T$  systems,  $\bar{N} = N_t/\mathcal{N}$ . If  $\mathcal{N}$  itself fluctuates ( $N \geq 1$ ), as we have been

considering above, we include averaging over  $\mathcal{N}$  as well as  $N$ :  $\bar{N} = N_t \bar{\mathcal{N}}^{-1}$ . But we are interested, as always, in the limit  $\mathcal{N} \rightarrow \infty$ , so that the probability distribution in  $\mathcal{N}$  is essentially a Dirac  $\delta$ -function. Thus  $\bar{\mathcal{N}}^{-1} = 1/\bar{\mathcal{N}}$  and

$$N_t = \bar{N} \bar{\mathcal{N}} = \text{constant}, \quad d\bar{\mathcal{N}} = -\frac{\bar{\mathcal{N}}}{\bar{N}} d\bar{N}.$$

Equation (10-114) becomes, then,

$$\begin{aligned} \bar{\mathcal{N}}^2 - \bar{\mathcal{N}}^2 &= kT \left( \frac{\partial \bar{\mathcal{N}}}{\partial \mathcal{E}} \right)_{T, p, N_t} = -\frac{kT \bar{\mathcal{N}}}{\bar{N}} \left( \frac{\partial \bar{N}}{\partial \mathcal{E}} \right)_{T, p} \\ &= -\frac{kT \bar{\mathcal{N}}}{\bar{N}} \left( \frac{\partial \mu}{\partial \mathcal{E}} \right)_{T, p} \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{T, p} \\ &= \frac{\bar{\mathcal{N}}(\bar{N}^2 - \bar{N}^2)}{\bar{N}^2} = \bar{\mathcal{N}} O(1), \end{aligned} \quad (10-118)$$

where we have used Eqs. (10-11c) and (10-38). The fluctuations in  $N$  are unusually large in a completely open system, as noted in the examples of Section 10-2. The fluctuations in  $\mathcal{N}$  are of the normal order of magnitude for an extensive property of a macroscopic system.

If the systems above are multicomponent,

$$\begin{aligned} d\bar{N}_i &= -\frac{\bar{N}_i}{\bar{\mathcal{N}}} d\bar{\mathcal{N}} \quad (N_{ti} \text{ constant}) \\ d\mathcal{E} &= \sum_i \left( \frac{\partial \mathcal{E}}{\partial \bar{N}_i} \right)_{p, T, \bar{N}} d\bar{N}_i \quad (p, T \text{ constant}), \end{aligned}$$

and therefore

$$\begin{aligned} \left( \frac{\partial \mathcal{E}}{\partial \bar{\mathcal{N}}} \right)_{p, T, N_{ti}} &= -\frac{1}{\bar{\mathcal{N}}} \sum_i \bar{N}_i \left( \frac{\partial \mathcal{E}}{\partial \bar{N}_i} \right)_{p, T, \bar{N}_j} \\ &= \frac{1}{\bar{\mathcal{N}}} \sum_{i, k} \bar{N}_i \bar{N}_k \left( \frac{\partial \mu_k}{\partial \bar{N}_i} \right)_{p, T, \bar{N}_j} > 0, \end{aligned} \quad (10-119)$$

where we have used Eq. (4-4). The inequality  $\sum_{i, k} > 0$  is applicable to any nonempty  $\mu_i, p, T$  system.

EXAMPLE OF SPONTANEOUS CHANGE IN  $\bar{\mathcal{N}}$ . Let us consider a closed ensemble of open linear aggregates as an illustration. The model we use is exactly the same as that treated at the beginning of Section 10-2, but here we impose the requirement (or definition) that a system must contain at least one molecule ( $N \geq 1$ ). We therefore subtract the  $N = 0$  term from  $\Upsilon$  in Eq. (10-27) and obtain

$$\Upsilon = \frac{1 - x + cx}{1 - x} - 1 = \frac{cx}{1 - x} \quad (x < 1). \quad (10-120)$$

Then

$$\mathcal{E} = -kT \ln \frac{cx}{1 - x} = -kT \ln c(\bar{N} - 1) \quad (10-121)$$

and

$$\bar{N} = - \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_T = \frac{1}{1 - x} = 1 + e^{-\epsilon/kT} e^{-\mathcal{E}/kT}. \quad (10-122)$$

Equation (10-121) gives  $\mathcal{E}$  as a function of  $\mu$  and  $T$  or as a function of  $\bar{N}$  and  $T$ .  $\mathcal{E}$  may be positive, negative, or zero. Equation (10-122) provides  $\bar{N}$  as a function of  $\mu$  and  $T$  or as a function of  $\mathcal{E}$  and  $T$ .

Other properties are easy to derive in the ordinary way:

$$\bar{E} = \bar{N} k T^2 \frac{d \ln j}{dT} + (\bar{N} - 1) \epsilon \quad (10-123)$$

$$S = \bar{N} k \ln j + \bar{N} k T \frac{d \ln j}{dT} + S(x) \quad (10-124)$$

$$\begin{aligned} S(x) &= -k \sum_{N=1}^{\infty} P(N) \ln P(N) \\ &= k \ln \bar{N} + (\bar{N} - 1) k \ln \frac{\bar{N}}{\bar{N} - 1}, \end{aligned} \quad (10-125)$$

where

$$P(N) = (1 - x)x^{N-1} \quad (N \geq 1). \quad (10-126)$$

Now we imagine that  $\bar{\mathcal{N}}$  is allowed to change spontaneously to a final equilibrium value, in a closed ensemble held at constant  $T$ . When this equilibrium is reached,

$$\begin{aligned} \mathcal{E} &= 0, \quad \Upsilon = 1, \quad \lambda = \frac{1}{j(1 + e^{-\epsilon/kT})} \\ \bar{N} &= 1 + e^{-\epsilon/kT}, \quad \bar{\mathcal{N}} = N_t / \bar{N}. \end{aligned} \quad (10-127)$$

If  $\epsilon < 0$ ,  $\bar{N} > 2$ . There is, of course, one less degree of freedom in this equilibrium state (for a single system, only  $T$  is independent).

It might be recalled, for comparison, that when we considered this model in Section 10-2, beginning with Eq. (10-27), and allowed empty systems in the ensemble, we had

$$Q(0, T) = 1, \quad Y \geq 1, \quad \text{and} \quad \mathcal{E} \leq 0. \quad (10-128)$$

The value  $\mathcal{E} = 0$  is achievable in this case only in the limit  $\lambda \rightarrow 0$ ,  $\bar{N} \rightarrow 0$  (and it does not have the physical significance of an equilibrium value).

Returning to Eq. (10-121), we observe that as  $x \rightarrow 1$ ,  $\bar{N} \rightarrow \infty$  and

$$\mathcal{E} \rightarrow -kT \ln \bar{N},$$

as in Eq. (10-32). Although  $\mathcal{E}$  is negligible for a macroscopic system (it has to be compared with terms of order  $\bar{N}kT$ ), it is *not* equal to zero in the strict sense that we are using  $\mathcal{E} = 0$  above as an equilibrium condition. The macroscopic state is therefore not to be confused with the equilibrium state.

COMPILATION OF  $\mathcal{E}$  VALUES. For the convenience of the reader, we collect here some of the expressions for  $\mathcal{E}$  found elsewhere for a few simple models and several choices of environmental variables.

#### *Ideal Lattice Gas*

$$N, B: \quad \mathcal{E} = -kT \left[ \frac{1}{2} \ln \frac{2\pi N(B-N)}{B} - \frac{B}{B-N} + \dots \right] \quad (15-94)$$

$$\frac{\mu}{T}, B: \quad \mathcal{E} = 0 \quad (6-54)$$

$$N, \frac{p}{T}: \quad \mathcal{E} = kT \ln (1 - e^{-p/kT}) \quad (2-81)$$

$$\frac{\mu}{T}, \frac{p}{T}: \quad \mathcal{E} = -kT \ln (1 + \bar{B}) \quad (N \geq 0). \quad (10-73)$$

*Classical Ideal Gas*

$$N, V, T: \quad \mathcal{E} = \frac{kT}{2} \ln \frac{2\pi N}{e^2} + \cdots \quad (15-64)$$

$$\mu, V, T: \quad \mathcal{E} = 0 \quad (10-82)$$

$$N, p, T: \quad \mathcal{E} = 0 \quad (10-84)$$

$$\mu, p, T: \quad \mathcal{E} = -kT \ln(1 + \bar{N}) \quad (N \geq 0). \quad (10-88)$$

*Spherical Aggregate*

$$N, T: \quad \mathcal{E} = \frac{1}{3} a N^{2/3} \quad (10-54)$$

$$\mu, T: \quad \mathcal{E} = -kT \ln \frac{3\pi \bar{N}}{16} \quad [\mu = \mu^{(0)}(T)]. \quad (10-59)$$

*Linear Aggregate*

$$N, T: \quad \mathcal{E} = -\epsilon \quad (10-22)$$

$$\mu, T: \quad \mathcal{E} = -kT \ln \frac{1-x+cx}{1-x} \quad (N \geq 0) \quad (10-30)$$

$$\mu, T: \quad \mathcal{E} = -kT \ln c(\bar{N}-1) \quad (N \geq 1). \quad (10-121)$$

Positive, negative, and zero values of  $\mathcal{E}$  are included above. Also, positive, negative, and zero values of the derivative  $(\partial \mathcal{E} / \partial N)_{T, p}$  may be noted. Equation (10-139), below, requires that this derivative be negative for a completely open system.

**STABILITY CONDITIONS.** We shall not attempt an exhaustive discussion here but rather shall confine ourselves to deductions which follow directly from standard statistical mechanical fluctuation formulas for one-component systems.

We have pointed out a number of times in this book that thermodynamic equations for small systems are the same for all environments, although thermodynamic functions differ (see the expressions for  $\mathcal{E}$ , above, for example). Stability conditions (inequalities) also prove to be different for different environments. For example,

$(\partial\mu/\partial N)_{V, T}$  can never be negative for a  $\mu, V, T$  system (see below), but this derivative may be negative for an  $N, V, T$  system (as in Fig. 8-1).

We first recall two stability conditions already encountered. Equation (5-78) states that  $\partial\bar{n}/\partial\psi < 0$  for a chemical reaction in an  $N, p, T$  system [see also Eq. (5-9)]. The second case is  $\partial\bar{\mathcal{N}}/\partial\mathcal{E} > 0$  in Eq. (10-114).

In an  $N, V, T$  system, the energy  $E$  fluctuates. From

$$Q(N, V, T) = \sum_E \Omega(N, V, E) e^{-E/kT}$$

we deduce

$$\frac{\overline{E^2} - \bar{E}^2}{kT^2} = \left( \frac{\partial \bar{E}}{\partial T} \right)_{N, V} = C_V = T \left( \frac{\partial S}{\partial T} \right)_{N, V} > 0. \quad (10-129)$$

We can say nothing in general about  $(\partial p/\partial V)_{N, T}$  and  $(\partial\mu/\partial N)_{V, T}$  for a small  $N, V, T$  system. Both signs are possible for both derivatives, even in exact theories (see Fig. 8-1), although of course  $\partial p/\partial V$  is usually negative and  $\partial\mu/\partial N$  is usually positive.

In a  $\mu, V, T$  system,  $N$  and  $E$  fluctuate. Equations (1-19) and (6-16) lead to

$$\frac{\overline{N^2} - \bar{N}^2}{kT} = \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{V, T} > 0 \quad (10-130)$$

$$\frac{\overline{L^2} - \bar{L}^2}{kT^2} = \left( \frac{\partial \bar{L}}{\partial T} \right)_{\mu, V} = T \left( \frac{\partial S}{\partial T} \right)_{\mu, V} > 0, \quad (10-131)$$

where

$$L = E - \mu N = TS - pV.$$

In view of Eq. (10-130), and because the first and third terms dominate in Eq. (8-30), in general  $(\partial p/\partial V)_{\bar{N}, T} < 0$ . But a more precise statement<sup>1</sup> follows from Eq. (6-8):

$$\left( \frac{\partial p}{\partial V/\bar{N}} \right)_{V, T} = - \frac{\bar{N}^3}{V^2} \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{V, T} < 0. \quad (10-132)$$

<sup>1</sup> This is the same as Eq. (28.10) in S.M. and Eq. (12) in T. L. Hill, *J. Phys. Chem.* **57**, 324 (1953).

In an  $N, p, T$  system, we derive from  $\Delta(N, p, T)$

$$-\frac{\bar{V}^2 - \bar{V}^2}{kT} = \left( \frac{\partial \bar{V}}{\partial p} \right)_{N, T} < 0 \quad (10-133)$$

$$\frac{\bar{H}^2 - \bar{H}^2}{kT^2} = \left( \frac{\partial \bar{H}}{\partial T} \right)_{N, p} = T \left( \frac{\partial S}{\partial T} \right)_{N, p} > 0, \quad (10-134)$$

where  $H = E + pV$ . From Eqs. (8-30) and (10-133),  $(\partial\mu/\partial N)_{\bar{V}, T} > 0$ , in general. More precisely, from Eq. (2-3),

$$\left( \frac{\partial \hat{\mu}}{\partial N/\bar{V}} \right)_{N, T} = -\frac{\bar{V}^3}{N^2} \left( \frac{\partial p}{\partial \bar{V}} \right)_{N, T} > 0. \quad (10-135)$$

In a  $\mu, p, T$  system,  $Y(\mu, p, T)$  leads to

$$\frac{\bar{N}^2 - \bar{N}^2}{kT} = \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{p, T} > 0 \quad (10-136)$$

$$-\frac{\bar{V}^2 - \bar{V}^2}{kT} = \left( \frac{\partial \bar{V}}{\partial p} \right)_{\mu, T} < 0 \quad (10-137)$$

$$\frac{\bar{Y}^2 - \bar{Y}^2}{kT^2} = \left( \frac{\partial \bar{Y}}{\partial T} \right)_{\mu, p} = T \left( \frac{\partial S}{\partial T} \right)_{\mu, p} > 0, \quad (10-138)$$

where

$$Y = \mathcal{E} + TS = E + pV - \mu N.$$

Equations (10-5), (10-136), and (10-137) then give the further relations

$$\left( \frac{\partial \mathcal{E}}{\partial \bar{N}} \right)_{p, T} = -\bar{N} \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{p, T} < 0 \quad (10-139)$$

$$\left( \frac{\partial \mathcal{E}}{\partial \bar{V}} \right)_{\mu, T} = \bar{V} \left( \frac{\partial p}{\partial \bar{V}} \right)_{\mu, T} < 0. \quad (10-140)$$

#### 10-4. PHASE TRANSITIONS IN $\mu, p, T$ SYSTEMS

Again, as in Sections 10-1 to 10-3, we consider an ensemble of distinguishable systems. The discussion here is a continuation of that in Sections 5-4 and 6-1. It can be brief because this subject proves to be less interesting for a  $\mu, p, T$  system than for  $N, p, T$

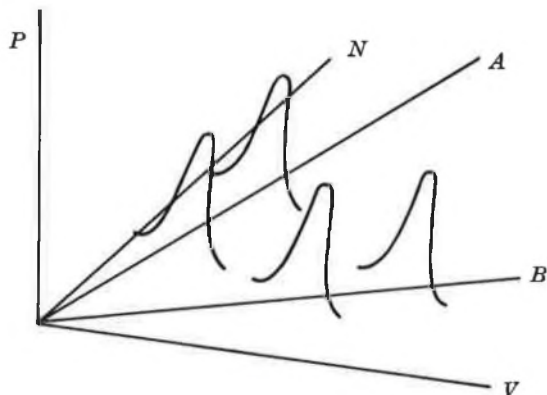


FIGURE 10-3. The probability function  $P(N, V)$  in a two-phase region (schematic).  $\mu, p$ , and  $T$  are constant.

or  $\mu, V, T$  systems. For variety, following the suggestion in the footnote on page 149 of Part I, we employ a statistical mechanical (rather than thermodynamic) approach here.

As we have pointed out on page 62, an exact or approximate  $Q(N, V, T)$  which leads to the two-state approximation for an  $N, p, T$  system also leads to this approximation for a  $\mu, V, T$  system. The essential point to be made here is that, still referring to the same  $Q(N, V, T)$ , the two-state approximation carries over to the next level in the hierarchy of ensembles—that is, to a  $\mu, p, T$  system. This can be seen, for example, by considering a series of neighboring values of the volume,  $V', V'', V'''$ , etc., for a  $\mu, V, T$  system in a phase-transition region. The probability curve  $P(N)$  will have two peaks ( $A$  and  $B$ ) for each of these values of  $V$  ( $\mu$  and  $T$  held constant). If we put these curves together to form a  $P(N, V)$  probability surface<sup>1</sup> for a  $\mu, p, T$  system, as in Fig. 10-2, the surface will have the form of two separated Gaussian mountain ranges, each range corresponding to one of the two states  $A$  and  $B$  (Fig. 10-3). Thus a vertical section through this surface, parallel to the  $V$  axis ( $N = N' = \text{constant}$ ), will give a  $P(N', V)$  curve as in Fig. 5-1c, whereas a vertical section parallel to the  $N$  axis ( $V = V' = \text{constant}$ ) will produce a two-peaked  $P(N, V')$  curve, as already mentioned.

<sup>1</sup>  $P(N, V)$  is defined as  $Q(N, V, T)e^{N\mu/kT}e^{-pV/kT}/Y$ .



Figure 7-2 is closely related to the  $P(N, V)$  surface in Fig. 10-3, but the former figure exhibits two Gaussian peaks rather than two Gaussian mountain ranges. This point will be referred to further in the next section.

We turn now to a more analytical discussion and begin with the equation on page 149 of Part I for a two-state  $N, p, T$  system:

$$\Delta = \Delta_A + \Delta_B. \quad (10-141)$$

We multiply by  $e^{N\mu/kT}$  and sum over  $N$  to obtain

$$\Upsilon = \Upsilon_A + \Upsilon_B. \quad (10-142)$$

Alternatively, we could have started with  $\Xi$  instead of  $\Delta$ .

Incidentally, although the additive form of  $\Delta$  or  $\Xi$  is retained on passing to the "higher" (more open) partition function  $\Upsilon$ , this form does not obtain in the lower partition function  $Q$ . The physical reason why  $\Delta$ ,  $\Xi$ , and  $\Upsilon$  are essentially additive at a phase transition is that density fluctuations are possible in all these cases and hence the system can *alternate* between states  $A$  and  $B$ . On the other hand, in an exact theory, an  $N, V, T$  system must have phases  $A$  and  $B$  present *simultaneously*, which leads to a  $Q$  in the form of a product rather than a sum.<sup>1</sup> In an approximate, uniform-density theory of a phase transition, there is just one expression (neither sum nor product) for  $Q(N, V, T)$ , but still  $\Delta$ ,  $\Xi$ , and  $\Upsilon$  are in general additive.

Returning now to Eq. (10-142), the probability of observing a given system in state  $A$ , or the fraction of systems of an ensemble which are in state  $A$ , is

$$P_A = \frac{\mathcal{N}_A}{\mathcal{N}} = \frac{\Upsilon_A}{\Upsilon}. \quad (10-143)$$

Therefore

$$\frac{\mathcal{N}_A}{\mathcal{N}_B} = \frac{e^{-\mathcal{E}_A/kT}}{e^{-\mathcal{E}_B/kT}}, \quad (10-144)$$

which is the analogue of Eqs. (5-118) and (6-35).

Equation (10-142) can be rewritten in the forms

$$e^{-\mathcal{E}/kT} = e^{-\mathcal{E}_A/kT} + e^{-\mathcal{E}_B/kT}, \quad (10-145)$$

or

$$\mathcal{E} = P_A \mathcal{E}_A + P_B \mathcal{E}_B + kT(P_A \ln P_A + P_B \ln P_B). \quad (10-146)$$

<sup>1</sup> See, for example, Eqs. (A9.21) to (A9.24) of S.M.

We find easily from Eq. (10-145) that

$$\bar{V} = \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, \mu} = P_A \bar{V}_A + P_B \bar{V}_B \quad (10-147)$$

and

$$\bar{N} = - \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{T, p} = P_A \bar{N}_A + P_B \bar{N}_B. \quad (10-148)$$

Although Eqs. (10-144) to (10-148) have the same formal appearance as the corresponding equations in Sections 5-4 and 6-1, they have less interesting implications here. This comes about as follows. Consider first an  $N, p, T$  system which exhibits a phase transition. If we hold the environmental variables  $N$  and  $T$  constant, and vary  $p$  over a suitable range (see Figs. 5-2 and 5-4), the system will pass through the transition—that is, it will start in one state, say  $A$ , and end in the other, say  $B$ . This is a consequence of the fact that the macroscopic system has two degrees of freedom; therefore, if we hold one intensive variable ( $T$ ) constant we can still span the transition region by varying a second intensive variable ( $p$ ). Similar comments can be made about a  $\mu, V, T$  system and Figs. 6-1 and 6-2.

But now consider a  $\mu, p, T$  system. If we hold any two environmental variables<sup>1</sup> constant, say  $p$  and  $T$ , then we can still vary  $\mu$ , but this variation will not cause the system to pass from one state to another; that is, nothing very interesting happens. This follows because specification of any two of  $\mu, p$ , and  $T$  fixes the macroscopic stable state as either  $A$  or  $B$  (except in the very special case where the values of the two specified variables correspond to the two macroscopic phases in equilibrium with each other; but even in this case the system does not pass from one state to the other as the third environmental variable is varied).

Figure 10-4 illustrates the above comments. The curves shown are the macroscopic chemical potentials  $\mu_A^{(0)}(p)$  and  $\mu_B^{(0)}(p)$  ( $T$  is held constant). The partition function  $\Upsilon_A$  converges for  $\mu < \mu_A^{(0)}$ , whereas  $\Upsilon_B$  converges for  $\mu < \mu_B^{(0)}$ . Hence  $\Upsilon$  in Eq. (10-142) converges in the crosshatched region (and possibly on the curves bordering this region). The vertical arrows indicate possible variation in

<sup>1</sup> Environmental variables are, essentially by definition, always the “natural” variables to hold constant.

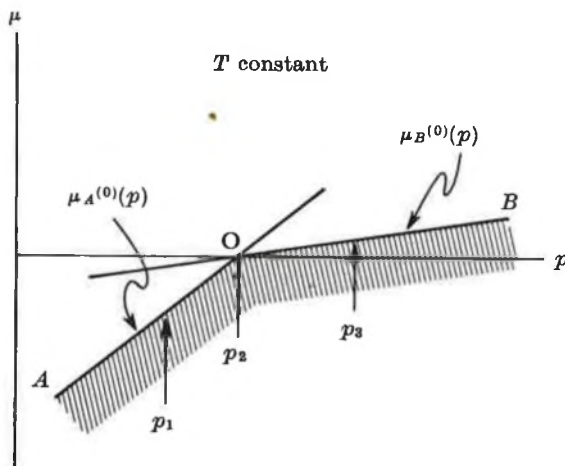


FIGURE 10-4. Phase transition in  $\mu, p, T$  system. See text for explanation.

the value of  $\mu$  at constant  $p$ . From Eq. (10-102),

$$\begin{aligned} \Upsilon &= \Upsilon_A + \Upsilon_B \\ &= \sum_N \exp \left[ \frac{(\mu - \mu_A^{(0)})N}{kT} \right] \exp \left( - \frac{N\hat{\mu}_A^{(x)}}{kT} \right) \\ &\quad + \sum_N \exp \left[ \frac{(\mu - \mu_B^{(0)})N}{kT} \right] \exp \left( - \frac{N\hat{\mu}_B^{(x)}}{kT} \right). \end{aligned} \quad (10-149)$$

At  $p = p_1$ ,  $\Upsilon_A$  and  $\bar{N}_A$  become significant in size only as  $\mu$  approaches the value  $\mu_A^{(0)}(p_1)$ . But for this value of  $\mu$ ,  $\Upsilon_B$  and  $\bar{N}_B$  are very small. Thus  $P_A \cong 1$  and, in the appropriate version of Fig. 10-3, "mountain range"  $B$  is very small compared to range  $A$ . For no value of  $\mu$  will  $\mathcal{E}_A = \mathcal{E}_B$ . For practical purposes, at  $p = p_1$  and  $\mu$  near  $\mu_A^{(0)}(p_1)$ , the system is confined to state  $A$  and has the properties of this state. Of course, the macroscopic stable state at  $p_1, T$  is  $A$ . The situation described above is exactly reversed with respect to  $A$  and  $B$  at  $p = p_3$ .

At  $p = p_2(T)$ ,  $\mu_A^{(0)} = \mu_B^{(0)}$  in Eq. (10-149). Thus  $\Upsilon_A$  and  $\Upsilon_B$  differ only by virtue of the relatively small quantities  $\hat{\mu}_A^{(x)}$  and  $\hat{\mu}_B^{(x)}$ . Hence

$\Upsilon_A$  and  $\Upsilon_B$  will be of the same order of magnitude, although  $P_A$  will in general vary somewhat with  $\mu$ . Mountain ranges  $A$  and  $B$  (Fig. 10-3) will be of similar size. A value of  $\mu$  may or may not exist at which  $\mathcal{E}_A = \mathcal{E}_B$ . Because of the limited opportunities for occurrence of this equality, Clausius-Clapeyron equations derived from  $d\mathcal{E}_A = d\mathcal{E}_B$  [compare Eq. (5-135)] are not very important.

For cases in which  $\Upsilon_A$  and  $\Upsilon_B$  converge at  $\mu = \mu_A^{(0)}$  and  $\mu = \mu_B^{(0)}$ , respectively, it would be possible to follow a transition from one state to another in a  $\mu, p, T$  system in this way: Hold only  $T$  constant, vary  $p$ , and choose  $\mu$  equal to the lesser of  $\mu_A^{(0)}(p)$  and  $\mu_B^{(0)}(p)$  for each  $p$  (curve  $AOB$  in Fig. 10-4). But this procedure seems too contrived to be worth pursuing in any detail.

Another procedure of the same sort is the following: Hold  $T$  constant, vary  $p$ , and adjust  $\mu$  for each  $p$  to give a constant  $\bar{N}$  (or  $\bar{V}$ ).

*Example.* The extension of Eqs. (6-72)ff. to a  $\mu, p, T$  system provides a simple example. For a  $\mu, B, T$  system, we assume

$$\begin{aligned}\hat{p}_1(\mu, T) &= \hat{p}_0(T) + \rho_1(T)[\mu - \mu_0(T)] \\ \hat{p}_2(\mu, T) &= \hat{p}_0(T) + \rho_2(T)[\mu - \mu_0(T)],\end{aligned}\quad (10-150)$$

where  $\rho_1$  and  $\rho_2$  are densities ( $\rho_1 > \rho_2$ ). Ordinarily  $\hat{p}_1$  and  $\hat{p}_2$  would be functions of  $B$ , but not in this simple model. Then

$$\begin{aligned}\Upsilon(\mu, p, T) &= \Upsilon_1 + \Upsilon_2 \\ &= \sum_{B=0}^{\infty} e^{\hat{p}_1 B/kT} e^{-pB/kT} + \sum_{B=0}^{\infty} e^{\hat{p}_2 B/kT} e^{-pB/kT} \\ &= \frac{1}{1 - e^{(\hat{p}_1 - p)/kT}} + \frac{1}{1 - e^{(\hat{p}_2 - p)/kT}}.\end{aligned}\quad (10-151)$$

Thus

$$\frac{P_1}{P_2} = \frac{\mathcal{N}_1}{\mathcal{N}_2} = \frac{\Upsilon_1}{\Upsilon_2} = \frac{e^{-\mathcal{E}_1/kT}}{e^{-\mathcal{E}_2/kT}} = \frac{1 - e^{(\hat{p}_2 - p)/kT}}{1 - e^{(\hat{p}_1 - p)/kT}}. \quad (10-152)$$

Figure 10-5 is the analogue of Fig. 10-4. Convergence of  $\Upsilon$  occurs in the crosshatched region. That is,  $\Upsilon_1$  converges for  $p > \hat{p}_1$  and  $\Upsilon_2$  converges for  $p > \hat{p}_2$ .

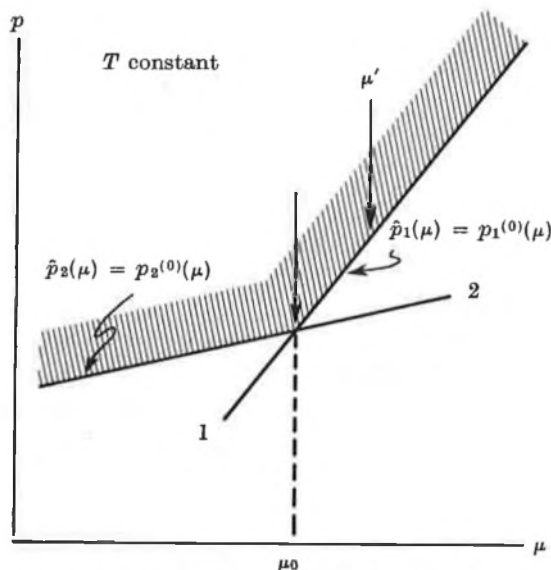


FIGURE 10-5. Example of phase transition in  $\mu, p, T$  system [see Eqs. (10-150) to (10-158)].

We find easily that

$$\bar{N}_1 = - \left( \frac{\partial \mathcal{E}_1}{\partial \mu} \right)_{p, T} = \frac{e^{(\hat{p}_1 - p)/kT} \rho_1}{1 - e^{(\hat{p}_1 - p)/kT}} \quad (10-153)$$

$$\bar{B}_1 = \left( \frac{\partial \mathcal{E}_1}{\partial p} \right)_{\mu, T} = \frac{\bar{N}_1}{\rho_1}, \quad \Upsilon_1 = 1 + \bar{B}_1, \quad (10-154)$$

with similar expressions for  $\bar{N}_2$ ,  $\bar{B}_2$ , and  $\Upsilon_2$ .

Let us consider a particular value of  $\mu$ , say  $\mu = \mu'$ , in Fig. 10-5. Then we have to choose  $p > \hat{p}_1(\mu')$ . In order that the small systems have a reasonable size, with  $\bar{N}_1 \gg 1$ ,  $(p - \hat{p}_1)/kT$  must be very small. Let us call this quantity  $\alpha$ . Now  $0 < \alpha \ll 1$  and

$$\Upsilon_1 = \frac{1}{\alpha}, \quad \bar{N}_1 = \frac{\rho_1}{\alpha}. \quad (10-155)$$

As  $\alpha \rightarrow 0$ ,  $\bar{N}_1 \rightarrow \infty$ .

The quantity

$$\beta \equiv e^{(\hat{p}_1 - \hat{p}_2)/kT} = e^{(\rho_1 - \rho_2)(\mu' - \mu_0)/kT}$$

might be of order, say, 2 to 10. Then ( $\alpha \rightarrow 0$ )

$$\Upsilon_2 = \frac{\beta}{\beta - 1} = O(1), \quad \bar{N}_2 = \frac{\rho_2}{\beta - 1} = O(1), \quad (10-156)$$

and

$$\frac{P_1}{P_2} = \frac{\beta - 1}{\alpha\beta} = O\left(\frac{1}{\alpha}\right) \quad (10-157)$$

$$\rightarrow \infty \text{ as } \alpha \rightarrow 0.$$

If we choose  $\mu$  equal to  $\mu_0$ ,

$$\hat{p}_1 = \hat{p}_2, \quad \Upsilon_1 = \Upsilon_2, \quad P_1 = P_2 = \frac{1}{2}. \quad (10-158)$$

The two states are equally probable in this case. The systems become large, as before, as  $p \rightarrow \hat{p}_1 = \hat{p}_2$ .

#### 10-5. $N_1, \mu_2, p, T$ SYSTEMS WITH $N_1$ CONSTANT

In Section 7-1 we considered an ensemble of distinguishable  $N_1, \mu_2, p, T$  systems. If  $N_1$  is always held constant, the remaining environmental variables are  $\mu_2, p$ , and  $T$ . This is formally equivalent to a  $\mu, p, T$  system. An example is the adsorption of component 2 at  $\mu_2$  onto an aggregate of  $N_1$  molecules (or sites) of component 1, where  $N_1 = \text{constant}$ . Essentially the same kind of system is obtained if we start with a  $\mu, V, T$  system (or  $\mu, B, T$  system, where  $B = \text{number of sites}$ ) and hold  $V$  (or  $B$ ) constant.

When we put  $N_1 = \text{constant}$ , Eqs. (7-2), (7-4), and (7-5) become

$$\hat{\mu}_1 N_1 = \bar{E} - TS + p\bar{V} - \mu_2 \bar{N}_2 \quad (10-159)$$

$$d\bar{E} = T dS - p d\bar{V} + \mu_2 d\bar{N}_2 \quad (10-160)$$

$$d(\hat{\mu}_1 N_1) = -S dT + \bar{V} dp - \bar{N}_2 d\mu_2. \quad (10-161)$$

These are the analogues of Eqs. (10-3), (10-1), and (10-5), respectively, for a  $\mu, p, T$  system:

$$\mathcal{E} = \bar{E} - TS + p\bar{V} - \mu\bar{N} \quad (10-162)$$

$$d\bar{E} = T dS - p d\bar{V} + \mu d\bar{N} \quad (10-163)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - \bar{N} d\mu. \quad (10-164)$$

Thus  $\hat{\mu}_1 N_1$  plays the role of  $\mathcal{E}$ . The functions  $\bar{E}, S$ , and  $\bar{V}$  in Eqs.

(10-159) to (10-161) include contributions from both components 1 and 2. The function  $\hat{\mu}_1 N_1$  will be small (like  $\mathcal{E}$ ) compared with the other terms in Eq. (10-159) only if  $\bar{N}_2 \gg N_1$ . This can occur in cases where there is no limit on the value of  $\bar{N}_2$  ( $\bar{N}_2 \rightarrow \infty$ )—for example, in multilayer adsorption of component 2 onto  $N_1$  sites (but not in the case of monolayer adsorption onto  $N_1$  sites).

Perhaps a more natural procedure is to subtract out of the functions in Eqs. (10-159) to (10-161) the properties of pure component 1. If we put  $\bar{N}_2 = 0$  ( $\mu_2 \rightarrow -\infty$ ) in these equations, we have (for the same constant value of  $N_1$ )

$$\begin{aligned}\hat{\mu}_{10} N_1 &= \bar{E}_0 - T S_0 + p \bar{V}_0 \\ d\bar{E}_0 &= T dS_0 - p d\bar{V}_0 \\ d(\hat{\mu}_{10} N_1) &= -S_0 dT + \bar{V}_0 dp.\end{aligned}$$

These relations are now subtracted from Eqs. (10-159) to (10-161) to give

$$(\hat{\mu}_1 - \hat{\mu}_{10}) N_1 = (\bar{E} - \bar{E}_0) - T(S - S_0) + p(\bar{V} - \bar{V}_0) - \mu_2 \bar{N}_2 \quad (10-165)$$

$$d(\bar{E} - \bar{E}_0) = T d(S - S_0) - p d(\bar{V} - \bar{V}_0) + \mu_2 d\bar{N}_2 \quad (10-166)$$

$$d[(\hat{\mu}_1 - \hat{\mu}_{10}) N_1] = -(S - S_0) dT + (\bar{V} - \bar{V}_0) dp - \bar{N}_2 d\mu_2. \quad (10-167)$$

These expressions involve, essentially, one-component thermodynamic functions and hence they are closer analogues of Eqs. (10-162) to (10-164) than are Eqs. (10-159) to (10-161). Again, however, the analogue of  $\mathcal{E}$ , namely,  $(\hat{\mu}_1 - \hat{\mu}_{10}) N_1$  will be "small" in Eq. (10-165) only when  $\bar{N}_2 \gg N_1$ .

Equations (10-165) to (10-167) resemble the relations of adsorption thermodynamics,<sup>1</sup> except that here  $N_1$  can be arbitrarily small. The quantity  $\hat{\mu}_{10} - \hat{\mu}_1$  is the analogue of the surface pressure.<sup>2</sup>

The connection with statistical mechanics is through the partition functions  $\Delta$  and  $\Gamma$  [see Eqs. (1-32) and (7-7)]:

$$-kT \ln \Delta(N_1, p, T) = \hat{\mu}_{10} N_1 \quad (10-168)$$

$$-kT \ln \Gamma(N_1, \mu_2, p, T) = \hat{\mu}_1 N_1. \quad (10-169)$$

<sup>1</sup> T. L. Hill, *J. Chem. Phys.*, **18**, 246 (1950).

<sup>2</sup> Loc. cit., Appendix III.

Therefore

$$(\hat{\mu}_1 - \hat{\mu}_{10})N_1 = -kT \ln \frac{\Gamma(N_1, \mu_2, p, T)}{\Delta(N_1, p, T)}. \quad (10-170)$$

*Example.* As an extremely simple example consider an ideal lattice gas of  $\bar{N}_2$  molecules adsorbed on a group of  $N_1$  independent and equivalent sites.<sup>1</sup> The partition function for the sites alone is taken to be  $Q(N_1, T) = j_1(T)^{N_1}$  ( $Q$  replaces  $\Delta$ ). For the binary system, we have

$$Q(N_1, N_2, T) = \frac{j_1(T)^{N_1} j_2(T)^{N_2} N_1!}{N_2! (N_1 - N_2)!} \quad (10-171)$$

and

$$\Gamma(N_1, \mu_2, T) = \sum_{N_2=0}^{N_1} Q(N_1, N_2, T) \lambda_2^{N_2} = j_1^{N_1} (1 + j_2 \lambda_2)^{N_1}. \quad (10-172)$$

The energy of adsorption of a component 2 molecule on a site is included in  $j_2$ . Then

$$\hat{\mu}_{10} N_1 = -N_1 kT \ln j_1 \quad (10-173)$$

$$\hat{\mu}_1 N_1 = -N_1 kT [\ln j_1 + \ln (1 + j_2 \lambda_2)] \quad (10-174)$$

and

$$(\hat{\mu}_1 - \hat{\mu}_{10})N_1 = -N_1 kT \ln (1 + j_2 \lambda_2). \quad (10-175)$$

From Eqs. (10-167) and (10-175),

$$\bar{N}_2 = - \frac{\partial [(\hat{\mu}_1 - \hat{\mu}_{10})N_1]}{\partial \mu_2} = \frac{N_1 j_2 \lambda_2}{1 + j_2 \lambda_2}. \quad (10-176)$$

In this model  $\bar{N}_2$  cannot exceed  $N_1$ . All terms in Eq. (10-165) are of order  $N_1 kT$ . The usual fluctuation formula

$$\overline{N_2^2} - \bar{N}_2^2 = kT \left( \frac{\partial \bar{N}_2}{\partial \mu_2} \right)_{N_1, T},$$

gives

$$\frac{\overline{N_2^2} - \bar{N}_2^2}{\bar{N}_2^2} = \frac{1}{N_1 j_2 \lambda_2} = O\left(\frac{1}{N_1}\right) = O\left(\frac{1}{\bar{N}_2}\right). \quad (10-177)$$

Unlike the examples of  $\mu, p, T$  systems in Section 10-2, the fluctuations here are "normal." The basic reason for this is that in a  $\mu, p, T$  system, no extensive variable is specified and hence the

<sup>1</sup> See also the discussion preceding Eq. (10-71).



size of the system can fluctuate widely. Here, although  $N_1$  is constant, it does serve to fix the size of the system (the system is "partially open" rather than "completely open").

We mentioned, in connection with Eq. (10-31), that the B.E.T. multilayer adsorption model amounts to having a "linear aggregate" of adsorbed molecules on each site. Thus, in the example above, if we allow B.E.T. multilayer adsorption of component 2 on each of the  $N_1$  sites (instead of a maximum of only one adsorbed molecule per site), we will have

$$\bar{N}_2 = \frac{N_1 cx}{(1-x)(1-x+cx)} \quad (10-178)$$

and

$$(\hat{\mu}_1 - \hat{\mu}_{10})N_1 = -N_1 kT \ln \frac{1-x+cx}{1-x}. \quad (10-179)$$

In this case  $\bar{N}_2 \rightarrow \infty$  as  $x \rightarrow 1$ . Thus we may have  $\bar{N}_2 \gg N_1$ . In Eq. (10-165), the terms on the right-hand side are of order  $\bar{N}_2 kT$  whereas the left-hand side is of order  $N_1 kT$ . The fluctuation in  $N_2$  is given by [see Eq. (10-39)]

$$\frac{\bar{N}_2^2 - \bar{N}_2^2}{\bar{N}_2^2} = \frac{1}{N_1} \left( \frac{1-x^2+cx^2}{cx} \right) = O\left(\frac{1}{N_1}\right). \quad (10-180)$$

This relative fluctuation is "normal" (small) if  $N_1$  is large, say, 50 to 100 or more, and of order unity if  $N_1$  is very small [in Eq. (10-39),  $N_1 = 1$ ]. This is because each linear aggregate has large fluctuations but the total relative fluctuation in a large number of aggregates is considerably reduced by cancellation.

Hence, in this case, as well as in others where  $\bar{N}_2 \rightarrow \infty$  is possible, the extreme fluctuations characteristic of  $\mu$ ,  $p$ ,  $T$  systems are found when  $N_1$  is very small but not when  $N_1 \gg 1$ . When the maximum possible value of  $\bar{N}_2$  is of order  $N_1$ , normal fluctuations are always encountered.

**BINDING ON PROTEINLIKE MOLECULES.** Suppose component 2 is bound on a macromolecule of fixed composition and molecular weight which, however, is not simply an aggregate or polymer of  $N_1$  identical monomers. A protein molecule is an example. It has a definite composition and may contain many different amino acids. Hence  $N_1$  and  $\hat{\mu}_1$  lose their separate meaning.

To take care of this situation, it is necessary only to make a trivial change in notation. We start with Eq. (7-1):

$$dE_t = T dS_t - p dV_t + \mu_2 dN_{t2} + X d\mathcal{N}.$$

From this we deduce Eqs. (10-159) to (10-161), but we retain the symbol  $X$  instead of using  $\hat{\mu}_1 N_1$ . Similarly, in the  $\bar{N}_2 = 0$  equations ("bare protein"), we replace  $\hat{\mu}_{10} N_1$  by  $X_0$ . Then Eqs. (10-165) to (10-167) are obtained, except that  $(\hat{\mu}_1 - \hat{\mu}_{10})N_1$  is replaced by  $X - X_0$ .

**TWO-STATE APPROXIMATION FOR PHASE TRANSITION.** There are two possibilities here, both of which have already been discussed. The  $P(N_2, V)$  probability function may appear as in Fig. 7-2 (fluctuations in  $N_2$  and  $V$  normal) or as in Fig. 10-3 (large fluctuations in  $N_2$  and  $V$ ). The latter behavior will obtain only when  $N_1$  is very small and  $\bar{N}_2 \rightarrow \infty$  is possible. Intermediate behavior may occur when  $N_1$  is, say, of order 10 to 20 and when  $\bar{N}_2 \rightarrow \infty$  is possible.

*Example of Phase Transition.* In Section 8-2, we discussed the exact canonical ensemble partition function for a lattice gas of  $N$  molecules, with nearest-neighbor interaction energy  $w$ , on  $B = 12$  sites arranged on the surface of a sphere. If this system is open, it becomes an example of a  $\mu_2, T$  ( $N_1 = \text{constant}$ ) system. The notational correspondences are  $N_1 = B = 12 = \text{constant}$ ,  $N_2 = N$ ,  $\mu_2 = \mu$ .

The partition function  $Q(N, T)$  for a closed system is given in Eq. (8-37). For an open system, the partition function is

$$\Gamma(\mu, T) = \sum_{N=0}^{12} Q(N, T) \lambda^N. \quad (10-181)$$

The probability that the open system contains  $N$  molecules is

$$P(N) = \frac{Q(N, T) \lambda^N}{\Gamma(\mu, T)}. \quad (10-182)$$

Figures 10-6 and 10-7 show examples of the function  $P(N)$ . In all these curves,  $w$  is negative. If we regard  $w$  as constant,  $y = e^{-w/kT}$  is a measure of the temperature. In Fig. 10-6, we have chosen  $\lambda = y^{-2}$  for each curve. This value of  $\lambda$  leads to symmetrical  $P(N)$  curves and hence corresponds to  $\bar{N}/B = \frac{1}{2}$  (i.e.,  $\bar{N} = 6$ ). Four temperatures are shown in Fig. 10-6:  $y = 5.00$  is well below the

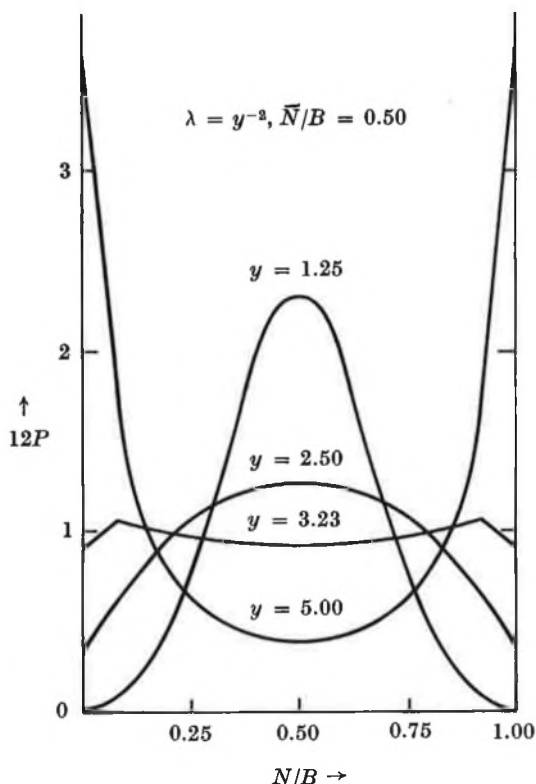


FIGURE 10-6. Probability function  $P(N)$  for open 12-site spherical lattice gas at  $\bar{N}/B = 0.50$ .

critical temperature;  $y = 3.23$  appears to be slightly below the critical temperature; on the other hand,  $y = 2.50$  and  $y = 1.25$  are above the critical temperature. The two peaks in  $P(N)$  at  $y = 5.00$  correspond to the two phases in a phase equilibrium. The peaks are not well separated or Gaussian in shape because  $B$  is so small ( $B = 12$ ). At the two highest temperatures, there is only one "phase" present and one peak.

In Fig. 10-7, the temperature is again  $y = 5.00$  but  $\lambda$  is smaller than in Fig. 10-6:  $\lambda = 0.90y^{-2}$ . There are still two peaks ("phases") in  $P(N)$ , but the curve is unsymmetrical. The dilute "phase" has a higher probability of occurrence than the concentrated phase.

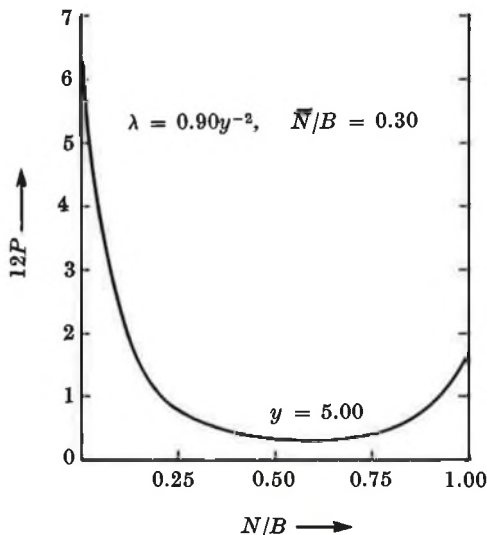


FIGURE 10-7. Probability function  $P(N)$  for open 12-site spherical lattice gas at  $\bar{N}/B = 0.30$ .

We calculate  $\bar{N}/B = 0.30$  from the  $P(N)$  curve. Thus we have three points on a  $\lambda$ - $\bar{N}/B$  plot for  $y = 5.00$ :  $\lambda = y^{-2}$ ,  $\bar{N}/B = 0.50$ ;  $\lambda = 0.90y^{-2}$ ,  $\bar{N}/B = 0.30$ ; and, by symmetry,  $\lambda = 1.11y^{-2}$ ,  $\bar{N}/B = 0.70$ . The derivative  $(\partial\bar{N}/\partial\mu)_T$  is therefore positive, as required by the fluctuation formula following (10-176); i.e., there is no "loop."

The above results should be compared with<sup>1</sup> Figs. 6-6 and 6-7. These figures, it will be recalled, are based on the Bragg-Williams approximation and on a  $B$  that can be varied.

#### 10-6. SMALL SYSTEMS IN SOLVENT OR GAS

Section 7-2 provides the foundation for much of the present section. We consider here a small system which is closed with respect to component 1 (moreover,  $N_1$  is invariable) and open with respect to component 2. There are two cases:  $N_1 \neq 0$  and  $N_1 = 0$ . The former case has essentially been covered in Chapter 7. The latter case is new and more interesting. It is concerned with the formation of

<sup>1</sup>See also D. A. Chesnut and Z. W. Salsburg, *J. Chem. Phys.*, **38**, 2861 (1963).

aggregates (of component 2) from solvent or gas (soap micelles, clusters in a gas, crystal nuclei in a liquid, etc.). A fundamental difference between the two cases is that when  $N_1 \neq 0$  the number of small systems in the macroscopic solvent or gas (i.e., the number of systems in the "ensemble") is a quantity which is an independent, experimental variable, whereas when  $N_1 = 0$ , the number of small systems (aggregates) is not independently controllable.

**SMALL SYSTEMS WITH  $N_1 \neq 0$ .** When the *solvent contains two or more components*, we can adopt pages 15 to 25, essentially without change, simply by putting  $N_1 = \text{constant}$ . Equations such as (7-103), in which  $N_1$  is varied, are not applicable. The environmental variables are  $\mu_2, p, T$  or  $m_1^s, p, T$ , with  $sc'$  constant. Section 10-5 is concerned with an ensemble of distinguishable systems of this type, and is of course very closely related to the present subsection.

Probably the most important special case is the binding of ions or molecules onto naturally occurring macromolecules, such as proteins, in solution. In this kind of system the macromolecule is not simply an aggregate of  $N_1$  identical monomers (see page 114). Hence,  $N_1$  and  $\hat{\mu}_1$  are not separately defined. However, the product  $X = N_1 \hat{\mu}_1$  is well defined. Thus, for example, we have [Eqs. (7-69) and (7-90)]

$$X = \bar{E} - TS + p\bar{V} - \bar{N}_2\mu_2 \quad (10-183)$$

and

$$dX = - (S - \bar{N}_2 \tilde{s}_1^\square) dT + (\bar{V} - \bar{N}_2 \tilde{v}_1^\square) dp - \bar{N}_2 kT d \ln m_1^s \quad (m_1^s \rightarrow 0, sc'). \quad (10-184)$$

When  $\bar{N}_2 = 0$ , as in Eq. (7-108),

$$\begin{aligned} dX_0 &= - S_0 dT + \bar{V}_0 dp \quad (m_1^s \rightarrow 0, sc') \\ X_0 &= \bar{E}_0 - TS_0 + p\bar{V}_0. \end{aligned} \quad (10-185)$$

Thus, on subtraction,

$$\begin{aligned} d(X - X_0) &= - (S - S_0 - \bar{N}_2 \tilde{s}_1^\square) dT + (\bar{V} - \bar{V}_0 - \bar{N}_2 \tilde{v}_1^\square) dp \\ &\quad - \bar{N}_2 kT d \ln m_1^s \quad (m_1^s \rightarrow 0, sc') \end{aligned} \quad (10-186)$$

$$X - X_0 = (\bar{E} - \bar{E}_0) - T(S - S_0) + p(\bar{V} - \bar{V}_0) - \bar{N}_2\mu_2. \quad (10-187)$$

Usually all these terms have the same order of magnitude.

From Eq. (10-186) we can find  $X - X_0$  by integration over  $m_1^s$  at constant  $T, p$ , and  $sc'$ , as in Eq. (7-113). If  $X - X_0$  is calculated in this way at several temperatures and pressures, we can then use [see Eq. (7-110)]

$$\left(\frac{\partial \ln m_1^s}{\partial T}\right)_{p, sc', X-X_0} = \frac{1}{kT} \left( \tilde{s}_1^\square - \frac{S - S_0}{\bar{N}_2} \right) \quad (m_1^s \rightarrow 0) \quad (10-188)$$

and

$$\left(\frac{\partial \ln m_1^s}{\partial p}\right)_{T, sc', X-X_0} = \frac{1}{kT} \left( \frac{\bar{V} - \bar{V}_0}{\bar{N}_2} - \tilde{v}_1^\square \right) \quad (m_1^s \rightarrow 0) \quad (10-189)$$

to obtain information about  $S$  and  $\bar{V}$ . Equations (10-188) and (10-189) follow from (10-186).

Equation (7-107) provides an analogous expression for  $(\partial S / \partial \bar{N}_2)_{T, p, sc'}$  which can be combined with Eqs. (10-186) and (10-188) to give

$$\begin{aligned} \left[ \frac{\partial(X - X_0)}{\partial T} \right]_{p, \bar{N}_2, sc'} &= \left[ \frac{\partial(X - X_0)}{\partial T} \right]_{p, sc} - \bar{N}_2 kT \left( \frac{\partial \ln m_1^s}{\partial T} \right)_{p, \bar{N}_2, sc'} \\ &= \bar{N}_2 \left( \frac{\partial S}{\partial \bar{N}_2} \right)_{T, p, sc'} - (S - S_0). \end{aligned}$$

Equation (10-229), below, may be consulted for further details.

If we put

$$\mu_2 = \mu_1^* = \tilde{E}_1^\square + p \tilde{v}_1^\square - T \tilde{s}_1^\square \quad (m_1^s \rightarrow 0)$$

in Eq. (10-187), there results

$$\begin{aligned} X - X_0 &= (\bar{E} - \bar{E}_0 - \bar{N}_2 \tilde{E}_1^\square) - T(S - S_0 - \bar{N}_2 \tilde{s}_1^\square) \\ &\quad + p(\bar{V} - \bar{V}_0 - \bar{N}_2 \tilde{v}_1^\square) \quad (m_1^s \rightarrow 0). \end{aligned} \quad (10-190)$$

Since we can find the terms in  $X, S$ , and  $\bar{V}$  from Eqs. (7-113), (10-188), and (10-189), respectively, the term in  $\bar{E}$  may be calculated from Eq. (10-190).

The above are practical equations applicable to adsorption or binding of a dilute solute from solution onto a macromolecule or colloidal particle. Very similar methods have been used in gas adsorption work (see page 25).

If a phase transition occurs in the small systems and the two-state approximation is used, pages 34 to 38 of Chapter 7 apply,

provided that we take  $N_1 = \text{constant}$ . The notation  $X_A = N_1\hat{\mu}_{1A}$  and  $X_B = N_1\hat{\mu}_{1B}$  may be introduced, if necessary. What appear to be experimental examples of phase transitions involving protein molecules have been encountered by Colvin<sup>1</sup> and Foster.<sup>2</sup> In the former case, the adsorbate (component 2) undergoes a transition, whereas in the latter case the protein itself (component 1) does.

When the *solvent contains only one component*, we put  $N_1 = \text{constant}$  in pages 27 to 30, and introduce  $X = N_1\hat{\mu}_1$  whenever  $N_1$  and  $\hat{\mu}_1$  are not separately defined. Examples are the hydration of a protein molecule in water and the adsorption of a gas onto gaseous colloidal particles with invariable  $N_1$ .

Most applications of this subsection will probably be of the type  $\bar{N}_2(\text{maximum}) = O(N_1)$  or  $O(N_1^{2/3})$ . But  $\bar{N}_2 \rightarrow \infty$  is also a possibility, as, for example, in heterogeneous nucleation (the small system serves as a nucleus to start a new phase). These two types of behavior are referred to in Section 10-5.

The remainder of this section is concerned with cases in which  $N_1 = 0$ .

**SMALL SYSTEMS, WITH  $N_1 = 0$ , IN SOLUTION.** We now turn to the important situation in which aggregates are formed in a solution ( $c \geq 2$ ). We consider one-component aggregates first, for simplicity. Two-component aggregates (open with respect to both components) are of considerable interest, but the necessary generalization of the present treatment is straightforward. Hence, we present a separate and brief discussion of this topic later.

First, we re-emphasize (see Section 7-2) that if one of the components of a solution, say 1<sup>s</sup>, produces aggregates or clusters in the solution, the only completely rigorous procedure is to ignore this fact in the thermodynamics. But if the aggregates are well enough defined to be measured (in, say, size and number) by some extra-thermodynamic method, then it is profitable and informative to treat the aggregates as a separate component of the macroscopic solution. The precise definition of an aggregate is arbitrary in so far as pure thermodynamics is concerned. All that is required is that the definition be unambiguous and self-consistent.<sup>3</sup> From an operational point of view, the experimental method used to detect and

<sup>1</sup> J. R. Colvin, *Can. J. Chem.*, **30**, 320 (1952).

<sup>2</sup> See, for example, J. F. Foster and P. Clark, *J. Biol. Chem.*, **237**, 3163 (1962).

<sup>3</sup> See S.M., p. 156.

measure the aggregates imposes the "definition" of an aggregate.

An extreme theoretical definition would be that any cluster (suitably defined) of two or more molecules of  $1^s$  is an "aggregate." There is no objection to this in principle but it does limit the small system thermodynamics (small system = aggregate) to solutions dilute in  $1^s$ . This follows because the macroscopic solution must be dilute enough in aggregates that interactions between them are negligible. A pair-pair interaction is fourth-order in  $1^s$  and would affect, for example, the fourth osmotic pressure virial coefficient. Hence only third-order terms in  $m_1^s$  would be allowable if a cluster of two molecules is considered an "aggregate."

Let us pursue this point a little further. Small system thermodynamics cannot be applied to a macroscopic collection of aggregates which interact significantly with each other. The aggregates must be defined in such a way (made large enough) that the macroscopic system is dilute in aggregates. Consider an example. Suppose that in a moderately dilute soap solution (with added electrolyte) the fraction of soap molecules involved in clusters of size  $N$  is plotted against  $N$ , as in Fig. 10-8 (strictly schematic). Small clusters of

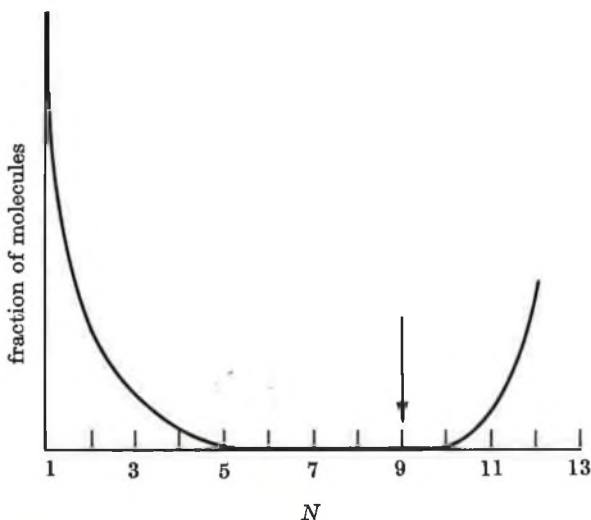


FIGURE 10-8. Fraction of soap molecules involved in clusters of size  $N$  (schematic). Clusters with  $N \geq 9$  are defined as aggregates or small systems.



size  $N = 2$  to 6 are considered to contribute to the nonideality of the solution, but large clusters (micelles;  $N \geq 9$ ) are treated as a new component (aggregates or small systems). The solution represented in the figure may be dilute in micelles or aggregates ( $N \geq 9$ ), but it is certainly not dilute in clusters ( $N \geq 2$ ).

We assume from this point on that aggregates in the macroscopic solution are suitably defined and very dilute. We can adopt the equations of Chapter 7, starting with Eq. (7-62), without a great deal of modification. In the notation of Eq. (7-62),  $N_1 = \text{constant} = 0$  (i.e., we are concerned here with homogeneous rather than heterogeneous nucleation). The number of aggregates (small systems) is  $\mathcal{N}$  and the mean number of molecules of component 2 (that same as  $1^s$ ), per aggregate, is  $\bar{N}_2$ . However, since the aggregate contains only one component, we now drop the subscript 2 from  $\mu_2$  and  $\bar{N}_2$ .

Consider a macroscopic solution containing  $\mathcal{N}$  small systems with mean size  $\bar{N}$  [see Eq. (7-62)]:

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu^\square d\mathcal{N} + \mu \mathcal{N} d\bar{N}. \quad (10-191)$$

It is useful to rewrite this in the form

$$dF_T = -S_T dT + V_T dp + \sum_{j=2}^c \mu_j^s dN_j^s + \mu_1^s d(N_1^s + N_t) \\ + (\mu - \mu_1^s) dN_t + (\mu^\square - \mu \bar{N}) d\mathcal{N}, \quad (10-192)$$

where  $N_t = \mathcal{N} \bar{N}$ . If the macroscopic solution is closed ( $N_j^s, N_1^s + N_t$  constant) and held at constant  $T$  and  $p$ ,

$$dF_T = (\mu - \mu_1^s) dN_t + (\mu^\square - \mu \bar{N}) d\mathcal{N} \leq 0. \quad (10-193)$$

The conditions for aggregation equilibrium are therefore

$$\mu = \mu_1^s, \quad \mu^\square = \mu \bar{N}. \quad (10-194)$$

These are "phase" and "chemical" equilibrium conditions, respectively.

For convenience, write  $\mu - \mu_1^s = \alpha_p$  and  $\mu^\square - \mu \bar{N} = \alpha_c$ . If  $\alpha_p$  and  $\alpha_c$  are chosen as environmental variables of the macroscopic solution instead of  $N_t$  and  $\mathcal{N}$ , we have [compare Eq. (10-112)]

$$d(F_T - \alpha_p \bar{N}_t - \alpha_c \mathcal{N}) = -S_T dT + V_T dp + \sum_{j=2}^c \mu_j^s dN_j^s \\ + \mu_1^s d(\bar{N}_1^s + \bar{N}_t) - \bar{N}_t d\alpha_p - \mathcal{N} d\alpha_c. \quad (10-195)$$

We have put bars over the macroscopic quantities  $N_t$ ,  $\mathcal{N}$ , and  $N_1^s$  here just to emphasize that these variables fluctuate under the conditions of actual interest ( $\alpha_p = \alpha_c = 0$ ):

$$\overline{N_t^2} - \bar{N}_t^2 = kT \left( \frac{\partial \bar{N}_t}{\partial \alpha_p} \right)_{T, p, N_1^s, \bar{N}_1 + \bar{N}_t, \alpha_c} > 0, \quad (10-196)$$

$$\overline{\mathcal{N}^2} - \bar{\mathcal{N}}^2 = kT \left( \frac{\partial \bar{\mathcal{N}}}{\partial \alpha_c} \right)_{T, p, N_1^s, \bar{N}_1 + \bar{N}_t, \alpha_p} > 0. \quad (10-197)$$

The relative fluctuations are normal (small). Stability conditions may be discussed<sup>1</sup> as in Eq. (10-114)ff.

At equilibrium ( $\alpha_p = \alpha_c = 0$ ), all the properties of the macroscopic solution are determined by  $T, p, \bar{N}_1^s, N_j^s$ . Thus, for example,  $\bar{\mathcal{N}}, \bar{N}, \mu$ , and  $\mu^\square$  are functions of these variables. In fact,  $\bar{N}, \mu$ , and  $\mu^\square$  are functions of  $p, T, sc$ , or  $p, T, m_1^s, sc'$ , only. Note especially that  $\bar{\mathcal{N}}$  is a dependent and not an independent variable.

We now return to Eq. (10-191) and proceed much as we did in Chapter 7, although many of the applicable equations in Chapter 7 will not be repeated here. At the outset, the equilibrium conditions ( $\alpha_p = \alpha_c = 0$ ) are not used and the aggregates are treated as an independent, dilute component of the macroscopic solution. That is, we consider temporarily that there are an assigned number  $\mathcal{N}$  of open systems with environmental variables  $\mu, p, T$  immersed in the solvent. Each of the  $\mathcal{N}$  small systems is, of course, in "internal" equilibrium with respect to fluctuations in  $N$  at the chemical potential  $\mu$ . We shall see that introduction of the condition  $\mu^\square = \mu \bar{N}$  determines the equilibrium value of  $\bar{\mathcal{N}}$  and hence removes  $\mathcal{N}$  as an independent variable, whereas the condition  $\mu = \mu_1^s$  serves to bring the solvent, as a reservoir for  $1^s$  molecules, into the picture explicitly.

The basic expressions for  $\mu^\square$  are

$$\mu^\square = \tilde{E}^\square - T\tilde{S}^\square + p\tilde{V}^\square \quad (10-198)$$

$$= F(\bar{N}, p, T, sc) + kT \ln x', \quad (10-199)$$

where

$$F = \mathcal{E}(\bar{N}, p, T, sc) + \bar{N}\mu(\bar{N}, p, T, sc) = \bar{N}\hat{\mu}(\bar{N}, p, T, sc) \quad (10-200)$$

<sup>1</sup> We shall see below that the coefficient of  $d\mathcal{N}$  in Eq. (10-193) is equal to  $\mathcal{E} + kT \ln x'$ , [instead of  $\mathcal{E}$ , as in Eq. (10-105)].

and

$$x' = \frac{\mathcal{N}}{\sum_i N_i^s} \quad \left( \text{or } \frac{\bar{\mathcal{N}}}{\bar{N}_1^s + \sum_j N_j^s} \right).$$

At equilibrium, as already pointed out,  $\bar{N}$  in  $F(\bar{N}, p, T, sc)$ , etc., is itself a function of  $p, T, sc$ .

We also have

$$d\mu^\square = -\bar{s}^\square dT + \bar{v}^\square dp + kT d \ln x' + \beta dm_1^s + \mu d\bar{N} \quad (sc'), \quad (10-201)$$

where  $\beta = (\partial F / \partial m_1^s)_{T, p, \bar{N}, sc}$ .

We define

$$S = \bar{s}^\square + k \ln x', \quad \bar{E} = \bar{e}^\square, \quad \bar{V} = \bar{v}^\square.$$

Equations (10-198) and (10-201) become, then,

$$F = \mathcal{E} + \bar{N}\mu = \bar{N}\hat{\mu} = \bar{E} - TS + p\bar{V} \quad (10-202)$$

$$dF = -S dT + \bar{V} dp + \mu d\bar{N} + \beta dm_1^s \quad (sc'). \quad (10-203)$$

Also,

$$d\mathcal{E} = -S dT + \bar{V} dp - \bar{N} d\mu + \beta dm_1^s \quad (sc'). \quad (10-204)$$

The environmental variables appear in this last equation. At equilibrium, of course,  $\mu$  and  $m_1^s$  are not independent. Unlike the  $N_1 \neq 0$  case (where  $X - X_0$  is the corresponding quantity),  $\mathcal{E}$  is a small term here.

At this point, we introduce the equilibrium conditions. We first note that, at equilibrium,

$$\mu^\square = \bar{N}\mu = \mathcal{E} + \bar{N}\mu + kT \ln x'$$

or

$$\mathcal{E} = \bar{N}(\hat{\mu} - \mu) = -kT \ln x', \quad \mathcal{S} = k \ln x'. \quad (10-205)$$

The number of small systems  $\bar{\mathcal{N}}$ , at equilibrium, is determined by this equation if we regard  $\mathcal{E}$  (and other properties of the individual small systems) as a function of  $\bar{p}, T, m_1^s, sc'$ . Conversely, if  $x'$  is measured experimentally,  $\mathcal{E}$  can be calculated directly from the equation. We observe that  $\mathcal{E}$  is positive and of order  $kT$ . The other terms in Eq. (10-202) are of order  $\bar{N}kT$ . Comparison with Eq. (10-7) shows that  $x'$  plays the formal role of a partition function. This point becomes important in the next subsection.

The second condition,  $\mu = \mu_1^s$ , can be introduced in different ways, as in Chapter 7. For example, if we eliminate  $d\mu$  from Eq. (10-204), we find

$$\begin{aligned} d\mathcal{E} &= -d(kT \ln x') \\ &= -(S - \bar{N}\bar{s}_1^*) dT + (\bar{V} - \bar{N}\bar{v}_1^*) dp \\ &\quad + \left[ \beta - \bar{N} \left( \frac{\partial \mu_1^*}{\partial m_1^s} \right)_{T, p, sc'} \right] dm_1^s \quad (sc'), \end{aligned} \quad (10-206)$$

which is the analogue of Eq. (7-81).

Equation (10-206), and others below that apply to a single small system, are unchanged from Chapter 7, except that here we are dealing with a special case ( $N_1 = \text{constant} = 0$ ). The equilibrium condition  $\mu = \mu_1^s$  has been used in both places. The other condition,  $\mu^\square = \mu\bar{N}$ , does not affect the small system equations *per se*; rather, it provides a subsidiary relation which determines  $x'$  in terms of small system properties. That is, as already mentioned above, the condition  $\mu^\square = \mu\bar{N}$  eliminates  $\mathcal{N}$  as an independent variable; in effect, the macroscopic solution selects that value of  $\bar{\mathcal{N}}$  which minimizes  $F_T$ . When  $N_1 \neq 0$ ,  $\mathcal{N}$  is not adjustable in this way. The present situation resembles that described on page 96ff., of course.

Another form of Eq. (10-206) is

$$\begin{aligned} -kT d \ln x' &= \left( \frac{\bar{N}\bar{h}_1^* - \bar{H}}{T} \right) dT + (\bar{V} - \bar{N}\bar{v}_1^*) dp \\ &\quad + \left( \beta - \bar{N} \frac{\partial \mu_1^*}{\partial m_1^s} \right) dm_1^s \quad (sc'), \end{aligned} \quad (10-207)$$

where

$$\bar{N}\bar{h}_1^* - \bar{H} = T(\bar{N}\bar{s}_1^* - S) - \mathcal{E}. \quad (10-208)$$

From Eq. (10-206), one can immediately obtain expressions for  $\partial\mathcal{E}/\partial T$ ,  $\partial\mathcal{E}/\partial p$ , and  $\partial\mathcal{E}/\partial m_1^s$ . Similarly, Eq. (10-207) provides equations for  $\partial \ln x'/\partial T$ ,  $\partial \ln x'/\partial p$ , and  $\partial \ln x'/\partial m_1^s$ . Also, Eqs. (10-206) and (10-207) give  $\partial m_1^s/\partial T$ ,  $\partial m_1^s/\partial p$ , and  $\partial p/\partial T$ , all at constant  $\mathcal{E}$ , or  $x'$ , respectively. The reader may wish to write out all these relations.

When the solvent is dilute in  $1^s$ , we have the more practical

equation

$$-kT d \ln x' = \left( \frac{\bar{N}_{H_1}^{\square} - \bar{H}}{T} \right) dT + (\bar{V} - \bar{N} \bar{v}_1^{\square}) dp - \bar{N} kT d \ln m_1^s \quad (m_1^s \rightarrow 0, sc'). \quad (10-209)$$

Then, for example,

$$\bar{N} = \left( \frac{\partial \ln x'}{\partial \ln m_1^s} \right)_{T, p, sc'}, \quad \left( \frac{\partial \ln x'}{\partial T} \right)_{p, sc} = \frac{\bar{H} - \bar{N} \bar{v}_1^{\square}}{kT^2} \quad (m_1^s \rightarrow 0) \quad (10-210)$$

$$\left( \frac{\partial \ln m_1^s}{\partial T} \right)_{p, x', sc'} = \frac{1}{kT^2} \left( \bar{v}_1^{\square} - \frac{\bar{H}}{\bar{N}} \right) \quad (m_1^s \rightarrow 0). \quad (10-211)$$

Equation (10-211) resembles Eq. (7-110).

If  $x'(m_1^s)$  is easier to measure than  $\bar{N}$ , Eq. (10-210a) provides a method for obtaining  $\bar{N}$ . On the other hand, if  $\bar{N}(m_1^s)$  is easy to measure, Eq. (10-210) may be integrated to give  $x'$ . The procedure is the following. In the limit  $m_1^s \rightarrow 0$ , suppose  $\bar{N} \rightarrow N_0(T, p, sc')$ .  $N_0$  is the minimum possible value of  $N$ ; it is a quantity independent of  $m_1^s$  but dependent on our definition of an "aggregate." On integrating Eq. (10-210a), we find that the limiting law for  $x'$  is

$$x'_0(m_1^s) = C(T, p, sc')(m_1^s)^{N_0}.$$

The constant of integration  $C$  remains undetermined unless some information is at hand which allows us to evaluate it. Next, we note that

$$\bar{N} - N_0 = \left( \frac{\partial \ln x'/x'_0}{\partial \ln m_1^s} \right)_{T, p, sc'} \quad (m_1^s \rightarrow 0). \quad (10-212)$$

If we integrate this equation from  $m_1^s = 0$  to  $m_1^s = m'$ , the desired result is

$$\ln x'(m') = \ln C m'^{N_0} + \int_0^{m'} \frac{[\bar{N}(m_1^s) - N_0]}{m_1^s} dm_1^s \quad (m_1^s \rightarrow 0). \quad (10-213)$$

Incidentally, the generalization of Henry's law is

$$\bar{N} - N_0 = k_1^s(T, p, sc') m_1^s. \quad (10-214)$$

Let us digress to consider an example. Suppose we are given (the notation is simplified in an obvious way)

$$\bar{N} = N_0 + am + bm^2 + \dots \quad (10-215)$$

and the "constant"  $C$ . Then Eq. (10-213) leads to

$$\ln x'(m) = \ln Cm^{N_0} + am + \frac{b}{2}m^2 + \dots = -\frac{\mathcal{E}}{kT} \quad (10-216)$$

and

$$x'(m) = Cm^{N_0} + aCm^{N_0+1} + \left(\frac{b+a^2}{2}\right)Cm^{N_0+2} + \dots \quad (10-217)$$

$$= x'_{N_0} + x'_{N_0+1} + x'_{N_0+2} + \dots, \quad (10-218)$$

where  $x'_N = \bar{\mathcal{N}}_N / \Sigma_i N_i^s$  and  $\bar{\mathcal{N}}_N$  is the mean number of aggregates of size  $N$ . An alternative expression for  $\bar{N}$  is

$$\bar{N} = \frac{N_0 x'_{N_0} + (N_0 + 1)x'_{N_0+1} + (N_0 + 2)x'_{N_0+2} + \dots}{x'}. \quad (10-219)$$

This follows from

$$\bar{N} = \frac{m}{x'} \frac{\partial x'}{\partial m}.$$

We have mentioned that  $x'$  resembles a partition function. This is confirmed in Eq. (10-219) where  $x'$  is a sum of weights (a standard property of a partition function).

If  $N_0$  is large, say,  $N_0 \geq 10-20$ ,  $x'(m)$  in Eq. (10-217) will be practically zero as  $m$  increases from zero until  $m$  reaches a fairly sharp critical value (the "critical micelle concentration"), at which point  $x'$  will increase rapidly. This follows because of the assumed high power of  $m$  in  $Cm^{N_0}$ . This "sharp" behavior is reminiscent of that in a phase transition (condensation), the more so as  $N_0$  increases. In fact, this discussion is closely related to the Frenkel-Band approximate theory of condensation.<sup>1</sup>

The conventional approach to this kind of example is in terms of aggregation equilibrium constants:

$$K_{N_0} = \frac{x'_{N_0}}{m^{N_0}}, \quad K_{N_0+1} = \frac{x'_{N_0+1}}{m^{N_0+1}}, \quad \text{etc.} \quad (10-220)$$

<sup>1</sup> See S.M., p. 147.

Then

$$x'_{N_0} = C m^{N_0} = K_{N_0} m^{N_0}, \quad x'_{N_0+1} = a C m^{N_0+1} = K_{N_0+1} m^{N_0+1}, \quad \text{etc.}$$

Thus the correspondences in notation are

$$C = K_{N_0}, \quad aC = K_{N_0+1}, \quad \left( \frac{b+a^2}{2} \right) C = K_{N_0+2}, \quad \text{etc.} \quad (10-221)$$

The advantage of the present treatment is that considerations of the above sort are tied into a complete discussion of the thermodynamic properties of the aggregates. For example, use of Eqs. (10-209) to (10-211) permits evaluation of the separate terms in

$$\mathcal{E} = -kT \ln x' = (\bar{E} - \bar{N} \bar{E}_1^\square) - T(S - \bar{N} \bar{S}_1^\square) + p(\bar{V} - \bar{N} \bar{V}_1^\square). \quad (10-222)$$

Instead of putting  $d\mu = d\mu_1^s$  in Eq. (10-204), we can use this relation directly. We start with

$$d\mu = \frac{\partial \mu}{\partial T} dT + \frac{\partial \mu}{\partial p} dp + \frac{\partial \mu}{\partial \bar{N}} d\bar{N} + \frac{\partial \mu}{\partial m_1^s} dm_1^s \quad (sc').$$

From Eq. (10-203),

$$\frac{\partial \mu}{\partial T} = - \left( \frac{\partial S}{\partial \bar{N}} \right)_{T, p, sc}, \quad \frac{\partial \mu}{\partial p} = \left( \frac{\partial \bar{V}}{\partial \bar{N}} \right)_{T, p, sc}, \quad \frac{\partial \mu}{\partial m_1^s} = \left( \frac{\partial \beta}{\partial \bar{N}} \right)_{T, p, sc}.$$

Therefore,

$$d\mu = - \left( \frac{\partial S}{\partial \bar{N}} \right)_{T, p, sc} dT + \left( \frac{\partial \bar{V}}{\partial \bar{N}} \right)_{T, p, sc} dp + \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{T, p, sc} d\bar{N} + \left( \frac{\partial \beta}{\partial \bar{N}} \right)_{T, p, sc} dm_1^s \quad (sc'). \quad (10-223)$$

We set this equal to  $d\mu_1^s$ , as given by Eq. (7-80). We can select six pairs from  $dT$ ,  $dp$ ,  $d\bar{N}$ , and  $dm_1^s$ , and hence there are six equations of the Clausius-Clapeyron type. Only three of these are independent, however. The most important set is probably

$$\left( \frac{\partial \bar{N}}{\partial T} \right)_{p, sc} = \left[ \left( \frac{\partial S}{\partial \bar{N}} \right)_{T, p, sc} - \bar{S}_1^* \right] / \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{T, p, sc} \quad (10-224)$$

$$\left( \frac{\partial \bar{N}}{\partial p} \right)_{T, sc} = \left[ \bar{V}_1^* - \left( \frac{\partial \bar{V}}{\partial \bar{N}} \right)_{T, p, sc} \right] / \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{T, p, sc} \quad (10-225)$$

$$\left(\frac{\partial \bar{N}}{\partial m_1^s}\right)_{T, p, sc'} = \left[ \left(\frac{\partial \mu_1^*}{\partial m_1^s}\right)_{T, p, sc'} - \left(\frac{\partial \beta}{\partial \bar{N}}\right)_{T, p, sc'} \right] / \left(\frac{\partial \mu}{\partial \bar{N}}\right)_{T, p, sc'}. \quad (10-226)$$

When  $m_1^s$  is small,

$$\left(\frac{\partial \bar{N}}{\partial m_1^s}\right)_{T, p, sc'} = \frac{kT/m_1^s}{(\partial \mu / \partial \bar{N})_{T, p, sc'}} \quad (m_1^s \rightarrow 0). \quad (10-227)$$

In the example in Eq. (10-215)ff.,

$$kT \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T, p, sc'} = m \left(\frac{\partial \bar{N}}{\partial m}\right)_{T, p, sc'} = m(a + 2bm + \dots).$$

If we use the inverse of Eq. (10-215), that is,

$$m = \frac{1}{a}(\bar{N} - N_0) - \frac{b}{a^3}(\bar{N} - N_0)^2 + \dots,$$

to eliminate  $m$ , we obtain

$$kT \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T, p, sc'} = (\bar{N} - N_0) + \frac{b}{a^2}(\bar{N} - N_0)^2 + \dots.$$

Integration shows that  $\mu(\bar{N})$  has the form

$$\frac{\mu}{kT} = f(T, p, sc') + \ln(\bar{N} - N_0) - \frac{b}{a^2}(\bar{N} - N_0) + \dots, \quad (10-228)$$

where  $f$  is an integration constant. The same result follows directly from Eq. (7-88). The notational correspondence is

$$f = \frac{\mu^\Delta}{kT} - \ln a.$$

If we eliminate  $\partial \mu / \partial \bar{N}$  from Eqs. (10-224) and (10-225) using (10-227), we see that measurement of  $\partial \bar{N} / \partial T$  and  $\partial \bar{N} / \partial m_1^s$  will provide  $(\partial S / \partial \bar{N}) - \bar{s}_1^\square$ , whereas measurement of  $\partial \bar{N} / \partial p$  and  $\partial \bar{N} / \partial m_1^s$  will give  $\bar{v}_1^\square - (\partial \bar{V} / \partial \bar{N})$ .

We can change independent variables in Eq. (10-206) from  $T, p, m_1^s$ , to  $T, p, \bar{N}$ , as in Eq. (2-23), by substituting

$$\begin{aligned} dm_1^s = & \left(\frac{\partial m_1^s}{\partial T}\right)_{p, \bar{N}, sc'} dT + \left(\frac{\partial m_1^s}{\partial p}\right)_{T, \bar{N}, sc'} dp \\ & + \left(\frac{\partial m_1^s}{\partial \bar{N}}\right)_{T, p, sc'} d\bar{N} \quad (sc'). \end{aligned}$$



Expressions for the coefficients appearing here follow from Eqs. (10-224) to (10-226). The resultant equation for  $d\mathcal{E}$  is rather complicated because of terms in  $\beta$ . But when  $m_1^s$  is small,

$$d\mathcal{E} = - \left[ S - \bar{N} \left( \frac{\partial S}{\partial \bar{N}} \right)_{T, p, sc'} \right] dT + \left[ \bar{V} - \bar{N} \left( \frac{\partial \bar{V}}{\partial \bar{N}} \right)_{T, p, sc'} \right] dp - \bar{N} \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{T, p, sc'} d\bar{N} \quad (m_1^s \rightarrow 0, sc'), \quad (10-229)$$

as in Eq. (2-23). In the derivatives  $\partial\mathcal{E}/\partial T$  and  $\partial\mathcal{E}/\partial p$ ,  $m_1^s$  is varied, along with  $T$  or  $p$ , respectively, in such a way that  $\bar{N}$  remains constant.

There is a final topic that should be mentioned, one which is also of interest in Chapters 2 and 7. In Eq. (10-199) we introduced the convenient composition variable  $x'$ . But this choice is somewhat arbitrary. Suppose we use a new variable  $x'/\epsilon$  instead of  $x'$ , where  $\epsilon$  is a constant or any function<sup>1</sup> of the  $N_i^s$ . That is,

$$\begin{aligned} \mu^\square &= F_\epsilon + kT \ln \frac{x'}{\epsilon} \\ F_\epsilon &= \mathcal{E}_\epsilon + \bar{N}\mu = \bar{N}\hat{\mu}_\epsilon \\ &= F + kT \ln \epsilon = \bar{N}\hat{\mu} + kT \ln \epsilon \\ &= \mathcal{E} + \bar{N}\mu + kT \ln \epsilon \\ \mathcal{E}_\epsilon &= \mathcal{E} + kT \ln \epsilon. \end{aligned}$$

The chemical potential  $\mu$  is defined in Eq. (10-191) and is unaffected. Also,  $\bar{E}$  and  $\bar{V}$  are unchanged. The definition of  $S_\epsilon$  is

$$S_\epsilon = \bar{s}^\square + k \ln \frac{x'}{\epsilon} = S - k \ln \epsilon.$$

Equations (10-202) to (10-204) become

$$\begin{aligned} F_\epsilon &= \bar{E} - TS_\epsilon + p\bar{V} \\ dF_\epsilon &= -S_\epsilon dT + \bar{V} dp + \mu d\bar{N} + \beta_\epsilon dm_1^s \quad (sc') \\ d\mathcal{E}_\epsilon &= -S_\epsilon dT + \bar{V} dp - \bar{N} d\mu + \beta_\epsilon dm_1^s \quad (sc'), \end{aligned}$$

<sup>1</sup> We do not allow  $\epsilon$  to be a function of  $p$  or  $T$  because this would introduce complications. For example, we could no longer replace  $\partial\mu^\square/\partial T$  by  $-\bar{s}^\square$  in Eq. (10-201). If  $\epsilon$  does depend on  $p$  or  $T$  (e.g.,  $x'/\epsilon$  is  $\mathcal{N}/V_T$ ), this dependence can be ignored—as a good approximation.

where

$$\beta_\epsilon = \left( \frac{\partial F_\epsilon}{\partial m_1^s} \right)_{T, p, \bar{N}, sc'} = \beta + kT \left( \frac{\partial \ln \epsilon}{\partial m_1^s} \right)_{sc'}.$$

The equilibrium condition  $\mu = \mu_1^s$  is not involved. But the other equilibrium condition becomes

$$\mu^\square = \bar{N}\mu = \mathcal{E}_\epsilon + \bar{N}\mu + kT \ln \frac{x'}{\epsilon},$$

or

$$\mathcal{E}_\epsilon = -kT \ln \frac{x'}{\epsilon}.$$

We see, in conclusion, that although some of the functions have different definitions, the formal appearance of all the basic equations is unchanged if  $x'$  is replaced by a different composition variable  $x'/\epsilon$ .

**DETAILED ANALYSIS OF EQUILIBRIUM.** It is instructive to investigate the alternative but equivalent approach in which we keep explicit account of each subspecies of aggregate:  $N = N_0, N_0 + 1, \dots$ . This is an essentially nonoperational or quasi statistical mechanical method as it presumes the knowledge or measurability of the properties of each of the separate subspecies. The same is true, of course, when we use  $K_{N_0}, K_{N_0+1}$ , etc., in Eq. (10-220). This type of discussion could also be applied to Section 7-2.

We start with [compare Eq. (10-191)]

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \sum_{N \geq N_0} \mu_N^\square d\mathcal{N}_N, \quad (10-230)$$

where subscript  $N$  refers to the subspecies of size  $N$ . The macroscopic solution is dilute with respect to all subspecies. The small systems interact with each other only through the aggregation equilibrium. At equilibrium, with

$$T, p, N_j^s, \text{ and } N_1^s + \sum_N \mathcal{N}_N \text{ constant,}$$

$$dF_T = 0 = \sum_N (\mu_N^\square - \mu_1^s N) d\mathcal{N}_N.$$

That is,

$$\mu_N^{\square} = \mu_1^s N \quad (N = N_0, N_0 + 1, \dots). \quad (10-231)$$

This set of conditions corresponds to the establishment of equilibrium with respect to fluctuations in  $N$  for each small system and also determines the equilibrium number of small systems of size  $N$ ,  $\bar{\mathcal{N}}_N$ .

Equations (10-191) and (10-230) are equivalent (i.e., refer to the same macroscopic system) at and only at equilibrium, when they both become

$$dF_T = -S_T dT + V_T dp + \sum_{j=2}^c \mu_j^s dN_j^s + \mu_1^s d(\bar{N}_1^s + \bar{\mathcal{N}}\bar{N}),$$

since

$$\sum_N N d\bar{\mathcal{N}}_N = d\left(\sum_N N \bar{\mathcal{N}}_N\right) = d(\bar{\mathcal{N}}\bar{N}).$$

We have put bars over the quantities which fluctuate at equilibrium. Also at equilibrium, from Eqs. (10-194) and (10-231),

$$\sum_N P_N \mu_N^{\square} = \mu_1^s \sum_N P_N N = \mu_1^s \bar{N} = \mu^{\square}, \quad (10-232)$$

where  $P_N = \bar{\mathcal{N}}_N / \bar{\mathcal{N}}$ , the fraction of aggregates of size  $N$ .

For subspecies  $N$ , we write [see Eq. (2-119)]

$$\mu_N^{\square} = N \hat{\mu}_N(p, T, sc) + kT \ln x'_N, \quad (10-233)$$

where  $x'_N = \bar{\mathcal{N}}_N / \sum_i \bar{\mathcal{N}}_i^s$ . At equilibrium,

$$\mu_N^{\square} = \mu_1^s N = N \hat{\mu}_N + kT \ln x'_N, \quad (10-234)$$

or

$$x'_N = \exp \left[ \frac{N(\mu_1^s - \hat{\mu}_N)}{kT} \right] = e^{-N \hat{\mu}_N / kT \lambda^N} \quad (N = N_0, N_0 + 1, \dots), \quad (10-235)$$

with  $\lambda = e^{\mu_1^s / kT}$ . This equation determines the equilibrium number of aggregates of size  $N$ ,  $\bar{\mathcal{N}}_N$ , if  $\hat{\mu}_N(p, T, sc)$  and  $\mu_1^s(p, T, sc)$  are known. It should be compared with Eqs. (10-218) and (10-220). Since  $\lambda = e^{\mu^{\Delta} / kT} m$  in this example, the correspondence in notation is

$$K_N = e^{-N \hat{\mu}_N / kT} e^{N \mu^{\Delta} / kT} \quad (N = N_0, N_0 + 1, \dots). \quad (10-236)$$

Let us sum Eq. (10-235) over  $N$ :

$$x' = \sum_{N \geq N_0} e^{-N \hat{\mu}_N / kT \lambda^N} = \sum_N \Delta_N(p, T, sc) \lambda(p, T, sc)^N, \quad (10-237)$$

where

$$\Delta_N \equiv e^{-N\hat{\mu}_N/kT}.$$

We see that  $x'$  has the formal appearance of a partition function<sup>1</sup> for a completely open system [see Eq. (10-10)]. Note that

$$P_N = \frac{\bar{\mathcal{N}}_N}{\bar{\mathcal{N}}} = \frac{x'_N}{x'} = \frac{\Delta_N \lambda^N}{\sum_N \Delta_N \lambda^N}. \quad (10-238)$$

If we multiply Eq. (10-234) by  $P_N$ , sum over  $N$ , and use Eq. (10-232), there results

$$\sum_N P_N \mu_N^\square = \mu_1^s \bar{N} = \mu^\square = \sum_N P_N N \hat{\mu}_N + kT \sum_N P_N \ln P_N + kT \ln x'. \quad (10-239)$$

The correspondence with the notation in Eqs. (10-199) and (10-200) is seen to be

$$\bar{N} \hat{\mu} = \sum_N P_N N \hat{\mu}_N + kT \sum_N P_N \ln P_N \quad (10-240)$$

and

$$\begin{aligned} \mathcal{E} &= \bar{N}(\hat{\mu} - \mu_1^s) \\ &= -kT \ln x' = -kT \ln \sum_N \Delta_N \lambda^N, \end{aligned} \quad (10-241)$$

as in Eq. (10-7). If we define  $\mathcal{E}_N$  by  $N(\hat{\mu}_N - \mu_1^s)$ , then

$$\mathcal{E} = \sum_N P_N \mathcal{E}_N + kT \sum_N P_N \ln P_N \quad (10-242)$$

and

$$x' = e^{-\mathcal{E}/kT} = \sum_N e^{-\mathcal{E}_N/kT}, \quad (10-243)$$

as in Eq. (10-10).

Now we turn to the relation

$$\mu_N^\square = \tilde{\mathbf{E}}_N^\square - T \tilde{\mathbf{S}}_N^\square + p \tilde{\mathbf{V}}_N^\square$$

for each subspecies (at equilibrium), multiply by  $P_N$ , and sum over  $N$ :

$$\begin{aligned} \sum_N P_N \mu_N^\square = \mu^\square &= \sum_N P_N \tilde{\mathbf{E}}_N^\square - T \sum_N P_N \tilde{\mathbf{S}}_N^\square + p \sum_N P_N \tilde{\mathbf{V}}_N^\square \\ &= \tilde{\mathbf{E}}^\square - T \tilde{\mathbf{S}}^\square + p \tilde{\mathbf{V}}^\square. \end{aligned} \quad (10-244)$$

<sup>1</sup> This is not surprising in view of the quasi statistical mechanical nature of the discussion.

Thus,  $\bar{s}^\square = \sum_N P_N \bar{s}_N^\square$ . Similarly, starting with the subspecies equation

$$d\mu_N^\square = -\bar{s}_N^\square dT + \bar{v}_N^\square dp + kT d \ln x'_N + \beta_N dm_1^s \quad (sc'),$$

we find on summing,

$$\sum_N P_N d\mu_N^\square = -\bar{s}^\square dT + \bar{v}^\square dp + kT \sum_N P_N d \ln x'_N + \beta dm_1^s \quad (sc'),$$

(10-245)

where  $\beta = \sum_N P_N \beta_N$ . If we use

$$d\mu^\square = \sum_N \mu_N^\square dP_N + \sum_N P_N d\mu_N^\square$$

$$\sum_N \mu_N^\square dP_N = \mu_1^s \sum_N N dP_N = \mu_1^s d\bar{N}$$

and

$$\sum_N P_N d \ln x'_N = \frac{1}{x'} \sum_N dx'_N = d \ln x',$$

Eq. (10-245) becomes

$$d\mu^\square = -\bar{s}^\square dT + \bar{v}^\square dp + kT d \ln x' + \beta dm_1^s + \mu_1^s d\bar{N} \quad (sc'),$$

(10-246)

which is the same as Eq. (10-201), at equilibrium. Incidentally, since

$$S_N = \bar{s}_N^\square + k \ln x'_N \quad \text{and} \quad S = \bar{s}^\square + k \ln x',$$

it follows that

$$S = \sum_N P_N S_N - k \sum_N P_N \ln P_N. \quad (10-247)$$

The last term has the same physical significance as, for example, in Eqs. (10-43) and (10-70). Equation (10-247) also follows from

$$\begin{aligned} \mathcal{E}_N &= \bar{E}_N - TS_N + p\bar{V}_N + \mu_1^s N, \\ \mathcal{E} &= \bar{E} - TS + p\bar{V} + \mu_1^s \bar{N}, \end{aligned} \quad (10-248)$$

and Eq. (10-242).

In all these equations the point of view would generally be that  $\mu_1^s(p, T, sc)$  and the  $\mu_N(p, T, sc)$  are known, and from these we can calculate the equilibrium aggregation properties:  $x'_N$ ,  $x'$ ,  $P_N$ ,  $\bar{N}$ ,  $\bar{\mu}$ ,  $\mathcal{E}$ , etc.

An exact equilibrium "constant" can be defined if we replace  $m_1^s$

by the molality activity  $a_1^s(p, T, sc)$  in Eq. (7-88):

$$\frac{x'_N}{(a_1^s)^N} = e^{-N\hat{\mu}_N/kT} e^{N\mu_1^A/kT} = K_N. \quad (10-249)$$

The quotient on the left does not have quite the usual significance, however, because the right-hand side is not "constant" in the conventional sense:  $\hat{\mu}_N$  is a function of  $m_1^s$  as well as of  $p, T, sc'$  (the interaction of the  $N$ -aggregate with the solvent depends on the solvent composition, which depends, in turn, on  $m_1^s$ ). But when  $m_1^s$  is small, the quotient  $x'_N/(m_1^s)^N$  is equal to a true equilibrium constant: the right-hand side of Eq. (10-249) becomes a function of  $p, T$ , and  $sc'$  only. In this case it is easy to show that

$$\left(\frac{\partial \ln K_N}{\partial p}\right)_{T, sc'} = \frac{N\bar{v}_1^\square - \bar{V}_N}{kT} \quad (m_1^s \rightarrow 0) \quad (10-250)$$

$$\left(\frac{\partial \ln K_N}{\partial T}\right)_{p, sc'} = \frac{\bar{H}_N - N\bar{H}_1^\square}{kT^2} \quad (m_1^s \rightarrow 0). \quad (10-251)$$

The fluctuation in  $N$ ,  $\overline{N^2} - \bar{N}^2$ , at equilibrium, follows from

$$\bar{N} = \frac{1}{x'} \sum_N N \Delta_N \lambda^N \quad \text{and} \quad \overline{N^2} = \frac{1}{x'} \sum_N N^2 \Delta_N \lambda^N. \quad (10-252)$$

There is also the formal relation

$$\lambda \left( \frac{\partial \bar{N}}{\partial \lambda} \right)_{\Delta_N} = \overline{N^2} - \bar{N}^2. \quad (10-253)$$

The differential coefficients in Eqs. (10-204) and (10-206) may be verified by differentiating the "partition function" in Eq. (10-237). In the former case, the derivatives are "formal," as in Eq. (10-253).

**TWO-COMPONENT AGGREGATES IN A SOLVENT.** Suppose an aggregate in solution can bind another species from the solution. An example is the binding of hydrogen ions by a soap micelle. The aggregate is then a two-component small system, open with respect to both components. There may also be cases in which such an aggregate contains two components of similar size.

We give a rather condensed treatment of two-component aggregates here. The reader may wish to employ the basic equations given below to pursue the analysis further.

For simplicity, we use a special notation to designate components in this subsection. The notation is not quite the same as in the remainder of the section. The species  $1^s$  and  $2^s$  in the solvent form aggregates with components designated 1 and 2, respectively ( $1^s \rightleftharpoons 1$ ;  $2^s \rightleftharpoons 2$ ). The other solvent species are  $3^s, \dots, c^s$ . The molality of  $1^s$  is  $m_1^s = 1000N_1^s/(N_3^s + \dots + N_c^s)M$  (see page 15), with a similar expression for  $2^s$ . We still denote  $\mathcal{N}/\sum_i N_i^s$  by  $x'$ . The solvent composition ( $sc$ ) depends on  $m_1^s$ ,  $m_2^s$ , and the relative composition of components  $3^s, \dots, c^s$  ( $sc'$ ).

Again, some criterion must be selected as the definition of an aggregate. This criterion may depend on one or both components (e.g., an aggregate might be defined by  $N_1 \geq N_0$ ,  $N_2 \geq 0$ ).

We write, for the macroscopic solution,

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu^\square d\mathcal{N} \\ + \mu_1 \mathcal{N} d\bar{N}_1 + \mu_2 \mathcal{N} d\bar{N}_2 \quad (10-254)$$

$$= -S_T dT + V_T dp + \sum_{j=3}^c \mu_j^s dN_j^s + \mu_1^s d(N_1^s + N_{t1}) \\ + (\mu_1 - \mu_1^s) dN_{t1} + \mu_2^s d(N_2^s + N_{t2}) + (\mu_2 - \mu_2^s) dN_{t2} \\ + (\mu^\square - \mu_1 \bar{N}_1 - \mu_2 \bar{N}_2) d\mathcal{N}, \quad (10-255)$$

where  $N_{t1} = \mathcal{N} \bar{N}_1$  and  $N_{t2} = \mathcal{N} \bar{N}_2$ . The equilibrium conditions are

$$\mu_1 = \mu_1^s, \quad \mu_2 = \mu_2^s, \quad \mu^\square = \mu_1 \bar{N}_1 + \mu_2 \bar{N}_2. \quad (10-256)$$

Equation (10-198) is unchanged but

$$\mu^\square = F(\bar{N}_1, \bar{N}_2, p, T, sc) + kT \ln x' \quad (10-257)$$

$$F = \mathcal{E} + \bar{N}_1 \mu_1 + \bar{N}_2 \mu_2 \quad (10-258)$$

$$d\mu^\square = -\tilde{s}^\square dT + \tilde{v}^\square dp + kT d \ln x' + \beta_1 dm_1^s + \beta_2 dm_2^s \\ + \mu_1 d\bar{N}_1 + \mu_2 d\bar{N}_2 \quad (sc'), \quad (10-259)$$

with

$$\beta_1 = \left( \frac{\partial F}{\partial m_1^s} \right)_{T, p, m_2^s, \bar{N}_1, \bar{N}_2, sc'}, \quad \text{etc.}$$

Note that  $\partial \beta_1 / \partial m_2^s = \partial \beta_2 / \partial m_1^s$  and  $\partial \mu_1 / \partial \bar{N}_2 = \partial \mu_2 / \partial \bar{N}_1$ .

The definitions of  $S$ ,  $\bar{E}$ , and  $\bar{V}$  are the same as before. Therefore Eqs. (10-198) and (10-259) lead to

$$F = \mathcal{E} + \bar{N}_1\mu_1 + \bar{N}_2\mu_2 = \bar{E} - TS + p\bar{V} \quad (10-260)$$

$$dF = -S dT + \bar{V} dp + \mu_1 d\bar{N}_1 + \mu_2 d\bar{N}_2 + \beta_1 dm_1^s + \beta_2 dm_2^s \quad (sc') \quad (10-261)$$

$$d\mathcal{E} = -S dT + \bar{V} dp - \bar{N}_1 d\mu_1 - \bar{N}_2 d\mu_2 + \beta_1 dm_1^s + \beta_2 dm_2^s \quad (sc'). \quad (10-262)$$

On combining Eqs. (10-256) to (10-258), we find that, at equilibrium, we still have the relation

$$\mathcal{E} = -kT \ln x'. \quad (10-263)$$

We now substitute

$$\begin{aligned} d\mu_1 = d\mu_1^s = d\mu_1^* = -\tilde{s}_1^* dT + \tilde{v}_1^* dp + \left(\frac{\partial\mu_1^*}{\partial m_1^s}\right)_{T, p, m_2^s, sc'} dm_1^s \\ + \left(\frac{\partial\mu_1^*}{\partial m_2^s}\right)_{T, p, m_1^s, sc'} dm_2^s \quad (sc'), \end{aligned} \quad (10-264)$$

and a similar expression for  $d\mu_2$ , in place of  $d\mu_1$  and  $d\mu_2$  in Eq. (10-262). The result is the equilibrium relation

$$\begin{aligned} d\mathcal{E} = (-S + \bar{N}_1\tilde{s}_1^* + \bar{N}_2\tilde{s}_2^*) dT + (\bar{V} - \bar{N}_1\tilde{v}_1^* - \bar{N}_2\tilde{v}_2^*) dp \\ + \left(\beta_1 - \bar{N}_1\frac{\partial\mu_1^*}{\partial m_1^s} - \bar{N}_2\frac{\partial\mu_2^*}{\partial m_1^s}\right) dm_1^s \\ + \left(\beta_2 - \bar{N}_1\frac{\partial\mu_1^*}{\partial m_2^s} - \bar{N}_2\frac{\partial\mu_2^*}{\partial m_2^s}\right) dm_2^s \quad (sc'). \end{aligned} \quad (10-265)$$

It is easy to verify that  $\partial\mu_1^*/\partial m_2^s = \partial\mu_2^*/\partial m_1^s$ . Equation (10-263) may be used to introduce  $d \ln x'$  in place of  $d\mathcal{E}$ . Equations for  $\partial\mathcal{E}/\partial T$ ,  $\partial\mathcal{E}/\partial m_1^s$ ,  $\partial m_1^s/\partial m_2^s$ , etc. (there are ten of these), may now be derived.

The equilibrium relation

$$\bar{N}_1\tilde{H}_2^* + \bar{N}_2\tilde{H}_2^* - \bar{H} = T(\bar{N}_1\tilde{s}_1^* + \bar{N}_2\tilde{s}_2^* - S) - \mathcal{E} \quad (10-266)$$

may be useful above.



When the solvent is dilute in both 1<sup>s</sup> and 2<sup>s</sup>,

$$\mu_{\alpha}^* = \mu_{\alpha}^{\Delta}(p, T, sc') + kT \ln m_{\alpha}^s \quad (\alpha = 1, 2). \quad (10-267)$$

Then

$$\begin{aligned} -kT d \ln x' = & \left( \frac{\bar{N}_1 \tilde{H}_1^{\square} + \bar{N}_2 \tilde{H}_2^{\square} - \bar{H}}{T} \right) dT \\ & + (\bar{V} - \bar{N}_1 \tilde{v}_1^{\square} - \bar{N}_2 \tilde{v}_2^{\square}) dp - \bar{N}_1 kT d \ln m_1^s \\ & - \bar{N}_2 kT d \ln m_2^s \quad (m_{\alpha}^s \rightarrow 0, sc'). \end{aligned} \quad (10-268)$$

Measurement of the dependence of  $x'$  on  $m_1^s$  and  $m_2^s$  gives  $\bar{N}_1$  and  $\bar{N}_2$ :

$$\bar{N}_1 = \left( \frac{\partial \ln x'}{\partial \ln m_1^s} \right)_{T, p, m_2^s, sc'}, \quad \bar{N}_2 = \left( \frac{\partial \ln x'}{\partial \ln m_2^s} \right)_{T, p, m_1^s, sc'} \quad (m_{\alpha}^s \rightarrow 0). \quad (10-269)$$

Also,

$$\left( \frac{\partial \bar{N}_1}{\partial \ln m_2^s} \right)_{T, p, m_1^s, sc'} = \left( \frac{\partial \bar{N}_2}{\partial \ln m_1^s} \right)_{T, p, m_2^s, sc'} \quad (m_{\alpha}^s \rightarrow 0). \quad (10-270)$$

Many other relations follow from Eq. (10-268), but we leave these to the reader.

Equations involving  $\bar{N}_1$  and  $\bar{N}_2$  as independent variables follow from

$$\begin{aligned} d\mu_1 = & - \frac{\partial S}{\partial \bar{N}_1} dT + \frac{\partial \bar{V}}{\partial \bar{N}_1} dp + \frac{\partial \mu_1}{\partial \bar{N}_1} d\bar{N}_1 + \frac{\partial \mu_2}{\partial \bar{N}_1} d\bar{N}_2 \\ & + \frac{\partial \beta_1}{\partial \bar{N}_1} dm_1^s + \frac{\partial \beta_2}{\partial \bar{N}_1} dm_2^s \\ = & d\mu_1^* = - \tilde{s}_1^* dT + \tilde{v}_1^* dp + \frac{\partial \mu_1^*}{\partial m_1^s} dm_1^s + \frac{\partial \mu_1^*}{\partial m_2^s} dm_2^s \quad (sc') \end{aligned} \quad (10-271)$$

and  $d\mu_2 = d\mu_2^*$ . All the derivatives in the first line are at constant  $T, p, \bar{N}_2$ , and  $sc$ . Equation (10-271) and the corresponding equation for component 2 involve six differentials ( $dT, dp$ , etc.), but provide two relations between them. Thus four variables are independent. When the solvent is dilute in 1<sup>s</sup> and 2<sup>s</sup>, we have the simpler pair of

equations

$$\begin{aligned}
 -\frac{\partial S}{\partial \bar{N}_1} dT + \frac{\partial \bar{V}}{\partial \bar{N}_1} dp + \frac{\partial \mu_1}{\partial \bar{N}_1} d\bar{N}_1 + \frac{\partial \mu_2}{\partial \bar{N}_1} d\bar{N}_2 &= -\tilde{s}_1^\square dT \\
 &+ \tilde{v}_1^\square dp + kT d \ln m_1^s \quad (m_\alpha^s \rightarrow 0, sc') \\
 -\frac{\partial S}{\partial \bar{N}_2} dT + \frac{\partial \bar{V}}{\partial \bar{N}_2} dp + \frac{\partial \mu_1}{\partial \bar{N}_2} d\bar{N}_1 + \frac{\partial \mu_2}{\partial \bar{N}_2} d\bar{N}_2 &= -\tilde{s}_2^\square dT \\
 &+ \tilde{v}_2^\square dp + kT d \ln m_2^s.
 \end{aligned} \quad (10-272)$$

Examples of deductions from Eqs. (10-272) are

$$\left( \frac{\partial \ln m_1^s}{\partial T} \right)_{p, \bar{N}_1, \bar{N}_2, sc'} = \frac{1}{kT} \left[ \tilde{s}_1^\square - \left( \frac{\partial S}{\partial \bar{N}_1} \right)_{T, p, \bar{N}_2, sc'} \right] \quad (m_\alpha^s \rightarrow 0) \quad (10-273)$$

$$\left( \frac{\partial \bar{N}_1}{\partial \ln m_1^s} \right)_{T, p, \bar{N}_2, sc'} = \frac{kT}{(\partial \mu_1 / \partial \bar{N}_1)_{T, p, \bar{N}_2, sc'}} \quad (m_\alpha^s \rightarrow 0) \quad (10-274)$$

$$\left( \frac{\partial \bar{N}_2}{\partial \ln m_1^s} \right)_{T, p, \bar{N}_1, sc'} = \frac{kT}{(\partial \mu_2 / \partial \bar{N}_1)_{T, p, \bar{N}_2, sc'}} = \left( \frac{\partial \bar{N}_1}{\partial \ln m_2^s} \right)_{T, p, \bar{N}_2, sc'} \quad (m_\alpha^s \rightarrow 0) \quad (10-275)$$

$$\left( \frac{\partial \ln m_1^s}{\partial \bar{N}_1} \right)_{T, p, m_2^s, sc'} = \frac{\frac{\partial \mu_1}{\partial \bar{N}_1} \frac{\partial \mu_2}{\partial \bar{N}_2} - \left( \frac{\partial \mu_2}{\partial \bar{N}_1} \right)^2}{kT \frac{\partial \mu_2}{\partial \bar{N}_2}} \quad (m_\alpha^s \rightarrow 0) \quad (10-276)$$

$$\left( \frac{\partial \ln m_1^s}{\partial \bar{N}_2} \right)_{T, p, m_2^s, sc'} = \frac{\left( \frac{\partial \mu_2}{\partial \bar{N}_1} \right)^2 - \frac{\partial \mu_1}{\partial \bar{N}_1} \frac{\partial \mu_2}{\partial \bar{N}_2}}{kT \frac{\partial \mu_1}{\partial \bar{N}_2}} \quad (m_\alpha^s \rightarrow 0) \quad (10-277)$$

$$\left( \frac{\partial \bar{N}_2}{\partial \bar{N}_1} \right)_{T, p, m_2^s, sc'} = - \left( \frac{\partial \mu_1}{\partial \mu_2} \right)_{T, p, \bar{N}_1, sc'} \quad (m_\alpha^s \rightarrow 0). \quad (10-278)$$

If the solvent is dilute in 1<sup>s</sup> and 2<sup>s</sup>, and if we regard  $m_1^s$  and  $m_2^s$  in Eq. (10-265) as functions of  $T, p, \bar{N}_1$ , and  $\bar{N}_2$ , we can derive

the generalization of Eq. (10-229):

$$d\mathcal{E} = - \left( S - \bar{N}_1 \frac{\partial S}{\partial \bar{N}_1} - \bar{N}_2 \frac{\partial S}{\partial \bar{N}_2} \right) dT + \left( \bar{V} - \bar{N}_1 \frac{\partial \bar{V}}{\partial \bar{N}_1} - \bar{N}_2 \frac{\partial \bar{V}}{\partial \bar{N}_2} \right) dp \\ - \left( \bar{N}_1 \frac{\partial \mu_1}{\partial \bar{N}_1} + \bar{N}_2 \frac{\partial \mu_2}{\partial \bar{N}_1} \right) d\bar{N}_1 - \left( \bar{N}_1 \frac{\partial \mu_1}{\partial \bar{N}_2} + \bar{N}_2 \frac{\partial \mu_2}{\partial \bar{N}_2} \right) d\bar{N}_2 \\ (m_\alpha^s \rightarrow 0, sc'). \quad (10-279)$$

This has the same formal appearance as Eq. (4-15).

ONE-COMPONENT SOLVENT. Aggregates (nuclei of a new phase) may form in a one-component gas, liquid, or solid, and these may be treated as small systems so long as they are dilute enough not to interact with each other. Up to a point [Eq. (10-206)], this is just a special case of our discussion beginning on page 120. Reference should also be made to pages 27 to 30 in Chapter 7. The solvent here has only one component, 1<sup>s</sup>. The variables  $N_2^s, \dots, N_c^s, m_1^s$ , and  $sc'$  are now all missing from the analysis. The definition of  $x'$  is  $\mathcal{N}/N_1^s$ . The fundamental equations are thus

$$dF_T = - S_T dT + V_T dp + \mu_1^s dN_1^s + \mu^\square d\mathcal{N} + \mu\mathcal{N} d\bar{N} \quad (10-280)$$

$$\mu = \mu_1^s, \quad \mu^\square = \mu\bar{N} \quad (\text{equilibrium}) \quad (10-281)$$

$$\mu^\square = F(\bar{N}, p, T) + kT \ln x'$$

$$F = \mathcal{E} + \bar{N}\mu = \bar{N}\hat{\mu} = \bar{E} - TS + p\bar{V} \quad (10-282)$$

$$dF = - S dT + \bar{V} dp + \mu d\bar{N} \quad (10-283)$$

$$d\mathcal{E} = - S dT + \bar{V} dp - \bar{N} d\mu \quad (10-284)$$

$$\mathcal{E} = - kT \ln x' \quad (\text{equilibrium}). \quad (10-285)$$

At equilibrium  $\mu = \mu_1^s = \mu_1^*$ , where  $\mu_1^*$  is a function of  $p$  and  $T$  only. We put

$$d\mu_1^* = - s_1^* dT + v_1^* dp$$

in place of  $d\mu$  in Eq. (10-284) with the result

$$d\mathcal{E} = - (S - \bar{N}s_1^*) dT + (\bar{V} - \bar{N}v_1^*) dp, \quad (10-286)$$

or

$$- kT d \ln x' = \left( \frac{\bar{N}H_1^* - \bar{H}}{T} \right) dT + (\bar{V} - \bar{N}v_1^*) dp. \quad (10-287)$$

If the solvent is a very dilute gas [see Eq. (7-126)],

$$d\mathcal{E} = - (S - \bar{N}s_1^\square) dT - (\bar{N} - 1)kT d \ln p \quad (p \rightarrow 0). \quad (10-288)$$

These equations give expressions for  $(\partial\mathcal{E}/\partial T)_p$ ,  $(\partial\mathcal{E}/\partial p)_T$ ,  $(\partial p/\partial T)_\mathcal{E}$ , etc.

We can use

$$\begin{aligned} d\mu &= - \left( \frac{\partial S}{\partial \bar{N}} \right)_{T,p} dT + \left( \frac{\partial \bar{V}}{\partial \bar{N}} \right)_{T,p} dp + \left( \frac{\partial \mu}{\partial \bar{N}} \right)_{T,p} d\bar{N} \\ &= d\mu_1^* = - s_1^* dT + v_1^* dp \end{aligned} \quad (10-289)$$

to obtain formulas for  $(\partial\bar{N}/\partial T)_p$ ,  $(\partial\bar{N}/\partial p)_T$ , and  $(\partial p/\partial T)_{\bar{N}}$  at equilibrium. Also, Eq. (10-289) may be employed to eliminate  $dp$  from Eq. (10-286) in favor of  $dT$  and  $d\bar{N}$ , thus giving  $(\partial\mathcal{E}/\partial\bar{N})_T$ , etc. If the solvent is a very dilute gas,

$$d\mathcal{E} = - \left[ S - (\bar{N} - 1) \left( \frac{\partial S}{\partial \bar{N}} \right)_{T,p} - s_1^\square \right] dT - (\bar{N} - 1) \left( \frac{\partial \mu}{\partial \bar{N}} \right)_T d\bar{N} \quad (p \rightarrow 0). \quad (10-290)$$

In the *dilute gas* case, it is advantageous to introduce the definitions employed in Eqs. (7-127) to (7-131). That is, we define  $S^{(3)}$  and  $\mathcal{E}^{(3)}$  by

$$S = S^{(3)} + k + k \ln \frac{\mathcal{N}^\dagger}{N_1^s} \quad \text{and} \quad \mathcal{E} = \mathcal{E}^{(3)} + kT \ln \frac{N_1^s}{\mathcal{N}^\dagger}, \quad (10-291)$$

and then  $F^{(3)}$ ,  $\hat{\mu}^{(3)}$ , and  $x^{(3)}$  by

$$\begin{aligned} F^{(3)} &= \mathcal{E}^{(3)} + \bar{N}\mu = \bar{N}\hat{\mu}^{(3)} \\ \mu^\square &= F^{(3)} + kT \ln x^{(3)}. \end{aligned} \quad (10-292)$$

Thus  $x^{(3)} = \mathcal{N}/\mathcal{N}^\dagger$ . Equations (10-283) to (10-285) become

$$dF^{(3)} = - S^{(3)} dT + \mu d\bar{N} \quad (10-293)$$

$$d\mathcal{E}^{(3)} = - S^{(3)} dT - \bar{N} d\mu \quad (10-294)$$

$$\mathcal{E}^{(3)} = - kT \ln \frac{\mathcal{N}}{\mathcal{N}^\dagger} \quad (\text{equilibrium}). \quad (10-295)$$

We have used here, as in Chapter 7,  $pV_T = N_1^s kT$  ( $V_T = \text{constant}$ ,

$N_1^s \gg \mathcal{N}$ ). Then,

$$d\mathcal{E}^{(3)} = - \left[ S^{(3)} - \bar{N} \left( \frac{\partial S^{(3)}}{\partial \bar{N}} \right)_T \right] dT - \bar{N} \left( \frac{\partial \mu}{\partial \bar{N}} \right)_T d\bar{N} \quad (10-296)$$

and, at equilibrium,

$$d\mathcal{E}^{(3)} = - (S^{(3)} - \bar{N} s_1^\square) dT - \bar{N} kT d \ln p. \quad (10-297)$$

*Example. Dilute Gas.* Consider a very dilute gas in which aggregates are formed (e.g., in the Frenkel-Band theory). We shall not characterize the aggregates explicitly (see pages 69 to 72 of Part I for two special cases), but simply write, for aggregates of size  $N$ ,

$$Q_N = \frac{1}{\mathcal{N}_N!} q_N^{\mathcal{N}_N}, \quad (10-298)$$

with  $q_N = V_T \psi_N(T)$ . The pressure in the gas mixture is given by  $pV_T = N_1^s kT$  since  $N_1^s \gg \mathcal{N}_N$  for all  $N$ . The chemical potential of aggregates of size  $N$  is then

$$\mu_N^\square = kT \ln \frac{\mathcal{N}_N}{\psi_N V_T} = kT \ln \frac{p}{\psi_N kT} + kT \ln x'_N, \quad (10-299)$$

with  $x'_N = \mathcal{N}_N / N_1^s$ . When the aggregates of various sizes are in equilibrium with each other (i.e., when the aggregates are open small systems),  $\mu_N^\square / N = \mu$  for all  $N$ . This, combined with Eq. (10-299), gives

$$x'_N(\mu, p, T) = \frac{kT \psi_N}{p} e^{N\mu/kT} \quad (10-300)$$

$$e^{-\mathcal{E}(\mu, p, T)/kT} = x'(\mu, p, T) = \frac{kT}{p} \sum_N \psi_N e^{N\mu/kT} \quad (10-301)$$

and

$$P_N(\mu, T) = \frac{\psi_N e^{N\mu/kT}}{\sum_N \psi_N e^{N\mu/kT}}. \quad (10-302)$$

The coefficients in Eq. (10-284) are found to be

$$-\bar{N}(\mu, T) = \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{p, T} = - \sum_N P_N N \quad (10-303)$$

$$\bar{V}(p, T) = \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{\mu, T} = \frac{kT}{p} \quad (= \bar{v}^\square = v_1^*) \quad (10-304)$$

$$\begin{aligned} -S(\mu, p, T) &= k \ln \frac{p}{kT} - k + k \sum_N P_N \left( \ln P_N - T \frac{d \ln \psi_N}{dT} - \ln \psi_N \right) \\ &= \frac{\mathcal{E}}{T} - k + \frac{\bar{N}\mu}{T} - \frac{\bar{E}}{T}, \end{aligned} \quad (10-305)$$

where

$$\bar{E} = kT^2 \sum_N P_N \frac{d \ln \psi_N}{dT}$$

and  $k = p\bar{V}/T$ .

To introduce the equilibrium condition  $\mu = \mu_1^*$  explicitly, we need [as in Eq. (3-32)]

$$\mu_1^*(p, T) = \mu_1^0(T) + kT \ln \frac{p}{p^\dagger}, \quad (10-306)$$

from which we derive

$$-s_1^\square = \left( \frac{\partial \mu_1^*}{\partial T} \right)_p = \frac{d\mu_1^0}{dT} + k \ln \frac{p}{p^\dagger}.$$

We now replace  $\mu$  by  $\mu_1^*$  in Eq. (10-301) and have

$$x'(p, T) = \frac{kT}{p} \sum_N \psi_N e^{N\mu_1^0/kT} \left( \frac{p}{p^\dagger} \right)^N. \quad (10-307)$$

This gives  $\mathcal{E}$  for use in Eq. (10-288). Differentiation of  $\mathcal{E}$  to obtain  $\bar{N} - 1$  and  $S - \bar{N}s_1^\square$  verifies Eqs. (10-303) and (10-305).

The dependence of  $x', S$  [Eqs. (10-301) and (10-305)], etc., on  $p$ , in this dilute gas case, is a rather artificial consequence of our definition of  $x'$  as  $\mathcal{N}/N_1^0$ . This dependence can be eliminated by use of

$$x^{(3)}(\mu, T) = \frac{1}{c^\dagger} \sum_N \psi_N e^{N\mu/kT}, \quad (10-308)$$

$$\begin{aligned} -S^{(3)}(\mu, T) &= k \ln c^\dagger + k \sum_N P_N \left( \ln P_N - T \frac{d \ln \psi_N}{dT} - \ln \psi_N \right), \\ &\quad (10-309) \end{aligned}$$

etc., where  $c^\dagger = \mathcal{N}^\dagger/V_T = \text{constant}$ . In other words,  $\mathcal{N}/N_1^s$  is a natural choice for a concentration variable when the solvent is a dense phase, but it is an unnatural, though quite proper, choice for a dilute gas.

*Example. Incompressible Solution.* This is essentially the same example as above but here we consider that molecules of component 1<sup>s</sup> in a liquid solution form aggregates. To achieve maximum simplicity, the solution is assumed incompressible, its volume is assumed additive, and  $m_1^s \rightarrow 0$ :

$$V_T = V^* + v \sum_N \mathcal{N}_N N, \quad (10-310)$$

where  $V^* = \text{volume of solvent} = \text{constant}$  and  $v = \text{volume per molecule of aggregate} = \text{constant}$ . From Eqs. (10-230) and (10-310),

$$\begin{aligned} dA_T &= -S_T dT - p dV_T + \sum_N \mu_N^\square d\mathcal{N}_N \quad (N_i^s \text{ constant}) \\ &= -S_T dT + \sum_N (\mu_N^\square - pvN) d\mathcal{N}_N \quad (N_i^s \text{ constant}). \end{aligned} \quad (10-311)$$

For the partition function  $Q_T$ , we write

$$Q_T = Q_{\text{solvent}} \prod_N Q_N, \quad (10-312)$$

where

$$Q_N = \frac{1}{\mathcal{N}_N!} [V_T \psi_N(T)]^{\mathcal{N}_N},$$

as in Eq. (10-298). Explicit examples of  $\psi_N(T)$  are provided by the function  $q/V$  in Eqs. (3-55) (rigid linear aggregate) and (3-61) (spherical aggregate).

From

$$\mu_N^\square - pvN = -kT \frac{\partial \ln Q_T}{\partial \mathcal{N}_N}$$

and the equilibrium condition  $\mu_N^\square/N = \mu$ , we find (in the limit  $\mathcal{N}_N \rightarrow 0$ , as usual)

$$\mu_N^\square = kT \ln \frac{\mathcal{N}_N}{V^* \psi_N} + pvN = \mu N.$$

Therefore

$$x'_N(\mu, p, T) = \frac{V^* \psi_N}{\sum_j N_j^s} e^{(\mu - p v) N / kT} \quad (10-313)$$

$$e^{-\mathcal{E}(\mu, p, T) / kT} = x'(\mu, p, T) = \frac{V^*}{\sum_j N_j^s} \sum_N \psi_N e^{(\mu - p v) N / kT} \quad (10-314)$$

and

$$P_N(\mu, p, T) = \frac{\psi_N e^{(\mu - p v) N / kT}}{\sum_N \psi_N e^{(\mu - p v) N / kT}}. \quad (10-315)$$

Equations (10-204) and (10-314) lead to

$$\bar{N}(\mu, p, T) = - \left( \frac{\partial \mathcal{E}}{\partial \mu} \right)_{T, p} = \sum_N P_N N \quad (10-316)$$

$$\bar{V}(\mu, p, T) = \left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, \mu} = \bar{N} v \quad (10-317)$$

$$-S(\mu, p, T) = \frac{\mathcal{E}}{T} - \frac{p \bar{N} v}{T} + \frac{\bar{N} \mu}{T} - \frac{\bar{E}}{T}, \quad (10-318)$$

where again, as in Eq. (10-305),

$$\bar{E} = kT^2 \sum_N P_N \frac{d \ln \psi_N}{dT}.$$

When we introduce the equilibrium condition

$$\mu = \mu_1^s = \mu_1^\Delta(p, T, sc') + kT \ln m_1^s,$$

we have

$$e^{-\mathcal{E}/kT} = x'(p, T, m_1^s) = \frac{V^*}{\sum_j N_j^s} \sum_N \psi_N e^{\mu_1^\Delta N / kT} e^{-p v N / kT} (m_1^s)^N. \quad (10-319)$$

We can then verify [see Eqs. (10-206) and (10-209)] that

$$\left( \frac{\partial \mathcal{E}}{\partial T} \right)_{p, m_1^s} = - (S - \bar{N} \tilde{s}_1^\square) \quad (10-320)$$

$$\left( \frac{\partial \mathcal{E}}{\partial p} \right)_{T, m_1^s} = \bar{V} - \bar{N} \tilde{v}_1^\square \quad (10-321)$$

$$\left( \frac{\partial \mathcal{E}}{\partial \ln m_1^s} \right)_{T, p} = - \bar{N} kT, \quad (10-322)$$

where  $S$ ,  $\bar{V}$ , and  $\bar{N}$  are given by Eqs. (10-316) to (10-318).



## 10-7. INTERACTING SMALL SYSTEMS IN SOLUTION

In parts of Chapters 2, 4, 5, 7, and the present one, we have considered small systems in solution. We have taken pains to emphasize that, in all cases, the solution must be infinitely dilute in small systems in order to define and measure thermodynamic functions that "belong" to a single small system.

The present section is essentially an appendix to all the chapters referred to above in which we discuss, for completeness, one example of a solution that is *not* infinitely dilute in small systems.

We choose, as our example, an  $N, p, T$  small system in a mixed solvent (see pages 56ff. of Part I). We use conventional solution thermodynamics, but we add  $N$ , the size of the small system, as a variable parameter. We employed the same kind of starting point in our treatment of an infinitely dilute solution.

The fundamental equations we need are

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \mu' d\mathcal{N} + \mu'' \mathcal{N} dN \quad (10-323)$$

$$d\mu' = -\bar{s} dT + \bar{v} dp + \frac{\partial \mu'}{\partial x'} dx' + \frac{\partial \mu'}{\partial N} dN \quad (sc) \quad (10-324)$$

$$\mu' = \bar{E} - T\bar{s} + p\bar{v} \quad (10-325)$$

$$\begin{aligned} &= N\hat{\mu}(N, p, T, sc) + kT \ln x' + B(N, p, T, sc)x' \\ &\quad + C(N, p, T, sc)x'^2 + \cdots, \end{aligned} \quad (10-326)$$

where  $\mu'$  is the chemical potential of the small systems and  $\mu''$  is defined by  $\mu'' \mathcal{N} \equiv \partial F_T / \partial N$ . In the limit  $x' \rightarrow 0$ ,  $\mu' \rightarrow \mu^\square$ ,  $\bar{s} \rightarrow \bar{s}^\square$ ,  $\mu'' \rightarrow \mu$ , etc., in our previous notation. The new feature here is the inclusion of the terms in  $B$ ,  $C$ , etc., in Eq. (10-326). These involve binary, ternary, etc., interactions, respectively, between small systems.

From Eq. (10-326), the derivative  $\partial \mu' / \partial x'$  in Eq. (10-324) is

$$\left( \frac{\partial \mu'}{\partial x'} \right)_{T, p, N, sc} = \frac{kT}{x'} + B + 2Cx' + \cdots \quad (10-327)$$

Similarly,

$$\left( \frac{\partial \mu'}{\partial N} \right)_{T, p, x', sc} = \mu + \left( \frac{\partial B}{\partial N} \right)_{p, T, sc} x' + \left( \frac{\partial C}{\partial N} \right)_{p, T, sc} x'^2 + \cdots \quad (10-328)$$

The quantity  $\mu''$  will also have an expansion of the form

$$\mu'' = \mu + bx' + cx'^2 + \dots$$

To find  $b$  and  $c$ , we use

$$\begin{aligned} \left( \frac{\partial \mu'}{\partial N} \right)_{T, p, x', sc} &= \left( \frac{\partial \mu'}{\partial N} \right)_{T, p, N', \mathcal{N}} = \left( \frac{\partial \mu'' \mathcal{N}}{\partial \mathcal{N}} \right)_{T, p, N', N} \\ &= \mu'' + x' \left( \frac{\partial \mu''}{\partial x'} \right)_{T, p, N, sc} \end{aligned} \quad (10-329)$$

and Eq. (10-328). By equating coefficients of like powers of  $x'$  we obtain

$$\mu'' = \mu + \frac{1}{2} \frac{\partial B}{\partial N} x' + \frac{1}{3} \frac{\partial C}{\partial N} x'^2 + \dots \quad (10-330)$$

We also have the series

$$\tilde{s} = - \left( \frac{\partial \mu'}{\partial T} \right)_{p, N, x', sc} = S - k \ln x' - \frac{\partial B}{\partial T} x' - \frac{\partial C}{\partial T} x'^2 - \dots \quad (10-331)$$

$$\tilde{v} = \left( \frac{\partial \mu'}{\partial p} \right)_{T, N, x', sc} = \bar{V} + \frac{\partial B}{\partial p} x' + \frac{\partial C}{\partial p} x'^2 + \dots \quad (10-332)$$

At this point, let us introduce the notation

$$\begin{aligned} \mu' &= F + kT \ln x' + F_B x' + F_C x'^2 + \dots \\ \tilde{s} &= S - k \ln x' + S_B x' + S_C x'^2 + \dots \\ \tilde{v} &= \bar{V} + V_B x' + V_C x'^2 + \dots, \end{aligned} \quad (10-333)$$

where

$$\begin{aligned} F &\equiv N\hat{\mu}, & F_B &\equiv B, & F_C &\equiv C \\ S_B &\equiv - \frac{\partial B}{\partial T} = - \frac{\partial F_B}{\partial T}, & S_C &\equiv - \frac{\partial C}{\partial T} = - \frac{\partial F_C}{\partial T} \\ V_B &\equiv \frac{\partial B}{\partial p} = \frac{\partial F_B}{\partial p}, & V_C &= \frac{\partial C}{\partial p} = \frac{\partial F_C}{\partial p}, & \text{etc.} \end{aligned}$$

Then

$$\begin{aligned} \tilde{E} &= \mu' + T\tilde{s} - p\tilde{v} \\ &= \bar{E} + E_B x' + E_C x'^2 + \dots, \end{aligned} \quad (10-334)$$

where

$$\begin{aligned} E &\equiv F + TS - p\bar{V} \\ E_B &\equiv F_B + TS_B - pV_B \\ E_C &\equiv F_C + TS_C - pV_C, \quad \text{etc.} \end{aligned} \quad (10-335)$$

The functions  $F$ ,  $S$ , etc., are intrinsic properties of a single small system; the functions  $F_B$ ,  $S_B$ , etc., are concerned with binary interactions between small systems; etc.

By the rules of calculus, we can of course always write

$$dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial p} dp + \frac{\partial F}{\partial N} dN \quad (sc)$$

$$dF_B = \frac{\partial F_B}{\partial T} dT + \frac{\partial F_B}{\partial p} dp + \frac{\partial F_B}{\partial N} dN \quad (sc)$$

$$dF_C = \frac{\partial F_C}{\partial T} dT + \frac{\partial F_C}{\partial p} dp + \frac{\partial F_C}{\partial N} dN \quad (sc)$$

etc., or

$$\begin{aligned} dF &= -S dT + \bar{V} dp + \mu dN \quad (sc) \\ dF_B &= -S_B dT + V_B dp + \mu_B dN \quad (sc) \\ dF_C &= -S_C dT + V_C dp + \mu_C dN \quad (sc), \end{aligned} \quad (10-336)$$

etc., where

$$\mu = \frac{\partial F}{\partial N}, \quad \mu_B \equiv \frac{\partial F_B}{\partial N} = \frac{\partial B}{\partial N}, \quad \mu_C \equiv \frac{\partial F_C}{\partial N} = \frac{\partial C}{\partial N}, \quad \text{etc.}$$

All equations in the sets (10-335) and (10-336) have the same form, but there is nothing remarkable about this. Only definitions and the rules of partial differentiation are involved. Also, in general,

$$\frac{F}{N} \neq \frac{\partial F}{\partial N} = \mu, \quad \frac{F_B}{N} \neq \frac{\partial F_B}{\partial N} = \mu_B, \quad \frac{F_C}{N} \neq \frac{\partial F_C}{\partial N} = \mu_C, \quad \text{etc.}$$

Again, this is nothing remarkable. These relations simply state that arbitrary functions  $F(N, p, T)$ ,  $F_B(N, p, T)$ , etc., are not usually linear homogeneous functions of  $N$  ( $p$  and  $T$  constant). The linear homogeneous relation  $F/N = (\partial F/\partial N)_{p, T}$  in macroscopic thermodynamics is the exception rather than the rule.

The basic reasons why Eqs. (10-335a) and (10-336a), out of the sets (10-335) and (10-336), are worth the special attention they have

been paid in this book are: (a) they refer to the intrinsic properties of a *single* small system; and (b) these equations and properties go over into conventional macroscopic results in the limit  $N \rightarrow \infty$ .

Finally, as a check on self-consistency, we substitute Eqs. (10-327), (10-328), and (10-333) into Eq. (10-324). After cancellation of various terms and comparison of coefficients of like powers of  $x'$ , we recover Eqs. (10-336).

# ELECTRIC AND MAGNETIC FIELDS

Since the extension of the thermodynamics presented in earlier chapters to small systems in electric or magnetic fields is quite straightforward, we limit the present chapter to a rather brief analysis and a few examples.

For a complete discussion, as background material, of the *macroscopic* thermodynamics of electric and magnetic fields, the reader is referred to the papers of Koenig and Guggenheim.<sup>1</sup>

The statistical mechanics of finite systems in a magnetic field is a well-known subject, especially the statistical mechanics of the so-called Ising model.<sup>2</sup> Among other things, the present chapter should furnish the appropriate thermodynamics to apply to this type of system. On the experimental side, so-called superparamagnetic particles serve as an example of small, magnetic systems.

There have been several recent treatments of the statistical mechanics of macroscopic systems in an electric field<sup>3</sup> which provide some of the point of view and notation to be used below.

## 11-1. ELECTRIC FIELD

As a simple case, let us consider first an ensemble of closed, small  $N$ ,  $T$  dielectric systems (see Chapter 3) in a uniform external electric field  $D$  (the dielectric displacement). The small systems are distinguishable, equivalent, independent, and with fixed centers of mass. The field  $D$  is imposed from outside the ensemble. The systems of the ensemble are sufficiently far apart (dilute) that each system is subject to the external field  $D$  but not to any additional contribution to the field, owing to polarization of neighboring systems of the ensemble. Thus, in this case, we could just as well write  $E$  as  $D$  ( $E = D$ ), where  $E$  is the electric field strength.

<sup>1</sup> F. O. Koenig, *J. Phys. Chem.*, **41**, 597 (1937); E. A. Guggenheim, *Proc. Roy. Soc. (London)*, **155A**, 49, 70 (1936).

<sup>2</sup> For a recent review, see C. Domb, *Advan. Phys.* **9**, 149, 245 (1960).

<sup>3</sup> S.T., Chapter 12; T. L. Hill, *J. Chem. Phys.*, **28**, 61 (1958); **30**, 1114 (1959); *J. Am. Chem. Soc.*, **80**, 2142 (1958).

For the basic ensemble equation we then have [compare Eq. (1-24)]

$$dE_t = T dS_t - M_t dD + \mu \mathcal{N} dN + X d\mathcal{N}, \quad (11-1)$$

where  $M_t = \bar{M}\mathcal{N}$  is the total dipole moment of the ensemble ( $\bar{M}$  is the mean moment per small system).  $M_t$  is an extensive property;  $D$  is intensive. As Koenig<sup>1</sup> has emphasized, there are a number of alternative choices of electric-field thermodynamic variables. The particular choice<sup>2</sup> in Eq. (11-1) is most convenient for present (but not all) purposes. In particular,  $E_t$  above includes the molecular kinetic energy of the molecules within each system, the potential energy of interaction of the molecules with the field  $D$ , and the potential energy of interaction between the molecules within each system.  $E_t$  does not include the energy of the field  $D$  in a vacuum ( $\mathcal{N} = 0$ ).

Integration of the macroscopic relation (11-1) yields

$$E_t = TS_t + X\mathcal{N},$$

or

$$X = \bar{E} - TS = A. \quad (11-2)$$

When this is used to eliminate  $X$  in Eq. (11-1), we obtain the following fundamental equations for a single system:

$$d\bar{E} = T dS - \bar{M} dD + \mu dN \quad (11-3)$$

$$dA = d(\hat{\mu}N) = -S dT - \bar{M} dD + \mu dN \quad (11-4)$$

$$d\mathcal{E} = -S dT - \bar{M} dD + \mu dN, \quad (11-5)$$

where  $A = \hat{\mu}N$  and

$$\mathcal{E} = N(\hat{\mu} - \mu) \quad (11-6)$$

$$= \bar{E} - TS - \mu N. \quad (11-7)$$

The connection with statistical mechanics is

$$A(N, T, D) = -kT \ln Q(N, T, D). \quad (11-8)$$

<sup>1</sup> Loc. cit.

<sup>2</sup> See S.T., p. 203.

Equation (11-4) provides the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial D}\right)_{T,N} &= \left(\frac{\partial \bar{M}}{\partial T}\right)_{D,N}, & -\left(\frac{\partial S}{\partial N}\right)_{T,D} &= \left(\frac{\partial \mu}{\partial T}\right)_{D,N}, \\ -\left(\frac{\partial \bar{M}}{\partial N}\right)_{T,D} &= \left(\frac{\partial \mu}{\partial D}\right)_{T,N}. \end{aligned} \quad (11-9)$$

From these we find

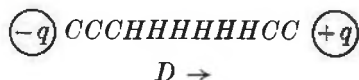
$$d\hat{\mu} = -\frac{S}{N}dT - \frac{\bar{M}}{N}dD - \frac{\mathcal{E}}{N^2}dN \quad (11-10)$$

$$d\mu = -\left(\frac{\partial S}{\partial N}\right)_{T,D}dT - \left(\frac{\partial \bar{M}}{\partial N}\right)_{T,D}dD - \frac{1}{N}\left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T,D}dN \quad (11-11)$$

$$\begin{aligned} d\mathcal{E} &= -\left[S - N\left(\frac{\partial S}{\partial N}\right)_{T,D}\right]dT - \left[\bar{M} - N\left(\frac{\partial \bar{M}}{\partial N}\right)_{T,D}\right]dD \\ &\quad + \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{T,D}dN. \end{aligned} \quad (11-12)$$

The reader may wish to derive further general relations for an  $N, T, D$  system, using analogies with earlier chapters.

*Example. Helix-Coil Transition.* This is a very simple example.<sup>1</sup> Suppose the linear macromolecular helix-coil model on page 45 of Part I has charges  $+q$  and  $-q$  at the ends of the chain and is in a uniform external electric field  $D$ . We take  $D \geq 0$  and  $q \geq 0$ . The macromolecule



is assumed to be oriented with the field. Hence the field tends to stretch the system by converting  $H$  units into longer  $C$  units ( $l_C > l_H$ ). The dipole moment is  $lq$  and the potential energy of the dipole in the field is  $-lqD$ .

For simplicity, we assume that  $C$  and  $H$  units have the same polarizability  $\alpha$ . The associated potential energy in the field, per unit, is  $-\alpha D^2/2$ . With this assumption, the polarizability will make no

<sup>1</sup> More complicated examples of similar type, but for macroscopic systems, are discussed in T. L. Hill, *J. Am. Chem. Soc.*, **80**, 2142 (1958).

contribution to the effect of  $D$  on the transition  $H \rightarrow C$ . A more general situation is obviously  $\alpha_C \neq \alpha_H$ .

If  $Q(N, l, T)$  is the canonical ensemble partition function of a macromolecule in the absence of a field (as on page 45 of Part I), in the presence of a field it is

$$Q(N, l, T, D) = Q(N, l, T) e^{lqD/kT} e^{N\alpha D^2/2kT}.$$

Also, if  $\Delta(N, f, T)$  is the  $N, f, T$  partition function in the absence of a field, in the presence of a field we have

$$\begin{aligned} \Delta(N, f, T, D) &= \sum_l Q(N, l, T, D) e^{fl/kT} \\ &= e^{N\alpha D^2/2kT} \sum_l Q(N, l, T) e^{(f+qD)l/kT} \\ &= e^{N\alpha D^2/2kT} \Delta(N, f + qD, T). \end{aligned} \quad (11-13)$$

Specifically, in the "unzipper-from-the-ends" model,<sup>1</sup>

$$\Delta(N, f, T, D) = e^{N\alpha D^2/2kT} r_C^N \frac{Nr(1-r) + 1 - 2r + r^{N+2}}{(1-r)^2}, \quad (11-14)$$

where

$$r_C = q_C(T) e^{(f+qD)l_C/kT}, \quad r_H = q_H(T) e^{(f+qD)l_H/kT},$$

$$r(f, T, D) = \frac{r_H}{r_C}.$$

This follows from Eqs. (2-86) and (11-13).

The basic thermodynamic equations are

$$d\bar{E} = T dS + f d\bar{l} - \bar{M} dD + \mu dN \quad (11-15)$$

$$d(\hat{\mu}N) = -S dT - \bar{l} df - \bar{M} dD + \mu dN \quad (11-16)$$

$$\hat{\mu}N = \bar{E} - TS - f\bar{l} \quad (11-17)$$

$$= \mu N + \mathcal{E} \quad (11-18)$$

$$= -kT \ln \Delta(N, f, T, D). \quad (11-19)$$

These are obvious generalizations of Eqs. (11-3) to (11-8). These relations, together with Eq. (11-14), lead to all the thermodynamic properties of the "unzipper" model in an electric field.

<sup>1</sup> Equation (11-13) is more general and applies to other  $HC$  models as well.



Equations (2-92) and (2-93) for the mean number of helical units in the chain still hold, but with  $r$  redefined as in Eq. (11-14). If we take  $f = 0$ , then the expression at the top of page 47 of Part I becomes

$$\ln r = \ln \frac{\omega_H}{\omega_C} + \frac{\epsilon_C - \epsilon_H}{kT} - \frac{qD(l_C - l_H)}{kT}$$

Figure 2-2 is still applicable. If  $D = \text{constant}$ , Fig. 2-2 is essentially a plot of the fraction of helical units ( $\bar{n}/N$ ) against  $1/T$ . When  $D = 0$ , the helical form predominates at low temperatures ( $\epsilon_C - \epsilon_H > 0$ ,  $1/T \rightarrow \infty$ ). But if  $D$  is sufficiently large,

$$qD(l_C - l_H) > \epsilon_C - \epsilon_H$$

and the longer coil form is favored at low temperatures ( $\ln r \rightarrow -\infty$ ). That is, the relative energetic stability of  $H$  and  $C$  units can be reversed by the electric field.

If  $T$  is held constant, Fig. 2-2 may be regarded as a plot of  $\bar{n}/N$  against  $-D$ . As  $D \rightarrow \infty$ ,  $\ln r \rightarrow -\infty$  and the coil form is obtained, as expected. Thus, the helix to coil transition can be induced by an electric field at constant  $T$ , if the macromolecule is charged, as assumed.

For the moment  $\bar{M}$  we find easily, from Eqs. (11-13), (11-16), and (11-19),

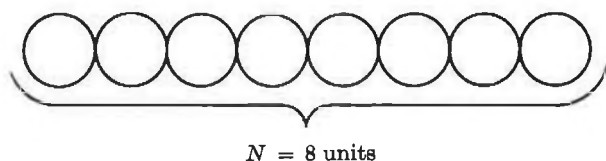
$$\bar{M} = - \left( \frac{\partial \hat{\mu}N}{\partial D} \right)_{T, f, N} = N\alpha D + \bar{l}q. \quad (11-20)$$

**DILUTE GAS OF SMALL SYSTEMS.** Here we consider a very dilute gas of small systems in a uniform, external electric field  $D$ . This involves a simple extension of Section 3-3. We have to add a term  $-M_i dD$  to Eq. (3-26), but Eq. (3-27) is unchanged. The definitions of  $\hat{\mu}$  and  $S$  are the same [Eqs. (3-28) and (3-30)]. We then find that Eqs. (11-3) to (11-7), above, are again the basic equations for a small system. Since the gas is infinitely dilute ( $\mathcal{N}/V \rightarrow 0$ ), we may again replace  $D$  by  $E$  if desired (i.e.,  $D = E$ ).

*Example. Rigid Linear Aggregate.* In this example we have the same model as on page 69 of Part I, except that here the gas<sup>1</sup> of

<sup>1</sup> As on p. 69 of Part I, we could have in mind here, instead, an incompressible small system in an inert solvent. In this case  $D$  should be replaced in the basic thermodynamic equations by  $E$ , where  $D = \epsilon^*E$  and  $\epsilon^*$  is the dielectric constant of the solvent. The definitions of  $E_i$  and  $p$  are then different [compare Koenig's Eqs. (35.1) and (37.8)]. See also Section 11-2.

aggregates is in an external field  $D$ . We assume that each unit of an aggregate, as, for example, in



has polarizability  $\alpha$  and a permanent moment  $\mu_0$  pointing along the chain. The total dipole moment of an aggregate is  $N\mu_0$ . Then, in Eq. (3-54),<sup>1</sup>

$$q(N, V, T, D) = q_0(N, V, T) e^{N\alpha D^2/2kT} \frac{\sinh y}{y}, \quad (11-21)$$

where  $q_0$  is the expression on the right-hand side of Eq. (3-55) and  $y = N\mu_0 D/kT$ . Note that  $q$  is an even function of  $D$ , as required on physical grounds.

With  $q(N, V, T, D)$  available, Eq. (3-54) and

$$A_t = -kT \ln Q(N, V, T, \mathcal{N}, D) \quad (11-22)$$

$$dA_t = -S_t dT - p dV - M_t dD + \mu_t d\mathcal{N} + \mu \mathcal{N} dN \quad (11-23)$$

make possible the calculation of all the thermodynamic functions of a small system (aggregate). We consider explicitly two limiting cases.

In the *macroscopic limit*, we let  $N \rightarrow \infty$  and take  $D$  positive, for definiteness. Because of the large dipole moment,  $N\mu_0$ , the aggregate is almost completely oriented in the field. We find

$$\ln q = \ln q_0 + \frac{N\alpha D^2}{2kT} + \frac{N\mu_0 D}{kT} - \ln \frac{2N\mu_0 D}{kT} + \dots \quad (11-24)$$

There are terms here in  $N$  and in  $\ln N$  ( $\ln q_0$  has terms in  $N$  and  $\ln N$ ). The macroscopic expression is

$$\ln q = \left( -\frac{\epsilon}{kT} + \frac{\alpha D^2}{2kT} + \frac{\mu_0 D}{kT} \right) N. \quad (11-25)$$

<sup>1</sup> Compare S.T., Eq. (12-25).

From Eq. (11-24) and

$$M_t = \bar{M} \mathcal{N} = kT \left( \frac{\partial \ln Q}{\partial D} \right)_{T, V, \mathcal{N}, N}$$

$$\mu \mathcal{N} = -kT \left( \frac{\partial \ln Q}{\partial N} \right)_{T, V, \mathcal{N}, D}$$

we find, for example,

$$\bar{M}(N, T, D) = N\alpha D + N\mu_0 - \frac{kT}{D} \quad (11-26)$$

$$\mu(N, T, D) = \epsilon - \frac{7kT}{2N} - \frac{\alpha D^2}{2} - \mu_0 D. \quad (11-27)$$

These are consistent with Eq. (11-9c).

In the *small-field limit* ( $D \rightarrow 0$ ), there is little orientation of the dipolar aggregates in the field. In this case  $N$  is finite (i.e., we do not allow  $N \rightarrow \infty$  because of the expansion used). On expanding  $y^{-1} \sinh y$  in powers of  $y$ , we obtain

$$\ln q = \ln q_0 + \frac{N\alpha D^2}{2kT} + \frac{1}{6} \left( \frac{N\mu_0 D}{kT} \right)^2 + O(D^4). \quad (11-28)$$

Note that there is a nonlinear term here in  $N^2$ , but this is not alarming since  $N \rightarrow \infty$  is not permissible. By the same procedure as above, we deduce

$$\bar{M}(N, T, D) = N\alpha D + \frac{1}{3} \frac{N^2 \mu_0^2 D}{kT} + O(D^3) \quad (11-29)$$

$$\mu = \epsilon - \frac{9kT}{2N} - \frac{\alpha D^2}{2} - \frac{N\mu_0^2 D^2}{3kT} + O(D^4). \quad (11-30)$$

Instead of calculating thermodynamic functions directly from Eq. (11-23), one could of course find  $\mu_t$  from Eq. (11-23), then  $\hat{\mu}$  from Eq. (3-28), and finally other functions from Eq. (11-4).

We have considered so far in this chapter only closed small systems ( $N$  units) in an electric field. Of course open systems in an electric field can be treated as well, as in Chapter 10, for example. One interesting effect, with an open system, is that the electric field will influence the distribution in aggregate sizes. This is easily illustrated by the present example of rigid linear aggregates. From Eqs. (10-298) and (10-302), we see that if aggregates of different

sizes are in equilibrium with each other, the fraction of aggregates of size  $N$  in the presence of a field  $D$  is given by

$$P_N(\mu, T, D) = \frac{\psi_N(T, D) e^{N\mu/kT}}{\sum_N \psi_N e^{N\mu/kT}}, \quad (11-31)$$

where  $\mu$  is the monomer chemical potential in the gas,

$$\psi_N(T, D) = \left( \frac{2\pi m N k T}{h^2} \right)^{3/2} \frac{\pi^2 k T m a^2 N^3}{3 h^2} e^{-(N-1)\epsilon/kT} e^{N\alpha D^2/2kT} \frac{\sinh y}{y}, \quad (11-32)$$

and  $y = N\mu_0 D/kT$ . Because  $P_N$  is a complicated function of  $N$ , even for this simple model, we have not made any numerical calculations.

## 11-2. SOLVENT EFFECTS IN AN ELECTRIC FIELD

We show here that it is easy to include an electric field in the treatment of solvent effects which was given in Section 2-3. We use the notation of that section.

The solvent is a dielectric with components 1, 2, ...,  $c$  (we can drop the usual superscript  $s$  here). The small systems (macromolecules, for example) are an additional, infinitely dilute component in the solution. The small systems are "closed," each with  $N$  units or monomers. There is a uniform external field  $D$  imposed on the solution.

Because of the presence of the solvent, a small system is subject to the field  $\mathbf{E}$ , not  $D$ , where  $\epsilon^* \mathbf{E} = D$  and  $\epsilon^*$  is the dielectric constant of the solvent. The generalization of Eq. (2-117) which we choose is therefore<sup>1</sup>

$$dE_T = T dS_T - p dV_T - M_T dE + \sum_{i=1}^c \mu_i dN_i + \mu^\square d\mathcal{N} + \mu \mathcal{N} dN, \quad (11-33)$$

where  $M_T$  is the total dipole moment of the macroscopic solution. The precise definitions of  $E_T$  and  $p$  are those given in Koenig's<sup>2</sup>

<sup>1</sup> See T. L. Hill, *J. Chem. Phys.*, **28**, 61 (1958); **30**, 1114 (1959).

<sup>2</sup> Loc. cit.

Eq. (37.8). It then follows that

$$F_T = E_T - TS_T + pV_T = \sum_i \mu_i N_i + \mu^\square \mathcal{N} \quad (11-34)$$

$$dF_T = -S_T dT + V_T dp - M_T dE + \sum_i \mu_i dN_i + \mu^\square d\mathcal{N} + \mu \mathcal{N} dN \quad (11-35)$$

$$\sum_i N_i d\mu_i + \mathcal{N} d\mu^\square = -S_T dT + V_T dp - M_T dE + \mu \mathcal{N} dN. \quad (11-36)$$

Partial molal quantities are defined by

$$\tilde{g} = \left( \frac{\partial G_T}{\partial \mathcal{N}} \right)_{T, p, E, N_i, N},$$

etc. Then

$$dG_T = \tilde{g} d\mathcal{N} + \sum_i \tilde{g}_i dN_i \quad (T, p, E, N \text{ constant})$$

$$G_T = \tilde{g} \mathcal{N} + \sum_i \tilde{g}_i N_i,$$

as usual.

On differentiating Eq. (11-34) with respect to  $\mathcal{N}$ ,

$$\mu^\square = \tilde{e}^\square - T\tilde{s}^\square + p\tilde{v}^\square. \quad (11-37)$$

Also, using Maxwell relations from Eq. (11-35), we find

$$d\mu^\square = -\tilde{s}^\square dT + \tilde{v}^\square dp - \tilde{m}^\square dE + \frac{\partial \mu^\square}{\partial x'} dx' + \frac{\partial \mu^\square}{\partial N} dN \quad (sc). \quad (11-38)$$

The argument in Eqs. (7-70) to (7-75) is applicable here and shows that  $\partial \mu^\square / \partial N$  in Eq. (11-38) is equal to  $\mu$ , as defined by Eq. (11-33).

We then define  $F$ ,  $\hat{\mu}$ , and  $S$  for a small system by

$$\begin{aligned} \mu^\square &= F(N, p, T, E, sc) + kT \ln x' \\ &= N\hat{\mu}(N, p, T, E, sc) + kT \ln x' \end{aligned} \quad (11-39)$$

$$\tilde{s}^\square = S(N, p, T, E, sc) - k \ln x'. \quad (11-40)$$

We also define

$$\tilde{v} \equiv \tilde{v}^\square, \quad \tilde{M} \equiv \tilde{m}^\square, \quad \tilde{E} \equiv \tilde{e}^\square. \quad (11-41)$$

Thus  $\tilde{M}$  is the mean change in  $M_T$  brought about by the addition of one small system to the infinitely dilute solution (with  $T$ ,  $p$ ,  $E$ ,

$N_i$ , and  $N$  held constant). There will be contributions to  $\bar{M}$  associated with the small system itself (permanent moment, polarizability) and also contributions from the effect the presence of the small system has on neighboring solvent molecules.

On combining Eqs. (11-37) to (11-41), we obtain the following fundamental relations for a small system:

$$F = N\hat{\mu} = \bar{E} - TS + p\bar{V} \quad (11-42)$$

$$d\bar{E} = T dS - p d\bar{V} - \bar{M} dE + \mu dN \quad (sc) \quad (11-43)$$

$$d(N\hat{\mu}) = -S dT + \bar{V} dp - \bar{M} dE + \mu dN \quad (sc) \quad (11-44)$$

$$d\mathcal{E} = d[N(\hat{\mu} - \mu)] = -S dT + \bar{V} dp - \bar{M} dE - N d\mu \quad (sc). \quad (11-45)$$

These should be compared with Eqs. (11-3) to (11-7) and (11-15) to (11-18). We leave it to the reader to continue from this point.

As a final topic, we derive a relation, which may have some practical value, between  $\bar{M}$  and the change of the dielectric constant  $\epsilon$  with  $x'$ . From

$$\epsilon E = D = E + \frac{4\pi M_T}{V_T}, \quad (11-46)$$

we have

$$4\pi M_T = (\epsilon - 1) E V_T.$$

Then, on differentiating with respect to  $\mathcal{N}$ ,

$$4\pi \bar{M} = (\epsilon - 1) E \bar{V} + E V_T \left( \frac{\partial \epsilon}{\partial \mathcal{N}} \right)_{T, p, E, N_i, N}. \quad (11-47)$$

We are interested in the infinitely dilute solution ( $x' \rightarrow 0$ ):

$$4\pi \bar{M} = \left[ (\epsilon^* - 1) \bar{V} + v^* \left( \frac{\partial \epsilon}{\partial x'} \right)_{T, p, E, N, sc}^{\square} \right] E, \quad (11-48)$$

where  $v^* = V^*/\Sigma_i N_i$ . At ordinary field strengths the quantity in brackets is independent of  $E$  (it can be expanded in even powers of  $E$ ) and  $\bar{M}$  is proportional to  $E$ . Measurement of  $(\partial \epsilon / \partial x')^{\square}$  would allow calculation of  $\bar{M}$ .

## 11-3. MAGNETIC FIELD

The thermodynamics of a magnetic field is formally identical with the thermodynamics of an electric field. Hence the preceding sections apply to a magnetic field provided we replace  $D$  by  $B$  (magnetic induction),  $E$  by  $H$  (magnetic field strength), and  $M$  by  $I$  (intensity of magnetization). Section 11-2 is applicable only to a dielectric (nonelectrolyte) solution. This restriction is not necessary here: The solution may be electrolytic.

*Example. Ising Model.* We conclude by rephrasing the general lattice-gas problem in "magnetic language" (the Ising model).

An approximate treatment of a finite lattice gas is given on pages 143 to 149 of Part I. Also, an exact treatment of a special case is considered on pages 62 to 64 and 70 to 72 of Part II. But there is no point in repeating this discussion for the magnetic case.

Let the small system be a lattice of  $B$  magnetic dipoles,<sup>1</sup> associated with the electron spins, each of which can exist in only two orientations or states:  $\uparrow$ , in the direction of the magnetic field  $H$ ; or  $\downarrow$ , against the field. The potential energy of a dipole or spin is  $-mH$  if oriented with the field ( $\uparrow$ ) and  $+mH$  if oriented against the field ( $\downarrow$ ), where  $m$  is the magnetic moment.

Let  $N$  be the number of  $\downarrow$  states and  $B - N$  the number of  $\uparrow$  states. For a given value of  $N$ , the potential energy of the dipoles in the field is then

$$mHN - mH(B - N) = (2N - B)mH.$$

For given  $H, B, T$  (the environmental variables), let  $\bar{N}$  be the mean value of  $N$  ( $0 \leq N \leq B$ ). Then the mean work necessary to increase  $H$  by  $dH$  is  $-I dH$ , where

$$\bar{I} = (B - 2\bar{N})m. \quad (11-49)$$

The range of  $I$  values is  $-Bm \leq I \leq +Bm$ .

There is an additional contribution to the potential energy: nearest-neighbor parallel spins ( $\uparrow\uparrow$  or  $\downarrow\downarrow$ ) are assumed to have an interaction energy  $-J$ , whereas nearest-neighbor antiparallel

<sup>1</sup> To maintain the lattice-gas notation, we use  $B$  for the number of dipoles rather than for the magnetic induction. In this example, the magnetic induction is equal to the magnetic field strength, so we use the symbol  $H$  for the field. We follow the discussion in S.T., pp. 209-211 and 250-252, where applicable.

spins ( $\uparrow\downarrow$ ) have an interaction energy  $+J$ . These interaction energies are due to quantum mechanical exchange forces; they are not dipole-dipole interactions (which are neglected). If  $J > 0$ , we have the ferromagnetic case, whereas if  $J < 0$ , we have the anti-ferromagnetic case.

In a small system, all the  $B$  dipoles may not be equivalent because of edge effects (a different number of nearest neighbors).

Since there are  $B$  spins in the system and each spin can be  $\uparrow$  or  $\downarrow$ , there are a total of  $2^B$  possible configurations for the whole system. In any one of these configurations,  $N$  has a definite value and we let  $N_{\uparrow\uparrow}$  be the number of nearest-neighbor  $\uparrow\uparrow$  pairs, etc. Then, in this configuration, the energy of the system is (we omit kinetic energy and other degrees of freedom)

$$E = (2N - B)mH + N_{\uparrow\downarrow}J - (N_{\uparrow\uparrow} + N_{\downarrow\downarrow})J. \quad (11-50)$$

The canonical ensemble partition function is then

$$Q(B, T, H) = \sum_{2^B} e^{-E/kT}, \quad (11-51)$$

where the sum is over all  $2^B$  configurations.

From Eqs. (11-3) to (11-5), the basic thermodynamic equations are

$$d\bar{E} = T dS - I dH + \mu dB \quad (11-52)$$

$$A = \bar{E} - TS = \hat{\mu}B, \quad \mathcal{E} = (\hat{\mu} - \mu)B \quad (11-53)$$

$$dA = d(\hat{\mu}B) = -S dT - I dH + \mu dB \quad (11-54)$$

$$d\mathcal{E} = -S dT - I dH - B d\mu \quad (11-55)$$

$$A = \hat{\mu}B = -kT \ln Q. \quad (11-56)$$

Note that the number of "units" in the system is  $B$ , instead of  $N$  as in Eq. (11-3).

We can easily verify the self-consistency of Eqs. (11-49) and (11-54):

$$\begin{aligned} I &= \frac{kT}{Q} \left( \frac{\partial Q}{\partial H} \right)_{B, T} = \frac{1}{Q} \sum_{2^B} (B - 2N) m e^{-E/kT} \\ &= (B - 2\bar{N})m. \end{aligned}$$



Different definitions of  $E$  are possible, as we have already mentioned on page 151. A common alternate choice is

$$E' = E + IH.$$

This leads to

$$\begin{aligned} d\bar{E}' &= T dS + H dI + \mu dB \\ d(\bar{E}' - TS - IH) &= -S dT - I dH + \mu dB, \quad \text{etc.} \end{aligned}$$

A great deal of exact work has been done on the above system, for both finite and infinite systems. Readers interested in pursuing the subject further should consult the recent review article by Domb, referred to above. Also, it should now be apparent<sup>1</sup> that the Ising (magnetic) problem is identical with the lattice-gas problem, which we have already discussed to some extent, except for notation. For example, the environmental variables  $H$ ,  $B$ ,  $T$  here are equivalent to  $\mu$ ,  $B$ ,  $T$  for a lattice gas.

In conclusion we consider the "ideal" Ising model: That is, we take the interaction energy  $J = 0$ . Then

$$\begin{aligned} Q(B, T, H) &= \sum_{2^B} e^{-(2N - B)mH/kT} \\ &= \sum_{N=0}^B \frac{B! e^{-(2N - B)mH/kT}}{N!(B - N)!} \\ &= (e^{mH/kT} + e^{-mH/kT})^B. \end{aligned} \quad (11-57)$$

Equations (11-49), (11-54), and (11-56) give

$$\frac{\bar{N}}{B} = \frac{e^{-2mH/kT}}{1 + e^{-2mH/kT}} \quad (11-58)$$

$$\begin{aligned} \mu &= -kT \ln (e^{mH/kT} + e^{-mH/kT}) \\ &= -mH + kT \ln \left( 1 - \frac{\bar{N}}{B} \right) = \hat{\mu} \end{aligned} \quad (11-59)$$

$$\mathcal{E} = 0 \quad (11-60)$$

$$\frac{S}{k} = B \ln B - (B - \bar{N}) \ln (B - \bar{N}) - \bar{N} \ln \bar{N}. \quad (11-61)$$

These results are equivalent to those on page 142 of Part I for an

<sup>1</sup> See also S.M., Chapter 7.

ideal lattice gas. The correspondence in notation is:

*Ideal Ising model*

*Ideal lattice gas*

$$\mu + mH$$

$$-p$$

$$\hat{\mu} + mH$$

$$-\hat{p}$$

$$-2mH$$

$$\mu$$

$B$ ,  $\bar{N}$ ,  $S$ , and  $T$  are the same in the two cases.

# SPHERICAL DROPS AND BUBBLES

This chapter is concerned with the properties of a spherical, isotropic nucleus of a stable phase ( $\alpha$ ) forming within a macroscopic metastable phase ( $\beta$ ). For definiteness, we shall use language appropriate to a liquid drop forming in a vapor. But the discussion could just as well be applied to bubbles in a liquid, or to the nucleation of melting or freezing. On the other hand, Section 10-6 has to do with the formation of aggregates within a stable equilibrium phase.

Our main object here is to show the relation between Gibbs' treatment of spherical surfaces and the "small system" approach which is being developed in this book. The two methods are equivalent but different when applied to the present problem. Of course small system thermodynamics is much more general in that it is not restricted to surface problems (see the other chapters in this book).

The small system method uses thermodynamic functions which pertain to the entire drop or small system. The Gibbs method uses excess functions (similar to those introduced on pages 38, 78, and 136 of Part I) which are defined by comparing small system functions with bulk functions. It is necessary to introduce the concept of a dividing surface in the Gibbs method but not in the small system method.

## 12-1. SMALL SYSTEM THERMODYNAMIC FUNCTIONS

Consider a spherical drop in a spherical container of volume  $V$  (Fig. 12-1). The center of mass of the drop is imagined restrained to the origin ( $r = 0$ ). The drop is in contact with a metastable vapor ( $\beta$ ) characterized by  $T, \mu_1, \dots, \mu_c$ . These variables completely determine the nature of the drop. The entire system (drop plus surrounding vapor) is an open one. There is a continuous transition, at the interface, from drop to vapor. There is no restriction on the size of the drop; it may be so small that properties of bulk liquid (at  $T, \mu_1, \dots, \mu_c$ ) do not obtain even at  $r = 0$ . Figure 12-1 illustrates this case. The interior phase (drop) is denoted by  $\alpha$ . The bulk liquid is indicated by  $\alpha^0$ . Ordinarily, though, the center of the drop has

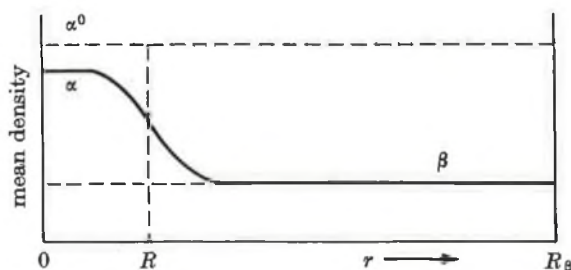


FIGURE 12-1. Radial dependence of density of spherical droplet. Bulk properties do not obtain at center ( $r = 0$ ).

bulk properties so that  $\alpha$  and  $\alpha^0$  coincide, as in Fig. 12-2. The volume  $V$  is taken as macroscopic and large enough that properties of bulk metastable vapor (at  $T, \mu_1, \dots, \mu_c$ ) are reached at least at the periphery of  $V$ ; otherwise  $V$  is arbitrary. The pressure at the periphery is  $p_\beta$  (determined by  $T, \mu_1, \dots, \mu_c$ ).

For an ensemble of  $\mathcal{N}$  of these open systems [compare Eq. (1-4)], we have

$$dE_t = T dS_t - p_\beta \mathcal{N} dV + \sum_{i=1}^c \mu_i dN_{ti} + X' d\mathcal{N}, \quad (12-1)$$

where  $X' = (\partial E_t / \partial \mathcal{N})_{S_t, V, N_{ti}}$ . Use of a macroscopic ensemble ( $\mathcal{N} \rightarrow \infty$ ) allows us to consider very small drops with large relative fluctuations in properties. Integration of Eq. (12-1) at constant  $T$ ,

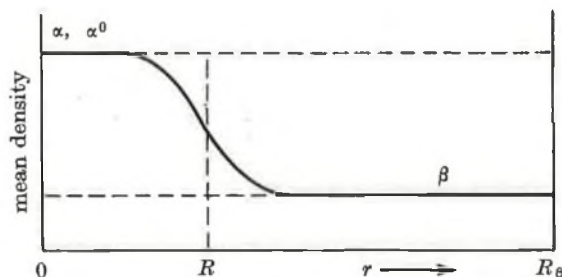


FIGURE 12-2. Radial dependence of density of spherical droplet. Bulk properties obtain at center ( $r = 0$ ).

$\mu_i$ ,  $V$  gives

$$E_t = TS_t + \sum_i \mu_i N_{ti} + X' \mathcal{N},$$

or

$$X' = \bar{E}' - TS' - \sum_i \mu_i \bar{N}'_i. \quad (12-2)$$

The functions in Eq. (12-2) refer to a single system, such as in Fig. 12-1 or 12-2. Substitution of Eq. (12-2) in Eq. (12-1) yields

$$d\bar{E}' = T dS' - p_\beta dV + \sum_i \mu_i d\bar{N}'_i. \quad (12-3)$$

We have given a treatment of the present problem from the Gibbs point of view elsewhere.<sup>1</sup> Equation (12-3) is the same as Eq. (P40).

Now consider, for reference,  $\mathcal{N}$  systems containing the same vapor at  $T$ ,  $\mu_i$  but with no drop in the center. Actually, since such a system is macroscopic and homogeneous, it would suffice to treat only one system. Then, for the ensemble of reference systems, in obvious notation.

$$dE_t^\beta = T dS_t^\beta - p_\beta \mathcal{N} dV + \sum_i \mu_i dN_{ti}^\beta + X_\beta d\mathcal{N} \quad (12-4)$$

$$E_t^\beta = TS_t^\beta + \sum_i \mu_i N_{ti}^\beta + X_\beta \mathcal{N}$$

$$X_\beta = \bar{E}_\beta - TS_\beta - \sum_i \mu_i \bar{N}_{i\beta}. \quad (12-5)$$

These last functions refer to a single system (volume  $V$ ) completely filled with vapor ( $\beta$ ), that is, with no drop in the center. Therefore, from ordinary thermodynamics,  $X_\beta = -p_\beta V$ . Substitution of Eq. (12-5) in Eq. (12-4) gives the macroscopic expression

$$d\bar{E}_\beta = T dS_\beta - p_\beta dV + \sum_i \mu_i d\bar{N}_{i\beta}. \quad (12-6)$$

We define  $\mathcal{E}$  by  $X' = \mathcal{E} - p_\beta V$ . Since  $X'$  and  $X_\beta = -p_\beta V$  differ only because of the presence of the drop, or nonhomogeneity, in the system to which  $X'$  pertains,  $\mathcal{E}$  is a property of the drop and is independent of the arbitrary choice of  $V$ .

<sup>1</sup> T. L. Hill, *J. Phys. Chem.*, **56**, 526 (1952), especially Section IV; we denote equations in this paper by P. Gibbs' own work is in "The Scientific Papers of J. Willard Gibbs," Dover Publications, New York, 1961. For recent analyses of this problem, with references, see the chapters by S. Ono and S. Kondo and by F. P. Buff in "Handbuch der Physik," S. Flügge (ed.), Springer-Verlag, Berlin, 1960, Vol. 10.

We subtract Eq. (12-5) from Eq. (12-2) and find

$$\mathcal{E} = \bar{E} - TS - \sum_i \mu_i \bar{N}_i, \quad (12-7)$$

where  $\bar{E} = \bar{E}' - \bar{E}_\beta$ , etc. Similarly, from Eqs. (12-3) and (12-6),

$$d\bar{E} = T dS + \sum_i \mu_i d\bar{N}_i. \quad (12-8)$$

All the functions appearing in the last two equations are characteristic of the drop (with the vapor subtracted out) and are independent of the arbitrary choice of  $V$ . They are determined (experimentally or from molecular theory) by the variables  $T, \mu_i$ . Also, they do *not* depend on the choice of a Gibbs "dividing surface." If  $T, \mu_i$  are chosen so as to make the drop become vanishingly small, then  $\mathcal{E}, \bar{E}, S$ , and  $\bar{N}_i$  approach zero.

The drop, with properties  $\mathcal{E}, \bar{E}, S$ , etc., may be regarded as a completely open, small system with independent environmental variables  $T, \mu_i$ , as in Chapter 10. The pressure  $p_\beta$  is not independent; in the notation of Section 10-2 we would denote it by  $p^{(0)}(T, \mu_i)$  for the macroscopic metastable vapor.

In the case of a bubble, the  $\bar{N}_i$  would of course be negative.

The equation

$$d\mathcal{E} = -S dT - \sum_i \bar{N}_i d\mu_i, \quad (12-9)$$

which follows from Eqs. (12-7) and (12-8), has the environmental variables as independent variables. It is therefore the fundamental differential relation. From it we deduce

$$-S = \left( \frac{\partial \mathcal{E}}{\partial T} \right)_{\mu_i}, \quad -\bar{N}_i = \left( \frac{\partial \mathcal{E}}{\partial \mu_i} \right)_{T, \mu_j} \quad (12-10)$$

$$\left( \frac{\partial \bar{N}_k}{\partial T} \right)_{\mu_i} = \left( \frac{\partial S}{\partial \mu_k} \right)_{T, \mu_j}. \quad (12-11)$$

Other relations of interest are

$$dA = d(\bar{E} - TS) = -S dT + \sum_i \mu_i d\bar{N}_i \quad (12-12)$$

$$d(\mathcal{E} + TS) = T dS - \sum_i \bar{N}_i d\mu_i. \quad (12-13)$$

These lead to equations analogous to (12-10) and (12-11).

The connection with statistical mechanics is

$$-dX' = d(kT \ln \Xi') = S' dT + p_\beta dV + \sum_i \bar{N}'_i d\mu_i \quad (12-14)$$

$$-dX_\beta = d(p_\beta V) = d(kT \ln \Xi_\beta) = S_\beta dT + p_\beta dV + \sum_i \bar{N}_{i\beta} d\mu_i \quad (12-15)$$

$$-d\mathcal{E} = d\left(kT \ln \frac{\Xi'}{\Xi_\beta}\right) = S dT + \sum_i \bar{N}_i d\mu_i, \quad (12-16)$$

where  $\Xi'$  and  $\Xi_\beta$  are grand partition functions for the volume  $V$ , with and without a central drop, respectively.

## 12-2. RELATION TO THE GIBBS METHOD

The functions  $\mathcal{E}$ ,  $S$ ,  $\bar{E}$ , etc., above, pertain to the drop (small system). In earlier chapters we found it useful to introduce excess functions which exhibit the difference between the small system functions and corresponding bulk or macroscopic functions. When we do this here, in a natural way, we find that our excess functions (for the present problem) are exactly the Gibbs surface excess functions.

Let us consider the entropy as an example of an extensive property. Let  $s_\beta$  be the entropy per unit volume of the metastable vapor  $\beta$  ( $s_\beta = S_\beta/V$ ). Similarly, let  $s_\alpha^0$  be the entropy per unit volume of the bulk liquid. Then  $s_\alpha^0 - s_\beta$  is the "bulk" entropy per volume which should be compared with  $S$  (since  $S_\beta$  has been subtracted from  $S'$  to give  $S$ ). For a multicomponent system, we have to introduce a Gibbs dividing surface in order to complete the definition of the excess entropy  $S^{(x)}$ . The specification of the dividing-surface condition is left arbitrary for the moment, but let us suppose that the surface is at  $r = R$  (Fig. 12-1). Then we write

$$V_\alpha = \frac{4}{3}\pi R^3, \quad V_\beta = \frac{4}{3}\pi(R_\beta^3 - R^3), \quad V = \frac{4}{3}\pi R_\beta^3 = V_\alpha + V_\beta.$$

Since  $V_\alpha$  is the "volume of the drop," using the dividing surface  $r = R$ , we define  $S^{(x)}$  by

$$S = V_\alpha(s_\alpha^0 - s_\beta) + S^{(x)}. \quad (12-17)$$

This is the analogue of Eq. (6-19). Although  $S$ ,  $s_\alpha^0$ , and  $s_\beta$  do not depend on the location chosen for the dividing surface,  $V_\alpha$  and  $S^{(x)}$  do depend on this choice.

Now we have

$$S = S' - S_\beta = S' - (V_\alpha + V_\beta)s_\beta$$

and hence, from Eq. (12-17),

$$\begin{aligned} S^{(x)} &= [S' - (V_\alpha + V_\beta)s_\beta] - V_\alpha(s_\alpha^0 - s_\beta) \\ &= S' - V_\alpha s_\alpha^0 - V_\beta s_\beta. \end{aligned} \quad (12-18)$$

But this is just the Gibbs definition of a surface excess. Hence we use the notation  $S^{(x)}$ ,  $\bar{N}_i^{(x)}$ , etc., for Gibbs surface excesses below.

The surface tension  $\gamma$ , for an arbitrary dividing-surface condition, is defined by [see Eq. (P42)]

$$\gamma\mathcal{A} = p_\alpha^0 V_\alpha + p_\beta V_\beta - \sum_i \mu_i \bar{N}_i' + \bar{E}' - TS', \quad (12-19)$$

where the surface area  $\mathcal{A} = 4\pi R^2$ . The first two terms on the right depend on the location of the dividing surface, but the rest of the right-hand terms do not. If we use Eq. (12-5) (recalling that  $X_\beta = -p_\beta V$ ) to eliminate  $p_\beta V_\beta$  above, and then introduce Eq. (12-7), we find

$$\gamma\mathcal{A} = V_\alpha(p_\alpha^0 - p_\beta) + \mathcal{E}, \quad (12-20)$$

where the first two terms depend on the dividing surface, but the last one does not.

If now we adopt the so-called surface of tension (s.o.t.) as a specific choice of dividing-surface condition [see Eq. (P45)], we have

$$\frac{2\gamma}{R} = p_\alpha^0 - p_\beta \quad (\text{s.o.t.}) \quad (12-21)$$

and hence

$$\mathcal{E} = \frac{1}{2}\gamma\mathcal{A} \quad (\text{s.o.t.}). \quad (12-22)$$

Gibbs<sup>1</sup> introduced a quantity  $W$ , which, as he showed, is the work required to form a drop in the vapor. The definition of  $W$  [Gibbs' Eq. (552)] is the same as our definition of  $\mathcal{E}$  in Eq. (12-7), although Gibbs does not seem to have derived a relation equivalent to our Eq. (12-9). Equation (12-22) above is the same as Gibbs' Eq. (560). The work property of  $\mathcal{E}$  is obvious from

$$\mathcal{E} = X' - X_\beta = \left( \frac{\partial E_t}{\partial \mathcal{N}} \right)_{S_t, V, N_{it}} - \left( \frac{\partial E_t^\beta}{\partial \mathcal{N}} \right)_{S_t^\beta, V, N_{it}^\beta}. \quad (12-23)$$

<sup>1</sup> Loc. cit., pp. 254-258.



The discussion of Eq. (10-107a) should be noted in this connection.

For the surface of tension [Eq. (P26)],

$$\mathcal{A} d\gamma = - S^{(x)} dT - \sum_i \bar{N}_i^{(x)} d\mu_i \quad (\text{s.o.t.}). \quad (12-24)$$

Equation (12-9) is the basic differential relation for the small system functions. Equation (12-24) is the corresponding relation for the excess functions. In Eq. (12-9), the first term is of order  $\bar{N}^{2/3}kT$ , whereas the other two terms are of order  $\bar{N}kT$ . All terms in Eq. (12-24) are of order  $\bar{N}^{2/3}kT$ .

It is probably worthwhile to verify the self-consistency of Eqs. (12-9) and (12-24). One way to do this is as follows. From Eq. (12-20),

$$\begin{aligned} \gamma d\mathcal{A} + \mathcal{A} d\gamma &= V_\alpha(dp_\alpha^0 - dp_\beta) + (p_\alpha^0 - p_\beta) dV_\alpha + d\mathcal{E}, \\ \text{or} \quad \mathcal{A} d\gamma &= V_\alpha(dp_\alpha^0 - dp_\beta) + d\mathcal{E} \quad (\text{s.o.t.}). \end{aligned} \quad (12-25)$$

We now substitute Eq. (12-9) and the macroscopic relationships

$$\begin{aligned} dp_\alpha^0 &= s_\alpha^0 dT + \sum_i n_{\alpha i}^0 d\mu_i \\ dp_\beta &= s_\beta dT + \sum_i n_{\beta i} d\mu_i \end{aligned}$$

into Eq. (12-25) to obtain the desired result:

$$\begin{aligned} \mathcal{A} d\gamma &= (V_\alpha s_\alpha^0 - V_\alpha s_\beta - S) dT + \sum_i (V_\alpha n_{\alpha i}^0 - V_\alpha n_{\beta i} - \bar{N}_i) d\mu_i \\ &= - S^{(x)} dT - \sum_i \bar{N}_i^{(x)} d\mu_i \quad (\text{s.o.t.}). \end{aligned} \quad (12-26)$$

Alternatively, if we start with Eq. (12-9) and substitute equations of the type (12-17) for  $S$  and  $\bar{N}_i$ , we find

$$d\mathcal{E} = - S^{(x)} dT - \sum_i \bar{N}_i^{(x)} d\mu_i - V_\alpha(dp_\alpha^0 - dp_\beta) \quad (12-27)$$

for an arbitrary dividing-surface condition. The difference  $dp_\alpha^0 - dp_\beta$  is independent of dividing surface, so the term in  $V_\alpha$  never drops out. Equations (12-25) and (12-27) give Eq. (12-26).

Very interesting approximate numerical calculations for one-component spherical drops of various sizes have been made by Plesner<sup>1</sup>, using the Gibbs approach.

<sup>1</sup> I. Plesner, *J. Chem. Phys.*, in press.

To recapitulate: In Section 12-1 it is shown that small system functions can be defined for spherical drops in such a way that equations of the same type [(12-7) and (12-9)] as in Chapter 10 result. The drops can be arbitrarily small. This formulation has the advantage of avoiding the dividing-surface concept. But, if we introduce a dividing surface, it is easy to establish the connection with Gibbs' treatment of spherical surfaces.

## POLYDISPERSE SYSTEMS

More often than not, an experimental polymeric or colloidal system is polydisperse rather than monodisperse. Up to this point in the book, only monodisperse samples have been considered. But we can still define thermodynamic functions for a small system, in the polydisperse case, by averaging over the degree of polymerization. The monodisperse situation then becomes a limiting case.

We are referring here, of course, to a polydisperse mixture of *closed* small systems. An ensemble of open small systems has polydispersity of a different kind (dynamic aggregation equilibrium). This type of system was analyzed in Chapter 10.

In Section 13-1 we discuss a polydisperse  $N, p, T$  system. Examples are polymer molecules in solution, colloidal particles in solution or gas, and a colloidal powder sample. We start with small system equations for the monodisperse case and simply introduce averaging. The same analysis applies to all the examples just referred to (except that  $p$  drops out as a variable in some cases). But separate discussions are required if one wants to examine explicit connections with macroscopic thermodynamics. We illustrate such connections, for a solution, in Section 13-2.

Another important case is binding on a polydisperse macromolecule in solution. This is an  $N_1, \mu_2, p, T$  system which is polydisperse in  $N_1$ . A synthesis of Sections 7-2 and 13-2 is required in order to treat such a system. This task is left to the interested reader.

## 13-1. SMALL SYSTEM EQUATIONS

The basic equations (see Chapter 2) for a monodisperse  $N, p, T$  small system with a fixed value of  $N$  are

$$F_N = N\hat{\mu}_N = \bar{E}_N - TS_N + p\bar{V}_N \quad (13-1)$$

and

$$dF_N = -S_N dT + \bar{V}_N dp \quad (N \text{ constant}). \quad (13-2)$$

The subscript  $N$  is introduced for clarity below. These functions refer to the average *intrinsic* properties of a small system [see, for example, Eq. (2-108)]. If we have a polydisperse sample, we are still interested in average intrinsic properties, but now the averaging must be extended over  $N$  as well. If  $P_N$  is the fraction of small

systems in the ensemble with size  $N$ , we choose not to include an entropy  $-k \sum_N P_N \ln P_N$  in the definition of  $S$  (and  $F$ ) for a small system in the polydisperse case, on grounds that this entropy is not an "intrinsic" property. Note that this choice differs from that made in Eqs. (10-240) and (10-247) where  $-k \sum_N P_N \ln P_N$  was included for open systems. But this is as it should be: Any one *open* small system can take on the various values of  $N$ ; its entropy is higher because there is an additional set of states (values of  $N$ ) available to the system. In a polydisperse sample, on the other hand, each small system has a permanent value of  $N$ .

We therefore define the following properties per small system:

$$\begin{aligned} F &= \sum_N P_N F_N, & S &= \sum_N P_N S_N, \\ \bar{E} &= \sum_N P_N \bar{E}_N, & \bar{V} &= \sum_N P_N \bar{V}_N. \end{aligned} \quad (13-3)$$

If we multiply Eq. (13-1) by  $P_N$  and sum, we have

$$F = \bar{E} - TS + pV. \quad (13-4)$$

We regard  $P_N$  as a function of a set of parameters  $\alpha_1, \alpha_2, \dots$ .<sup>1</sup> For example, if the distribution is Gaussian and assumed continuous, there would be two parameters, the mean value  $\bar{N}$  and the standard deviation  $\sigma$ :

$$P_N(\bar{N}, \sigma) = \frac{\exp[-(N - \bar{N})^2/2\sigma^2]}{(2\pi)^{1/2}\sigma}. \quad (13-5)$$

In practical cases the number of parameters might range, say, from one to four. For convenience, we shall always make the assignment  $\alpha_1 = \bar{N}$ . The complete list of independent parameters determining the form of  $P_N$  is then  $\bar{N}, \alpha_2, \alpha_3, \dots$ .

Now from  $F = \sum_N P_N F_N$ , we deduce

$$\begin{aligned} dF &= \sum_N P_N dF_N + \sum_N F_N dP_N \\ &= \sum_N P_N (-S_N dT + \bar{V}_N dp) \\ &\quad + \sum_N F_N \left( \frac{\partial P_N}{\partial \bar{N}} d\bar{N} + \frac{\partial P_N}{\partial \alpha_2} d\alpha_2 + \dots \right) \\ &= -S dT + \bar{V} dp + \mu d\bar{N} + \Phi_2 d\alpha_2 + \dots, \end{aligned} \quad (13-6)$$

<sup>1</sup> See T. L. Hill, *J. Chem. Phys.*, **34**, 1974 (1961). This paper anticipates the present chapter in some respects and goes beyond it.

where we have introduced

$$\mu \equiv \sum_N F_N \left( \frac{\partial P_N}{\partial \bar{N}} \right)_{\alpha_2, \dots}, \quad \Phi_2 \equiv \sum_N F_N \left( \frac{\partial P_N}{\partial \alpha_2} \right)_{\bar{N}, \alpha_3, \dots}, \dots \quad (13-7)$$

Equations (13-4) and (13-6) are the basic equations for a polydisperse small system. Compared to Eq. (2-3) for a monodisperse  $N$ ,  $p$ ,  $T$  system, Eq. (13-6) requires extra terms in  $\alpha_2, \alpha_3, \dots$ , because of the dispersion of the distribution about the mean value  $\bar{N}$ . The variables  $F, S, \bar{V}, \bar{E}, \mu$ , etc., are functions of  $p, T, \bar{N}, \alpha_2, \dots$ . One is interested not only in the dependence of various properties on the average size  $\bar{N}$  of the small systems but also in the dependence on the shape of the distribution, determined by  $\alpha_2, \alpha_3, \dots$ .

We can define  $\hat{\mu}$  and  $\mathcal{E}$  by

$$\bar{N}\hat{\mu} \equiv F \quad \text{and} \quad \mathcal{E} \equiv \bar{N}(\hat{\mu} - \mu). \quad (13-8)$$

Then

$$\hat{\mu} = \frac{F}{\bar{N}} = \frac{1}{\bar{N}} \sum_N P_N N \hat{\mu}_N \quad (13-9)$$

and

$$d\mathcal{E} = -S dT + \bar{V} dp - \bar{N} d\mu + \Phi_2 d\alpha_2 + \dots \quad (13-10)$$

By differentiating  $\bar{N} = \sum_N P_N N$ , we obtain the following properties which we shall need below:

$$1 = \sum_N N \frac{\partial P_N}{\partial \bar{N}}, \quad 0 = \sum_N N \frac{\partial P_N}{\partial \alpha_2}, \quad \dots \quad (13-11)$$

The "macroscopic limit" here means that, even though there is a distribution in small system sizes, all small systems become very large. An example would be  $\bar{N} \rightarrow \infty$  with  $\alpha_2, \alpha_3, \dots$  held constant. In this case the distribution function  $P_N$  shifts toward large values of  $N$  without changing its shape. For systems of size  $N$  in the macroscopic limit,  $F_N = N\mu^{(0)}(p, T)$  [see Eq. (2-55)]. Then

$$F = \sum_N P_N N \mu^{(0)} = \bar{N} \mu^{(0)},$$

with a similar result for  $S, \bar{V}$ , etc. Also,

$$\mu = \sum_N N \mu^{(0)} \frac{\partial P_N}{\partial \bar{N}} = \mu^{(0)}, \quad \Phi_2 = \sum_N N \mu^{(0)} \frac{\partial P_N}{\partial \alpha_2} = 0, \quad \dots$$

Thus we have the usual macroscopic relations (despite the distribution):

$$\begin{aligned} F &= E - TS + p\bar{V} \\ \mu^{(0)} &= E^{(0)} - TS^{(0)} + pV^{(0)} \\ dF &= -SdT + \bar{V}dp + \mu^{(0)}d\bar{N}. \end{aligned} \quad (13-12)$$

Since

$$\hat{\mu} = F/\bar{N} = \mu^{(0)}, \quad \mathcal{E} = 0.$$

The equations in Section 2-1 are applicable here if the shape of the distribution  $(\alpha_2, \alpha_3, \dots)$  is held constant [see Eq. 13-6]. In addition, there will be various new relations involving changes in  $\alpha_2, \alpha_3, \dots$ . Examples are

$$\Phi_2 = \left( \frac{\partial F}{\partial \alpha_2} \right)_{T, p, \bar{N}, \alpha_3, \dots} = \left( \frac{\partial \mathcal{E}}{\partial \alpha_2} \right)_{T, p, \mu, \alpha_3, \dots} \quad (13-13)$$

$$\left( \frac{\partial S}{\partial \alpha_2} \right)_{T, p, \bar{N}, \alpha_3, \dots} = - \left( \frac{\partial \Phi_2}{\partial T} \right)_{p, \bar{N}, \alpha_2, \dots} \quad (13-14)$$

$$\begin{aligned} \left( \frac{\partial \Phi_2}{\partial \alpha_3} \right)_{T, p, \bar{N}, \alpha_j} &= \left( \frac{\partial \Phi_3}{\partial \alpha_2} \right)_{T, p, \bar{N}, \alpha_j} \\ \left( \frac{\partial \mu}{\partial \alpha_2} \right)_{T, p, \bar{N}, \alpha_3, \dots} &= \left( \frac{\partial \Phi_2}{\partial \bar{N}} \right)_{T, p, \alpha_2, \dots} \end{aligned} \quad (13-15)$$

*Example. Polydisperse Colloidal Particles.* Suppose we have a sample of colloidal particles with Gaussian polydispersity. We assume that (see pages 41 and 129 to 132 of Part I)

$$F_N = Nf(p, T) + a(p, T)N^{2/3} \quad (13-16)$$

and use Eq. (13-5) for  $F_N$ . If  $\sigma$  is small, we are interested only in values of  $N$  near  $N = \bar{N}$ . Hence we expand  $F_N$  about  $N = \bar{N}$ :

$$F_N = F_{\bar{N}} + \left( \frac{\partial F_N}{\partial N} \right)_{N=\bar{N}} (N - \bar{N}) + \frac{1}{2!} \left( \frac{\partial^2 F_N}{\partial N^2} \right)_{N=\bar{N}} (N - \bar{N})^2 + \dots \quad (13-17)$$

Then we find, from Eqs. (13-3a), (13-5), and (13-17),

$$\begin{aligned} F(\bar{N}, p, T, \sigma) &= \bar{N}f(p, T) \\ &+ a(p, T)\bar{N}^{2/3} \left[ 1 - \frac{1}{9} \left( \frac{\sigma}{\bar{N}} \right)^2 - \frac{7}{81} \left( \frac{\sigma}{\bar{N}} \right)^4 - \dots \right]. \end{aligned} \quad (13-18)$$

When  $\sigma/\bar{N} \rightarrow 0$  (monodisperse system), this reduces to the applicable terms in Eq. (2-68).

We use the notation  $\alpha_2 = \sigma$  and  $\Phi_2 = \Phi$  in Eq. (13-6). Equations (13-6) and (13-18) then give

$$-S = \bar{N} \frac{\partial f}{\partial T} + \frac{\partial a}{\partial T} \bar{N}^{2/3} \left[ 1 - \frac{1}{9} \left( \frac{\sigma}{\bar{N}} \right)^2 - \frac{7}{81} \left( \frac{\sigma}{\bar{N}} \right)^4 - \dots \right] \quad (13-19)$$

$$\bar{V} = \bar{N} \frac{\partial f}{\partial p} + \frac{\partial a}{\partial p} \bar{N}^{2/3} \left[ 1 - \frac{1}{9} \left( \frac{\sigma}{\bar{N}} \right)^2 - \frac{7}{81} \left( \frac{\sigma}{\bar{N}} \right)^4 - \dots \right] \quad (13-20)$$

$$\mu = f + \frac{2}{3} a \bar{N}^{-1/3} \left[ 1 + \frac{2}{9} \left( \frac{\sigma}{\bar{N}} \right)^2 + \frac{35}{81} \left( \frac{\sigma}{\bar{N}} \right)^4 + \dots \right] \quad (13-21)$$

$$\Phi = -\frac{2}{9} a \bar{N}^{-1/3} \left[ \left( \frac{\sigma}{\bar{N}} \right) + \frac{14}{9} \left( \frac{\sigma}{\bar{N}} \right)^3 + \dots \right] \quad (13-22)$$

$$\mathcal{E} = \frac{1}{3} a \bar{N}^{2/3} \left[ 1 - \frac{7}{9} \left( \frac{\sigma}{\bar{N}} \right)^2 - \frac{91}{81} \left( \frac{\sigma}{\bar{N}} \right)^4 - \dots \right]. \quad (13-23)$$

The self-consistency of these equations can be checked by Maxwell relations such as Eqs. (13-14a) and (13-15).

### 13-2. SMALL SYSTEMS IN SOLUTION

In this section we show, as an illustration, the explicit connections between the small system functions of the previous section and the usual functions of macroscopic solution thermodynamics, in the case that the small systems are in a solution. This is an extension of Section 2-3, which should be referred to.

We have, for the macroscopic solution,

$$dF_T = -S_T dT + V_T dp + \sum_{i=1}^c \mu_i^s dN_i^s + \sum_N \mu_N^\square d\mathcal{N}_N, \quad (13-24)$$

where  $\mathcal{N}_N$  is the number of small systems of size  $N$  and  $\mu_N^\square$  is the chemical potential of these small systems. The solution is infinitely dilute in all components  $N$  but not (usually) in the solvent components  $i$ . The integrated form of Eq. (13-24) is

$$F_T = \sum_i \mu_i^s N_i^s + \sum_N \mu_N^\square \mathcal{N}_N. \quad (13-25)$$

The chemical potential of component  $N$  has the properties

$$\mu_N^\square = \bar{E}_N^\square - T\bar{S}_N^\square + p\bar{V}_N^\square \quad (13-26)$$

$$d\mu_N^\square = -\bar{S}_N^\square dT + \bar{V}_N^\square dp + \frac{kT}{x'_N} dx'_N \quad (sc), \quad (13-27)$$

where  $x'_N = \mathcal{N}_N / (N_1^s + \cdots + N_c^s)$ . These expressions are the same as if  $N$  were the only small system component because all small system components are infinitely dilute in the solution. If we now define  $\hat{\mu}_N$ ,  $S_N$ , etc., by

$$\mu_N^\square = N\hat{\mu}_N(p, T, sc) + kT \ln x'_N \quad (13-28)$$

$$\bar{S}_N^\square = S_N(p, T, sc) - k \ln x'_N \quad (13-29)$$

$$\bar{E}_N^\square = \bar{E}_N, \quad \bar{V}_N^\square = \bar{V}_N, \quad (13-30)$$

just as in Section 2-3, and substitute these in Eqs. (13-26) and (13-27), we obtain Eqs. (13-1) and (13-2), the starting points of the preceding section.

This completes the necessary part of the argument, but it is instructive to consider an alternative point of view as well. Instead of using the  $\mathcal{N}_N$  as independent variables in Eq. (13-24), we introduce<sup>1</sup> the set of variables  $\mathcal{N}$ ,  $\bar{N}$ ,  $\alpha_2$ ,  $\alpha_3$ ,  $\cdots$ . Then

$$\begin{aligned} dF_T = & -S_T dT + V_T dp + \sum_i \mu_i^s dN_i^s + \mu^\square d\mathcal{N} \\ & + \mu' \mathcal{N} d\bar{N} + \Phi'_2 \mathcal{N} d\alpha_2 + \cdots \end{aligned} \quad (13-31)$$

This equation defines  $\mu^\square$ ,  $\mu'$ ,  $\Phi'_2$ ,  $\cdots$ . The mixture of components  $N$  is treated here as a pseudo single component just as in Eq. (13-3)ff. Integration of Eq. (13-31) yields

$$F_T = \sum_i \mu_i^s N_i^s + \mu^\square \mathcal{N}. \quad (13-32)$$

Comparison with Eq. (13-25) shows that

$$\begin{aligned} \mu^\square &= \sum_N P_N \mu_N^\square \\ &= \sum_N P_N (N\hat{\mu}_N + kT \ln P_N + kT \ln x') \\ &= \bar{N}\hat{\mu} + kT \sum_N P_N \ln P_N + kT \ln x', \end{aligned} \quad (13-33)$$

<sup>1</sup> See T. L. Hill, loc. cit.



where  $x' = \mathcal{N}/(N_1^s + \dots + N_c^s)$ . If we regard Eq. (13-33) as the definition of  $\hat{\mu}$  in terms of  $\mu^\square$ , we note that the two entropy terms  $-k \sum_N P_N \ln P_N$  and  $-k \ln x'$ , which are both present in  $\mu^\square$ , are subtracted out of this quantity in order to define an intrinsic  $\hat{\mu}$ .

By differentiating

$$F_T = E_T - TS_T + pV_T,$$

we obtain

$$\mu^\square = \left( \frac{\partial F_T}{\partial \mathcal{N}} \right)_{T, p, N_1^s, \bar{N}, \alpha_2, \dots} = \tilde{E}^\square - T\tilde{S}^\square + p\tilde{V}^\square. \quad (13-34)$$

Since

$$\mu^\square = \sum_N P_N \mu_N^\square = \sum_N P_N \tilde{E}_N^\square - T \sum_N P_N \tilde{S}_N^\square + p \sum_N P_N \tilde{V}_N^\square,$$

we then have

$$\tilde{E}^\square = \sum_N P_N \tilde{E}_N^\square = \sum_N P_N \bar{E}_N = \bar{E} \quad (13-35)$$

$$\tilde{V}^\square = \sum_N P_N \tilde{V}_N^\square = \sum_N P_N \bar{V}_N = \bar{V} \quad (13-36)$$

$$\begin{aligned} \tilde{S}^\square &= \sum_N P_N \tilde{S}_N^\square = \sum_N P_N S_N - k \sum_N P_N \ln(P_N x') \\ &= S - k \sum_N P_N \ln P_N - k \ln x'. \end{aligned} \quad (13-37)$$

This last result is consistent with the comments we made above about Eq. (13-33).

Finally, we have to establish the connections between the coefficients  $\mu, \Phi_2, \dots$  in Eq. (13-6) and  $\mu', \Phi'_2, \dots$  in Eq. (13-31). The argument is essentially the same as that beginning with Eq. (7-70). We find, instead of Eqs. (7-71) and (7-72),

$$\mu_k^s = \mu_k^* + \sum_N P_N \left[ (N_1^s + \dots + N_c^s) \frac{\partial N \hat{\mu}_N}{\partial N_k^s} - kT \right] x' \quad (13-38)$$

and

$$\sum_k N_k^s \sum_N P_N \frac{\partial N \hat{\mu}_N}{\partial N_k^s} = 0, \quad (13-39)$$

respectively, but Eq. (7-73) is unchanged. Then, from Eq. (13-32),

$$\begin{aligned}
 \mu' &= \left( \frac{\partial \mu^\square}{\partial \bar{N}} \right)_{T, p, N_1', \mathcal{N}, \alpha_2, \dots} \\
 &= \sum_N \frac{\partial P_N}{\partial \bar{N}} (N \hat{\mu}_N + kT \ln x'_N) + kT \sum_N \frac{\partial P_N}{\partial \bar{N}} \\
 &= \sum_N \frac{\partial P_N}{\partial \bar{N}} (N \hat{\mu}_N + kT \ln P_N) \\
 &= \sum_N \frac{\partial P_N}{\partial \bar{N}} N \hat{\mu}_N + kT \frac{\partial}{\partial \bar{N}} \sum_N P_N \ln P_N = \mu, \quad (13-40)
 \end{aligned}$$

since  $\sum_N P_N \ln P_N$  depends only on the shape ( $\alpha_2, \alpha_3, \dots$ ) of the distribution and not on the value of the mean  $\bar{N}$ . In the same way we find

$$\begin{aligned}
 \Phi'_j &= \sum_N \frac{\partial P_N}{\partial \alpha_j} N \hat{\mu}_N + kT \frac{\partial}{\partial \alpha_j} \sum_N P_N \ln P_N \\
 &= \Phi_j + kT \frac{\partial}{\partial \alpha_j} \sum_N P_N \ln P_N \quad (j = 2, 3, \dots). \quad (13-41)
 \end{aligned}$$

## HIGHER MOMENTS OF DISTRIBUTION FUNCTIONS

Macroscopic thermodynamics is concerned with mean values of fluctuating extensive variables ( $E$ ,  $N$ ,  $V$ , etc.). But a variable that fluctuates has a probability distribution of possible values, and the mean is only one property of the distribution. The complete distribution can be characterized, for example, by the mean and the second and higher central moments. The second central moment is the square of the standard deviation. The neglect of second and higher moments in macroscopic thermodynamics is justified by the fact that relative fluctuations about mean values are extremely small indeed, except in very special circumstances.

On the other hand, small systems have appreciable fluctuations about mean values. In this book we have so far confined ourselves to "mean-value thermodynamics" as in macroscopic thermodynamics. That is, fluctuating extensive variables are represented in the basic small system thermodynamic equations by mean values only. It thus appears that we may be overlooking a "higher-order" thermodynamics of small systems (although not of macroscopic systems): There may be equations connecting higher moments of fluctuating extensive properties of small systems which are higher analogues of the mean-value equations already encountered.

Such equations do exist and we derive some examples in this chapter. However, we do not pursue the subject very far because, at least in one important respect (see below), nothing fundamentally new comes out of the analysis. Also, the equations found are rather cumbersome.

We confine ourselves to one special but important type of small system: The small system has one extensive and two intensive environmental variables (e.g.,  $N$ ,  $p$ ,  $T$  and  $\mu$ ,  $V$ ,  $T$  systems). We use a generalized notation applicable to any such case.

Consider a system with environmental variables  $g_1$ ,  $g_2$  (small  $g$  = intensive), and  $G_3$  (large  $G$  = extensive), chosen so that<sup>1</sup>

<sup>1</sup> The brackets are inserted for purposes of comparison with other groups of terms below. We use special numbering on some equations in order to associate those equations belonging to the same hierarchy. For example: I, I<sup>(1)</sup>, I<sup>(2)</sup>, ...; II, II<sup>(1)</sup>, II<sup>(2)</sup>, ...; etc.

$$\left[ \frac{S}{k} + \hat{g}_3 G_3 \right] + g_1 \bar{G}_1 + g_2 \bar{G}_2 = 0. \quad (14-I)$$

For example:

$$\begin{aligned} g_1 &= -\frac{1}{kT}, & g_2 &= \frac{\mu}{kT}, & G_3 &= V, \\ G_1 &= E, & G_2 &= N, & g_3 &= -\frac{p}{kT}; \end{aligned} \quad (14-1)$$

or

$$\begin{aligned} g_1 &= -\frac{1}{kT}, & g_2 &= -\frac{p}{kT}, & G_3 &= N, \\ G_1 &= E, & G_2 &= V & g_3 &= \frac{\mu}{kT}; \end{aligned} \quad (14-2)$$

or

$$\begin{aligned} g_1 &= -\frac{p}{kT}, & g_2 &= \frac{\mu}{kT}, & G_3 &= E, \\ G_1 &= V, & G_2 &= N, & g_3 &= -\frac{1}{kT}. \end{aligned} \quad (14-3)$$

That is,  $G_1$  and  $G_2$  fluctuate, but  $G_3$  does not. The assignment (14-1) corresponds to Chapter 6, whereas (14-2) corresponds to Chapter 2.

Equation (14-I) is a basic "mean-value" equation [see Eq. (2-2), for example]. Besides Eq. (14-I), other important mean-value equations are

$$d\left(\frac{S}{k}\right) + g_1 d\bar{G}_1 + g_2 d\bar{G}_2 + g_3 dG_3 = 0 \quad (14-II)$$

$$d(\hat{g}_3 G_3) + \bar{G}_1 dg_1 + \bar{G}_2 dg_2 - g_3 dG_3 = 0 \quad (14-III)$$

$$d[(\hat{g}_3 - g_3)G_3] + \bar{G}_1 dg_1 + \bar{G}_2 dg_2 + G_3 dg_3 = 0. \quad (14-IV)$$

These are generalizations, for example, of Eqs. (2-1), (2-3), and (2-4), respectively. Our object, in this chapter, is to derive higher-moment analogues of Eqs. (14-I) to (14-IV).

We have to appeal to statistical mechanics in order to relate probability distribution moments to thermodynamics. Thus, in so far as higher moments are brought in, the argument is no longer

purely thermodynamic. The appropriate partition function here is

$$e^{-\bar{g}_3 G_3} = \sum_{G_1, G_2} \Omega(G_1, G_2, G_3) e^{g_1 G_1} e^{g_2 G_2} \quad (14-4)$$

and the probability of observing a  $g_1, g_2, G_3$  system with particular values of  $G_1$  and  $G_2$  is

$$\frac{\Omega(G_1, G_2, G_3) e^{g_1 G_1} e^{g_2 G_2}}{e^{-\bar{g}_3 G_3}}$$

Then,<sup>1</sup> for  $n + m = 1$  or  $2$ ,

$$\left[ \frac{\partial^{n+m} \bar{G}_1}{\partial g_1^n \partial g_2^m} \right]_{G_3} = \overline{(G_1 - \bar{G}_1)^{n+1} (G_2 - \bar{G}_2)^m}, \quad (14-5)$$

or we can exchange subscripts 1 and 2 in this equation. For  $n + m \geq 3$ , the left-hand side of Eq. (14-5) contains additional terms (lower-order derivatives of the same type). Hence the central moments of the  $G_1, G_2$  distribution are related to derivatives of  $\bar{G}_1$  and  $\bar{G}_2$  with respect to  $g_1$  and  $g_2$ . Therefore, if  $\bar{G}_1(g_1, g_2, G_3)$  and  $\bar{G}_2(g_1, g_2, G_3)$  are known, all higher central moments follow by differentiation. Thus, in a sense, the mean-value thermodynamic equations tell the whole story after all, and nothing basically new should be expected. But we still look for equations explicitly involving the higher moments [actually, we use the equivalent derivatives from Eq. (14-5)]. There does not appear to be a unique set of such equations, incidentally. We derive the simplest set we have encountered.

If  $Y$  is a function of  $g_1, g_2$ , and  $G_3$ , we define  $Y'$  by the operation

$$Y' = g_1 \left( \frac{\partial Y}{\partial g_1} \right)_{g_2, G_3} + g_2 \left( \frac{\partial Y}{\partial g_2} \right)_{g_1, G_3}, \quad (14-6)$$

and  $Y''$  by  $(Y')'$ , etc. We also define

$$Y^{(1)} = g_1 \frac{\partial Y}{\partial g_1} + g_2 \frac{\partial Y}{\partial g_2} = Y' \quad (14-7)$$

$$\begin{aligned} Y^{(2)} &= g_1^2 \frac{\partial^2 Y}{\partial g_1^2} + 2g_1 g_2 \frac{\partial^2 Y}{\partial g_1 \partial g_2} + g_2^2 \frac{\partial^2 Y}{\partial g_2^2} \\ &= Y'' - Y', \end{aligned} \quad (14-8)$$

<sup>1</sup> R. F. Greene and H. B. Callen, *Phys. Rev.*, **83**, 1231 (1951).

and so forth (using binomial coefficients in the definition of  $Y^{(n)}$ ). Thus we find

$$Y^{(3)} = Y''' - 3Y'' + 2Y' \quad (14-9)$$

$$Y^{(4)} = Y'''' - 6Y''' + 11Y'' - 6Y', \quad (14-10)$$

and so forth.

We start with Eq. (14-I) and apply to each term the "prime" operation defined in Eq. (14-6). We use the fact that

$$(-\hat{g}_3 G_3)' = g_1 \bar{G}_1 + g_2 \bar{G}_2 = -\left[\frac{S}{k} + \hat{g}_3 G_3\right]$$

and find

$$\left[\frac{S^{(1)}}{k}\right] + g_1 \bar{G}_1^{(1)} + g_2 \bar{G}_2^{(1)} = 0. \quad (14-I^{(1)})$$

By repeating the "prime" operation we also find

$$\left[\frac{S^{(2)} - S^{(1)}}{k}\right] + g_1 \bar{G}_1^{(2)} + g_2 \bar{G}_2^{(2)} = 0 \quad (14-I^{(2)})$$

$$\left[\frac{S^{(3)} - 2S^{(2)} + 2S^{(1)}}{k}\right] + g_1 \bar{G}_1^{(3)} + g_2 \bar{G}_2^{(3)} = 0 \quad (14-I^{(3)})$$

$$\left[\frac{S^{(4)} - 3S^{(3)} + 6S^{(2)} - 6S^{(1)}}{k}\right] + g_1 \bar{G}_1^{(4)} + g_2 \bar{G}_2^{(4)} = 0. \quad (14-I^{(4)})$$

These equations are the higher-moment analogues of Eq. (14-I). The coefficients in the first terms are simply related to binomial coefficients.

From Eq. (14-I<sup>(1)</sup>) we have

$$-\frac{S'}{k} = g_1 \bar{G}'_1 + g_2 \bar{G}'_2 = g_1 \frac{\partial(-S/k)}{\partial g_1} + g_2 \frac{\partial(-S/k)}{\partial g_2}.$$

Therefore

$$\frac{\partial(-S/k)}{\partial g_1} = \bar{G}'_1, \quad \frac{\partial(-S/k)}{\partial g_2} = \bar{G}'_2,$$

and

$$d\left(-\frac{S}{k}\right) = \bar{G}'_1 dg_1 + \bar{G}'_2 dg_2 + \frac{\partial(-S/k)}{\partial G_3} dG_3.$$

This is similar to Eq. (14-III) above. If we use Eq. (14-I) for  $S/k$ , we find

$$\begin{aligned}\frac{\partial(-S/k)}{\partial G_3} &= g_1 \frac{\partial \bar{G}_1}{\partial G_3} + g_2 \frac{\partial \bar{G}_2}{\partial G_3} + \frac{\partial(\hat{g}_3 G_3)}{\partial G_3} \\ &= -g_1 \frac{\partial g_3}{\partial g_1} - g_2 \frac{\partial g_3}{\partial g_2} + g_3 = -g'_3 + g_3.\end{aligned}$$

Therefore,

$$d\left(\frac{S}{k}\right) + \bar{G}_1^{(1)} dg_1 + \bar{G}_2^{(1)} dg_2 + (-g_3^{(1)} + g_3) dG_3 = 0 \quad (14-III^{(1)})$$

is the next higher analogue of Eq. (14-III).

Similarly, if we start with Eqs. (14-I<sup>(2)</sup>), (14-I<sup>(3)</sup>), etc., we can derive

$$\begin{aligned}d\left(\frac{S^{(1)} - 2S}{k}\right) + \bar{G}_1^{(2)} dg_1 + \bar{G}_2^{(2)} dg_2 \\ + (-g_3^{(2)} + 2g_3^{(1)} - 2g_3) dG_3 = 0 \quad (14-III^{(2)})\end{aligned}$$

$$\begin{aligned}d\left(\frac{S^{(2)} - 4S^{(1)} + 6S}{k}\right) + \bar{G}_1^{(3)} dg_1 + \bar{G}_2^{(3)} dg_2 + (-g_3^{(3)}) \\ + 3g_3^{(2)} - 6g_3^{(1)} + 6g_3) dG_3 = 0. \quad (14-III^{(3)})\end{aligned}$$

The coefficients in Eq. (14-III<sup>(4)</sup>) are 1, -6, +18, -24 and -1, +4, -12, +24, -24, respectively.

If we differentiate Eq. (14-I<sup>(1)</sup>) and combine it with Eq. (14-III<sup>(1)</sup>), we get

$$\begin{aligned}d\left(\frac{S^{(1)} - S}{k}\right) + g_1 d\bar{G}_1^{(1)} + g_2 d\bar{G}_2^{(1)} \\ + (g_3^{(1)} - g_3) dG_3 = 0. \quad (14-II^{(1)})\end{aligned}$$

Similarly, from Eqs. (14-I<sup>(2)</sup>) and (14-III<sup>(2)</sup>), etc.,

$$\begin{aligned}d\left(\frac{S^{(2)} - 2S^{(1)} + 2S}{k}\right) + g_1 d\bar{G}_1^{(2)} + g_2 d\bar{G}_2^{(2)} \\ + (g_3^{(2)} - 2g_3^{(1)} + 2g_3) dG_3 = 0 \quad (14-II^{(2)})\end{aligned}$$

$$\begin{aligned}d\left(\frac{S^{(3)} - 3S^{(2)} + 6S^{(1)} - 6S}{k}\right) + g_1 d\bar{G}_1^{(3)} + g_2 d\bar{G}_2^{(3)} \\ + (g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3) dG_3 = 0. \quad (14-II^{(3)})\end{aligned}$$

The coefficients in Eq. (14-II<sup>(4)</sup>) are 1, -4, +12, -24, +24. These are the higher-moment analogues of Eq. (14-II).

Finally, from Eqs. (14-III<sup>(1)</sup>), (14-III<sup>(2)</sup>), etc., we have

$$d\left[\left(-g_3^{(1)} + g_3 + \frac{S}{G_3 k}\right)G_3\right] + \bar{G}_1^{(1)} dg_1 + \bar{G}_2^{(1)} dg_2 + G_3 d(g_3^{(1)} - g_3) = 0 \quad (14-IV^{(1)})$$

$$d\left[\left(-g_3^{(2)} + 2g_3^{(2)} - 2g_3 + \frac{S^{(1)} - 2S}{G_3 k}\right)G_3\right] + \bar{G}_1^{(2)} dg_1 + \bar{G}_2^{(2)} dg_2 + G_3 d(g_3^{(2)} - 2g_3^{(1)} + 2g_3) = 0, \quad (14-IV^{(2)})$$

and so forth. These are the analogues of Eq. (14-IV).

On comparing the functions playing equivalent roles in the above hierarchies of equations, we note the sequences

$$\begin{array}{ccccccc} \bar{G}_1, & \bar{G}_1^{(1)}, & \bar{G}_1^{(2)}, & \dots & & & \\ \bar{G}_2, & \bar{G}_2^{(1)}, & \bar{G}_2^{(2)}, & \dots & & & \\ \hat{g}_3 G_3, & \frac{S}{k}, & \frac{S^{(1)} - 2S}{k}, & \frac{S^{(2)} - 4S^{(1)} + 6S}{k}, & \dots & & \\ g_3, & g_3^{(1)} - g_3, & g_3^{(2)} - 2g_3^{(1)} + 2g_3, & \dots, & & & \end{array}$$

from which the other sequences can be constructed.

There is some simplification in these equations in the case of macroscopic systems. In Eqs. (14-I), (14-III), and (14-IV),  $\hat{g}_3$  is replaced by  $g_3$ . In the sequences of equations beginning with (14-III<sup>(1)</sup>), (14-II<sup>(1)</sup>), and (14-IV<sup>(1)</sup>), we replace

$$g_3^{(1)} - g_3, \quad g_3^{(2)} - 2g_3^{(1)} + 2g_3, \quad g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3, \quad \dots$$

by

$$\frac{S}{G_3 k}, \quad \frac{S^{(1)} - 2S}{G_3 k}, \quad \frac{S^{(2)} - 4S^{(1)} + 6S}{G_3 k}, \quad \dots,$$

as is apparent from the sequence (14-III<sup>(1)</sup>), (14-III<sup>(2)</sup>), ... . Thus the leading term in each of the equations (14-IV), (14-IV<sup>(1)</sup>), ... , vanishes.

It may be that more compact higher-order equations exist, but we have not found them.



In summary, we have derived the hierarchies beginning with Eqs. (14-I<sup>(1)</sup>), (14-II<sup>(1)</sup>), (14-III<sup>(1)</sup>), and (14-IV<sup>(1)</sup>). These are higher analogues of Eqs. (14-I) to (14-IV), respectively. Quantities of the type  $\bar{G}_1^{(n)}$  and  $\bar{G}_2^{(n)}$  appear. These involve  $n$ th derivatives of  $\bar{G}_1$  and  $\bar{G}_2$  with respect to  $g_1$  and  $g_2$ . These derivatives, in turn, are related to higher central moments in the  $G_1, G_2$  distribution.

# DIFFERENCE EQUATIONS AND VERY SMALL SYSTEMS

Differential equations are used in macroscopic thermodynamics and we have carried over their use to small systems. However, as has been mentioned several times in earlier chapters, this cannot be done indiscriminately. Specifically, the concept of the *differential* of a *discrete* thermodynamic variable cannot be extended to arbitrarily small values of the variable. For very small values, it is necessary to employ differences instead of differentials. Hence we have the task, in this chapter, of introducing some new definitions of thermodynamic functions for very small systems and of deriving new equations interrelating these and other functions. The new equations provide an extension of small system thermodynamics in much the same way that small system thermodynamics extends ordinary thermodynamics.

There are some cases, incidentally, for which, on letting the system become small, it is necessary to make the transition directly from macroscopic thermodynamics to very small system thermodynamics (omitting the intermediate stage). This arises when discreteness influences first-order small terms. Some examples are given in the present chapter.

Discrete extensive environmental variables are the ones of primary concern to us. Examples are: the variable  $N$  in an  $N, p, T$  system; the variable  $B$  in a  $\mu, B, T$  system ( $B$  = number of sites, as in Chapter 6); the variable  $N$  in an  $N, V, T$  system ( $V$  continuous); the variables  $N$  and  $B$  in an  $N, B, T$  system (Chapter 8); and the variables  $N, B$ , and  $E$  in an  $N, B, E$  system (Chapter 9). The first four of these cases serve as the subjects of the respective sections of this chapter.

An extensive variable that fluctuates, and is averaged, is of course continuous, not discrete. Examples are: the variables  $\bar{E}$  and  $\bar{V}$  in an  $N, p, T$  system;  $\bar{N}$  and  $\bar{E}$  in a  $\mu, B, T$  system; etc. The variables  $\mu, p$ , and  $T$  are also continuous. Thus, in a  $\mu, p, T$  system, all variables are continuous.

One could discuss the thermodynamics of very small systems with discrete variables in considerable detail, much as small systems

have been treated in Chapters 1 to 14. But we intend just the opposite here. We shall merely choose a few special cases and indicate some of the new features that arise. One important point might be mentioned at the outset: the thermodynamic equations are no longer the same for all environments.

### 15-1. $N, p, T$ SYSTEMS

The basic equations of Chapter 2 are valid here, and can be used as a starting point, *provided* we hold  $N$  (the only discrete environmental variable) constant. This statement applies to a theoretical ensemble of small systems or to experimental small systems in a solvent. It can be verified by dropping the term in  $dN$  in Eq. (1-49) or Eq. (2-122), but otherwise using the same arguments as before. We then have [Eqs. (2-2) and (2-3)], in obvious notation,

$$F_N = \hat{\mu}_N N = E_N - TS_N + p\bar{V}_N \quad (15-1)$$

$$dF_N = d(\hat{\mu}_N N) = -S_N dT + \bar{V}_N dp \quad (N \text{ constant}). \quad (15-2)$$

Of course  $\hat{\mu}_N$ ,  $E_N$ ,  $S_N$ , and  $\bar{V}_N$  are all continuous functions of  $p$  and  $T$ .

We now want to introduce variations in  $N$  in Eq. (15-2). But when  $N$  is sufficiently small,<sup>1</sup> it must be treated as a discrete rather than continuous variable. Let us digress to consider the effect of discrete variations in  $N$  on an arbitrary variable  $f_N(p, T)$ .

If  $N$ ,  $p$ , and  $T$  are all treated as continuous variables ( $N$  large),

$$df_N = \left( \frac{\partial f_N}{\partial T} \right)_{p, N} dT + \left( \frac{\partial f_N}{\partial p} \right)_{T, N} dp + \left( \frac{\partial f_N}{\partial N} \right)_{T, p} dN. \quad (15-3)$$

The three terms on the right are additive because the variations  $dT$ ,  $dp$ , and  $dN$  are infinitesimals. Any or all of  $dT$ ,  $dp$ , and  $dN$  may be nonzero in this equation. The situation is somewhat different when  $N$  is discrete. Without loss of generality, we let the variation  $\Delta N$  have only two possible values:  $\Delta N = 0$  or  $\Delta N = +1$ . If  $\Delta N = +1$  and  $T$ ,  $p = \text{constant}$ , we use the notation  $\delta f_N = f_{N+1} - f_N$  for the variation in  $f_N$ . The variation in  $f_N$  when  $N$  decreases from  $N$  to  $N - 1$  would then be written  $-\delta f_{N-1}$ . If we allow variations

<sup>1</sup> This depends on the accuracy desired or experimental error involved. For example, if the value of  $N$  is accurate to two per cent, the smallest possible change in  $N$ ,  $\Delta N = 1$ , could be considered a differential change ( $N$  is effectively continuous) for  $N > 0(50)$ . But  $N$  should be regarded as discrete for  $N < 0(50)$ .

in any or all of  $T$ ,  $p$ , and  $N$ , the complete expression for  $\delta f_N$ , which replaces Eq. (15-3), is easily seen to be

$$\begin{aligned} \delta f_N = & \left( \frac{\partial f_N}{\partial T} \right)_{p, N} dT + \left( \frac{\partial f_N}{\partial p} \right)_{T, N} dp + (f_{N+1} - f_N) \Delta N \\ & + \left[ \frac{\partial(f_{N+1} - f_N)}{\partial T} dT + \frac{\partial(f_{N+1} - f_N)}{\partial p} dp \right] \Delta N, \end{aligned} \quad (15-4)$$

where, as always,  $\Delta N = 0$  or  $+1$ . Thus if  $dT$  and  $dp$  are nonzero and  $\Delta N = +1$ ,

$$\delta f_N = f_{N+1} - f_N + \frac{\partial f_{N+1}}{\partial T} dT + \frac{\partial f_{N+1}}{\partial p} dp \quad (\Delta N = +1) \quad (15-5)$$

as it should be.

The differing uses of the three symbols  $\Delta$ ,  $\delta$ , and  $d$ , above, should be noted. Whenever  $\Delta N = +1$ ,  $\delta f_N$  represents a finite change and not a differential.

In view of

$$\delta f_N = \left( \frac{\partial f_N}{\partial T} \right)_{p, N} dT \quad (p, N \text{ constant})$$

and

$$\delta f_N = (f_{N+1} - f_N) \Delta N \quad (p, T \text{ constant}),$$

we introduce the notation

$$\begin{aligned} \left( \frac{\delta f_N}{\partial T} \right)_{p, N} &= \left( \frac{\partial f_N}{\partial T} \right)_{p, N}, & \left( \frac{\delta f_N}{\partial p} \right)_{T, N} &= \left( \frac{\partial f_N}{\partial p} \right)_{T, N}, \\ \left( \frac{\delta f_N}{\Delta N} \right)_{T, p} &= f_{N+1} - f_N. \end{aligned} \quad (15-6)$$

Since

$$\left[ \frac{\delta}{\Delta N} \left( \frac{\partial f_N}{\partial p} \right)_{T, N} \right]_{T, p} = \left( \frac{\partial f_{N+1}}{\partial p} \right)_{T, N} - \left( \frac{\partial f_N}{\partial p} \right)_{T, N}, \quad (15-7)$$

we have the Maxwell relation

$$\left[ \frac{\delta}{\Delta N} \left( \frac{\partial f_N}{\partial p} \right)_{T, N} \right]_{T, p} = \left[ \frac{\delta(f_{N+1} - f_N)}{\partial p} \right]_{T, N}, \quad (15-8)$$

and a similar one between  $T$  and  $N$  (the conventional relation between  $T$  and  $p$  is of course also valid).

For most purposes it suffices to consider variations in *either* the continuous variables *or* the discrete variable, but not both [as allowed in Eq. (15-4)]. In this case we write

$$\delta f_N^* = \left( \frac{\partial f_N}{\partial T} \right)_{p, N} dT + \left( \frac{\partial f_N}{\partial p} \right)_{T, N} dp + (f_{N+1} - f_N) \Delta N, \quad (15-9)$$

where the asterisk indicates the restriction just referred to. Equations (15-6) to (15-8), for example, follow from Eq. (15-9) as well as from Eq. (15-4).

A derivative such as  $(\partial p / \Delta N)_{T, f_N}$  is meaningless in the present calculus, although not in ordinary calculus. The reason for this is that when  $\Delta N = +1$  and  $T = \text{constant}$ , a *finite* change in  $p$ ,  $\delta p$ , would be required in order to hold  $f_N$  constant, i.e., in order that  $f_N(T, p) = f_{N+1}(T, p + \delta p)$ . But Eq. (15-4) is restricted to infinitesimal changes in  $p$ . Equation (15-9) would not apply in any case since both  $N$  and  $p$  are varied.

We can verify from the definition of  $\delta f_N$  in Eq. (15-4) that

$$\delta(f_N + g_N) = \delta f_N + \delta g_N,$$

a property which we shall need presently.

Let us return now to Eqs. (15-1) and (15-2). If we apply Eq. (15-4) to the function  $F_N(p, T)$  and define<sup>1</sup> the chemical potential

$$\mu_N(p, T) \equiv F_{N+1}(p, T) - F_N(p, T), \quad (15-10)$$

then we have

$$\delta F_N = -S_N dT + \bar{V}_N dp + \mu_N \Delta N + \left[ \left( \frac{\partial \mu_N}{\partial T} \right)_{p, N} dT + \left( \frac{\partial \mu_N}{\partial p} \right)_{T, N} dp \right] \Delta N \quad (15-11)$$

and also

$$\begin{aligned} \left( \frac{\delta F_N}{\partial T} \right)_{p, N} &= \left( \frac{\partial F_N}{\partial T} \right)_{p, N} = -S_N \\ \left( \frac{\delta F_N}{\partial p} \right)_{T, N} &= \left( \frac{\partial F_N}{\partial p} \right)_{T, N} = \bar{V}_N \end{aligned} \quad (15-12)$$

<sup>1</sup> The choice between  $F_N - F_{N-1}$  and  $F_{N+1} - F_N$  is of course arbitrary. The two quantities are not quite equivalent. The difference  $F_{N+1/2} - F_{N-1/2}$  is closer in value to the derivative (see the Appendix), but this definition is excluded because the number of molecules or units in the system must be an integer.

$$\left(\frac{\delta F_N}{\Delta N}\right)_{T,p} = \mu_N, \quad \left(\frac{\partial \bar{V}_N}{\partial T}\right)_{p,N} = -\left(\frac{\partial S_N}{\partial p}\right)_{T,N} \quad (15-13)$$

$$-\left(\frac{\delta S_N}{\Delta N}\right)_{T,p} = \left(\frac{\partial \mu_N}{\partial T}\right)_{p,N} = -S_{N+1} + S_N \quad (15-14)$$

$$\left(\frac{\delta \bar{V}_N}{\Delta N}\right)_{T,p} = \left(\frac{\partial \mu_N}{\partial p}\right)_{T,N} = \bar{V}_{N+1} - \bar{V}_N. \quad (15-15)$$

Thus alternative forms of Eq. (15-11) are

$$\begin{aligned} \delta F_N = & -S_N dT + \bar{V}_N dp + \mu_N \Delta N \\ & + \left[ -\left(\frac{\delta S_N}{\Delta N}\right)_{T,p} dT + \left(\frac{\delta \bar{V}_N}{\Delta N}\right)_{T,p} dp \right] \Delta N \end{aligned} \quad (15-16)$$

$$^* = -S_N dT + \bar{V}_N dp + \mu_N \Delta N. \quad (15-17)$$

Equations (15-11) and (15-16) are the extensions of Eq. (2-3) to very small systems. They reduce to Eq. (2-3) when  $N$  is large enough for  $\Delta N$  to be considered a differential.<sup>1</sup>

At this point, the reader may wish to consult the Appendix to this chapter. It compares the difference  $\mu_N$  and the derivative  $\mu(N)$  for a number of simple types of small terms.

It might also be mentioned here that  $\mu_N$  for a very small system does not have the conventional physical significance of a potential which determines the approach to, and point of, material transport equilibrium. The primary reason for this is that the system under discussion is closed, not open. The same comment applies, of course, to a closed, small  $N, p, T$  system. One should view  $\mu_N$  as merely an interesting property that provides a logical mathematical extension of the function  $\mu(N)$  to very small systems.

From Eq. (15-4) we have

$$\delta(TS_N) = T \delta S_N + S_N dT + \left(\frac{\delta S_N}{\Delta N}\right)_{T,p} dT \Delta N \quad (15-18)$$

$$\delta(p\bar{V}_N) = p \delta \bar{V}_N + \bar{V}_N dp + \left(\frac{\delta \bar{V}_N}{\Delta N}\right)_{T,p} dp \Delta N. \quad (15-19)$$

<sup>1</sup> See the footnote on p. 188.

Then

$$\begin{aligned}\delta A_N &= \delta(\bar{E}_N - TS_N) = \delta(F_N - p\bar{V}_N) \\ &= -S_N dT - p \delta\bar{V}_N + \mu_N \Delta N - \left(\frac{\delta S_N}{\Delta N}\right)_{T,p} dT \Delta N\end{aligned}\quad (15-20)$$

$$\begin{aligned}\delta H_N &= \delta(\bar{E}_N + p\bar{V}_N) = \delta(F_N + TS_N) \\ &= T \delta S_N + \bar{V}_N dp + \mu_N \Delta N + \left(\frac{\delta\bar{V}_N}{\Delta N}\right)_{T,p} dp \Delta N\end{aligned}\quad (15-21)$$

$$\begin{aligned}\delta\bar{E}_N &= \delta(F_N + TS_N - p\bar{V}_N) \\ &= T \delta S_N - p \delta\bar{V}_N + \mu_N \Delta N.\end{aligned}\quad (15-22)$$

It should be noted that, for example,

$$\begin{aligned}\left(\frac{\delta A_N}{\delta\bar{V}_N}\right)_{T,N} &= \left(\frac{\partial A_N}{\partial\bar{V}_N}\right)_{T,N} = -p \\ \left(\frac{\delta A_N}{\partial T}\right)_{\bar{V}_N,N} &= \left(\frac{\partial A_N}{\partial T}\right)_{\bar{V}_N,N} = -S_N \\ \left(\frac{\delta\bar{E}_N}{\delta S_N}\right)_{\bar{V}_N,N} &= \left(\frac{\partial\bar{E}_N}{\partial S_N}\right)_{\bar{V}_N,N} = T,\end{aligned}$$

because only ordinary differentials are encountered when  $N$  is constant. But quantities like  $(\delta A_N/\Delta N)_{T,\bar{V}_N}$ , etc., are not defined, for a finite  $\delta p$  is required to keep  $\bar{V}_N$  constant and only differentials of  $p$  and  $T$  are allowed in Eq. (15-20).

We define  $\mathcal{E}_N$  by

$$\mathcal{E}_N \equiv F_N - \mu_N N = N(\hat{\mu}_N - \mu_N), \quad (15-23)$$

and seek expressions for  $\delta\mathcal{E}_N$ . We find

$$\begin{aligned}\delta\mathcal{E}_N &= \delta F_N - \delta(\mu_N N) \\ &= -\left[S_N - N\left(\frac{\delta S_N}{\Delta N}\right)_{T,p}\right] dT + \left[\bar{V}_N - N\left(\frac{\delta\bar{V}_N}{\Delta N}\right)_{T,p}\right] dp \\ &\quad - (N+1)(\mu_{N+1} - \mu_N) \Delta N \\ &\quad - (N+1)\left[\frac{\partial(\mu_{N+1} - \mu_N)}{\partial T} dT + \frac{\partial(\mu_{N+1} - \mu_N)}{\partial p} dp\right] \Delta N\end{aligned}\quad (15-24)$$

$$\begin{aligned}
 &= - \left[ S_N - N \left( \frac{\delta S_N}{\Delta N} \right)_{T,p} \right] dT + \left[ \bar{V}_N - N \left( \frac{\delta \bar{V}_N}{\Delta N} \right)_{T,p} \right] dp \\
 &\quad + \left( \frac{\delta \mathcal{E}_N}{\Delta N} \right)_{T,p} \Delta N, \quad (15-25)
 \end{aligned}$$

where

$$\left( \frac{\delta \mathcal{E}_N}{\Delta N} \right)_{T,p} = - (N + 1) (\mu_{N+1} - \mu_N). \quad (15-26)$$

Equations (15-24) and (15-25) should be compared with Eq. (2-23).

Since [compare Eq. (2-17)]

$$\begin{aligned}
 \delta \mu_N &= - \left( \frac{\delta S_N}{\Delta N} \right)_{T,p} dT + \left( \frac{\delta \bar{V}_N}{\Delta N} \right)_{T,p} dp + (\mu_{N+1} - \mu_N) \Delta N \\
 &\quad + \left[ \frac{\partial(\mu_{N+1} - \mu_N)}{\partial T} dT + \frac{\partial(\mu_{N+1} - \mu_N)}{\partial p} dp \right] \Delta N \quad (15-27)
 \end{aligned}$$

$$\begin{aligned}
 &= - \left( \frac{\delta S_N}{\Delta N} \right)_{T,p} dT + \left( \frac{\delta \bar{V}_N}{\Delta N} \right)_{T,p} dp \\
 &\quad - \frac{1}{(N + 1)} \left( \frac{\delta \mathcal{E}_N}{\Delta N} \right)_{T,p} \Delta N, \quad (15-28)
 \end{aligned}$$

we can write Eq. (15-24) in the alternative form

$$\delta \mathcal{E}_N = - S_{N+1} dT + \bar{V}_{N+1} dp - (N + 1) \delta \mu_N. \quad (15-29)$$

A similar relation which is easy to prove is

$$\delta(F_{N+1} - \mu_N N) = - S_{N+1} dT + \bar{V}_{N+1} dp - N \delta \mu_N. \quad (15-30)$$

The derivatives  $(\delta \mathcal{E}_N / \partial T)_{p, \mu_N}$  and  $(\delta \mathcal{E}_N / \partial p)_{T, \mu_N}$  are meaningless but, in view of

$$\delta \mathcal{E}_N = - (N + 1) (\mu_{N+1} - \mu_N) \Delta N \quad (T, p \text{ constant})$$

and

$$\delta \mu_N = (\mu_{N+1} - \mu_N) \Delta N \quad (T, p \text{ constant}),$$

we have

$$\left( \frac{\delta \mathcal{E}_N}{\delta \mu_N} \right)_{T,p} = - (N + 1). \quad (15-31)$$



The expressions for  $\delta\hat{\mu}_N$  are

$$\begin{aligned}\delta\hat{\mu}_N = & -\frac{S_N}{N}dT + \frac{\bar{V}_N}{N}dp - \frac{\mathcal{E}_N}{N(N+1)}\Delta N \\ & + \left[ \frac{\partial(\hat{\mu}_{N+1} - \hat{\mu}_N)}{\partial T}dT + \frac{\partial(\hat{\mu}_{N+1} - \hat{\mu}_N)}{\partial p}dp \right] \Delta N\end{aligned}\quad (15-32)$$

$$= -\frac{S_N}{N}dT + \frac{\bar{V}_N}{N}dp - \frac{\mathcal{E}_N}{N(N+1)}\Delta N. \quad (15-33)$$

These are the extensions of Eq. (2-13). Thus

$$\begin{aligned}\left(\frac{\delta\hat{\mu}_N}{\Delta N}\right)_{T,p} &= -\frac{\mathcal{E}_N}{N(N+1)} \\ &= \hat{\mu}_{N+1} - \hat{\mu}_N = \frac{\mu_N - \hat{\mu}_{N+1}}{N} = \frac{\mu_N - \hat{\mu}_N}{N+1}.\end{aligned}\quad (15-34)$$

As an example of the effect of size on an intensive variable of the type  $G_N/N$  (see page 34 of Part I), we consider  $\bar{V}_N/N$ . We have

$$\left(\frac{\delta(\bar{V}_N/N)}{\Delta N}\right)_{T,p} = \frac{\bar{V}_{N+1}}{N+1} - \frac{\bar{V}_N}{N} = \frac{N\bar{V}_{N+1} - (N+1)\bar{V}_N}{N(N+1)}$$

and

$$\left(\frac{\delta\mathcal{E}_N}{\partial p}\right)_{T,N} = \bar{V}_N - N\left(\frac{\delta\bar{V}_N}{\Delta N}\right)_{T,p} = -N\bar{V}_{N+1} + (N+1)\bar{V}_N.$$

Therefore

$$\left(\frac{\delta\bar{V}_N/N}{\Delta N}\right)_{T,p} = -\frac{1}{N(N+1)}\left(\frac{\delta\mathcal{E}_N}{\partial p}\right)_{T,N}. \quad (15-35)$$

For the heat capacity (see page 33 of Part I) we write

$$DQ_N = C_N dT = T dS_N \quad (p, N \text{ constant}),$$

or

$$C_N = T\left(\frac{\partial S_N}{\partial T}\right)_{p,N} = -NT\left(\frac{\partial^2\hat{\mu}_N}{\partial T^2}\right)_{p,N}. \quad (15-36)$$

Then

$$\begin{aligned}\left[\frac{\delta(C_N/N)}{\Delta N}\right]_{p,T} &= \frac{C_{N+1}}{N+1} - \frac{C_N}{N} = T\frac{\partial^2(\hat{\mu}_N - \hat{\mu}_{N+1})}{\partial T^2} \\ &= \frac{T}{N(N+1)}\left(\frac{\partial^2\mathcal{E}_N}{\partial T^2}\right)_{p,N}.\end{aligned}\quad (15-37)$$

EXPANSIONS IN POWERS OF  $N^{-1}$ . In some cases, an expansion of  $\hat{\mu}_N$  in powers of  $N^{-1}$  may exist (compare page 136 of Part I):

$$\hat{\mu}_N(p, T) = \mu^{(0)}(p, T) + N^{-1}\hat{\mu}^{(1)}(p, T) + N^{-2}\hat{\mu}^{(2)}(p, T) + \dots \quad (15-38)$$

The smaller the system, the greater the number of terms required. But if the system is small enough, the equations satisfied by  $\hat{\mu}_N$  are those of the present section rather than of Chapter 2. Therefore, even if the expansion exists, Eq. (15-38) should not in general be used in Chapter 2. For example,

$$\begin{aligned} \mu_N &= (N + 1) \hat{\mu}_{N+1} - N \hat{\mu}_N \\ &= \mu^{(0)} - N^{-2}\hat{\mu}^{(2)} + N^{-3}(\hat{\mu}^{(2)} - 2\hat{\mu}^{(3)}) - \dots, \end{aligned} \quad (15-39)$$

whereas, from Chapter 2,

$$\mu = \left( \frac{\partial N \hat{\mu}_N}{\partial N} \right)_{T, p} = \mu^{(0)} - N^{-2}\hat{\mu}^{(2)} - 2N^{-3}\hat{\mu}^{(3)} - \dots \quad (15-40)$$

A discrepancy between  $\mu_N$  and  $\mu$  appears beginning with the term in  $N^{-3}$ . Thus, for a system that allows expansions in powers of  $N^{-1}$ , difference equations must be employed if the system is small enough that the  $N^{-3}$  term in  $\hat{\mu}_N$ , or the  $N^{-2}$  term in  $F_N$ , is required in order to achieve sufficient accuracy.

Other functions are

$$\mathcal{E}_N = N(\hat{\mu}_N - \mu_N) = \hat{\mu}^{(1)} + 2N^{-1}\hat{\mu}^{(2)} + N^{-2}(-\hat{\mu}^{(2)} + 3\hat{\mu}^{(3)}) + \dots \quad (15-41)$$

$$-\frac{S_N}{N} = \left( \frac{\partial \hat{\mu}_N}{\partial T} \right)_{p, N} = \frac{\partial \mu^{(0)}}{\partial T} + N^{-1} \frac{\partial \hat{\mu}^{(1)}}{\partial T} + N^{-2} \frac{\partial \hat{\mu}^{(2)}}{\partial T} + \dots \quad (15-42)$$

$$\frac{\bar{V}_N}{N} = \left( \frac{\partial \hat{\mu}_N}{\partial p} \right)_{T, N} = \frac{\partial \mu^{(0)}}{\partial p} + N^{-1} \frac{\partial \hat{\mu}^{(1)}}{\partial p} + N^{-2} \frac{\partial \hat{\mu}^{(2)}}{\partial p} + \dots \quad (15-43)$$

*Examples.* In treating simple examples on pages 43 and 69 of Part I, it was necessary to point out that differentiation with respect to  $N$  could not be carried to arbitrarily small  $N$ . We have eliminated this restriction in the present section by replacing the derivative  $\mu$  by the difference  $\mu_N$ . But it happens that in the two examples referred to above,  $\hat{\mu}_N N$  is *linear* in  $N$ . In such a case,  $\mu$  and  $\mu_N$  are identical. Hence we now find that our earlier precautionary remarks,

in these two cases, happened to be unnecessary. In general, of course,  $\mu$  and  $\mu_N$  will differ, and  $\mu_N$  must be used for very small  $N$ .

Pages 46 and 48 of Part I provide simple examples of models in which  $\mu$  and  $\mu_N$  differ. We leave it to the reader to write out the expressions for  $\mu_N$ . Note that the formula for  $\bar{n}$  involves differentiation with respect to  $r$  at constant  $N$  [this is equivalent to Eq. (15-12b)] and hence is valid, as it stands, for very small  $N$ .

### 15-2. $\mu, B, T$ SYSTEMS

This case is formally identical with that treated in the preceding section. We can take over all the equations<sup>1</sup> of Section 15-1 by using the transcription [see (6-5)]

$$\begin{aligned} \bar{E}_N &\rightarrow \bar{E}_B, & T &\rightarrow T, & S_N &\rightarrow S_B \\ N &\rightarrow B, & \bar{V}_N &\rightarrow \bar{N}_B, & \mathcal{E}_N &\rightarrow \mathcal{E}_B \\ \mu_N &\rightarrow -p_B, & \hat{\mu}_N &\rightarrow -\hat{p}_B, & p &\rightarrow -\mu. \end{aligned} \quad (15-44)$$

*Examples.* The function  $\hat{p}B$  for an ideal lattice gas (page 142 of Part I) is linear in  $B$ . Hence  $p$  and  $p_B$  are identical. This situation is analogous to that on pages 43 and 69 of Part I, referred to above.

In the treatment of a Bragg-Williams lattice gas on pages 145 to 149 of Part I,  $B$  and  $N$  are regarded as continuous variables. There seems to be little point, however, in "improving" this treatment by the introduction of discreteness because the potential energy term,  $\alpha N^2/B$ , is an approximation which itself is based on a "continuous" argument.

### 15-3. $N, V, T$ SYSTEMS

Here  $N$  is a discrete variable but we consider  $V$  to be continuous, as in many theoretical models. Because there is one discrete variable, the situation is quite similar to that in Sections 15-1 and 15-2.

The fundamental equations are (page 18, Part I)

$$A_N = \bar{E}_N - TS_N \quad (15-45)$$

$$dA_N = -S_N dT - p_N dV \quad (N \text{ constant}), \quad (15-46)$$

<sup>1</sup>But  $DQ_B$  has to be omitted from the equation preceding (15-36). See the bottom of p. 135, Part I.

where  $A_N$ ,  $\bar{E}_N$ ,  $S_N$ , and  $p_N$  are all functions of  $V$  and  $T$ . For the variation in an arbitrary function  $f_N(V, T)$ , we have

$$\begin{aligned} \delta f_N = & \left( \frac{\partial f_N}{\partial T} \right)_{V, N} dT + \left( \frac{\partial f_N}{\partial V} \right)_{T, N} dV + (f_{N+1} - f_N) \Delta N \\ & + \left[ \frac{\partial(f_{N+1} - f_N)}{\partial T} dT + \frac{\partial(f_{N+1} - f_N)}{\partial V} dV \right] \Delta N. \end{aligned} \quad (15-47)$$

We define

$$\mu_N(V, T) \equiv A_{N+1}(V, T) - A_N(V, T). \quad (15-48)$$

Then

$$\begin{aligned} \delta A_N = & -S_N dT - p_N dV + \mu_N \Delta N \\ & + \left[ \left( \frac{\partial \mu_N}{\partial T} \right)_V dT + \left( \frac{\partial \mu_N}{\partial V} \right)_T dV \right] \Delta N \end{aligned} \quad (15-49)$$

$$=^* -S_N dT - p_N dV + \mu_N \Delta N. \quad (15-50)$$

All the deductions made directly from Eq. (15-11) follow as well from Eq. (15-49), if we introduce the transcription

$$\begin{aligned} F_N &\rightarrow A_N, & S_N &\rightarrow S_N, & T &\rightarrow T, & \bar{V}_N &\rightarrow -p_N \\ p &\rightarrow V, & \mu_N &\rightarrow \mu_N, & N &\rightarrow N. \end{aligned} \quad (15-51)$$

For example,

$$\left( \frac{\delta p_N}{\Delta N} \right)_{T, V} = - \left( \frac{\partial \mu_N}{\partial V} \right)_{T, N} = p_{N+1} - p_N. \quad (15-52)$$

From the expressions for  $\delta(TS_N)$  and  $\delta(p_NV)$  we deduce

$$\begin{aligned} \delta(A_N + p_NV) &= \delta F_N \\ &= -S_N dT + V \delta p_N + \mu_N \Delta N - \left( \frac{\delta S_N}{\Delta N} \right)_{T, V} dT \Delta N \end{aligned} \quad (15-53)$$

$$\begin{aligned} \delta(A_N + TS_N) &= \delta \bar{E}_N \\ &= T \delta S_N - p_N dV + \mu_N \Delta N - \left( \frac{\delta p_N}{\Delta N} \right)_{T, V} dV \Delta N \end{aligned} \quad (15-54)$$

$$\begin{aligned} \delta(A_N + TS_N + p_NV) &= \delta H_N \\ &= T \delta S_N + V \delta p_N + \mu_N \Delta N. \end{aligned} \quad (15-55)$$

Let us define  $\mathcal{E}_N$  by

$$\mathcal{E}_N \equiv A_N + p_N V - \mu_N N = F_N - \mu_N N. \quad (15-56)$$

This leads to

$$\begin{aligned} \delta \mathcal{E}_N^* = & - \left[ S_N - N \left( \frac{\delta S_N}{\Delta N} \right)_{T, V} - V \left( \frac{\delta S_N}{\partial V} \right)_{T, N} \right] dT \\ & + \left[ N \left( \frac{\delta p_N}{\Delta N} \right)_{T, V} + V \left( \frac{\delta p_N}{\partial V} \right)_{T, N} \right] dV \\ & - \left[ (N + 1) \left( \frac{\delta \mu_N}{\Delta N} \right)_{T, V} + V \left( \frac{\delta \mu_N}{\partial V} \right)_{T, N} \right] \Delta N. \end{aligned} \quad (15-57)$$

Closely related is the expression

$$\delta(A_N + p_{N+1} V - \mu_N N)^* = -S_{N+1} dT + V \delta p_{N+1} - (N + 1) \delta \mu_N. \quad (15-58)$$

*Example. Gas of Hard Spheres.* We shall consider here the first few terms in the exact virial expansion of a finite gas of hard spheres in a cube with periodic boundary conditions.<sup>1</sup> But first we have to investigate the limit  $V \rightarrow \infty$  for  $N$  large but finite, where the gas would behave ideally.

In the above limit,

$$Q_N(V, T) = \frac{V^N}{N! \Lambda^{3N}} \quad (V \rightarrow \infty), \quad (15-59)$$

where

$$\Lambda = \frac{h}{(2\pi m k T)^{1/2}}.$$

For  $N$  large but not infinite,

$$\begin{aligned} -\frac{A_N}{kT} = \ln Q_N = & N \ln V - N \ln \Lambda^3 - N \ln N + N - \frac{1}{2} \ln 2\pi N \\ & - \frac{1}{12N} + \dots \end{aligned} \quad (15-60)$$

<sup>1</sup> I. Oppenheim and P. Mazur, *Physica*, **23**, 197 (1957); B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, **33**, 1439 (1960); *Phys. Rev.*, **127**, 359 (1962); J. L. Lebowitz and J. K. Percus, *Phys. Rev.*, **124**, 1673 (1961). This problem is also referred to at the end of Chapter 6, Part I.

Then, from Eq. (15-48),

$$-\frac{\mu_N}{kT} = \ln \frac{V}{\Lambda^3 N} - \frac{1}{N} + \frac{1}{2N^2} + \dots \quad (15-61)$$

Let us compare this with

$$-\frac{\mu}{kT} = \left( \frac{\partial \ln Q_N}{\partial N} \right)_{T, V} = \ln \frac{V}{\Lambda^3 N} - \frac{1}{2N} + \frac{1}{12N^2} + \dots \quad (15-62)$$

We note that here we have a case in which discreteness influences the first small term. This occurs because the "macroscopic" term  $-N \ln N$  in Eq. (15-60) contributes to the  $N^{-1}$  term<sup>1</sup> in Eq. (15-61). As a check on Eq. (15-61), we can work with Eq. (15-59) directly, without introducing Stirling's approximation. We find

$$-\frac{\mu_N}{kT} = \ln \frac{Q_{N+1}}{Q_N} = \ln \frac{V}{\Lambda^3(N+1)} = \ln \frac{V}{\Lambda^3 N} - \frac{1}{N} + \frac{1}{2N^2} + \dots$$

Other functions are

$$\frac{p_N}{kT} = \left( \frac{\partial -A_N/kT}{\partial V} \right)_{T, N} = \frac{N}{V} \quad (15-63)$$

$$\frac{\mathcal{E}_N}{kT} = \frac{A_N}{kT} + \frac{p_N V}{kT} - \frac{\mu_N N}{kT} = \ln \frac{N! e^N}{(N+1)^N} = \frac{1}{2} \ln \frac{2\pi N}{e^2} + \frac{7}{12N} + \dots \quad (15-64)$$

When  $V$  is not infinite, a virial expansion of  $p$  is required. The first terms<sup>2</sup> are

$$\frac{pV}{NkT} = 1 + B_2^{(0)} \left( 1 - \frac{1}{N} \right) \frac{N}{V} + B_3^{(0)} \left( 1 + \frac{1}{5N} - \frac{6}{5N^2} \right) \left( \frac{N}{V} \right)^2 + \dots, \quad (15-65)$$

where  $B_2^{(0)}$  and  $B_3^{(0)}$  are the macroscopic virial coefficients for hard spheres,

$$B_2^{(0)} = \frac{2\pi a^3}{3}, \quad B_3^{(0)} = \frac{5}{8} (B_2^{(0)})^2,$$

<sup>1</sup> This cannot happen with an  $N, p, T$  system because the macroscopic term in  $F_N$  has the form  $Nf(p, T)$ . For such a term, the difference and derivative ( $p$  and  $T$  constant) are the same for all  $N$ . In Eq. (15-60) for  $A_N$ , the macroscopic term has the form  $Nf(N/V, T)$ . In this case, the difference and derivative ( $V$  and  $T$  constant) are not, in general, the same for small  $N$ .

<sup>2</sup> Loc. cit.

with  $a$  = diameter of hard sphere. The functions of  $N^{-1}$  in parentheses are polynomials, not infinite series.

With the information given by statistical mechanics in Eq. (15-65), we proceed to derive the other thermodynamic functions. We start with

$$\frac{A_N(V)}{kT} - \frac{A_N(V^*)}{kT} = - \int_{V^*}^V \frac{p_N}{kT} dV, \quad (15-66)$$

where  $V^*$  is a very large volume. Equation (15-60) gives  $A_N(V^*)$ . Then, from Eqs. (15-65) and (15-66), we have

$$\begin{aligned} \frac{A_N(V, T)}{NkT} &= \ln \frac{\Lambda^3 N}{V e} + \frac{1}{2N} \ln 2\pi N + \frac{1}{12N^2} + \dots \\ &+ B_2^{(0)} \left(1 - \frac{1}{N}\right) \left(\frac{N}{V}\right) + \frac{1}{2} B_3^{(0)} \left(1 + \frac{1}{5N} - \frac{6}{5N^2}\right) \left(\frac{N}{V}\right)^2 + \dots \end{aligned} \quad (15-67)$$

This leads to

$$\begin{aligned} \frac{\mu_N}{kT} &= \ln \frac{\Lambda^3 N}{V} + \frac{1}{N} - \frac{1}{2N^2} + \dots \\ &+ \frac{2}{1} B_2^{(0)} \left(\frac{N}{V}\right) + \frac{3}{2} B_3^{(0)} \left(1 + \frac{17}{15N}\right) \left(\frac{N}{V}\right)^2 + \dots \end{aligned} \quad (15-68)$$

$$\begin{aligned} \frac{\mathcal{E}_N}{kT} &= \frac{1}{2} \ln \frac{2\pi N}{e^2} + \frac{7}{12N} + \dots \\ &- 2B_2^{(0)} \left(\frac{N}{V}\right) - \frac{1}{6} B_3^{(0)} \left(7 + \frac{9}{N}\right) \left(\frac{N}{V}\right)^2 + \dots \end{aligned} \quad (15-69)$$

and

$$\bar{E}_N = -T^2 \left( \frac{\partial A_N/T}{\partial T} \right)_{V, N} = \frac{3NkT}{2}. \quad (15-70)$$

As a check on self-consistency, we find that both sides of [see Eq. (15-57)]

$$\left( \frac{\delta \mathcal{E}_N}{\Delta N} \right)_{T, V} = - \left[ (N+1) \left( \frac{\delta \mu_N}{\Delta N} \right)_{T, V} + V \left( \frac{\delta \mu_N}{\partial V} \right)_{T, N} \right]$$

are equal to

$$- \frac{2B_2^{(0)}}{V} - \frac{2B_3^{(0)}}{5V^2} (7N+8).$$

15-4.  $N, B, T$  SYSTEMS

Here we have two discrete variables—for example,  $N$  molecules on  $B$  sites of a lattice gas. Rather obviously, the variation of an arbitrary function  $f_{N,B}(T)$  is given by

$$\begin{aligned} \delta f_{N,B} = & \left( \frac{\partial f_{N,B}}{\partial T} \right)_{N,B} dT \\ & + \left[ f_{N,B+1} - f_{N,B} + \frac{\partial(f_{N,B+1} - f_{N,B})}{\partial T} dT \right] \Delta B \\ & + \left[ f_{N+1,B} - f_{N,B} + \frac{\partial(f_{N+1,B} - f_{N,B})}{\partial T} dT \right] \Delta N \\ & + \left[ \left\{ f_{N+1,B+1} - f_{N,B+1} - f_{N+1,B} + f_{N,B} \right\} + \frac{\partial\{\}}{\partial T} dT \right] \Delta B \Delta N, \end{aligned} \quad (15-71)$$

where  $\Delta B, \Delta N = 0$  or  $+1$ . If  $\Delta B = \Delta N = +1$ ,

$$\delta f_{N,B}(T) = f_{N+1,B+1} - f_{N,B} + \frac{\partial f_{N+1,B+1}}{\partial T} dT.$$

Because of the complexity of Eq. (15-71), we turn to

$$\begin{aligned} \delta f_{N,B}^* = & \left( \frac{\partial f_{N,B}}{\partial T} \right)_{N,B} dT + (f_{N,B+1} - f_{N,B}) \Delta B \\ & + (f_{N+1,B} - f_{N,B}) \Delta N, \end{aligned} \quad (15-72)$$

where the asterisk means that only one of  $dT$ ,  $\Delta B$ , and  $\Delta N$  can be nonzero at a time.

Our starting point is [see Eqs. (15-45) and (15-46)]

$$A_{N,B} = \bar{E}_{N,B} - TS_{N,B} \quad (15-73)$$

$$dA_{N,B} = -S_{N,B} dT \quad (N, B \text{ constant}). \quad (15-74)$$

We define

$$\text{and} \quad -p_{N,B} \equiv A_{N,B+1} - A_{N,B} \quad (15-75)$$

$$\mu_{N,B} \equiv A_{N+1,B} - A_{N,B}.$$

Then

$$\delta A_{N,B}^* = -S_{N,B} dT - p_{N,B} \Delta B + \mu_{N,B} \Delta N \quad (15-76)$$



and

$$\left(\frac{\delta A_{N,B}}{\partial T}\right)_{N,B} = \left(\frac{\partial A_{N,B}}{\partial T}\right)_{N,B} = -S_{N,B} \quad (15-77)$$

$$\left(\frac{\delta A_{N,B}}{\Delta B}\right)_{T,N} = -p_{N,B}, \quad \left(\frac{\delta A_{N,B}}{\Delta N}\right)_{T,B} = \mu_{N,B}.$$

Also, we have the Maxwell relations

$$\left(\frac{\delta p_{N,B}}{\partial T}\right)_{N,B} = S_{N,B+1} - S_{N,B} = \left(\frac{\delta S_{N,B}}{\Delta B}\right)_{T,N} \quad (15-78)$$

$$\left(\frac{\partial \mu_{N,B}}{\partial T}\right)_{N,B} = -S_{N+1,B} + S_{N,B} = -\left(\frac{\delta S_{N,B}}{\Delta N}\right)_{T,B} \quad (15-79)$$

It is also true that

$$\left(\frac{\delta \mu_{N,B}}{\Delta B}\right)_{T,N} = -\left(\frac{\delta p_{N,B}}{\Delta N}\right)_{T,B}, \quad (15-80)$$

for each of these "derivatives" is equal to  $A_{N+1,B+1} - A_{N+1,B} - A_{N,B+1} + A_{N,B}$ . An alternative form of Eq. (15-80) is

$$\mu_{N,B+1} - \mu_{N,B} = -(p_{N+1,B} - p_{N,B}). \quad (15-81)$$

The same sorts of comments can be made here about  $p_{N,B}$  and  $\mu_{N,B}$  as were made about  $\mu_N$  in the paragraph preceding Eq. (15-18). Thus, a pressure  $p$  determines the approach to, and point of, mechanical equilibrium only for a system which is open with respect to volume changes. Here  $B$  is the environmental variable, not  $p$ . Furthermore,  $p_{N,B} \Delta B$  cannot be associated with a reversible work because a variation  $\Delta B = +1$  (even for an ensemble of very small systems) cannot be carried out reversibly.

We shall have need below for

$$\begin{aligned} \delta(p_{N,B}B)^* &= B \frac{\delta S_{N,B}}{\Delta B} dT + \left(B \frac{\delta p_{N,B}}{\Delta B} + p_{N,B+1}\right) \Delta B \\ &\quad - B \frac{\delta \mu_{N,B}}{\Delta B} \Delta N \end{aligned} \quad (15-82)$$

$$^* = B \delta p_{N,B} + p_{N,B+1} \Delta B \quad (15-83)$$

and

$$\begin{aligned} \delta(\mu_{N,B} N)^* &= -N \frac{\delta S_{N,B}}{\Delta N} dT - N \frac{\delta p_{N,B}}{\Delta N} \Delta B \\ &\quad + \left( N \frac{\delta \mu_{N,B}}{\Delta N} + \mu_{N+1,B} \right) \Delta N \end{aligned} \quad (15-84)$$

$$^* = N \delta \mu_{N,B} + \mu_{N+1,B} \Delta N. \quad (15-85)$$

Using the above relations we can now derive the following:

$$\begin{aligned} \delta \mathcal{E}_{N,B} &= \delta(A_{N,B} + p_{N,B} B - \mu_{N,B} N) \\ &= - \left( S_{N,B} - N \frac{\delta S_{N,B}}{\Delta N} - B \frac{\delta S_{N,B}}{\Delta B} \right) dT \\ &\quad + \left[ N \frac{\delta p_{N,B}}{\Delta N} + (B+1) \frac{\delta p_{N,B}}{\Delta B} \right] \Delta B \\ &\quad - \left[ (N+1) \frac{\delta \mu_{N,B}}{\Delta N} + B \frac{\delta \mu_{N,B}}{\Delta B} \right] \Delta N \end{aligned} \quad (15-86)$$

$$\begin{aligned} \delta(A_{N+1,B+1} + p_{N+1,B} B - \mu_{N+1,B} N) \\ &= - S_{N+1,B+1} dT + B \delta p_{N+1,B} - N \delta \mu_{N+1,B} \end{aligned} \quad (15-87)$$

$$\begin{aligned} \delta(A_{N,B} + T S_{N,B}) &= \delta \bar{E}_{N,B} \\ &= T \delta S_{N,B} - p_{N,B} \Delta B + \mu_{N,B} \Delta N. \end{aligned} \quad (15-88)$$

*Example. Ideal Lattice Gas.* This simple model has already been discussed in Eqs. (2-77) to (2-84) and (6-51) to (6-57) for the environmental variables  $N$ ,  $p/T$  and  $\mu/T$ ,  $B$ , respectively.

The energy of the system is  $E = \text{constant} = 0$  and the environmental variables are  $N$ ,  $B$ . The partition function is

$$\Omega_{N,B} = \frac{B!}{N!(B-N)!}, \quad (15-89)$$

and

$$S_{N,B} = k \ln \Omega_{N,B}. \quad (15-90)$$

In place of Eq. (15-76), we have

$$\delta \left( \frac{S_{N,B}}{k} \right)^* = p'_{N,B} \Delta B - \mu'_{N,B} \Delta N, \quad (15-91)$$

where

$$p'_{N,B} = \frac{p_{N,B}}{kT} \quad \text{and} \quad \mu'_{N,B} = \frac{\mu_{N,B}}{kT}.$$

Equations (15-89) to (15-91) lead to

$$p'_{N,B} = \left( \frac{\delta \ln \Omega_{N,B}}{\Delta B} \right)_N = \ln \frac{\Omega_{N,B+1}}{\Omega_{N,B}} = \ln \frac{B+1}{B+1-N} \quad (15-92)$$

$$- \mu'_{N,B} = \ln \frac{\Omega_{N+1,B}}{\Omega_{N,B}} = \ln \frac{B-N}{N+1} \quad (15-93)$$

$$\begin{aligned} - \frac{\mathcal{E}_{N,B}}{kT} &= \frac{S_{N,B}}{k} - p'_{N,B} B + \mu'_{N,B} N \\ &= \ln \frac{B!}{N!(B-N)!} \left( \frac{B+1-N}{B+1} \right)^B \left( \frac{N+1}{B-N} \right)^N \\ &= -\frac{1}{2} \ln \frac{2\pi N(B-N)}{B} + \frac{B}{B-N} + \dots \end{aligned} \quad (15-94)$$

We can check these results using, for example,

$$\left( \frac{\delta p'_{N,B}}{\Delta N} \right)_B = - \left( \frac{\delta \mu'_{N,B}}{\Delta B} \right)_N \quad (15-95)$$

and [see Eq. (15-86)]

$$\left( \frac{\delta \mathcal{E}_{N,B}/kT}{\Delta N} \right)_B = - \left[ (N+1) \frac{\delta \mu'_{N,B}}{\Delta N} + B \frac{\delta \mu'_{N,B}}{\Delta B} \right]. \quad (15-96)$$

This is another example in which the first-order small term is affected by discreteness. To see this, we use the Stirling approximation and write

$$\begin{aligned} \frac{S_{N,B}}{k} &= \ln \Omega_{N,B} = B \ln B - N \ln N - (B-N) \ln (B-N) \\ &\quad - \frac{1}{2} \ln \frac{2\pi N(B-N)}{B} + \dots \end{aligned} \quad (15-97)$$

Then, if we treat  $N$  and  $B$  as continuous,

$$\frac{p}{kT} = \left[ \frac{\partial(S/k)}{\partial B} \right]_N = \ln \frac{B}{B-N} - \frac{N}{2B(B-N)} + \dots \quad (15-98)$$

$$-\frac{\mu}{kT} = \left[ \frac{\partial(S/k)}{\partial N} \right]_B = \ln \frac{B-N}{N} + \frac{2N-B}{2N(B-N)} + \dots \quad (15-99)$$

The corresponding expressions from Eqs. (15-92) and (15-93) [or from Eq. (15-97), using differences] are

$$p'_{N,B} = \ln \frac{B}{B-N} - \frac{N}{B(B-N)} + \dots \quad (15-100)$$

and

$$-\mu'_{N,B} = \ln \frac{B-N}{N} - \frac{1}{N} + \dots \quad (15-101)$$

Hence the small terms in Eqs. (15-98) and (15-99) have no proper range of validity. Incidentally, Eq. (15-99) can easily be shown to be equivalent to Eq. (5.35) of James and Guth,<sup>1</sup> which gives the force as a function of length for a finite one-dimensional freely folding ruler model of a polymer chain.

*Example. Ideal Binary Mixture.* This example is considered on pages 87 and 88 of Part I, with  $N_1$  and  $N_2$  continuous. In view of the discussion above, a correction for discreteness is in order. The problem is practically identical with the preceding example.

The basic equations are

$$\delta A_{N_1, N_2}^* = -S_{N_1, N_2} dT + \mu_{N_1, N_2}^{(1)} \Delta N_1 + \mu_{N_1, N_2}^{(2)} \Delta N_2 \quad (15-102)$$

$$\mu_{N_1, N_2}^{(1)} = A_{N_1+1, N_2} - A_{N_1, N_2}, \quad \text{etc.}, \quad (15-103)$$

$$A_{N_1, N_2} = -kT \ln Q_{N_1, N_2}, \quad (15-104)$$

where  $Q_{N_1, N_2}$  is given by Eqs. (4-77) and (4-79). Then

$$\frac{\mu_{N_1, N_2}^{(1)}}{kT} = \ln \frac{(N_1 + 1)}{j_1(N_1 + N_2 + 1)} = -\ln j_1 + \ln x_1 + \frac{1}{N} \frac{x_2}{1 - x_2} + \dots, \quad (15-105)$$

<sup>1</sup> H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).

with a similar expression for  $\mu_{N_1, N_2}^{(2)}$ . Also

$$\begin{aligned}\frac{\mathcal{E}_{N_1, N_2}}{kT} &= \frac{A_{N_1, N_2} - N_1 \mu_{N_1, N_2}^{(1)} - N_2 \mu_{N_1, N_2}^{(2)}}{kT} \\ &= \ln \frac{N_1! N_2! (N_1 + N_2 + 1)^{N_1 + N_2}}{N! (N_1 + 1)^{N_1} (N_2 + 1)^{N_2}} = \frac{1}{2} \ln \frac{2\pi N_1 N_2}{N e^2} + \dots\end{aligned}\quad (15-106)$$

*Other Examples.* We recall that the “twelve-site spherical lattice gas” is a good example of a very small  $N, B, T$  system. It is discussed on pages 62 to 64.

The Bragg-Williams lattice gas for an  $N, B, T$  system is considered on pages 67 and 68, using continuous variables. We do not correct this treatment for the reason given on page 196.

## APPENDIX

It is instructive to compare differences with derivatives in a few simple cases. For example, in an  $N, p, T$  system,  $F_N(p, T)$  might have terms, among others, with  $N$  dependences of the following types:  $N$  (macroscopic), constant,  $N^{2/3}$ ,  $N^{1/3}$ ,  $\ln N$ ,  $1/N$ , etc. We can omit the coefficients (functions of  $p$  and  $T$ ), in each case, without loss of generality. For each term, let us compare  $\mu_N = F_{N+1} - F_N$  with  $\mu = \partial F / \partial N$ .

In the first two cases  $\mu_N = \mu$ .

If  $F_N = N^{2/3}$ , then

$$\mu = \frac{2}{3} N^{-1/3}, \quad \mu_N = \frac{2}{3} N^{-1/3} + O(N^{-4/3})$$

$$F_{N+1/2} - F_{N-1/2} = \frac{2}{3} N^{-1/3} + O(N^{-7/3}).$$

If  $F_N = N^{1/3}$ , then

$$\mu = \frac{1}{3} N^{-2/3}, \quad \mu_N = \frac{1}{3} N^{-2/3} + O(N^{-5/3})$$

$$F_{N+1/2} - F_{N-1/2} = \frac{1}{3} N^{-2/3} + O(N^{-8/3}).$$

If  $F_N = \ln N$ ,

$$\mu = \frac{1}{N}, \quad \mu_N = \frac{1}{N} - \frac{1}{2N^2} + \dots$$

$$F_N - F_{N-1} = \frac{1}{N} + \frac{1}{2N^2} + \dots$$

$$F_{N+1/2} - F_{N-1/2} = \frac{1}{N} + O(N^{-3}).$$

If  $F_N = 1/N$ ,

$$\mu = -\frac{1}{N^2}, \quad \mu_N = -\frac{1}{N^2} + O(N^{-3})$$

$$F_{N+1/2} - F_{N-1/2} = -\frac{1}{N^2} + O(N^{-4}).$$

In each of these cases we see that the first "small system term" is the same for  $\mu$  and  $\mu_N$ , but the next smaller term differs. Also, in each case, as expected, the difference between  $\mu$  and  $F_{N+1/2} - F_{N-1/2}$  is of smaller order than the difference between  $\mu$  and  $\mu_N$ .



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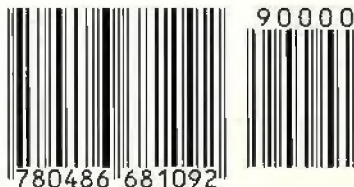
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