

MIXTURES

THE THEORY OF THE
EQUILIBRIUM PROPERTIES OF SOME
SIMPLE CLASSES OF MIXTURES
SOLUTIONS AND ALLOYS

BY

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PREFACE

My aim in this book has been to give an account of the application of statistical thermodynamics to certain models of solid, liquid, and gaseous mixtures. There has been no attempt to explore more than a small part of the wide field covered by the word 'mixture'. In fact the only models discussed are those so simple that theory can be applied to them quantitatively with the minimum of assumptions superposed on those implied in the models and can, moreover, be applied with the use of only elementary mathematics. In spite of the great simplicity of these models their study leads to problems sufficiently complicated to be interesting.

The models can be expected to be useful representations of only the simplest mixtures. In particular, mixtures containing electrolytes or highly polar molecules are entirely excluded from consideration. Comparison between theory and fact is limited by the scarcity of precise experimental measurements on the simpler systems. Where comparison is possible the result is nearly always surprisingly gratifying.

There is a clear need for more extensive and precise measurements of all the equilibrium properties of the simplest mixtures. If such research work is stimulated by the theories described, then this book will have served a useful purpose.

Here I should like to point out how much this subject owes to one of the founder-editors of this series, the late Sir Ralph Fowler. Although much of the theory has been developed since his death, there is scarcely a section which does not bear the imprint of ideas and techniques originated or inspired by him.

I have great pleasure in acknowledging my debt of gratitude to Dr. M. L. McGlashan for his invaluable assistance in preparing this book for the press. As well as contributing original work described in the book, he has read the manuscript, checked the formulae, prepared the diagrams, compiled the indexes, and corrected the proofs.

I am indebted to the Royal Society and to the North Holland Publishing Company for permission to copy certain diagrams.

E. A. G.

UNIVERSITY OF READING,

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CLASSICAL THERMODYNAMICS OF MIXTURES

1.01. Introduction. Free energy

THE classical thermodynamics of mixtures is such a vast subject that an exhaustive treatment of it would require a book comparable in size to this one. No attempt will be made to give such a treatment here. We must rather be content with a brief summary of the fundamental principles and the most important formulae. The reader must go elsewhere for detailed derivations.

We shall in this book be concerned only with systems in complete thermal equilibrium, so that the temperature will always be uniform throughout the system. As long as the temperature is kept constant, that is to say under isothermal conditions, the most important thermodynamic function is the *free energy*, so named by Helmholtz and denoted by F . In any isothermal reversible process the increase in F , denoted by ΔF , is equal to the work done on the system; alternatively the decrease in F , denoted by $-\Delta F$, is equal to the work done by the system. Thus in reversible isothermal processes the free energy is analogous to the potential energy in reversible mechanical processes.

The particular kind of isothermal process which most concerns us here is that of the mixing of two or more substances. We shall denote by $-\Delta_m F$ the decrease in free energy when one mole of a mixture is formed from the constituent pure substances. A considerable part of this book will be concerned with the quantity $\Delta_m F$ called the *molar free energy of mixing*. It is important to know how this quantity is determined experimentally, but this can be explained more conveniently in § 1.05 after we have considered some other thermodynamic functions.

1.02. Independent variables

The state of a liquid mixture may be completely defined by specifying the absolute temperature T , the pressure P , and the composition of the liquid. This is moreover nearly always the most convenient manner of specification. The same choice of independent variables is appropriate to a solid mixture provided all stresses other than an isotropic pressure are excluded. For gaseous mixtures, on the other hand, it is sometimes more convenient to choose the volume V rather than the

pressure P as an independent variable. Since a much greater part of this book is devoted to liquids and solids than to gases, the set of independent variables T, P will be appropriate more often than the set T, V and therefore more detailed attention will be paid to the former.

The composition of a mixture is conveniently described by specifying the number n_r of moles of each species r . When we are interested only in the relative composition, but not in the total amount of a mixture, it is convenient to use the mole fractions x_r defined by

$$x_r = n_r / \sum_r n_r. \quad (1.02.1)$$

The mole fractions are thus not independent, being related by

$$\sum_r x_r = 1. \quad (1.02.2)$$

We shall be mostly concerned with binary mixtures for which (2) reduces to

$$x_1 + x_2 = 1. \quad (1.02.3)$$

In this case it will be convenient to simplify our notation by writing x instead of x_2 and $1-x$ instead of x_1 .

With this notation the molar free energy of mixing $\Delta_m F$ of a binary mixture is related to the molar free energy F_m of the mixture and the molar free energies F_1^0, F_2^0 of the two pure components by the definition

$$-\Delta_m F = (1-x)F_1^0 + xF_2^0 - F_m. \quad (1.02.4)$$

1.03. Thermodynamic potentials and fundamental equations

When the free energy F of any homogeneous phase is regarded as a function of the independent variables T, V, n_r its partial differential coefficients with respect to the first two variables are given by the simple relations†

$$\partial F / \partial T = -S, \quad (1.03.1)$$

$$\partial F / \partial V = -P, \quad (1.03.2)$$

where S denotes the *entropy*. The partial differential coefficient of F with respect to each n_r is called the *chemical potential* of r and is denoted by μ_r . Thus

$$\partial F / \partial n_r = \mu_r. \quad (1.03.3)$$

Formulae (1), (2), and (3) may be combined to give

$$dF = -S dT - P dV + \sum_r \mu_r dn_r. \quad (1.03.4)$$

† The notation for all thermodynamic quantities is the same as used in the author's book *Thermodynamics* (1949), North-Holland Publishing Co., and conforms with the recommendations of the International Union of Physics (1948) and the International Union of Chemistry (1949). Derivations of all the required thermodynamic relations will be found in this or other standard text-books on chemical thermodynamics.

The free energy F is said to be the *thermodynamic potential* for the independent variables T , V , n_r , and formula (4) is called the *fundamental equation* for these variables.

Turning now to the more generally useful set of variables T , P , n_r , the relevant thermodynamic potential is the *Gibbs function* G defined by

$$G = F + PV, \quad (1.03.5)$$

and the fundamental equation for these variables is

$$dG = -S dT + V dP + \sum_r \mu_r dn_r. \quad (1.03.6)$$

Isothermal changes in G are closely related to *net work* defined as follows. The work done on a system plus the increase in the quantity PV is called the net work done on the system. Alternatively the work done by the system less the increase in the quantity PV is called the net work done by the system. In particular, if the pressure is kept constant then the net work done by the system may be defined as the work done by the system other than the work due to the change ΔV of its volume. With this definition of net work it follows from (5) that in a reversible isothermal process the decrease $-\Delta G$ of the Gibbs function is equal to the net work done by the system.

The *entropy* S has the property that in any infinitesimal reversible process the heat absorbed by the system is $T dS$. Consequently in any reversible isothermal process the heat absorbed is $T \Delta S$ or $\Delta(TS)$, where as usual the symbol Δ is used to denote the increase of any quantity during the process considered. If, on the other hand, we consider an isothermal process in which the pressure is maintained constant throughout, such a process being usually not reversible, then the heat absorbed is equal to the increase ΔH of the heat function H .

The functions G , S , and H are related by

$$H = G + TS, \quad (1.03.7)$$

$$S = -\frac{\partial G}{\partial T}, \quad (1.03.8)$$

$$H = G - T \frac{\partial G}{\partial T}. \quad (1.03.9)$$

Here and elsewhere when we use partial differential coefficients the independent variables are always T , P , n_r , unless the contrary is stated. It follows immediately that for an isothermal process in which the

initial and final pressures have specified values, usually but not necessarily the same, we have

$$\Delta H = \Delta G + T\Delta S, \quad (1.03.10)$$

$$\Delta S = -\frac{\partial}{\partial T} \Delta G, \quad (1.03.11)$$

$$\Delta H = \Delta G - T \frac{\partial}{\partial T} \Delta G. \quad (1.03.12)$$

The last formula is called the *Gibbs-Helmholtz relation*.

1.04. Partial molar quantities

The relations between partial molar quantities and the corresponding extensive property may be illustrated by the case where the property in question is the volume V . For the sake of brevity and simplicity we shall consider a mixture of only two components, 1 and 2. As usual we take as independent variables T, P, n_1, n_2 . The *partial molar volumes* V_1, V_2 are defined by

$$V_1 = \partial V / \partial n_1, \quad (1.04.1)$$

$$V_2 = \partial V / \partial n_2. \quad (1.04.2)$$

Incidentally the other partial differential coefficients of V are

$$\partial V / \partial T = \alpha V, \quad (1.04.3)$$

$$\partial V / \partial P = -\kappa V, \quad (1.04.4)$$

where α is the coefficient of thermal expansion and κ is the isothermal compressibility.

The total volume is related to the partial molar volumes by

$$V = n_1 V_1 + n_2 V_2. \quad (1.04.5)$$

When the composition of the mixture is varied at constant temperature and pressure the variations of the two partial molar volumes are interrelated by

$$n_1 dV_1 + n_2 dV_2 = 0 \quad (T, P \text{ const.}). \quad (1.04.6)$$

Applying the above formulae to a quantity of mixture containing in all one mole and denoting the mean molar volume by V_m , we have

$$V_m = (1-x)V_1 + xV_2, \quad (1.04.7)$$

$$\frac{\partial V_m}{\partial x} = V_2 - V_1, \quad (1.04.8)$$

$$(1-x) \frac{\partial V_1}{\partial x} + x \frac{\partial V_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.04.9)$$

Precisely analogous formulae apply to any other extensive property

such as F , G , S , or H . In particular we see from (1.03.6) and the definition of partial molar quantities that

$$G_1 = \mu_1, \quad G_2 = \mu_2. \quad (1.04.10)$$

Consequently for variations in the composition of a binary mixture at constant temperature and pressure we have

$$(1-x)\frac{\partial\mu_1}{\partial x} + x\frac{\partial\mu_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.04.11)$$

This important formula is called the *Gibbs-Duhem relation*.

Provided we keep to the independent variables T , P , n_1 , n_2 or T , P , x , then for each relation between extensive properties there is an analogous relation between the corresponding partial molar quantities. In particular as analogues of (1.03.7), (1.03.8), and (1.03.9) we have

$$H_1 = G_1 + TS_1, \quad H_2 = G_2 + TS_2, \quad (1.04.12)$$

$$S_1 = -\frac{\partial G_1}{\partial T}, \quad S_2 = -\frac{\partial G_2}{\partial T}, \quad (1.04.13)$$

$$H_1 = G_1 - T\frac{\partial G_1}{\partial T}, \quad H_2 = G_2 - T\frac{\partial G_2}{\partial T}. \quad (1.04.14)$$

By virtue of (10) we may rewrite these formulae as

$$H_1 = \mu_1 + TS_1, \quad H_2 = \mu_2 + TS_2, \quad (1.04.15)$$

$$S_1 = -\frac{\partial\mu_1}{\partial T}, \quad S_2 = -\frac{\partial\mu_2}{\partial T}, \quad (1.04.16)$$

$$H_1 = \mu_1 - T\frac{\partial\mu_1}{\partial T}, \quad H_2 = \mu_2 - T\frac{\partial\mu_2}{\partial T}. \quad (1.04.17)$$

1.05. Chemical potentials and absolute activities

We have already collected many of the most important formulae involving chemical potentials, but have not yet said anything about the physical significance of these quantities. The chemical potentials have two fundamental properties closely related to each other.

We have already drawn attention to the fact that the chemical potential is identical with the partial molar Gibbs function. We have also mentioned that in any reversible isothermal process the decrease in the Gibbs function is equal to the net work done by the system. It follows that if we consider the process of transferring one mole of the substance r reversibly and isothermally from a large quantity of one phase to a large quantity of another phase, then the decrease $-\Delta\mu_r$ in the value of the chemical potential μ_r is equal to the net work done

by the system. This is the first fundamental property of the chemical potential.

The second fundamental property of the chemical potential is the following. When two phases are at the same temperature the condition for equilibrium distribution of the substance r between the two phases is that the chemical potential μ_r should have the same value in both phases. This condition is valid even when the two phases are at different pressures, for example when separated by a semi-permeable membrane, provided always that they are at the same temperature.

The first fundamental property of the chemical potential enables us to relate the difference in chemical potential between two phases to experimentally determinable quantities. For the sake of simplicity we shall initially assume that the saturated vapour over each phase may with sufficient accuracy be treated as a perfect gas. It must be emphasized that this is an assumption relating only to the behaviour of the vapour; there is no restriction concerning the nature of the liquid or solid phases. The transfer of one mole of the substance r from a large quantity of a liquid or solid phase α to a large quantity of another liquid or solid phase β can in principle be performed reversibly and isothermally by what may be called an *isothermal three-stage distillation*. By means of pistons and appropriate semi-permeable membranes, which the interested reader can readily devise, the process can be performed in the following three stages:

- (a) Evaporate one mole of r from a large quantity of the phase α against a pressure equal to the saturated partial vapour pressure p_r^α of r in the phase α .
- (b) Expand or compress the one mole of vapour isothermally from the pressure p_r^α to a pressure equal to the saturated vapour pressure p_r^β of r in the phase β .
- (c) Condense the one mole into a large quantity of the phase β by applying a constant pressure p_r^β .

At all stages the temperature is supposed maintained constant by use of a suitable thermostat.

The work done by the system in the three stages when the vapour is treated as a perfect gas is as follows:

$$(a) \quad RT - p_r^\alpha V_r^\alpha, \quad (1.05.1)$$

$$(b) \quad RT \ln \frac{p_r^\alpha}{p_r^\beta}, \quad (1.05.2)$$

$$(c) \quad -RT + p_r^\beta V_r^\beta, \quad (1.05.3)$$

where R denotes the gas constant and V_r^α, V_r^β denote the partial molar volumes of r in the phases α, β respectively. By addition we find that the work done by the system is

$$\delta T \ln \frac{p_r^\alpha}{p_r^\beta} + (p_r^\beta V_r^\beta - p_r^\alpha V_r^\alpha). \quad (1.05.4)$$

It follows by definition that the net work done by the system is

$$RT \ln \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.5)$$

Thus for any two phases α, β at the same temperature we have

$$\mu_r^\alpha - \mu_r^\beta = RT \ln \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.6)$$

At this stage it is convenient to introduce another thermodynamic quantity λ_r , called the *absolute activity* defined by

$$\mu_r = RT \ln \lambda_r. \quad (1.05.7)$$

Since λ_r and μ_r are so intimately and simply interrelated mathematically it is obviously unnecessary to use both. Nevertheless in practice it is often convenient to use λ_r rather than μ_r . The convenience of the absolute activity will reveal itself with use especially in statistical derivations.

Using the definition (7) we can rewrite (6) as

$$\frac{\lambda_r^\alpha}{\lambda_r^\beta} = \frac{p_r^\alpha}{p_r^\beta}. \quad (1.05.8)$$

Returning now to the second fundamental property of the chemical potential, we see that the condition that two phases α, β at the same temperature should be in equilibrium with respect to the substance r may be expressed in the mathematically equivalent forms

$$\mu_r^\alpha = \mu_r^\beta, \quad (1.05.9)$$

$$\lambda_r^\alpha = \lambda_r^\beta, \quad (1.05.10)$$

or provided only that the vapour may be treated as a perfect gas,

$$p_r^\alpha = p_r^\beta. \quad (1.05.11)$$

Even if the vapour may not be treated as a perfect gas these relations still hold good provided p_r is redefined as the *fugacity* instead of the partial vapour pressure. The fugacity may be regarded simply as a partial vapour pressure corrected for deviations from the behaviour of perfect gases. The manner of applying such corrections will be described in Chapter VIII.

Let us now consider a binary mixture of substances 1 and 2, and compare it with the two pure substances. We shall use the superscript 0 in symbols relating to either of the pure substances and shall omit superscripts from symbols relating to the mixture. We then have the following relations between several thermodynamic functions and the partial vapour pressures:

$$\mu_1^0 - \mu_1 = RT \ln \frac{\lambda_1^0}{\lambda_1} = RT \ln \frac{p_1^0}{p_1}, \quad (1.05.12)$$

$$\mu_2^0 - \mu_2 = RT \ln \frac{\lambda_2^0}{\lambda_2} = RT \ln \frac{p_2^0}{p_2}, \quad (1.05.13)$$

$$\begin{aligned} -\frac{\Delta_m G}{RT} &= (1-x) \ln \frac{\lambda_1^0}{\lambda_1} + x \ln \frac{\lambda_2^0}{\lambda_2} \\ &= (1-x) \ln \frac{p_1^0}{p_1} + x \ln \frac{p_2^0}{p_2}. \end{aligned} \quad (1.05.14)$$

The Gibbs-Duhem relation (1.04.11) may be rewritten in terms of absolute activities

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.05.15)$$

If we treat the vapour as a perfect gas, or alternatively if we let p denote fugacity instead of partial vapour pressure, we may replace (15) by

$$(1-x) \frac{\partial \ln p_1}{\partial x} + x \frac{\partial \ln p_2}{\partial x} = 0 \quad (T, P \text{ const.}). \quad (1.05.16)$$

This important formula is called the *Duhem-Margules relation*.

1.06. Useful formulae for liquids and solids

As we have emphasized at an early stage, the convenient choice of independent variables for liquid and solid phases is T , P , n_1 , n_2 , or T , P , x and therefore the appropriate thermodynamic potential is G not F . To avoid any possibility of confusion we have set out in full the most important formulae in terms of the chosen independent variables. Having done so, we may now point out that at ordinary pressures, for liquids at temperatures not too near the critical point and for solids, all terms in PV or VdP are entirely negligible. This is the case when the pressure is comparable to atmospheric, or is less. Thus, although it is important to remember that G , not F , is the thermodynamic potential for the independent variables T , P , yet the experimental or theoretical values of G are usually indistinguishable

from those of F . We may therefore usually, for liquids and solids, omit all terms in PV or $V dP$. We then obtain for binary mixtures, independently of the pressure provided it is not too great, such formulae as

$$dG = dF = -S dT + \mu_1 dn_1 + \mu_2 dn_2, \quad (1.06.1)$$

$$dG_m = dF_m = -S_m dT + (\mu_2 - \mu_1) dx, \quad (1.06.2)$$

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T \text{ const.}, P \text{ not too great}), \quad (1.06.3)$$

$$(1-x) \frac{\partial \ln p_1}{\partial x} + x \frac{\partial \ln p_2}{\partial x} = 0 \quad (T \text{ const.}, P \text{ not too great}). \quad (1.06.4)$$

To the same approximation there is no need to distinguish between the heat function H and the total energy $U = H - PV$.

To sum up, except when we are dealing with gases, we shall usually make no mention of pressure. The implied assumption is that the pressure is sufficiently small not to affect appreciably the values of the relevant thermodynamic functions. An exceptional case is that of osmotic equilibrium. The osmotic pressure Π , of a binary mixture in which the substance 1 is regarded as the solvent, is defined as the extra pressure which must be applied to the mixture to raise the partial vapour pressure of the solvent in the mixture to that of the pure solvent at ordinary low pressure. The osmotic pressure is related to the partial vapour pressure of the solvent by the formula

$$\Pi = \frac{RT}{V_1} \ln \frac{p_1^0}{p_1}, \quad (1.06.5)$$

where p_1 , p_1^0 denote partial vapour pressures over the solution and the pure solvent respectively *at the same external pressure*. V_1 as usual denotes the partial molar volume of the solvent in the mixture, and is here assumed indistinguishable from the molar volume V_1^0 of the pure solvent.

1.07. Activity coefficients

We have mentioned that the absolute activities of the two components depend on the composition so as to be interrelated by the Duhem–Margules relation

$$(1-x) \frac{\partial \ln \lambda_1}{\partial x} + x \frac{\partial \ln \lambda_2}{\partial x} = 0 \quad (T \text{ const.}). \quad (1.07.1)$$

The simplest solution of this equation has the form

$$\lambda_1 = \lambda_1^0(1-x), \quad \lambda_2 = \lambda_2^0 x. \quad (1.07.2)$$

The same relations may be expressed in terms of partial vapour pressures, or strictly fugacities,

$$p_1 = p_1^0(1-x), \quad p_2 = p_2^0x. \quad (1.07.3)$$

As we shall see in Chapter III, the simplest kind of mixture which exists in fact satisfies the above relations. Such mixtures are called *ideal*. Whereas ideal mixtures are the exception rather than the rule, they provide a conveniently useful standard with which to compare other real mixtures. For this purpose it is expedient to introduce *activity coefficients* f_1, f_2 defined by

$$\lambda_1 = \lambda_1^0(1-x)f_1, \quad \lambda_2 = \lambda_2^0x f_2, \quad (1.07.4)$$

or $p_1 = p_1^0(1-x)f_1, \quad p_2 = p_2^0x f_2. \quad (1.07.5)$

It then follows by substitution of (4) into (1) that the variations with composition of the activity coefficients of the two species are interrelated by

$$(1-x)\frac{\partial \ln f_1}{\partial x} + x\frac{\partial \ln f_2}{\partial x} = 0 \quad (T \text{ const.}). \quad (1.07.6)$$

The introduction of activity coefficients of course gives us no quantitative information concerning the properties of the mixture until their values have been determined experimentally. Their introduction is merely a convenience and a worthwhile one because the same activity coefficients enter into all the equilibrium relations of the mixture. We have already seen that the partial vapour pressures of the two components are given by (5). By comparison with (1.06.5) we see that the osmotic pressure Π (for osmotic equilibrium with respect to the species 1) is given by

$$\Pi = \frac{RT}{V_1} \ln \frac{1}{(1-x)f_1}. \quad (1.07.7)$$

We shall now record without proof the formulae relating to equilibrium between the liquid solution and the pure solid phase of one of the components. For equilibrium at the temperature T between the solution and the solid phase consisting of the pure substance 1 the relation is

$$\ln \frac{1}{(1-x)f_1} = \frac{\Delta_f H_1^0}{R} \left(\frac{1}{T} - \frac{1}{T_1^0} \right), \quad (1.07.8)$$

where T_1^0 denotes the equilibrium temperature for the pure liquid 1 and $\Delta_f H_1^0$ denotes the molar heat of fusion of the pure substance 1. To be more precise $\Delta_f H_1^0$ denotes an average value of this quantity over the temperature range T to T_1^0 , but usually the variation of the

heat of fusion with temperature is neglected. For equilibrium between the solution and the solid phase of the pure substance 2 we have the analogous relation

$$\ln \frac{i}{x f_2} = \frac{\Delta_f H_2^0}{R} \left(\frac{1}{T} - \frac{1}{T_2^0} \right), \quad (1.07.9)$$

where T_2^0 denotes the equilibrium temperature for the pure liquid 2 and $\Delta_f H_2^0$ is the molar heat of fusion for the pure substance 2. Although formulae (8) and (9) are entirely analogous it is common practice to use different terminologies to describe them. Formula (8) is usually described as relating the *freezing-point* T of the solution to its composition x , while formula (9) is described as relating the *solubility*, or composition x of the *saturated* solution, to the temperature T .

1.08. Useful formulae for gases

Many of the formulae already quoted for liquids and solids, though not those in which the PV terms have been neglected, are also applicable to gaseous mixtures when the independent variables are chosen to be T, P, n_1, n_2 or T, P, x . But for gases it is sometimes convenient to use the set of independent variables T, V, n_1, n_2 or T, V, x . For this purpose quite a different set of formulae is required. Many of these formulae have a close resemblance to those in which P is an independent variable. We shall quote some of the most important of these formulae without proof, restricting ourselves to binary mixtures.

The thermodynamic potential for these independent variables is, as already mentioned, the free energy F and the fundamental equation is

$$dF = -SdT - PdV + n_1d\mu_1 + n_2d\mu_2. \quad (1.08.1)$$

The total energy U , the free energy F , and the entropy S are interrelated by

$$U = F + TS, \quad (1.08.2)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad (1.08.3)$$

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V. \quad (1.08.4)$$

We recall that in a reversible isothermal process the work done by the system is $-\Delta F$ and the heat absorbed is $T\Delta S$. Thus (2) expresses the law of conservation of total energy U for an isothermal reversible process. In an isothermal process at constant total volume, such a process being usually not reversible, the heat absorbed to keep the temperature constant is ΔU .

If we have a formula expressing the free energy F in terms of T , V , n_1 , n_2 , then we obtain other important properties from the formulae

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, n_1, n_2}, \quad (1.08.5)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, n_1, n_2}, \quad (1.08.6)$$

$$\mu_1 = \left(\frac{\partial F}{\partial n_1} \right)_{T, V, n_2}, \quad (1.08.7)$$

$$\mu_2 = \left(\frac{\partial F}{\partial n_2} \right)_{T, V, n_1}. \quad (1.08.8)$$

II

STATISTICAL THERMODYNAMICS OF MIXTURES

2.01. Introduction. Independent variables

In this chapter we shall give a brief synopsis of the most general formulae of statistical thermodynamics, especially those required in the treatment of mixtures. Detailed derivations will not be given, but must be sought elsewhere.†

In statistical, as in classical, thermodynamics one uses alternative functions and formulae according to the choice of independent variables. The simplest and most fundamental law of statistical thermodynamics relates to a completely isolated system, that is to say a system of prescribed energy, volume, and content. The observed equilibrium properties of such a system are correctly obtained by averaging over all accessible quantum states of the system attaching the same weight to each non-degenerate quantum state. This formulation is the simplest possible, but it is by no means the most useful in application. It is far more useful to have a formulation applicable to a system of prescribed temperature instead of to a system of prescribed energy. In other words, the choice of independent variables T , V is more useful than U , V .

The alternative formulation for a system of prescribed temperature, volume, and content is as follows. The observed equilibrium properties of such a system are correctly obtained by averaging over all accessible quantum states of the system, attaching a statistical weight $\exp(-E_r/kT)$ to each non-degenerate quantum state, where E_r is the energy of the quantum state r and k is a universal constant determining the size of the degree in the temperature scale. This constant k is called *Boltzmann's constant* and the weighting factor $\exp(-E_r/kT)$ is called a *Boltzmann factor*.

2.02. Distribution law and partition function

According to the law enunciated in the previous section, the fraction of time spent by a system at given temperature and volume

† For example Mayer and Mayer (1940), *Statistical Mechanics*, Wiley; Fowler and Guggenheim (1939), *Statistical Thermodynamics*, Cambridge University Press; Slater (1939), *Introduction to Chemical Physics*, McGraw-Hill; or for a more elementary treatment, Rushbrooke (1949), *Statistical Mechanics*, Oxford University Press.

in the state r is

$$\frac{e^{-E_r/kT}}{\sum_r e^{-E_r/kT}}, \quad (2.02.1)$$

and the observed equilibrium value $\bar{\mathcal{P}}$ of a property \mathcal{P} whose value is \mathcal{P}_r when the system is in the state r is given by

$$\bar{\mathcal{P}} = \frac{\sum_r \mathcal{P}_r e^{-E_r/kT}}{\sum_r e^{-E_r/kT}}. \quad (2.02.2)$$

The quantity occurring in the denominators of (1) and (2) is called the *partition function*. If then we denote the partition function by Q we have the definition

$$Q = \sum_r e^{-E_r/kT}. \quad (2.02.3)$$

2.03. Free energy and total energy

If we now define a quantity F by the relation

$$F = -kT \ln Q, \quad (2.03.1)$$

it can be shown that F has all the properties of the thermodynamic free energy. In particular the observed value of the pressure is given by

$$P = \frac{\sum_r \mathcal{P}_r e^{-E_r/kT}}{\sum_r e^{-E_r/kT}} = \frac{\sum_r -(\partial E_r / \partial V) e^{-E_r/kT}}{\sum_r e^{-E_r/kT}} = kT \frac{\partial}{\partial V} \ln Q = -\frac{\partial F}{\partial V}, \quad (2.03.2)$$

in agreement with formula (1.03.2).

Similarly the observed value of the total energy U is given by

$$U = \bar{E} = \frac{\sum_r E_r e^{-E_r/kT}}{\sum_r e^{-E_r/kT}} = kT^2 \frac{\partial}{\partial T} \ln Q = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = F - T \frac{\partial F}{\partial T}, \quad (2.03.3)$$

in agreement with formula (1.08.4).

If from our knowledge of the detailed structure of the system, or of a model representing the system to a useful degree of approximation, we can construct the partition function Q of the system, then the free energy is given by (1). When we are concerned with liquid or solid phases we may without sensible error usually replace (1) by the formula for the Gibbs function G

$$G = -kT \ln Q. \quad (2.03.4)$$

We can then obtain formulae for the entropy, heat function, and chemical potentials by appropriate differentiations.

2.04. Separation of degrees of freedom

It often happens that the behaviour of the system with respect to some degrees of freedom is independent of that with respect to the others. This is called *separation of degrees of freedom*. The energy of the system can then be expressed as a sum of energies in the separated degrees of freedom, and consequently the partition function of the system can be expressed as a product of factors relating to the separated degrees of freedom.

Throughout this book we shall treat the degrees of freedom relating to the positions and motions of the centres of mass of the molecules as separable from all other degrees of freedom. These other degrees of freedom will be referred to as *internal degrees of freedom*, although they include molecular rotations which are not strictly internal. We accordingly write

$$Q = Q_{\text{int}} Q_{\text{tr}}, \quad (2.04.1)$$

where the *internal partition function* Q_{int} relates to all internal degrees of freedom including rotations, and the *translational partition function* Q_{tr} relates to the motions of the centres of mass of the molecules.

Formula (1) is an approximation essential to the treatment of mixtures throughout this book. It is of course only an approximation. Its use implies that the rotational degrees of freedom of the molecules of each kind are the same in any mixture as in the pure substance. Its use does not, however, imply that the rotational degrees of freedom are the same in the liquid state as in the gas state, nor yet as in the solid state.

It follows from (1) that the free energy of mixing is determined entirely by the translational partition function Q_{tr} , since on comparing a mixture with its constituents as pure substances all contributions to the free energy of mixing from the internal partition function Q_{int} will clearly cancel.

2.05. Configurational free energy

We have seen in the preceding section that for the purpose of determining a free energy of mixing we may effectively ignore all degrees of freedom other than those relating to the motion of the centres of mass of the molecules. When the system is a crystalline solid we can use a still further simplification. For any given quantum state of the crystal we may regard the energy as the sum of two terms which for convenience we may call *configurational* and *acoustic*. By *configurational energy* we mean the energy the crystal would have if

the centre of mass of every molecule were at rest on its lattice point. By *acoustic energy* we mean the energy of the vibrations of the centres of mass of the molecules about their lattice points.

We shall, without any attempt at justification, use the approximation of treating the configurational and acoustic energies as independent. We accordingly write for the translational partition function Q_{tr}

$$Q_{\text{tr}} = Q_{\text{ac}} \Omega, \quad (2.05.1)$$

where Q_{ac} is the partition function for the acoustic modes of vibration and Ω is the *configurational partition function* for the molecules supposed fixed on their lattice points. The approximation, used throughout this book, consists in regarding Q_{ac} as determined by the number of molecules of each species but as unaffected by the mixing of these molecules. To this approximation the molar free energy of mixing $\Delta_m F$ of a binary mixture is determined by

$$-\Delta_m F/kT = \ln \Omega_m - (1-x)\ln \Omega_1^0 - x\ln \Omega_2^0, \quad (2.05.2)$$

where Ω_m denotes the configurational partition function of one mole of the mixture while Ω_1^0 , Ω_2^0 denote those of one mole of the pure substances 1, 2 respectively.

The foregoing discussion shows that for crystals Q_{ac} and Ω are well-defined quantities and that the weak point in the treatment is the assumption of their mutual independence. For liquids also we shall assume that the acoustical partition function and the configurational partition function are independent, but there is the further weakness that for liquids these functions are difficult to define since there is now no lattice. Nevertheless it is useful, even though untrue, to treat a liquid as if the molecules were arranged on a lattice. Analysis by X-rays has shown that a liquid is much more like a solid than like a gas, and the structure which we shall accept as the most plausible for a liquid is conveniently referred to as *quasi-crystalline*. Whereas in a crystal each molecule is surrounded by a definite invariable number of nearest neighbours, this number is not definite in a liquid. Nevertheless, at temperatures well below the critical temperature, the number of nearest neighbours has a fairly well-defined average value, and, although there are fluctuations about this average, these fluctuations are not serious and the geometrical relationship of each molecule to its immediate neighbours is on the average very similar to that in a crystal. Moreover, the fluctuations are not sufficiently serious to disturb the regularity of the geometrical relationship between immediate neighbours for more than a rather unimportant fraction of centres in the liquid. The

fluctuations or occasional irregularities in the configurations of immediate neighbours are, however, usually sufficient to destroy completely any regularity between the configurations of distant molecules. We shall then, without further apology, treat liquid mixtures as quasi-crystalline. This means that we shall use the terminology applicable to a lattice although we know that in fact no precise lattice exists. Formula (2) will accordingly be used for liquid mixtures as well as for solid mixtures.

2.06. Two simple examples

It may be helpful at this stage to illustrate the use of partition functions by considering certain particularly simple systems. We accordingly discuss two such examples.

Our first example is the determination of the free energy of mixing of two isotopes. Consider a mixture containing $N(1-x)$ molecules of the isotope 1 and Nx molecules of the isotope 2, that is to say N molecules in all. Let us begin by imagining that every individual molecule were distinguishable and let us denote the configurational partition function for this imaginary system by Ω^* . Then by definition we have

$$\Omega^* = \sum e^{-E/kT}, \quad (2.06.1)$$

where E denotes the energy of the crystal and the summation extends over all arrangements of the N supposedly distinguishable molecules over the N lattice points. Since the molecules are all isotopic we may safely assume that the energy E is independent of the arrangement of the molecules on the lattice and indeed independent of x . We may therefore take the Boltzmann factor outside the summation, and since the number of possible arrangements of the supposedly distinguishable molecules on the lattice is evidently $N!$, we have

$$\Omega^* = N! e^{-E/kT}. \quad (2.06.2)$$

In the real mixture the individual molecules are of course not distinguishable, but only the two kinds. We must count as separate states only such as are distinguishable. Hence the configurational partition function Ω for the real mixture is obtained by dividing Ω^* by

$$\{N(1-x)\}! \{Nx\}!.$$

Consequently $\Omega = \frac{N!}{\{N(1-x)\}! \{Nx\}!} e^{-E/kT}. \quad (2.06.3)$

If we now consider N molecules of the pure isotope 1, since E will

have the same value as in the mixture, we can obtain the configurational partition function Ω_1^0 by setting $x = 0$ in (3). Thus

$$\Omega_1^0 = e^{-E/kT}. \quad (2.06.4)$$

Similarly for the configurational partition function of N molecules of the pure isotope 2

$$\Omega_2^0 = e^{-E/kT}. \quad (2.06.5)$$

Hence the free energy of the mixture exceeds that of the constituent pure isotopes by the negative quantity

$$\begin{aligned} -kT\{\ln\Omega-(1-x)\ln\Omega_1^0-x\ln\Omega_2^0\} &= -kT\ln\frac{N!}{\{N(1-x)\}!\{Nx\}!} \\ &= NkT\{(1-x)\ln(1-x)+x\ln x\}, \end{aligned} \quad (2.06.6)$$

when we use Stirling's theorem for the factorials. If we now equate N to Avogadro's number, the number of molecules in a mole, so that $Nk = R$, we obtain for the molar free energy of mixing for isotopes the negative value given by

$$\Delta_m F = RT\{(1-x)\ln(1-x)+x\ln x\}. \quad (2.06.7)$$

The corresponding entropy of mixing has the positive value given by

$$\Delta_m S = -R\{(1-x)\ln(1-x)+x\ln x\}. \quad (2.06.8)$$

Our second example is the comparison of the free energy of a mixture of two perfect gases occupying a volume V with that of the two unmixed gases each occupying an equal volume V . By a perfect gas we mean a system of molecules so dilute that interaction between the molecules may be neglected. Since, then, we ignore all interactions between molecules, we ignore in particular interactions between different kinds of molecules. Thus the states and behaviour of each gaseous species will be independent of the presence of any other gaseous species. Hence the partition function of the mixture is equal to the product of partition functions for the separate gases each occupying the same volume V and consequently the free energy of the mixture is equal to the sum of the free energies of the separate gases each occupying the same volume. This result may be expressed by the formula

$$F(T, V, N_1, N_2) = F(T, V, N_1, 0) + F(T, V, 0, N_2). \quad (2.06.9)$$

Correspondingly for the entropies we have

$$S(T, V, N_1, N_2) = S(T, V, N_1, 0) + S(T, V, 0, N_2). \quad (2.06.10)$$

2.07. Characteristic of macroscopic system

Let us rewrite formula (2.02.3) as

$$Q = \sum g(E)e^{-E/kT}, \quad (2.07.1)$$

where $g(E)$ denotes the number of non-degenerate states having the same value of the energy E . Let us further denote the largest term in the sum by

$$Q_m = g(E_m)e^{-E_m/kT}, \quad (2.07.2)$$

and the ratio of the sum to its largest term by α . Since all terms of the sum are positive, it is evident that

$$Q/Q_m = \alpha > 1. \quad (2.07.3)$$

Substituting equations (2) and (3) into (2.03.1) we obtain

$$-\frac{F}{kT} = \ln Q_m + \ln \alpha. \quad (2.07.4)$$

It can be shown mathematically that in systems with a very large number of degrees of freedom, that is to say all macroscopic systems, the positive term $\ln \alpha$ is entirely negligible compared with the other term. For any macroscopic system we may therefore, without appreciable loss of accuracy, replace (4) by

$$F = -kT \ln Q_m. \quad (2.07.5)$$

In other words, for purposes of evaluating the free energy, or any thermodynamic property derived therefrom, we may always replace the partition function Q by its maximum term in the sum (1).

2.08. Grand partition function

We emphasized at the beginning of this chapter that the functions and formulae used depend on the choice of independent variables. We have hitherto concentrated our attention on the commonest and most generally useful set of independent variables, namely T, V, N_1, N_2 , where N_1, N_2 denote numbers of molecules of the species 1, 2 respectively. This is, however, not the only useful set. It is for some purposes convenient to use instead the independent variables $T, V, \lambda_1, \lambda_2$, where λ_1, λ_2 are the absolute activities. We shall not at this stage discuss the possible advantages of this choice. These will rather become evident from applications at various places in this book. We shall now merely describe the procedure and formulae appropriate to this set of independent variables.

We begin by constructing the *grand partition function* Ξ defined by†

$$\Xi(T, \lambda_1, \lambda_2) = \sum_{N_1} \sum_{N_2} \sum_r e^{-E_r/kT} \lambda_1^{N_1} \lambda_2^{N_2}, \quad (2.08.1)$$

where the triple summation extends over all values of N_1, N_2 as well as over all states r for each N_1, N_2 . It can be shown that the observed

† Fowler (1938), *Proc. Cambridge Phil. Soc.* 34, 382.

value of any property \mathcal{P} of the system is correctly given by averaging over all possible values of N_1, N_2 as well as r attaching to each such state as weight the relevant term in the sum (1). Thus the average or observed value $\bar{\mathcal{P}}$ of \mathcal{P} is given by

$$\bar{\mathcal{P}} = \frac{\sum_{N_1} \sum_{N_2} \sum_r \mathcal{P}_r(N_1, N_2) e^{-E_r/kT} \lambda_1^{N_1} \lambda_2^{N_2}}{\sum_{N_1} \sum_{N_2} \sum_r e^{-E_r/kT} \lambda_1^{N_1} \lambda_2^{N_2}}. \quad (2.08.2)$$

By application of (2) we find in particular that the equilibrium values of N_1, N_2 are given by

$$N_1 = \frac{\partial \ln \Xi}{\partial \ln \lambda_1}, \quad N_2 = \frac{\partial \ln \Xi}{\partial \ln \lambda_2}. \quad (2.08.3)$$

Similarly the equilibrium value of the energy, that is the total energy, is given by

$$U = \bar{E} = kT^2 \frac{\partial \ln \Xi}{\partial T}. \quad (2.08.4)$$

We must now consider how Ξ is related to the thermodynamic functions. As the partition function Q is closely related to the free energy F , which is a thermodynamic potential for the independent variables T, V, N_1, N_2 , so we may expect the grand partition function Ξ to be closely related to a thermodynamic potential for the independent variables $T, V, \lambda_1, \lambda_2$. Such a thermodynamic potential is the product PV of pressure and volume or alternatively the ratio PV/kT . We have for a system of two components

$$\frac{PV}{kT} = \frac{G - F}{kT} = \frac{N_1 \mu_1 + N_2 \mu_2 - F}{kT} = N_1 \ln \lambda_1 + N_2 \ln \lambda_2 - \frac{F}{kT}. \quad (2.08.5)$$

According to formula (1.03.4) for a system of two components, we have

$$dF = -SdT - PdV + kT \ln \lambda_1 dN_1 + kT \ln \lambda_2 dN_2, \quad (2.08.6)$$

which is equivalent to

$$d\left(\frac{F}{kT}\right) = -\frac{U}{kT^2}dT - \frac{P}{kT}dV + \ln \lambda_1 dN_1 + \ln \lambda_2 dN_2. \quad (2.08.7)$$

Differentiating (5) and using (7) we obtain

$$d\left(\frac{PV}{kT}\right) = \frac{U}{kT^2}dT + \frac{P}{kT}dV + N_1 d\ln \lambda_1 + N_2 d\ln \lambda_2. \quad (2.08.8)$$

We may regard (8) as a fundamental equation for the variables $T, V, \lambda_1, \lambda_2$ and PV/kT as a thermodynamic potential for these variables.

Formulae (3), (4), and (8) are consistent with the assumption, which can in fact be rigorously justified, that

$$\ln \Xi = \frac{PV}{kT}, \quad (2.08.9)$$

or

$$kT \ln \Xi = PV. \quad (2.08.10)$$

From (10) it follows that for liquid or solid phases the value of $(\Xi)^{1/N}$ will be extremely close to unity, since PV/NkT is negligible.

We may evidently rewrite (1) in the form

$$\Xi = \sum_{N_1} \sum_{N_2} Q(N_1, N_2) \lambda_1^{N_1} \lambda_2^{N_2}, \quad (2.08.11)$$

where $Q(N_1, N_2)$ denotes the ordinary partition function for given values of N_1, N_2 . In the previous section we saw that for the purpose of deriving the thermodynamic properties of a macroscopic system we may always replace the partition function Q by its largest term in the sum (2.07.1). For similar reasons we may, for the purpose of evaluating thermodynamic properties, always replace the double sum in (11) by its maximum term. If we denote this maximum term by Ξ_m , we have from its definition

$$\frac{\partial \ln \Xi_m}{\partial N_1} = 0, \quad \frac{\partial \ln \Xi_m}{\partial N_2} = 0. \quad (2.08.12)$$

Substituting the value of Ξ_m from (11) into (12) we have

$$\frac{\partial \ln Q}{\partial N_1} + \ln \lambda_1 = 0, \quad \frac{\partial \ln Q}{\partial N_2} + \ln \lambda_2 = 0, \quad (2.08.13)$$

which are equivalent to the familiar thermodynamic relations

$$\frac{\partial F}{\partial N_1} = kT \ln \lambda_1, \quad \frac{\partial F}{\partial N_2} = kT \ln \lambda_2. \quad (2.08.14)$$

The relations (14) provide a check on the mutual consistency of our statements concerning the properties of the grand partition function Ξ .

2.09. Semi-grand partition functions

It is sometimes convenient to use as independent variables neither N_1, N_2 nor λ_1, λ_2 but N_1, λ_2 or λ_1, N_2 . This causes no new difficulty and the required procedure is evident. We construct a *semi-grand partition function* $\Xi(T, N_1, \lambda_2)$ defined by

$$\Xi(T, N_1, \lambda_2) = \sum_{N_2} \sum_r e^{-E_r/kT} \lambda_2^{N_2}, \quad (2.09.1)$$

where the double summation extends over all values of N_2 as well as over all states r for each N_2 and the given N_1 . It can be shown that the

observed value of any property \mathcal{P} of the system is correctly given by averaging over all possible values of N_2 as well as r , attaching to each such state as weight the relevant term in the sum (1). Thus the average or observed value $\bar{\mathcal{P}}$ of \mathcal{P} is given by

$$\bar{\mathcal{P}} = \frac{\sum_{N_2} \sum_r \mathcal{P}_r(N_1, N_2) e^{-E_r/kT} \lambda_2^{N_2}}{\sum_{N_2} \sum_r e^{-E_r/kT} \lambda_2^{N_2}}. \quad (2.09.2)$$

By application of (2) we find in particular that the equilibrium value of N_2 is given by

$$N_2 = \frac{\partial \ln \Xi}{\partial \ln \lambda_2}. \quad (2.09.3)$$

We may evidently write (1) in the alternative form

$$\Xi(N_1, \lambda_2) = \sum_{N_2} Q(N_1, N_2) \lambda_2^{N_2}, \quad (2.09.4)$$

where $Q(N_1, N_2)$ denotes the ordinary partition function for given values of N_1, N_2 . As usual we may for a macroscopic system replace the sum in (4) by its maximum term Ξ_m determined by

$$\frac{\partial \ln \Xi_m}{\partial N_2} = 0. \quad (2.09.5)$$

Comparing (5) with (4) we have

$$\frac{\partial \ln Q}{\partial N_2} + \ln \lambda_2 = 0, \quad (2.09.6)$$

where N_2 now denotes its value in the maximum term and so its equilibrium value. Formula (6) is equivalent to the familiar thermodynamic relation

$$\frac{\partial F}{\partial N_2} = kT \ln \lambda_2. \quad (2.09.7)$$

III

IDEAL SOLUTIONS

3.01. Sufficient conditions for ideality

We have already in § 2.06 obtained a formula for the free energy of mixing of two isotopes. Actually this formula can apply at least approximately to a much wider class of mixtures. Such mixtures are called *ideal mixtures* or *ideal solutions*.† We shall now study the conditions sufficient for a mixture to be ideal. We shall begin by considering crystals with a well-defined lattice and shall then briefly extend the discussion to liquids treated on the quasi-crystalline model.

Consider a regular crystalline lattice in which each lattice-point has z nearest neighbours. This number z will be called the *coordination number*. For a simple cubic lattice $z = 6$, for a body-centred cubic lattice $z = 8$, and for a face-centred cubic lattice $z = 12$. A lattice with $z = 12$ is called *close-packed* because no higher value of z is geometrically possible.

We now consider two kinds of molecules A and B sufficiently similar in size and shape so that they are interchangeable on the lattice. Let a crystal of the pure substance A containing N molecules have an energy $-N\chi_A$ when all the molecules are at rest on their lattice points and the zero of energy is defined as that of the molecules at rest at infinite separation. If then we neglect interactions between pairs of molecules which are not nearest neighbours, we may regard $-2\chi_A/z$ as the mutual energy of a pair of neighbours both at rest on their lattice points. If we define χ_B similarly, then $-2\chi_B/z$ may be regarded as the mutual energy of a pair of neighbouring B molecules both at rest on their lattice points. If the lattice is filled partly by A molecules and partly by B molecules, then there will be contributions to the potential energy of the crystal from AB pairs of neighbours as well as from AA and BB pairs. It is convenient to denote the mutual energy of a pair of neighbours, one A the other B , by $(-\chi_A - \chi_B + w)/z$. This defines an *interchange energy*‡ w such that if we start with the two pure crystals and interchange an interior A molecule with an interior

† Lewis (1908), *J. Am. Chem. Soc.* **30**, 688; Brönsted (1908), *Z. physikal. Chem.* **64**, 649; Washburn (1910), *Z. physikal. Chem.* **74**, 537.

‡ This name is taken from Hildebrand and Scott (1950), *Solubility of Non-electrolytes*, p. 144, Reinhold.

B molecule the total increase of energy is $2w$, all molecules being assumed at rest on their lattice points.

We now assert that a sufficient condition for the mixed crystal to be ideal is that w should be zero. This implies that the mutual energy of an *AB* pair is equal to the arithmetic mean of the mutual energies of *AA* and *BB* pairs. In any interchange of molecules on the lattice of the mixed crystal the number of *AA* pairs destroyed (or created) is equal to the number of *BB* pairs destroyed (or created) and the number of *AB* pairs created (or destroyed) is equal to twice either of these. Hence, when $w = 0$, the interchange of molecules on the lattice of the mixed crystal leaves the energy unchanged. In other words, all configurations with the molecules at rest on their lattice points have equal energy.

If the mixed crystal contains $N(1-x)$ molecules *A* and Nx molecules *B*, the energy when all the molecules are at rest on their lattice points is

$$-N(1-x)\chi_A - Nx\chi_B, \quad (3.01.1)$$

regardless of how the two kinds of molecules are distributed.

The number of distinguishable ways of arranging these molecules on the lattice is

$$\frac{N!}{\{N(1-x)\}! \{Nx\}!}. \quad (3.01.2)$$

Hence the configurational partition function Ω is

$$\Omega = \frac{N!}{\{N(1-x)\}! \{Nx\}!} \exp[\{N(1-x)\chi_A + Nx\chi_B\}/kT]. \quad (3.01.3)$$

We must now consider briefly how the above analysis can be extended to liquids. We regard the liquid as quasi-crystalline as explained in § 2.05. This means that we continue to use a coordination number z denoting the number of molecules which are closest neighbours of a chosen molecule even though z may not have a well-defined value but may rather have to be regarded as an average. We must further assume that the molecules are sufficiently alike in size and shape to be able to pack in the same manner when mixed as in the pure liquids. For spherical molecules this requires a ratio of molecular volumes between 1 and 2 or a ratio of diameters between† 1.26 and 1. In addition we have to use, as we do throughout this book, the approximation of treating the internal degrees of freedom as separable from the translational degrees of freedom and further treating the acoustic

† Estimate due to Bernal. See Fowler and Guggenheim (1939), *Statistical Thermodynamics*, p. 351, Cambridge University Press.

factor in the translational partition function as separable from the configurational factor.

With all these assumptions formula (3) may still require correction by some unspecified geometrical factor to take account of the absence of a well-defined lattice, but it is assumed that this correction factor will be independent of the mole fraction x and so will not affect the value for the molar free energy of mixing.

3.02. Free energy and entropy of mixing

The configurational term in the free energy is $-kT \ln \Omega$. When we use formula (3.01.3) for Ω , this becomes

$$\begin{aligned} & -N(1-x)\chi_A - Nx\chi_B - kT \ln \frac{N!}{\{N(1-x)\}! \{Nx\}!} \\ & = -N(1-x)\chi_A - Nx\chi_B + NkT\{(1-x)\ln(1-x) + x\ln x\}, \quad (3.02.1) \end{aligned}$$

when Stirling's theorem is used. The corresponding values for the configurational free energy in crystals of the pure substances containing the same total number N of molecules are $-N\chi_A$ and $-N\chi_B$. Consequently the free energy of mixing is

$$NkT\{(1-x)\ln(1-x) + x\ln x\}, \quad (3.02.2)$$

and the molar free energy of mixing $\Delta_m F$ is given by

$$\Delta_m F = RT\{(1-x)\ln(1-x) + x\ln x\}. \quad (3.02.3)$$

This is the same formula as (2.06.7) derived for a mixture of isotopes. We emphasize that no restriction has been put on the relative magnitudes of χ_A and χ_B . The condition sometimes imposed that χ_A and χ_B should be equal or nearly equal is unnecessarily restrictive.

We have throughout disregarded interactions between pairs of molecules which are not nearest neighbours. It may be noted that this procedure does not imply that molecules farther apart than nearest neighbours have negligible energies of interaction but merely that such distant interactions may be regarded as equal for the several kinds of pairs AA , BB , and AB . This is less restrictive than treating such distant interactions as vanishing.

The extension to liquids of formula (3) for the molar free energy of mixing is immediate. We saw in the preceding section that account may be taken of the quasi-crystalline nature of the liquid by introducing into Ω an unspecified factor depending on N but assumed independent of x . It may readily be verified that such a factor contributes nothing to $\Delta_m F$.

For the molar entropy of mixing we obtain from (3) by differentiation with respect to T

$$\Delta_m S = R\{-(1-x)\ln(1-x)-x \ln x\}. \quad (3.02.4)$$

We notice that $\Delta_m F$ is negative and $\Delta_m S$ is positive. The energy of mixing is zero.

3.03. Raoult's law for vapour pressures

If we write N_A for $N(1-x)$ and N_B for Nx the configurational part of the free energy becomes, according to (3.02.1),

$$-N_A \chi_A - N_B \chi_B + kT \left\{ N_A \ln \frac{N_A}{N_A + N_B} + N_B \ln \frac{N_B}{N_A + N_B} \right\}. \quad (3.03.1)$$

Differentiating with respect to N_A we obtain for the configurational contribution to the chemical potential μ_A

$$-\chi_A + kT \ln \frac{N_A}{N_A + N_B} = -\chi_A + kT \ln(1-x). \quad (3.03.2)$$

The configurational contribution to the chemical potential of the pure substance A , obtained by putting $x = 0$, is $-\chi_A$. Consequently for the difference between the chemical potential μ_A of A in the mixture and its chemical potential μ_A^0 in the pure state we have

$$\mu_A - \mu_A^0 = kT \ln(1-x). \quad (3.03.3)$$

Formula (3) relates to the chemical potential per molecule. The more usual chemical potential per mole is obtained by multiplying by Avogadro's number. This changes k to R and we have

$$\mu_A - \mu_A^0 = RT \ln(1-x). \quad (3.03.4)$$

For the sake of brevity we do not trouble to distinguish between molecular and molar values for such quantities as μ unless there is danger of confusion. We would only mention that the absolute activity λ is defined on the molecular scale by

$$\mu = kT \ln \lambda, \quad (3.03.5)$$

and on the molar scale by

$$\mu = RT \ln \lambda, \quad (3.03.6)$$

so that the same formula is obtained for λ in both cases.

The relation between the absolute activity λ_A of A in the mixture and its value in the pure substance is thus

$$\lambda_A / \lambda_A^0 = 1-x. \quad (3.03.7)$$

The corresponding formula for the substance B is

$$\lambda_B / \lambda_B^0 = x. \quad (3.03.8)$$

If the vapour phase in equilibrium with the liquid or solid mixture may be regarded as a perfect gas, the partial vapour pressures p_A , p_B over the mixture are related to the vapour pressures p_A^0 , p_B^0 of the pure substances by

$$p_A/p_A^0 = 1 - x, \quad (3.03.9)$$

$$p_B/p_B^0 = x. \quad (3.03.10)$$

Formulae (9) and (10) are expressions of *Raoult's law*. If the vapour

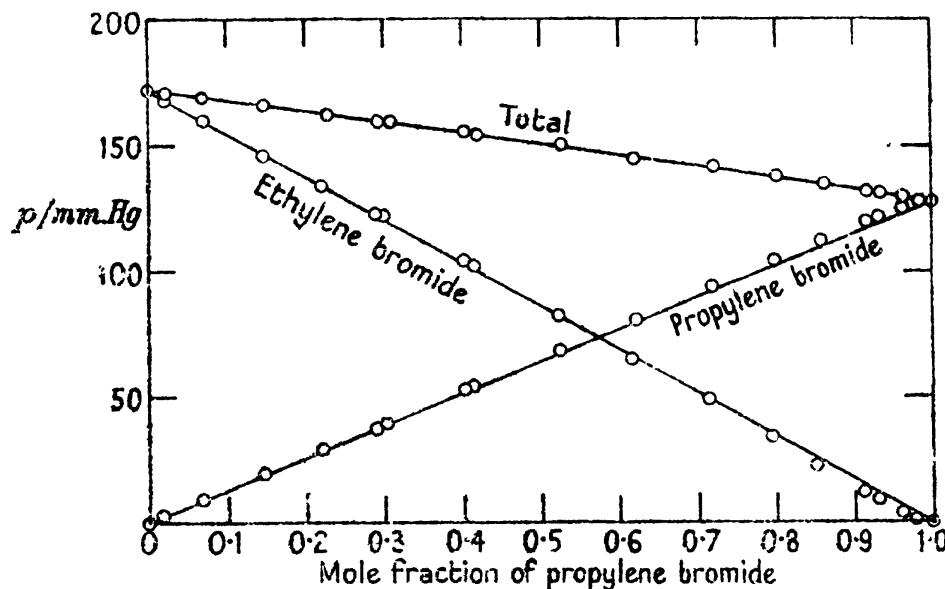


FIG. 3.1. Partial and total vapour pressures of mixtures of ethylene bromide and propylene bromide at 85° C.

phase may not be treated as a perfect gas, formulae (9) and (10) remain formally correct if each p is interpreted as a fugacity. The method of correcting vapour pressures to fugacities is discussed in Chapter VIII.

Raoult's law has been approximately verified experimentally for a few liquid mixtures of very similar substances. In particular Fig. 3.1 shows the experimental measurements by von Zawidzki of partial vapour pressures in mixtures of ethylene bromide and propylene bromide.

3.04. Osmotic pressure

If we substitute (9) into (1.06.5), we obtain for the osmotic pressure

$$\Pi_A = -\frac{RT}{V_A} \ln(1-x), \quad (3.04.1)$$

where we have used the subscript A in Π_A to denote that the osmotic pressure relates to a membrane permeable to A , but impermeable to B .

† von Zawidzki (1909), *Z. physikal. Chem.* 35, 129.

3.05. Several components

The treatment and formulae of this chapter are readily extended to mixtures of more than two substances. The general formula for the molar free energy of mixing is

$$\Delta_m F = RT \sum_r x_r \ln x_r, \quad (3.05.1)$$

and the general formula expressing Raoult's law for each component is

$$p_r/p_r^0 = x_r. \quad (3.05.2)$$

IV

REGULAR SOLUTIONS

4.01. Sufficient conditions for regularity

THE name *regular solution* was invented by Hildebrand† to describe mixtures whose behaviour was found experimentally to have certain regularities. The definition was essentially an empirical one. The name will here be used to denote a rather more restricted class of mixtures of molecules having properties amenable to theoretical treatment. Whenever it is necessary to distinguish this use of the name from Hildebrand's original use of it, we may speak of *strictly regular solutions*, or for brevity, *s-regular solutions*.

We define‡ as an *s-regular mixture* or *s-regular solution* any mixture of molecules satisfying all the conditions for forming an ideal mixture except that the interchange energy w defined in § 3.01 is not zero. The molecules are thus assumed to be sufficiently alike in size and shape to be interchangeable on a lattice or quasi-lattice, but the configurational energy is no longer independent of the mutual disposition of the two or more kinds of molecules.

4.02. Classification of neighbouring pairs

We consider a binary mixture containing $N_A = N(1-x)$ molecules *A* and $N_B = Nx$ molecules *B* on a lattice of N sites with a co-ordination number z . Since each molecule has z closest neighbours there are in all $\frac{1}{2}zN$ pairs of closest neighbours. Such pairs are of three kinds, namely *AA*, *BB*, and *AB*. We shall be much concerned with the numbers of pairs of each kind.

Let us denote the number of *AB* pairs in a particular configuration by zX . Then the number of neighbours of *A* molecules which are not *B* molecules is $z(N_A - X)$ and hence the number of *AA* pairs is $\frac{1}{2}z(N_A - X)$. Similarly the number of *BB* pairs is $\frac{1}{2}z(N_B - X)$. It is convenient to display these numbers and certain related quantities as follows:

<i>Kind of pair</i>	<i>Number of pairs</i>	<i>Energy per pair</i>	<i>Energy of all such pairs</i>
<i>AA</i>	$\frac{1}{2}z(N_A - X)$	$-2\chi_A/z$	$-(N_A - X)\chi_A$
<i>AB</i>	zX	$(-\chi_A - \chi_B + w)/z$	$X(-\chi_A - \chi_B + w)$
<i>BB</i>	$\frac{1}{2}z(N_B - X)$	$-2\chi_B/z$	$-(N_B - X)\chi_B$
All	$\frac{1}{2}z(N_A + N_B)$	—	$-N_A \chi_A - N_B \chi_B + Xw$

† Hildebrand (1929), *J. Am. Chem. Soc.* **51**, 66.

‡ Guggenheim (1935), *Proc. Roy. Soc. A* **148**, 304.

For a given value of X the configurational energy E_c is accordingly given by

$$\begin{aligned} E_c &= -(N_A - X)\chi_A + X(-\chi_A - \chi_B + w) - (N_B - X)\chi_B \\ &= -N_A \chi_A - N_B \chi_B + Xw. \end{aligned} \quad (4.02.1)$$

The quantities χ_A , χ_B , w are those defined in § 3.01. Part of our problem is to determine, either accurately or approximately, the average or equilibrium value \bar{X} of X . The equilibrium value of the configurational energy is then given by

$$U_c = \bar{E}_c = -N_A \chi_A - N_B \chi_B + \bar{X}w, \quad (4.02.2)$$

and the energy of mixing is $\bar{X}w$.

4.03. Nature of crude treatment (zeroth approximation)

We begin by describing the most crude treatment of the problem, because this treatment has been much used† and is a useful approximation to another more refined, but somewhat more complicated, treatment.

The essence of the crude treatment is to assume a completely random distribution of the two kinds of molecules in spite of the non-zero energy of mixing. Such an assumption of complete randomness leads to an average value \bar{X} of X given by

$$\bar{X}^2 = (N_A - \bar{X})(N_B - \bar{X}), \quad (4.03.1)$$

or
$$\bar{X} = \frac{N_A N_B}{N_A + N_B}. \quad (4.03.2)$$

This will be referred to as the zeroth approximation in contrast to the first approximation to be described in §§ 4.09–4.18.

4.04. Free energy and total energy

The configurational partition function Ω is according to definition given by
$$\Omega = \sum e^{-E/kT} = e^{N_A \chi_A/kT} e^{N_B \chi_B/kT} \sum e^{-Xw/kT}, \quad (4.04.1)$$

where the summation extends over the $N!/N_A! N_B!$ distinguishable configurations. Let us now define a quantity $\bar{\bar{X}}$ by writing

$$\sum e^{-Xw/kT} = \frac{N!}{N_A! N_B!} e^{-\bar{\bar{X}}w/kT}, \quad (4.04.2)$$

so that $\bar{\bar{X}}$ is related to X by averaging $\exp(-Xw/kT)$.

† Porter (1920), *Trans. Faraday Soc.* 16, 336; van Laar and Lorenz (1925), *Z. anorg. Chem.* 145, 239; Heitler (1926), *Ann. d. Phys.* 80, 629; Hildebrand (1929), *J. Am. Chem. Soc.* 51, 69. See also Fowler and Guggenheim (1939), *Statistical Thermodynamics*, p. 356, Cambridge University Press.

Having thus defined \bar{X} , we can formally express the several thermodynamic functions in terms of \bar{X} . We have

$$\Omega = e^{N_A \chi_A / kT} e^{N_B \chi_B / kT} \frac{N!}{N_A! N_B!} e^{-\bar{X}w/kT}, \quad (4.04.3)$$

so that the configurational free energy F_c is given by

$$\begin{aligned} F_c &= -N_A \chi_A - N_B \chi_B - kT \ln \frac{N!}{\{N(1-x)\}! \{Nx\}!} + \bar{X}w \\ &= -N_A \chi_A - N_B \chi_B + NkT\{(1-x)\ln(1-x) + x\ln x\} + \bar{X}w, \end{aligned} \quad (4.04.4)$$

when Stirling's theorem is used. The configurational total energy U_c is then given by

$$U_c = F_c - T \frac{\partial F_c}{\partial T}, \quad (4.04.5)$$

and the total energy of mixing is

$$\left(\bar{X} - T \frac{d\bar{X}}{dT} \right) w. \quad (4.04.6)$$

But we have in § 4.02 already identified the energy of mixing with $\bar{X}w$. Consequently we must have

$$\bar{X} = \bar{X} - T \frac{d\bar{X}}{dT}, \quad (4.04.7)$$

or

$$\bar{X} = T \int_0^{1/T} \bar{X} d\left(\frac{1}{T}\right), \quad (4.04.8)$$

the lower limit of integration being determined by the condition that as $w/kT \rightarrow 0$ the formulae should approach those of an ideal solution.

Returning now to the zeroth approximation, we have

$$\bar{X} = \frac{N_A N_B}{N_A + N_B}, \quad (4.04.9)$$

which is independent of T , and so to this approximation

$$\bar{X} = \bar{X} = \frac{N_A N_B}{N_A + N_B} = Nx(1-x). \quad (4.04.10)$$

Substituting (10) into (4) we obtain for the configurational free energy

$$F_c = -N_A \chi_A - N_B \chi_B + NkT\{(1-x)\ln(1-x) + x\ln x\} + Nx(1-x)w, \quad (4.04.11)$$

and so for the molar free energy of mixing

$$\Delta_m F = RT\{(1-x)\ln(1-x) + x\ln x\} + x(1-x)Nw, \quad (4.04.12)$$

where N denotes Avogadro's number.

The molar total energy of mixing and molar heat of mixing are given by

$$\Delta_m U = \Delta_m H = x(1-x)Nw. \quad (4.04.13)$$

The molar entropy of mixing $\Delta_m S$ is given by

$$\Delta_m S = \frac{\Delta_m U - \Delta_m F}{T} = -R\{(1-x)\ln(1-x) + x \ln x\}, \quad (4.04.14)$$

just as in an ideal mixture. Incidentally Hildebrand's original definition† of a regular solution was one having the same entropy of mixing as an ideal solution of the same mole fraction.

4.05. Partial pressures

If we use N_A, N_B as variables instead of N, x we can rewrite formula (4.04.11) for the configurational free energy as

$$F_c = -N_A \chi_A - N_B \chi_B + kT \left\{ N_A \ln \frac{N_A}{N_A + N_B} + N_B \ln \frac{N_B}{N_A + N_B} \right\} + \frac{N_A N_B}{N_A + N_B} w. \quad (4.05.1)$$

Differentiating with respect to N_A , we obtain for the chemical potential μ_A , and the absolute activity λ_A

$$\begin{aligned} \mu_A - \mu_A^0 &= kT \ln \frac{N_A}{N_A + N_B} + \left(\frac{N_B}{N_A + N_B} \right)^2 w \\ &= kT \ln(1-x) + x^2 w, \end{aligned} \quad (4.05.2)$$

$$\frac{\lambda_A}{\lambda_A^0} = (1-x)e^{x^2 w/kT}, \quad (4.05.3)$$

where μ_A^0, λ_A^0 denote, as usual, values of μ_A, λ_A respectively for the pure substance A and are obtained by setting $x = 0$. The formulae for the component B are precisely analogous. In particular

$$\frac{\lambda_B}{\lambda_B^0} = xe^{(1-x)^2 w/kT}. \quad (4.05.4)$$

For the partial vapour pressures, or more strictly the fugacities, we deduce from (3) and (4)

$$\frac{p_A}{p_A^0} = (1-x)e^{x^2 w/kT}, \quad (4.05.5)$$

$$\frac{p_B}{p_B^0} = xe^{(1-x)^2 w/kT}. \quad (4.05.6)$$

In Figs. 4.1, 4.2, and 4.3 values of p_A/p_A^0 and p_B/p_B^0 calculated from (4.05.5) and (4.05.6) respectively have been plotted against the mole fraction x for one negative and three positive values of w/kT , namely $-2, 1, 2$, and 3 . The shapes of these curves will be further discussed in § 4.07.

† Hildebrand (1929), *J. Am. Chem. Soc.* 51, 66.

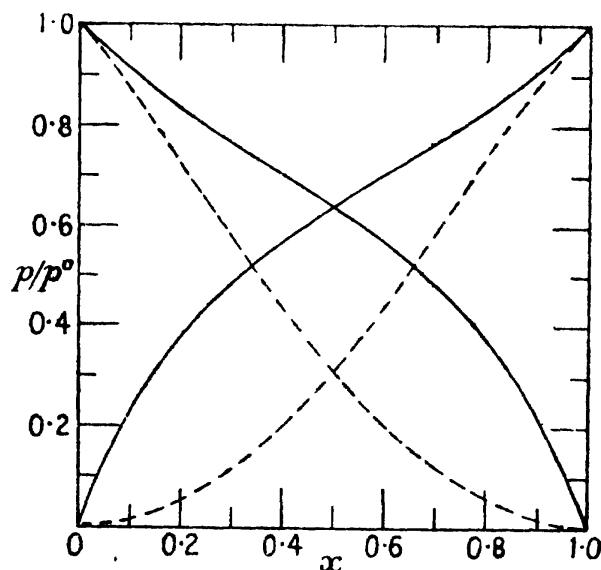


FIG. 4.1. Partial vapour pressures of regular solutions. Complete mixing.
— $w/kT = 1$; - - - $w/kT = -2$.

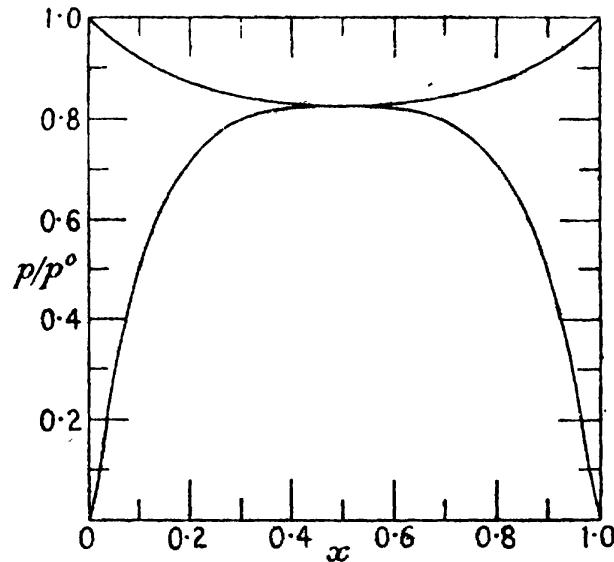


FIG. 4.2. Partial vapour pressures of regular solution
at temperature of critical mixing, $w/kT = 2$.

4.06. Activity coefficients

As already indicated briefly in § 1.07 it is convenient to measure the deviations from ideality by means of *activity coefficients* f_A, f_B defined as the ratio of the actual absolute activity or fugacity to its value if Raoult's law were obeyed. According to this definition

$$\frac{p_A}{p_A^0} = (1-x)f_A, \quad (4.06.1)$$

$$\frac{p_B}{p_B^0} = xf_B. \quad (4.06.2)$$

Thus according to formulae (4.05.5) and (4.05.6) the values of the activity coefficients are given by

$$f_A = e^{x^2 w/kT}, \quad (4.06.3)$$

$$f_B = e^{(1-x)^2 w/kT}. \quad (4.06.4)$$

It can readily be verified that these formulae satisfy the formula (1.07.6) required by the Gibbs-Duhem relation.

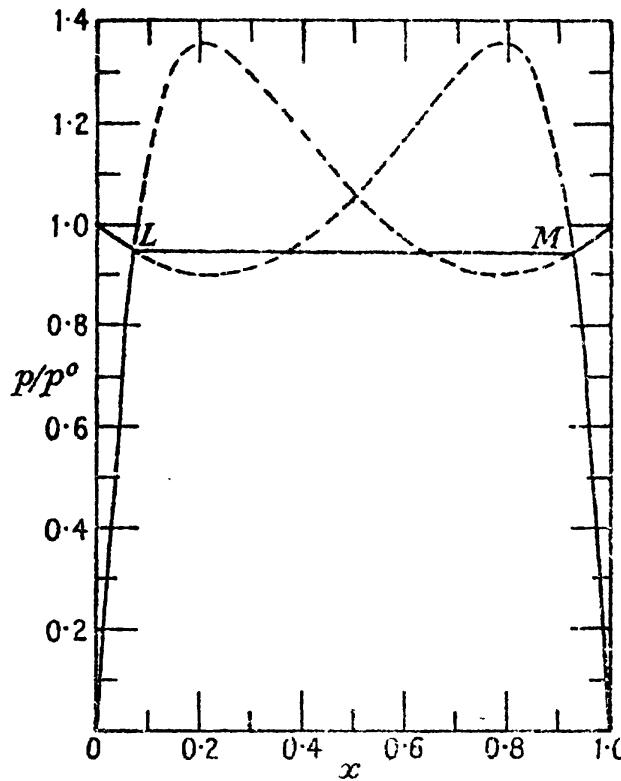


FIG. 4.3. Partial vapour pressures of regular solution.
Incomplete mixing, $w/kT = 3$.
— stable. - - - unstable.

4.07. Separation into two phases

It is evident that as the value of $|w|/kT$ increases, so do the deviations from Raoult's law. These deviations are called positive or negative according to the sign of w . The curves of p/p^0 plotted against x lie above or below the straight line corresponding to Raoult's law according as w is positive or negative.

When $w/kT = 2$ the curves have a point of horizontal inflection at the composition $x = \frac{1}{2}$ of an equimolecular mixture. This behaviour is shown in Fig. 4.2. For still higher positive values of w/kT the curves have a maximum and a minimum. An example of this behaviour is shown in Fig. 4.3 for $w/kT = 3$. The middle part of the curves corresponds to unstable phases; these split into two phases such that the

partial vapour pressure of each component has the same value in both phases. Since the curves for p_A/p_A^0 and p_B/p_B^0 are mirror images of each other about $x = \frac{1}{2}$, the two coexisting phases must have the compositions given by the two outer intersections of the two curves. These are the points marked L , M in the diagram. The dotted parts of the curve between L and M refer to an unrealizable single unstable phase.

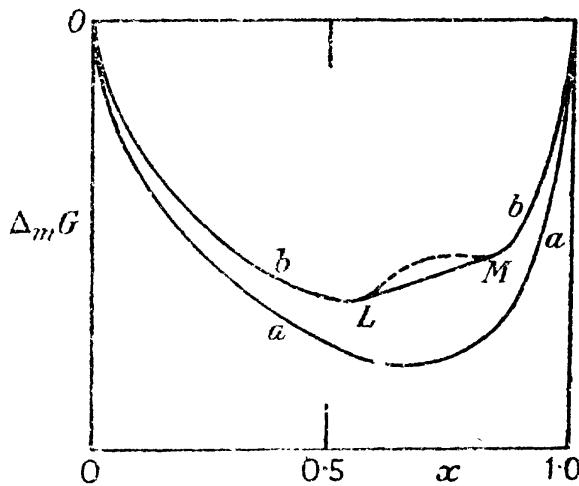


FIG. 4.4. Free energy of mixing of solution plotted against mole fraction. Curve a , complete mixing.
Curve b , incomplete mixing.

The condition for the mutual equilibrium of two phases such as L and M is conveniently obtained by studying how the molar Gibbs function of mixing $\Delta_m G$ depends on the mole fraction x . In general the curve obtained on plotting $\Delta_m G$ against x can have a shape like either curve a or curve b in Fig. 4.4. If the shape is like curve a , then all values of x are stable. If on the contrary the shape is like curve b , then values of x are unstable between those of L and M , the two points of contact of the double tangent LM . A phase of any composition intermediate between those of L and M will split into two phases having the compositions of L and M . Thus the characteristic of the two phases L and M which are in mutual equilibrium is equal values of $\partial\Delta_m G/\partial x$. This condition applies to any mixture whatever. When $\Delta_m G$ is symmetrical with respect to x and $1-x$, as it is for a regular mixture, the curves take the symmetrical form shown in Fig. 4.5. The condition at both L and M is then

$$\frac{\partial\Delta_m G}{\partial x} = 0. \quad (4.07.1)$$

Since for liquid or solid phases the difference between F and G is negligible, we may equally well write the condition as

$$\frac{\partial \Delta_m F}{\partial x} = 0. \quad (4.07.2)$$

Using formula (4.04.12) for $\Delta_m F$ in (2), we obtain

$$\ln \frac{x}{1-x} = (2x-1) \frac{w}{kT}. \quad (4.07.3)$$

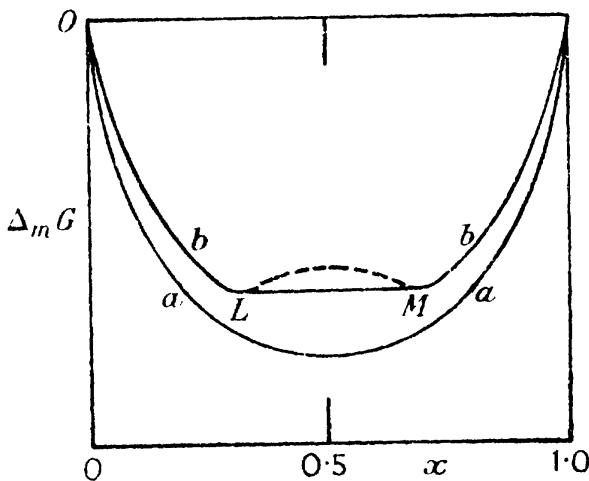


FIG. 4.5. Free energy of mixing of regular solution plotted against mole fraction. Curve a , complete mixing. Curve b , incomplete mixing.

One solution of equation (3) is $x = \frac{1}{2}$, but, at the relevant low temperatures where splitting into two phases occurs, this solution corresponds to a maximum of F . There are at these temperatures two other solutions of (3) distributed symmetrically on each side of $x = \frac{1}{2}$ which correspond to minima of F . These are the solutions which give the compositions of the two phases in mutual equilibrium.

If we use the substitution

$$s = 2x-1, \quad (4.07.4)$$

we can rewrite (3) in the form

$$\frac{w}{kT} = \frac{1}{s} \ln \frac{1+s}{1-s} = \frac{2}{s} \tanh^{-1} s. \quad (4.07.5)$$

The last form is especially convenient for numerical computation using tables of hyperbolic tangents.

4.08. Critical mixing

The point of horizontal inflection in the curves of Fig. 4.2 represents the condition called *critical mixing* and the temperature corresponding to this curve is called the *temperature of critical mixing* or sometimes, provided there is no danger of confusion, the *critical temperature*.

From the diagram it is clear that the conditions for critical mixing are

$$\frac{\partial p_A}{\partial x} = 0, \quad \frac{\partial^2 p_A}{\partial x^2} = 0, \quad (4.08.1)$$

$$\frac{\partial p_B}{\partial x} = 0, \quad \frac{\partial^2 p_B}{\partial x^2} = 0. \quad (4.08.2)$$

These conditions are mathematically equivalent to

$$\frac{\partial \ln p_A}{\partial x} = 0, \quad \frac{\partial^2 \ln p_A}{\partial x^2} = 0, \quad (4.08.3)$$

$$\frac{\partial \ln p_B}{\partial x} = 0, \quad \frac{\partial^2 \ln p_B}{\partial x^2} = 0. \quad (4.08.4)$$

By using the definitions of activity coefficients in (4.06.1) and (4.06.2), these conditions can in turn be transformed to

$$\frac{\partial \ln f_A}{\partial x} = \frac{1}{1-x}, \quad \frac{\partial^2 \ln f_A}{\partial x^2} = \frac{1}{(1-x)^2}, \quad (4.08.5)$$

$$-\frac{\partial \ln f_B}{\partial x} = \frac{1}{x}, \quad \frac{\partial^2 \ln f_B}{\partial x^2} = \frac{1}{x^2}. \quad (4.08.6)$$

These conditions for critical mixing are quite general. They do not imply that the solution must be regular. If the solution is regular, then according to the zeroth approximation the activity coefficients f_A and f_B are given by (4.06.3) and (4.06.4) respectively. Substituting these values into (5) and (6) we obtain the conditions

$$2x \frac{w}{kT_c} = \frac{1}{1-x}, \quad 2 \frac{w}{kT_c} = \frac{1}{(1-x)^2}, \quad (4.08.7)$$

$$2(1-x) \frac{w}{kT_c} = \frac{1}{x}, \quad 2 \frac{w}{kT_c} = \frac{1}{x^2}, \quad (4.08.8)$$

where T_c denotes the temperature of critical mixing.

The solution of these equations is

$$x = \frac{1}{2}, \quad (4.08.9)$$

$$kT_c = \frac{1}{2}w. \quad (4.08.10)$$

The condition (9) could have been foretold from considerations of symmetry. The condition (10) confirms that the curves of Fig. 4.2 in fact correspond to the temperature of critical mixing.

According to Fig. 4.5 we could alternatively have used the conditions of critical mixing,

$$\frac{\partial \Delta_m F}{\partial x} = 0, \quad \frac{\partial^2 \Delta_m F}{\partial x^2} = 0 \quad (x = \frac{1}{2}). \quad (4.08.11)$$

These lead immediately to (10).

4.09. Nature of quasi-chemical treatment (first approximation)

The assumption (4.03.1) corresponding to complete randomness cannot be strictly correct. It is in fact physically obvious that as $w/kT \rightarrow 0$ (high temperature) \bar{X} will tend to the random value given by (4.03.2), but that at finite temperatures \bar{X} will be less than or greater than the random value according as w is positive or negative.

We can improve† on the zeroth approximation by replacing (4.03.1) by

$$\bar{X}^2 = (N_A - \bar{X})(N_B - \bar{X})e^{-2w/zkT}. \quad (4.09.1)$$

Since $2w/z$ is the energy required to change an AA pair and a BB pair into two AB pairs and \bar{X} , $\frac{1}{2}(N_A - \bar{X})$, $\frac{1}{2}(N_B - \bar{X})$ are proportional to the number of AB , AA , and BB pairs respectively, (1) is an equation of the form to be expected if the several kinds of pairs of neighbours were gaseous molecular species in chemical equilibrium. The approximate treatment embodied in equation (1) is accordingly called the *quasi-chemical treatment*. It is also referred to as the *first approximation*, in contrast to the zeroth approximation corresponding to the assumption of complete randomness.

It is convenient to introduce the abbreviation η for the quantity $e^{w/zkT}$. We accordingly rewrite (1) as

$$(N_A - \bar{X})(N_B - \bar{X}) - \eta^2 \bar{X}^2 = 0. \quad (4.09.2)$$

4.10. Total energy and free energy

Formula (4.09.2) is a quadratic equation for \bar{X} . It is convenient to define a quantity β by

$$\bar{X} = \frac{N_A N_B}{N_A + N_B} \frac{2}{\beta + 1}, \quad (4.10.1)$$

so that the zeroth approximation corresponds to setting $\beta = 1$. Using (1) we can transform equation (4.09.2) into the quadratic equation for β

$$\beta^2 - (1 - 2x)^2 = 4\eta^2 x(1 - x), \quad (4.10.2)$$

having the solution

$$\beta = \{1 + 4x(1 - x)(\eta^2 - 1)\}^{\frac{1}{2}}. \quad (4.10.3)$$

The molecular total energy of mixing is then given by

$$\Delta_m U = \frac{2}{\beta + 1} x(1 - x) N w, \quad (4.10.4)$$

with β given by (3).

† Rushbrooke (1938), *Proc. Roy. Soc. A* 166, 296. This paper corrects an error in an earlier treatment, Guggenheim (1935), *Proc. Roy. Soc. A* 148, 304. See also Fowler and Guggenheim (1939), *Statistical Thermodynamics*, p. 358, C.U.P.

To obtain the free energy of mixing we have to evaluate \bar{X} , which is related to \bar{X} by (4.04.8). Since \bar{X} is given by (1), we need to obtain a relation between $d(1/T)$ and $d\beta$. We have

$$\frac{2w}{zk} d\left(\frac{1}{T}\right) = d \ln \eta^2 = \frac{2\beta d\beta}{\beta^2 - (1-2x)^2}. \quad (4.10.5)$$

Substituting (1) and (5) into (4.04.8) we have

$$\frac{\bar{X}}{N_A + N_B} = x(1-x) \frac{zkT}{2w} \int_1^\beta \frac{4\beta d\beta}{(\beta-1+2x)(\beta+1-2x)(\beta+1)}, \quad (4.10.6)$$

the lower limit of integration being determined by the condition that \bar{X} must remain finite as $T \rightarrow \infty$, when $\beta \rightarrow 1$, corresponding to complete randomness. Performing the integration in (6) we obtain

$$\frac{\bar{X}}{N_A + N_B} = \frac{zkT}{2w} \left\{ (1-x) \ln \frac{\beta+1-2x}{(1-x)(\beta+1)} + x \ln \frac{\beta-1+2x}{x(\beta+1)} \right\}. \quad (4.10.7)$$

Substituting (7) into (4.04.4) we obtain for the configurational free energy

$$F_c = -N_A \chi_A - N_B \chi_B + NkT \{(1-x) \ln(1-x) + x \ln x\} + N \frac{1}{2} zkT \left\{ (1-x) \ln \frac{\beta+1-2x}{(1-x)(\beta+1)} + x \ln \frac{\beta-1+2x}{x(\beta+1)} \right\}. \quad (4.10.8)$$

Consequently the molar free energy of mixing $\Delta_m F$ is given by

$$\frac{\Delta_m F}{RT} = (1-x) \ln(1-x) + x \ln x + \frac{1}{2} z \left\{ (1-x) \ln \frac{\beta+1-2x}{(1-x)(\beta+1)} + x \ln \frac{\beta-1+2x}{x(\beta+1)} \right\}. \quad (4.10.9)$$

4.11. Partial pressures and activity coefficients

We obtain the absolute activities from (4.10.8) by means of the relations

$$kT \ln \lambda_A = \frac{\partial F}{\partial N_A}, \quad kT \ln \lambda_B = \frac{\partial F}{\partial N_B}. \quad (4.11.1)$$

In using (1) we must remember that β , as well as x , is a function of N_A , N_B . The algebra is straightforward, but rather long. The final result obtained is

$$\frac{\lambda_A}{\lambda_A^0} = (1-x) \left\{ \frac{\beta+1-2x}{(1-x)(\beta+1)} \right\}^{1/2}, \quad (4.11.2)$$

$$\frac{\lambda_B}{\lambda_B^0} = x \left\{ \frac{\beta-1+2x}{x(\beta+1)} \right\}^{1/2}. \quad (4.11.3)$$

The partial pressures, or strictly fugacities, are given by the analogous formulae

$$\frac{p_A}{p_A^0} = (1-x) \left\{ \frac{\beta+1-2x}{(1-x)(\beta+1)} \right\}^{1/z}, \quad (4.11.4)$$

$$\frac{p_B}{p_B^0} = x \left\{ \frac{\beta-1+2x}{x(\beta+1)} \right\}^{1/z}. \quad (4.11.5)$$

The activity coefficients are given by

$$f_A = \left\{ \frac{\beta+1-2x}{(1-x)(\beta+1)} \right\}^{1/z}, \quad (4.11.6)$$

$$f_B = \left\{ \frac{\beta-1+2x}{x(\beta+1)} \right\}^{1/z}. \quad (4.11.7)$$

4.12. Coexisting phases. Critical mixing

At temperatures below the critical, phases of composition around $x = \frac{1}{2}$ are unstable and split into two phases of different compositions. The two coexisting phases are such that the partial vapour pressure of each component has the same value in both phases. In regular mixtures owing to symmetry the curves for p_A/p_A^0 and p_B/p_B^0 against x are mirror images of each other about $x = \frac{1}{2}$. Consequently in Fig. 4.3 the two coexisting phases are represented by the points L , M where the two curves intersect. These points are determined by

$$\frac{p_A}{p_A^0} = \frac{p_B}{p_B^0}. \quad (4.12.1)$$

Substituting from (4.11.4) and (4.11.5) into (1) we obtain

$$\frac{\beta-1+2x}{\beta+1-2x} = \left(\frac{x}{1-x} \right)^{(z-2)/z} = r^{(z-2)/z}, \quad (4.12.2)$$

where r is the *molecular ratio* defined by

$$r = \frac{x}{1-x}. \quad (4.12.3)$$

It is convenient to use the further abbreviation γ defined by

$$\gamma = r^{(z-2)/z}, \quad (4.12.4)$$

so that we write (2) as $\frac{\beta-1+2x}{\beta+1-2x} = \gamma$. (4.12.5)

Solving (5) for β we obtain

$$\frac{\beta}{1-2x} = \frac{1+\gamma}{1-\gamma}, \quad (4.12.6)$$

and consequently

$$\frac{\beta - 1 + 2x}{1 - 2x} = \frac{2\gamma}{1 - \gamma}, \quad (4.12.7)$$

$$\frac{\beta + 1 - 2x}{1 - 2x} = \frac{2}{1 - \gamma}. \quad (4.12.8)$$

Multiplying (7) by (8) we have

$$\beta^2 - (1 - 2x)^2 = \frac{4\gamma(1 - 2x)^2}{(1 - \gamma)^2}. \quad (4.12.9)$$

Comparing (9) with (4.10.2) we find

$$\eta = \left\{ \frac{\gamma}{x(1-x)} \right\}^{\frac{1}{z}} \frac{1-2x}{1-\gamma}. \quad (4.12.10)$$

Inserting the value of γ from (4) and using (3) we obtain

$$e^{w/zkT} = \eta = \frac{1-r}{r^{1/z} - r^{(z-1)/z}}. \quad (4.12.11)$$

Formula (11) is the required relation† between the molecular ratio of either of the coexisting phases and the temperature. It is readily verified that if one solution of (11) is $r = r_1$ then the other solution is $r_2 = 1/r_1$.

At the critical temperature the two coexisting phases become identical having the composition $x = \frac{1}{2}$ or $r = 1$. If we put $r = 1$ in (11) we obtain an indefinite form. We therefore put $r = 1 + \delta$, expand in powers of δ , and then make $\delta \rightarrow 0$. We thus obtain for the critical temperature T_c

$$e^{w/zkT_c} = \eta_c = \frac{z}{z-2}, \quad (4.12.12)$$

$$\text{or } \frac{w}{kT_c} = z \ln \frac{z}{z-2}. \quad (4.12.13)$$

For body-centred cubic packing $z = 8$ and (13) becomes

$$\frac{w}{kT_c} = 8 \ln \frac{8}{6} = 2.301 \quad (z = 8); \quad (4.12.14)$$

while for a face-centred cubic lattice $z = 12$ and (13) becomes

$$\frac{w}{kT_c} = 12 \ln \frac{12}{10} = 2.188 \quad (z = 12). \quad (4.12.15)$$

If in (13) we make $z \rightarrow \infty$ we recover the zeroth approximation (4.08.10), namely

$$\frac{w}{kT_c} = 2 \quad (z \rightarrow \infty). \quad (4.12.16)$$

† This relation obtained by McGlashan has not previously been published.

4.13. Relationship of zeroth to first approximation

We have just seen that as the coordination number z increases the value of w/kT_c decreases and that if we make $z \rightarrow \infty$ then $w/kT_c \rightarrow 2$, its value according to the zeroth approximation. It can be shown that the zeroth approximation is in fact the limiting form taken by the first approximation when z is made infinite. Consequently any formula of the zeroth approximation can be obtained from the corresponding formula of the first approximation by expanding in powers of z^{-1} and then putting $z^{-1} = 0$. We shall now verify this for a few of the most important formulae.

We begin with formula (4.10.3) for β . Expanding in powers of w/kT and retaining only the first power, we have

$$\beta = \left\{ 1 + 4x(1-x) \frac{2w}{zkT} \right\}^{\frac{1}{2}} = 1 + 4x(1-x) \frac{w}{zkT}. \quad (4.13.1)$$

We shall now use (1) in formula (4.11.6) for the activity coefficient f_A . We have, correct to the first power of w/zkT ,

$$\beta + 1 - 2x = 2(1-x) \left(1 + 2x \frac{w}{zkT} \right), \quad (4.13.2)$$

$$\beta + 1 = 2 \left(1 + 2x(1-x) \frac{w}{zkT} \right), \quad (4.13.3)$$

so that $\frac{\beta+1-2x}{(1-x)(\beta+1)} = \left(1 + 2x^2 \frac{w}{zkT} \right)$, (4.13.4)

and so finally, by substitution of (4) into (4.11.6),

$$f_A = \lim_{z \rightarrow \infty} \left(1 + \frac{2}{z} x^2 \frac{w}{kT} \right)^{\frac{1}{z}} = \exp \left(x^2 \frac{w}{kT} \right), \quad (4.13.5)$$

in agreement with formula (4.06.3) of the zeroth approximation.

When we substitute (1) into (4.10.1) and then make $z^{-1} = 0$ we recover formula (4.04.9) of the zeroth approximation. Again when $z \rightarrow \infty$ the quasi-chemical equilibrium formula (4.09.1) reduces to the formula for complete randomness (4.03.1). Finally when we make $z \rightarrow \infty$ in formula (4.12.13) for the critical temperature we recover formula (4.08.10) of the zeroth approximation.

4.14. Combinatory formula

We have so far treated formula (4.09.1) as the fundamental hypothesis of the quasi-chemical method, which has been introduced, without further support than its own inherent reasonableness, by analogy with the law for gaseous chemical equilibria. We shall now show that formula (4.09.1) is equivalent to an approximate combinatory

formula† for the number of configurations of the assembly with given values of N_A , N_B , and X .

If we could assume that the number of such configurations may be calculated as if the various types of pairs do not interfere with one another, then since there are $\frac{1}{2}z(N_A + N_B)$ pairs as tabulated in § 4.02, the number of configurations would be

$$\frac{\{\frac{1}{2}z(N_A + N_B)\}!}{\{\frac{1}{2}z(N_A - X)\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}z(N_B - X)\}!}. \quad (4.14.1)$$

It will be observed that in the denominator of (1) we have placed two factors each $\{\frac{1}{2}zX\}!$ where at first sight a single factor $\{zX\}!$ might seem more appropriate. This means that we are regarding the pairs of sites as orientated so that we distinguish between the two manners of occupation AB and BA . If we took the opposite view of ignoring orientations of the pairs of sites we should have to introduce symmetry factors and the final result would be the same.

Formula (1) is of course inexact, firstly because the different pairs do in fact necessarily interfere with one another and secondly because (1) would not give, when summed over all values of X , the correct total number of configurations. We can remove the second defect by inserting a normalizing factor independent of X and writing for the number of configurations $g(N_A, N_B, X)$ for given N_A , N_B , X

$$g(N_A, N_B, X) = h(N_A, N_B) \frac{\{\frac{1}{2}z(N_A + N_B)\}!}{\{\frac{1}{2}z(N_A - X)\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}z(N_B - X)\}!}. \quad (4.14.2)$$

We can evaluate $h(N_A, N_B)$ in (2), at least approximately, without much trouble. For if we sum $g(N_A, N_B, X)$ over all values of X we must obtain the total number of ways of placing N_A molecules A and N_B molecules B on $(N_A + N_B)$ sites. Hence

$$\sum_X g(N_A, N_B, X) = \frac{(N_A + N_B)!}{N_A! N_B!}. \quad (4.14.3)$$

Now we can with sufficient accuracy replace the sum in (3) by its maximum term. By differentiating (2) with respect to X we find that, if we denote the value of X in the maximum term by X^* , then

$$X^{*2} = (N_A - X^*)(N_B - X^*). \quad (4.14.4)$$

† The following treatment of regular mixtures is an adaptation of the method developed for superlattices by Fowler and Guggenheim (1940), *Proc. Roy. Soc. A* 174, 189. It may alternatively be regarded as a specially simple case of the treatment described by Guggenheim (1944), *Proc. Roy. Soc. A* 183, 213.

This gives

$$X^* = \frac{N_A N_B}{N_A + N_B}, \quad (4.14.5)$$

which means that X^* is the value of X corresponding to complete randomness.

We have then

$$g(N_A, N_B, X) = \frac{(N_A + N_B)!}{N_A! N_B!} \frac{\{\frac{1}{2}z(N_A - X^*)\}! \{\frac{1}{2}zX^*\}! \{\frac{1}{2}zX^*\}! \{\frac{1}{2}z(N_B - X^*)\}!}{\{\frac{1}{2}z(N_A - X)\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}zX\}! \{\frac{1}{2}z(N_B - X)\}!}, \quad (4.14.6)$$

where X^* is defined by (5).

4.15. Maximization

So far we have merely been investigating the form of $g(N_A, N_B, X)$ to which our suggested approximation for the number of configurations of given X leads us. We have now to apply the result to the thermodynamic problem. Since according to the table in § 4.02 the configurational energy for given X is $-N_A \chi_A - N_B \chi_B + Xw$, the configurational partition function is given by

$$\Omega = \sum_X g(N_A, N_B, X) \exp\{(N_A \chi_A + N_B \chi_B - Xw)/kT\}. \quad (4.15.1)$$

As usual we may replace the sum by its maximum term. If we denote the value of X in the maximum term by \bar{X} , we have

$$\Omega = g(N_A, N_B, \bar{X}) \exp\{(N_A \chi_A + N_B \chi_B - \bar{X}w)/kT\}, \quad (4.15.2)$$

where \bar{X} is determined by

$$\frac{\partial \ln \Omega}{\partial \bar{X}} = 0 \quad (\bar{X} = \bar{X}). \quad (4.15.3)$$

When we use formula (4.14.6) for $g(N_A, N_B, X)$, equation (3) becomes

$$\frac{1}{2}z \ln(N_A - \bar{X}) - z \ln \bar{X} + \frac{1}{2}z \ln(N_B - \bar{X}) - \frac{w}{kT} = 0,$$

or $\bar{X}^2 = (N_A - \bar{X})(N_B - \bar{X})e^{-2w/zkT}, \quad (4.15.4)$

which is identical with the quasi-chemical formula (4.09.1).

It follows that the hypothesis of the non-interference of pairs and the approximate combinatory formula for the number of configurations to which it leads also lead to all the equilibrium results which we have already deduced by the quasi-chemical method. The two assumptions are in fact exactly equivalent to each other. We have just proved that the hypothesis of non-interference of pairs implies also the results of the quasi-chemical method. We shall complete the proof of the

equivalence of the two methods by verifying that they lead to the same formula for the free energy.

4.16. Free energy and chemical potentials

The configurational free energy is given by

$$\begin{aligned} F_c &= -kT \ln \Omega \\ &= -kT \ln g(N_A, N_B, \bar{X}) - N_A \chi_A - N_B \chi_B + \bar{X}w, \end{aligned} \quad (4.16.1)$$

with $g(N_A, N_B, X)$ given by (4.14.6) and \bar{X} determined by (4.15.4) and X^* by (4.14.5). Instead of evaluating F_c directly, it is more convenient first to obtain formulae for the chemical potentials μ_A, μ_B , by differentiation of F_c with respect to N_A, N_B respectively. In performing these differentiations we must remember that \bar{X} is a function of N_A, N_B , but since by definition of \bar{X} we know that $\partial F_c / \partial \bar{X} = 0$, it follows that all terms coming from differentiations with respect to \bar{X} in fact cancel. We may therefore omit all such terms and this greatly reduces the work. At the same time from the definition of X^* one can readily verify that $\partial \ln g / \partial X^*$ vanishes, so that terms in $\partial X^* / \partial N_A$ or $\partial X^* / \partial N_B$ also cancel. Taking note of these simplifications we obtain immediately

$$\frac{\mu_A - \mu_A^0}{kT} = \ln \frac{N_A}{N_A + N_B} + \frac{1}{2}z \ln \frac{N_A - \bar{X}}{N_A - X^*}, \quad (4.16.2)$$

$$\frac{\mu_B - \mu_B^0}{kT} = \ln \frac{N_B}{N_A + N_B} + \frac{1}{2}z \ln \frac{N_B - \bar{X}}{N_B - X^*}. \quad (4.16.3)$$

Consequently for the absolute activities λ_A, λ_B , the partial pressures (strictly fugacities) p_A, p_B , and the activity coefficients f_A, f_B we have

$$\frac{\lambda_A}{\lambda_A^0(1-x)} = \frac{p_A}{p_A^0(1-x)} = f_A = \left(\frac{N_A - \bar{X}}{N_A - X^*} \right)^{\frac{1}{2}z}, \quad (4.16.4)$$

$$\frac{\lambda_B}{\lambda_B^0x} = \frac{p_B}{p_B^0x} = f_B = \left(\frac{N_B - \bar{X}}{N_B - X^*} \right)^{\frac{1}{2}z}. \quad (4.16.5)$$

When we substitute (2) and (3) into the relation

$$F = N_A \mu_A + N_B \mu_B = N(1-x) \mu_A + Nx \mu_B, \quad (4.16.6)$$

we obtain for the molar free energy of mixing $\Delta_m F$

$$\frac{\Delta_m F}{RT} = (1-x) \ln(1-x) + x \ln x + \frac{1}{2}z \left\{ (1-x) \ln \frac{N_A - \bar{X}}{N_A - X^*} + x \ln \frac{N_B - \bar{X}}{N_B - X^*} \right\}. \quad (4.16.7)$$

We recall that in all these formulae \bar{X}^* is given by

$$X^* = \frac{N_A N_B}{N_A + N_B}, \quad (4.16.8)$$

while \bar{X} is determined by the quasi-chemical equation

$$(N_A - \bar{X})(N_B - \bar{X}) = \bar{X}^2 e^{2w/zkT}. \quad (4.16.9)$$

It is clear that the method of deriving these formulae is appreciably more direct and more elegant than that of § 4.10 and § 4.11. The equivalence between the formulae of those sections and the formulae of the present section follows immediately from the relations

$$\frac{\bar{X}}{N} = x(1-x) \frac{2}{\beta+1}, \quad \frac{X^*}{N} = x(1-x), \quad (4.16.10)$$

$$\frac{N_A - \bar{X}}{N} = \frac{(1-x)(\beta+1-2x)}{\beta+1}, \quad \frac{N_A - X^*}{N} = (1-x)^2, \quad (4.16.11)$$

$$\frac{N_B - \bar{X}}{N} = \frac{x(\beta-1+2x)}{\beta+1}, \quad \frac{N_B - X^*}{N} = x^2. \quad (4.16.12)$$

4.17. Description of Bethe's method

We shall now describe a different method for deriving the equilibrium properties of an s -regular mixture. The method was devised by Bethe[†] for the study of the equilibrium properties of superlattices. It is therefore generally known as Bethe's method. It was applied to the study of s -regular mixtures by Rushbrooke.[‡] Although Bethe's method is apparently quite different from the quasi-chemical treatment, the two methods of approach are, as we shall see later, completely equivalent to each other. As the quasi-chemical treatment is more direct and more powerful, we need describe Bethe's method only briefly.

The essence of Bethe's method is the construction of a grand partition function for a sample group of sites, namely a site called the central site together with its z nearest neighbours. The grand partition function for this group of $z+1$ sites is written as

$$E_{z+1} = q_A \lambda_A (\epsilon_A \eta + \epsilon_B)^z + q_B \lambda_B (\epsilon_A + \epsilon_B \eta)^z, \quad (4.17.1)$$

where λ_A, λ_B are the absolute activities of A and B and q_A, q_B are the partition functions of molecules of type A and B respectively which take account of all degrees of freedom and motion of these molecules supposed attached to their lattice sites. The factors $q_A \lambda_A$ and $q_B \lambda_B$ relate to the occupation of the central site by an A or B molecule respectively. The other factors relate to the manners of occupation of each of the z neighbouring sites, namely

[†] Bethe (1935), *Proc. Roy. Soc. A* **150**, 552.

[‡] Rushbrooke (1938), *Proc. Roy. Soc. A* **166**, 296.

- $\epsilon_A \eta$ relates to the occupation of a neighbour site by A when the central site is also occupied by A ;
- ϵ_B relates to the occupation of a neighbour site by B when the central site is occupied by A ;
- ϵ_A relates to the occupation of a neighbour site by A when the central site is occupied by B ;
- $\epsilon_B \eta$ relates to the occupation of a neighbour site by B when the central site is also occupied by B .

The probabilities of occupation of the $z+1$ sites in the several alternative manners are assumed proportional to the respective terms in the expanded form of Ξ and for the present purpose these may be taken as sufficient definitions of the parameters ϵ_A , ϵ_B , η . Formula (1) can be simplified, at some sacrifice of symmetry, by making the substitutions

$$\xi_A = q_A \lambda_A \epsilon_B^z, \quad \xi_B = q_B \lambda_B \epsilon_A^z, \quad (4.17.2)$$

$$\epsilon = \epsilon_A / \epsilon_B. \quad (4.17.3)$$

We then obtain

$$\Xi_{z+1} = \xi_A (\epsilon \eta + 1)^z + \xi_B (\epsilon + \eta)^z. \quad (4.17.4)$$

The usual method of procedure, following Bethe, is to determine the parameter ϵ from the condition that the probability that the central site is occupied by A and a given neighbour site by B must by symmetry be equal to the probability that the central site is occupied by B and the given neighbour site by A . This condition gives

$$\xi_A (\epsilon \eta + 1)^{z-1} = \xi_B (\epsilon + \eta)^{z-1} \epsilon, \quad (4.17.5)$$

or using (2)
$$\frac{q_B \lambda_B}{q_A \lambda_A} \epsilon = \left(\frac{\epsilon \eta + 1}{\epsilon + \eta} \right)^{z-1}. \quad (4.17.6)$$

This is an equation for ϵ in terms of the known quantities q_A , q_B , λ_A , λ_B , and the parameter η . All the equilibrium properties, including for example \bar{X} , can then be expressed in terms of these quantities, but, owing to the intractable nature of equation (6), Bethe's method in this original form is far from convenient for obtaining explicit results.

We are, however, not compelled to follow Bethe in determining ϵ by means of (6). We shall instead obtain a relation from which ϵ has been eliminated. Before doing this we would point out that the form of (1) or (4) implies that, for a specified manner of occupation of the central site, the manners of occupation of the several neighbour sites are independent of one another. This implication is very similar to, if not identical with, our previous hypothesis of non-interference of pairs. It should therefore not be surprising if we can show that formula

(4) leads to the equation of quasi-chemical equilibrium. Let us denote by $[A, A]$ the probability that the central site be occupied by A and a given neighbour site by A ; by $[A, B]$ the probability that the central site be occupied by A and the given neighbour site by B ; and similarly for $[B, A]$ and $[B, B]$. We have therefore

$$\begin{aligned}[A, A] &= \xi_A \epsilon \eta (\epsilon \eta + 1)^{z-1}, \\ [A, B] &= \xi_A (\epsilon \eta + 1)^{z-1}, \\ [B, A] &= \xi_B \epsilon (\epsilon + \eta)^{z-1}, \\ [B, B] &= \xi_B \eta (\epsilon + \eta)^{z-1}.\end{aligned}\tag{4.17.7}$$

From (7) we deduce immediately

$$\frac{[A, B][B, A]}{[A, A][B, B]} = \eta^{-2}.\tag{4.17.8}$$

Since from symmetry $[A, B] = [B, A]$ we can write (8) in the alternative form

$$\frac{(\frac{1}{2}[A, B] + \frac{1}{2}[B, A])^2}{[A, A][B, B]} = \eta^{-2},\tag{4.17.9}$$

which we recognize as the equation of quasi-chemical equilibrium if we identify η with the η of § 4.09.

We see then that Bethe's method leads directly to the same result as the quasi-chemical treatment.

From the way in which the extra factors $(\quad)^{z-1}$ in (7) eliminate themselves from (8), it is clear that it is unnecessary in Bethe's manner to consider a group of $z+1$ sites. A group of a pair of neighbouring sites is sufficient.† If we construct the grand partition function Ξ_2 for a pair of sites analogous to Bethe's Ξ_{z+1} we find

$$\Xi_2 = q_A \lambda_A (\zeta_A \eta + \zeta_B) + q_B \lambda_B (\zeta_A + \zeta_B \eta).\tag{4.17.10}$$

It is possible, but not necessary, to correlate ζ_A, ζ_B with ϵ_A, ϵ_B occurring in Ξ_{z+1} . From (10) we have

$$\begin{aligned}[AA] &= q_A \lambda_A \zeta_A \eta, & [AB] &= q_A \lambda_A \zeta_B, \\ [BB] &= q_B \lambda_B \zeta_B \eta, & [BA] &= q_B \lambda_B \zeta_A,\end{aligned}\tag{4.17.11}$$

from which we immediately recover (8).

4.18. Critique of Bethe's method

We have seen that Bethe's method leads directly to the equation of quasi-chemical equilibrium. It might then be thought, and indeed it has been suggested, that Bethe's method may be regarded as a basis for the quasi-chemical treatment. Actually such an attitude puts the

† Guggenheim (1938), *Proc. Roy. Soc. A* 169, 134.

cart before the horse. We shall now show that Bethe's form for Ξ_{z+1} assumes the condition of quasi-chemical equilibrium.†

Let $[A, A, S]$ denote the term in the grand partition function corresponding to a selected central site being occupied by an A molecule, a selected nearest neighbour being occupied by an A molecule, and all the remaining sites central and neighbours being occupied in some specified manner denoted symbolically by S . Let $[B, B, S]$ be similarly defined. Let $[A, B, S]$ denote the term corresponding to the selected central site being occupied by an A molecule, the selected neighbour site by a B molecule, all the remaining sites, central and neighbours, being occupied in the manner S . Let $[B, A, S]$ be defined similarly and correspond to the converse manner of occupation of the selected central and neighbour sites.

One of the essential approximations of Bethe's method is the assumption

$$\left. \begin{array}{l} [A, A, S]/[A, B, S] \text{ independent of } S, \\ [B, A, S]/[B, B, S] \text{ independent of } S. \end{array} \right\} \quad (4.18.1)$$

According to this assumption the two Bethe parameters ϵ and η can be defined by

$$[A, A, S]/[A, B, S] = \epsilon\eta, \quad (4.18.2)$$

$$[B, A, S]/[B, B, S] = \epsilon/\eta. \quad (4.18.3)$$

We now sum (2) and (3) over all S obtaining

$$[A, A]/[A, B] = \epsilon\eta, \quad (4.18.4)$$

$$[B, A]/[B, B] = \epsilon/\eta. \quad (4.18.5)$$

Now divide (5) by (4), thus eliminating ϵ and obtaining

$$\frac{[A, B][B, A]}{[A, A][B, B]} = \eta^{-2}. \quad (4.18.6)$$

This is the same as (4.17.8), which we have already shown to be equivalent to the condition of quasi-chemical equilibrium, if we identify η with $e^{w/zkT}$, which is precisely the value assumed for η in Bethe's method.

To recapitulate, the two essential approximate assumptions of Bethe's method are (1) and the identification of η defined by (2) and (3) with $e^{w/zkT}$. These two assumptions are completely equivalent to the condition of quasi-chemical equilibrium.

4.19. Higher approximations

We have seen that the essential basis of the first approximation is the hypothesis of the non-interference of pairs. This hypothesis is

† Guggenheim (1944), *Proc. Roy. Soc. A* 183, 221.

most obviously false in the case of a close-packed lattice. For such a lattice there is an obvious method of obtaining a better approximation by considering triangular triplets of sites or tetrahedral quadruplets instead of pairs. The method of attack† is closely analogous to that of the first approximation, but the equations of quasi-chemical equilibrium for triangles and tetrahedra require the solution of cubic and quartic equations respectively.

4.20. System of triangles

We shall now construct an approximate combinatory formula for triplets of sites, forming equilateral triangles, analogous to that obtained in § 4.14 for pairs of sites. We begin by constructing the following table analogous to that in § 4.02.

<i>Kind of triplet</i>	<i>Number of triplets</i>	<i>Energy of all such triplets</i>
<i>AAA</i>	$\frac{1}{6}zN(1-x-2\zeta-\xi)$	$-N(1-x-2\zeta-\xi)\chi_A$
<i>AAB</i>	$\frac{1}{6}zN3\zeta$	$N\zeta(-2\chi_A-\chi_B+w)$
<i>ABB</i>	$\frac{1}{6}zN3\xi$	$N\xi(-\chi_A-2\chi_B+w)$
<i>BBB</i>	$\frac{1}{6}zN(x-\zeta-2\xi)$	$-N(x-\zeta-2\xi)\chi_B$
All	$\frac{1}{6}zN$	$-N(1-x)\chi_A-Nx\chi_B+N(\zeta+\xi)w$

As previously the number of *A* molecules is $N_A = N(1-x)$ and the number of *B* molecules is $N_B = Nx$. The number of nearest neighbours of each site is z . The total number of pairs of closest neighbours is $\frac{1}{2}zN$. Each such *AA* pair contributes $-2\chi_A/z$ to the energy; each *BB* pair contributes $-2\chi_B/z$; each *AB* pair contributes $(-\chi_A-\chi_B+w)/z$. In order that the energy of the imaginary system of triplets shall be a reasonable representation of the energy of the real system we must use the right total number of pairs. Since each triplet contains 3 pairs, the total number of triplets required to provide $\frac{1}{6}zN$ pairs is $\frac{1}{6}zN$. We have accordingly constructed the table for an imaginary system of $\frac{1}{6}zN$ triplets. This is less than the total number of distinguishable triplets in the real system by a factor 4 in a close-packed face-centred cubic lattice. The two parameters ζ and ξ are defined by the statement that the number of *AAB* and *ABB* triplets are $\frac{1}{6}zN3\zeta$ and $\frac{1}{6}zN3\xi$ respectively. The factors 3 are inserted for convenience to take account of the fact that a given triplet of sites can be occupied in three distinguishable ways by two *A* molecules and one *B* molecule or conversely. The numbers of *AAA* and *BBB* triplets are then obtained by counting the total number of pairs containing at least one *A* and at least one *B* respectively.

† Guggenheim and McGlashan (1951), Proc. Roy. Soc. A 206, 335.

If we could assume that the triplets did not interfere with one another, the number of configurations for given ζ, ξ would be

$$\frac{\{\frac{1}{3}zN\}!}{\{\frac{1}{3}zN(1-x-2\zeta-\xi)\}!\{\frac{1}{3}zN\zeta\}!\}^3\{\frac{1}{3}zN\xi\}!\}^3\{\frac{1}{3}zN(x-\zeta-2\xi)\}!. \quad (4.20.1)$$

It will be observed that in the denominator we have placed three factors $(\frac{1}{3}zN\zeta)!$ rather than one factor $(\frac{1}{3}zN^3\zeta)!$. This means that we are regarding the triplets as orientated so that the three manners of occupation AAB, ABA , and BAA are distinguishable. If we took the opposite view of ignoring orientations of triplets of sites we should have to introduce symmetry factors and the final result would be the same.

Formula (1), like (4.14.1), is of course inexact, firstly because the different triplets do in fact necessarily interfere with one another and secondly because (1) would not give when summed over all values of ζ, ξ the correct total number of configurations. We can remove the second defect by inserting a suitable normalizing factor independent of ζ, ξ . The manner of choosing this factor is precisely analogous to that used in § 4.14. We then obtain for $g(N, x, \zeta, \xi)$ the number of configurations of given N, x, ζ, ξ

$$g(N, x, \zeta, \xi) = \frac{N!}{\{N(1-x)\}!\{Nx\}!} \times \\ \times \frac{\{\frac{1}{3}zN(1-x-2\zeta^*-2\xi^*)\}!\{\frac{1}{3}zN\zeta^*\}!\}^3\{\frac{1}{3}zN\xi^*\}!\}^3\{\frac{1}{3}zN(x-\zeta^*-2\xi^*)\}!}{\{\frac{1}{3}zN(1-x-2\zeta-\xi)\}!\{\frac{1}{3}zN\zeta\}!\}^3\{\frac{1}{3}zN\xi\}!\}^3\{\frac{1}{3}zN(x-\zeta-2\xi)\}!, \quad (4.20.2)$$

where ζ^*, ξ^* are the values of ζ, ξ respectively which maximize (1). They are determined by the simultaneous equations

$$(1-x-2\zeta^*-2\xi^*)^2(x-\zeta^*-2\xi^*) = \zeta^{*3}, \quad (4.20.3)$$

$$(1-x-2\zeta^*-2\xi^*)(x-\zeta^*-2\xi^*)^2 = \xi^{*3}. \quad (4.20.4)$$

The solution of these equations is

$$\zeta^* = x(1-x)^2, \quad (4.20.5)$$

$$\xi^* = x^2(1-x). \quad (4.20.6)$$

These values of ζ^*, ξ^* correspond, as would be expected, to complete randomness.

The configurational energy for given N, x, ζ, ξ is given at the end of the above table. Consequently the configurational partition function Ω is given by

$$\Omega = \sum_{\zeta, \xi} g(N, x, \zeta, \xi) \exp[\{N(1-x)\chi_A + Nx\chi_B - N(\zeta+\xi)w\}/kT]. \quad (4.20.7)$$

As usual we may replace the double sum by its maximum term. If we denote the values of ζ , ξ in the maximum term by $\bar{\zeta}$, $\bar{\xi}$ respectively, we obtain

$$\Omega = g(N, x, \bar{\zeta}, \bar{\xi}) \exp[\{N(1-x)\chi_A + Nx\chi_B - N(\bar{\zeta} + \bar{\xi})w\}/kT], \quad (4.20.8)$$

where $\bar{\zeta}$, $\bar{\xi}$ are determined by

$$\frac{\partial \ln \Omega}{\partial \zeta} = 0 \quad (\zeta = \bar{\zeta}), \quad (4.20.9)$$

$$\frac{\partial \ln \Omega}{\partial \xi} = 0 \quad (\xi = \bar{\xi}). \quad (4.20.10)$$

Using formula (2) for $g(N, x, \zeta, \xi)$ equations (9) and (10) become

$$\frac{1}{6}zN\{2\ln(1-x-2\bar{\zeta}-\bar{\xi})-3\ln\bar{\zeta}+\ln(x-\bar{\zeta}-2\bar{\xi})\}-\frac{Nw}{kT}=0, \quad (4.20.11)$$

$$\frac{1}{6}zN\{\ln(1-x-2\bar{\zeta}-\bar{\xi})-3\ln\bar{\xi}+2\ln(x-\bar{\zeta}-2\bar{\xi})\}-\frac{Nw}{kT}=0. \quad (4.20.12)$$

These can be written as

$$(1-x-2\bar{\zeta}-\bar{\xi})^2(x-\bar{\zeta}-2\bar{\xi})=\bar{\xi}^3\eta^6, \quad (4.20.13)$$

$$(1-x-2\bar{\zeta}-\bar{\xi})(x-\bar{\zeta}-2\bar{\xi})^2=\bar{\zeta}^3\eta^6, \quad (4.20.14)$$

where η is used, as in § 4.09, to denote $e^{w/kT}$. If we compare equations (13) and (14) with the table at the beginning of this section, we recognize them as having the form of a quasi-chemical equilibrium. Equations (13) and (14) can be rearranged to give

$$\bar{\zeta}(x-\bar{\zeta}-2\bar{\xi})=\bar{\xi}^2\eta^2, \quad (4.20.15)$$

$$\bar{\xi}(1-x-2\bar{\zeta}-\bar{\xi})=\bar{\zeta}^2\eta^2, \quad (4.20.16)$$

which are also of quasi-chemical form.

The configurational free energy is given by

$$\begin{aligned} F_c &= -kT \ln \Omega \\ &= -kT \ln g(N, x, \bar{\zeta}, \bar{\xi}) - N(1-x)\chi_A - Nx\chi_B + N(\bar{\zeta} + \bar{\xi})w, \end{aligned} \quad (4.20.17)$$

with $g(N, x, \zeta, \xi)$ given by (2) and $\bar{\zeta}$, $\bar{\xi}$ determined by (15), (16). Instead of proceeding further with this formula for F_c , it is more convenient to obtain formulae for the chemical potentials μ_A , μ_B by first changing the variables from N , x to N_A , N_B and then differentiating with respect to N_A , N_B respectively. In performing these differentiations we must remember that $\bar{\zeta}$, $\bar{\xi}$ are functions of N_A , N_B , but since from the definitions of $\bar{\zeta}$, $\bar{\xi}$ they must satisfy $\partial F_c / \partial \zeta = 0$ and $\partial F_c / \partial \xi = 0$, it follows that all terms coming from differentiation with respect to $\bar{\zeta}$ and $\bar{\xi}$ in fact cancel. At the same time from the definitions of ζ^* , ξ^* one can

readily verify that $\partial \ln g / \partial \zeta^*$ and $\partial \ln g / \partial \xi^*$ both vanish so that terms coming from differentiation with respect to ζ^* , ξ^* also cancel. We may therefore omit all such terms and this greatly reduces the work. We then obtain immediately

$$\frac{\mu_A - \mu_A^0}{kT} = \ln(1-x) + \frac{1}{k} z \ln \frac{1-x-2\bar{\zeta}-\bar{\xi}}{1-x-2\zeta^*-2\xi^*}, \quad (4.20.18)$$

$$\frac{\mu_B - \mu_B^0}{kT} = \ln x + \frac{1}{k} z \ln \frac{x-\bar{\zeta}-2\bar{\xi}}{x-\zeta^*-2\xi^*}. \quad (4.20.19)$$

The absolute activities λ_A , λ_B , the partial pressures (strictly fugacities) p_A , p_B and the activity coefficients f_A , f_B are then given by

$$\frac{\lambda_A}{\lambda_A^0(1-x)} = \frac{p_A}{p_A^0(1-x)} = f_A = \left(\frac{1-x-2\bar{\zeta}-\bar{\xi}}{1-x-2\zeta^*-2\xi^*} \right)^{\frac{1}{k} z} = \left(\frac{1-x-2\bar{\zeta}-\bar{\xi}}{(1-x)^3} \right)^{\frac{1}{k} z}, \quad (4.20.20)$$

$$\frac{\lambda_B}{\lambda_B^0 x} = \frac{p_B}{p_B^0 x} = f_B = \left(\frac{x-\bar{\zeta}-2\bar{\xi}}{x-\zeta^*-2\xi^*} \right)^{\frac{1}{k} z} = \left(\frac{x-\bar{\zeta}-2\bar{\xi}}{x^3} \right)^{\frac{1}{k} z}, \quad (4.20.21)$$

where as usual the superscript 0 denotes the value for the pure substance.

The molar free energy of mixing $\Delta_m F$ is given by

$$\begin{aligned} \frac{\Delta_m F}{RT} &= \frac{(1-x)(\mu_A - \mu_A^0) + x(\mu_B - \mu_B^0)}{kT} \\ &= (1-x)\ln(1-x) + x\ln x + \\ &\quad + \frac{1}{k} z \left\{ (1-x)\ln \frac{1-x-2\bar{\zeta}-\bar{\xi}}{(1-x)^3} + x\ln \frac{x-\bar{\zeta}-2\bar{\xi}}{x^3} \right\}. \end{aligned} \quad (4.20.22)$$

The molar total energy of mixing and molar heat of mixing are given by

$$\Delta_m U = \Delta_m H = (\bar{\zeta} + \bar{\xi})Nw, \quad (4.20.23)$$

where N is Avogadro's number.

We have now obtained rather simple formulae for the most important thermodynamic quantities expressed in terms of $\bar{\zeta}$, $\bar{\xi}$ which are determined by the quasi-chemical equations (15), (16). Thus the whole problem is reduced to solving two simultaneous quadratic equations for $\bar{\zeta}$ and $\bar{\xi}$. For the purpose of studying these equations we shall drop the bars and write simply ζ , ξ instead of $\bar{\zeta}$, $\bar{\xi}$.

We introduce the new variable ρ defined by

$$\xi = \rho\zeta. \quad (4.20.24)$$

Substituting for ξ from (24) into (15) and (16) we obtain

$$x - \zeta - 2\rho\zeta = \rho^2 \eta^2 \zeta, \quad (4.20.25)$$

$$1 - x - 2\zeta - \rho\zeta = \rho^{-1} \eta^2 \zeta. \quad (4.20.26)$$

Solving (25) and (26) in turn for ζ we find

$$\zeta = \frac{x}{\rho^2 \eta^2 + 2\rho + 1} = \frac{\rho(1-x)}{\eta^2 + 2\rho + \rho^2}. \quad (4.20.27)$$

This is, for given values of η and x , a cubic equation in ρ which can be solved numerically. Substitution of the value of ρ back into (27) gives ζ and then ξ is given by (24). These values of ζ , ξ when substituted into the various equations of this section lead to values for the several thermodynamic properties of the mixture. Numerical results thus obtained will be quoted in § 4.22.

At temperatures below the critical, phases of compositions near $x = \frac{1}{2}$ will be unstable and split into two phases of different composition. The values of p_A (and of p_B) must be the same in the two coexisting phases. Owing to the free energy of mixing being symmetrical in x and $(1-x)$ the curves of p_A/p_A^0 and p_B/p_B^0 plotted against x are mirror images of each other in $x = \frac{1}{2}$. It follows that both the coexisting phases satisfy the relation

$$\frac{p_A}{p_A^0} = \frac{p_B}{p_B^0}. \quad (4.20.28)$$

Substituting (20) and (21) into (28) we have

$$\frac{x-\zeta-2\xi}{1-x-2\zeta-\xi} = \left(\frac{x}{1-x}\right)^{3(z-2)/z}. \quad (4.20.29)$$

If, on the other hand, we divide (15) by (16) we have

$$\frac{x-\zeta-2\xi}{1-x-2\zeta-\xi} = \frac{\xi^3}{\zeta^3} = \rho^3, \quad (4.20.30)$$

using (24). Comparing (29) and (30) we obtain

$$\rho = \left(\frac{x}{1-x}\right)^{(z-2)/z} = r^{(z-2)/z}, \quad (4.20.31)$$

where r denotes the molecular ratio $x/(1-x)$. We now solve (27) for η^2 obtaining

$$\eta^2 = \rho \frac{(2+\rho)x - (2\rho+1)(1-x)}{\rho^3(1-x)-x}, \quad (4.20.32)$$

and substituting for ρ from (31) we obtain

$$e^{2w/zkT} = \eta^2 = \frac{(1-2r)+(2-r)r^{(z-2)/z}}{r^{2/z}-r^{2(z-2)/z}}. \quad (4.20.33)$$

Formula (33) is an explicit relation between the temperature and the composition of either of the coexisting phases.

At the critical temperature T_c the two coexisting phases become

identical at $r = 1$. If we put $r = 1$ into (33) we obtain an indefinite form. We therefore put $r = 1 + \delta$, expand in powers of δ , and then make $\delta \rightarrow 0$. We thus obtain

$$e^{2w/zkT_0} = \eta_c^2 = \frac{z+1}{z-3}, \quad (4.20.34)$$

which may be compared with the first approximation (pairs) formula (4.12.12)

$$\eta_c = \frac{z}{z-2}. \quad (4.20.35)$$

4.21. System of tetrahedra

We now turn to a treatment in terms of quadruplets of sites, forming regular tetrahedra. As the treatment is closely analogous to that of triplets, described in the preceding section, we shall give only a brief outline. In order that the imaginary system of quadruplets shall contain in all the correct number $\frac{1}{2}zN$ of pairs, since each tetrahedral quadruplet contains 6 pairs of nearest neighbours, we consider a system of $\frac{1}{12}zN$ quadruplets. We begin by constructing the following table analogous to that for triplets in the preceding section.

Kind of quadruplet	Number of quadruplets	Energy of all such quadruplets
AAAA	$\frac{1}{12}zN(1-x-3\zeta-3v-\xi)$	$-N(1-x-3\zeta-3v-\xi)\chi_A$
AAAB	$\frac{1}{12}zN4\zeta$	$N\zeta(-3\chi_A-\chi_B+w)$
AABB	$\frac{1}{12}zN6v$	$Nv(-3\chi_A-3\chi_B+2w)$
ABBB	$\frac{1}{12}zN4\xi$	$N\xi(-\chi_A-3\chi_B+w)$
BBBB	$\frac{1}{12}zN(x-\zeta-3v-3\xi)$	$-N(x-\zeta-3v-3\xi)\chi_B$
All	$\frac{1}{12}zN$	$-N(1-x)\chi_A-Nx\chi_B+N(\zeta+2v+\xi)w$

As previously the number of A molecules is $N_A = N(1-x)$ and the number of B molecules is $N_B = Nx$. Each AA pair of closest neighbours contributes $-2\chi_A/z$ to the energy; each BB pair contributes $-2\chi_B/z$; each AB pair contributes $(-\chi_A-\chi_B+w)/z$. The three parameters ζ, v, ξ are defined by the statements that the number of $AAAB$ quadruplets is $\frac{1}{12}zN4\zeta$, the number of $AABB$ quadruplets $\frac{1}{12}zN6v$, and the number of $ABBB$ quadruplets $\frac{1}{12}zN4\xi$. The factors 4, 6, 4 are inserted for convenience to take account of the distinguishable orientations of the sets of 4 molecules on a given set of 4 sites. The numbers of $AAAA$ and $BBBB$ quadruplets are then obtained by counting.

By reasoning precisely analogous to that used for triplets we obtain

the approximate formula for $g(N, x, \zeta, v, \xi)$ the number of configurations of given N, x, ζ, v, ξ

$$g(N, x, \zeta, v, \xi) = \frac{N!}{\{N(1-x)\}! \{Nx\}!} \frac{\{\frac{1}{12}zN(1-x-3\zeta^*-3v^*-\xi^*)\}!}{\{\frac{1}{12}zN(1-x-3\zeta-3v-\xi)\}!} \times \\ \times \frac{\{\frac{1}{12}zN(\zeta^*)\}^4 \{\frac{1}{12}zN(v^*)\}^6 \{\frac{1}{12}zN(\xi^*)\}^4 \{\frac{1}{12}zN(x-\zeta^*-3v^*-3\xi^*)\}!}{\{\frac{1}{12}zN(\zeta)\}^4 \{\frac{1}{12}zN(v)\}^6 \{\frac{1}{12}zN(\xi)\}^4 \{\frac{1}{12}zN(x-\zeta-3v-3\xi)\}!}, \quad (4.21.1)$$

where ζ^*, v^*, ξ^* are the values of ζ, v, ξ corresponding to complete randomness. They are given by

$$\zeta^* = x(1-x)^8, \quad (4.21.2)$$

$$v^* = x^2(1-x)^2, \quad (4.21.3)$$

$$\xi^* = x^3(1-x), \quad (4.21.4)$$

respectively.

The configurational energy for given N, x, ζ, v, ξ is given at the end of the above table. Consequently the configurational partition function Ω is given by

$$\Omega = \sum_{\zeta, v, \xi} g(N, x, \zeta, v, \xi) \times \exp[\{N(1-x)\chi_A + Nx\chi_B - N(\zeta + 2v + \xi)w\}/kT]. \quad (4.21.5)$$

As usual we may replace the triple sum by its largest term, so that

$$\Omega = g(N, x, \zeta, v, \xi) \exp[\{N(1-x)\chi_A + Nx\chi_B - N(\zeta + 2v + \xi)w\}/kT], \quad (4.21.6)$$

where now and henceforth ζ, v, ξ denote the values $\bar{\zeta}, \bar{v}, \bar{\xi}$ determined by the conditions of quasi-chemical equilibrium. When we use the abbreviation η for $e^{w/kT}$ these become

$$(1-x-3\zeta-3v-\xi)^3(x-\zeta-3v-3\xi) = \zeta^4\eta^{12}, \quad (4.21.7)$$

$$(1-x-3\zeta-3v-\xi)^3(x-\zeta-3v-3\xi)^3 = v^6\eta^{24}, \quad (4.21.8)$$

$$(1-x-3\zeta-3v-\xi)(x-\zeta-3v-3\xi)^3 = \xi^4\eta^{12}. \quad (4.21.9)$$

These three equations can be rearranged to give

$$v(1-x-3\zeta-3v-\xi) = \zeta^2\eta^2, \quad (4.21.10)$$

$$v(x-\zeta-3v-3\xi) = \xi^2\eta^2, \quad (4.21.11)$$

$$\zeta\xi = v^2\eta^2. \quad (4.21.12)$$

These simultaneous equations for ζ, v, ξ have to be solved numerically when x, η are given.

The configurational free energy is given by

$$\begin{aligned} F_c &= -kT \ln \Omega \\ &= -kT \ln g(N, x, \zeta, v, \xi) - N(1-x)\chi_A - Nx\chi_B + N(\zeta + 2v + \xi)w, \end{aligned} \quad (4.21.13)$$

with ζ, v, ξ determined by the quasi-chemical equations (10), (11), (12).

Changing the variables from N, x to N_A, N_B and differentiating with respect to N_A, N_B we obtain formulae for the chemical potentials μ_A, μ_B . By the same kind of reasoning as in §§ 4.16, 4.20 one can readily verify that in performing these differentiations all terms coming from differentiations with respect to $\zeta, v, \xi, \zeta^*, v^*, \xi^*$ must cancel. Taking advantage of this we obtain immediately

$$\begin{aligned} \frac{\mu_A - \mu_A^0}{kT} &= \ln(1-x) + \frac{1}{12}z \ln \frac{1-x-3\zeta-3v-\xi}{1-x-3\zeta^*-3v^*-\xi^*} \\ &= \ln(1-x) + \frac{1}{12}z \ln \frac{1-x-3\zeta-3v-\xi}{(1-x)^4}, \end{aligned} \quad (4.21.14)$$

$$\begin{aligned} \frac{\mu_B - \mu_B^0}{kT} &= \ln x + \frac{1}{12}z \ln \frac{x-\zeta-3v-3\xi}{x-\zeta^*-3v^*-3\xi^*} \\ &= \ln x + \frac{1}{12}z \ln \frac{x-\zeta-3v-3\xi}{x^4}. \end{aligned} \quad (4.21.15)$$

The absolute activities, partial pressures (strictly fugacities), and the activity coefficients are given by

$$\frac{\lambda_A}{\lambda_A^0(1-x)} = \frac{p_A}{p_A^0(1-x)} = f_A = \left(\frac{1-x-3\zeta-3v-\xi}{(1-x)^4} \right)^{\frac{1}{12}z}, \quad (4.21.16)$$

$$\frac{\lambda_B}{\lambda_B^0 x} = \frac{p_B}{p_B^0 x} = f_B = \left(\frac{x-\zeta-3v-3\xi}{x^4} \right)^{\frac{1}{12}z}, \quad (4.21.17)$$

where as usual the superscript 0 denotes the value for the pure substance.

The molar total energy of mixing is given by

$$\Delta_m U = (\zeta + 2v + \xi)Nw, \quad (4.21.18)$$

where N is Avogadro's number.

To solve the quasi-chemical equations we introduce a new variable κ defined by

$$\xi = \kappa \eta v, \quad (4.21.19)$$

so that, owing to (12),

$$\zeta = \kappa^{-1} \eta v. \quad (4.21.20)$$

Substituting (19) and (20) into (10) and (11) we have

$$1-x-3\kappa^{-1}\eta v-3v-\kappa\eta v=\kappa^{-2}\eta^4 v, \quad (4.21.21)$$

$$x-\kappa^{-1}\eta v-3v-3\kappa\eta v=\kappa^2\eta^4 v. \quad (4.21.22)$$

Solving (22) and (21) in turn for v we obtain

$$v = \frac{x}{\kappa^2\eta^4 + 3\kappa\eta + \kappa^{-1}\eta + 3} = \frac{1-x}{\kappa^{-2}\eta^4 + 3\kappa^{-1}\eta + \kappa\eta + 3}. \quad (4.21.23)$$

This is, for given η and x , a quartic equation in κ which can be solved numerically. Substitution of the value of κ back into (23) gives v and then ξ , ζ are given by (19), (20) respectively. These values of ζ , v , ξ when substituted into the various equations of this section lead to values for the several thermodynamic properties of the mixture. Numerical results thus obtained will be quoted in § 4.22.

Below the critical temperature the two coexisting phases must satisfy the relation

$$\frac{p_A}{p_A^0} = \frac{p_B}{p_B^0}. \quad (4.21.24)$$

Substituting (16) and (17) into (24) we have

$$\frac{x-\zeta-3v-3\xi}{1-x-3\zeta-3v-\xi} = \left(\frac{x}{1-x}\right)^{4(z-3)/z} = r^{4(z-3)/z}, \quad (4.21.25)$$

where r denotes the molecular ratio $x/(1-x)$. Dividing (11) by (10) on the other hand we find

$$\frac{x-\zeta-3v-3\xi}{1-x-3\zeta-3v-\xi} = \frac{\xi^2}{\zeta^2} = \kappa^4, \quad (4.21.26)$$

using (19) and (20). Comparing (25) with (26) we have

$$\kappa = r^{(z-3)/z}. \quad (4.21.27)$$

We now arrange equation (23) in powers of η , obtaining

$$(\kappa^2 - r\kappa^{-2})\eta^4 + \{(3\kappa + \kappa^{-1}) - r(3\kappa^{-1} + \kappa)\}\eta + 3(1-r) = 0, \quad (4.21.28)$$

and, when we substitute for κ from (27),

$$(r^{(2z-6)/z} - r^{(-z+3)/z})\eta^4 + \{3(r^{(z-3)/z} - r^{3/z}) + (r^{-(z+3)/z} - r^{(2z-3)/z})\}\eta + 3(1-r) = 0. \quad (4.21.29)$$

Formula (29) is a quartic equation for η which can be solved for a given value of r .

To obtain the value η_c of η at the critical temperature we put $r = 1 + \delta$ in (29) expand in powers of δ and then make $\delta \rightarrow 0$. We obtain

$$\left(3 - \frac{12}{z}\right)\eta_c^4 - \frac{12}{z}\eta_c - 3 = 0. \quad (4.21.30)$$

The left side of (30) has a factor $\eta_c + 1$ which we may remove, since η_c is essentially positive. We then obtain the cubic equation

$$\eta_c^3 - \eta_c^2 + \eta_c = \frac{z}{z-4}. \quad (4.21.31)$$

When we put $z = 12$ for a close-packed lattice equation (31) becomes

$$\eta_c^3 - \eta_c^2 + \eta_c - \frac{3}{2} = 0, \quad (4.21.32)$$

having the solution $\eta_c = 1.204$.

4.22. Comparison of several approximations

We shall now compare some of the quantitative results obtained according to the several approximations. The zeroth approximation corresponds formally to $z \rightarrow \infty$. In the other approximations we shall put $z = 12$, the value for closest packing.

We begin by comparing the critical values η_c and w/kT_c . These are summarized in Table 4.1.

TABLE 4.1

*Values of Critical Temperature according to Several Approximations
for Close-packed Lattice*

Approximation	η_c	w/kT_c
Zeroth ($z \rightarrow \infty$)	—	2
First (pairs)	1.2 exactly	2.1878
Triplets	1.20185	2.2063
Quadruplets	1.20409	2.2288

The remaining comparisons involve the evaluation of the parameters such as X , ζ , ξ , v whose values have then to be substituted into the formulae for the various thermodynamic quantities. We first compare values of the molar free energy of mixing $\Delta_m F$, the molar energy of mixing $\Delta_m U$, and the molar entropy of mixing $\Delta_m S$ all at the critical temperature. The comparison is shown in Tables 4.2, 4.3, and 4.4.

Table 4.5 shows a comparison of the partial vapour pressure (strictly fugacity) of the component B at the critical temperature. There is no need to give a separate comparison for the component A since from symmetry the value of p_A/p_A^0 at x is equal to that of p_B/p_B^0 at $1-x$. The activity coefficient f_B is in each case obtained by dividing p_B/p_B^0 by x .

Table 4.6 shows a similar comparison at a temperature $T = \frac{3}{2}T_c$ and Table 4.7 for the stable region of concentrations at a temperature $0.9T_c$. Table 4.8 shows the relation between the composition of the two co-existing phases and the temperature according to the several approximations.

TABLE 4.2

Values of $-\Delta_m F/RT$ at Critical Temperature according to Several Approximations for Close-packed Lattice

<i>x</i>	<i>Zeroth</i>	<i>First (pairs)</i>	<i>Triplets</i>	<i>Quadruplets</i>
0.1	0.1451	0.1317	0.1303	0.1279
0.2	0.1804	0.1610	0.1587	0.1557
0.3	0.1909	0.1693	0.1667	0.1635
0.4	0.1930	0.1710	0.1683	0.1651
0.5	0.1931	0.1711	0.1684	0.1652
0.6	0.1930	0.1710	0.1683	0.1651
0.7	0.1909	0.1693	0.1667	0.1635
0.8	0.1804	0.1610	0.1587	0.1557
0.9	0.1451	0.1317	0.1303	0.1279

TABLE 4.3

Values of $\Delta_m U/RT$ at Critical Temperature according to Several Approximations for Close-packed Lattice

<i>x</i>	<i>Zeroth</i>	<i>First (pairs)</i>	<i>Triplets</i>	<i>Quadruplets</i>
0.1	0.1800	0.1897	0.1909	0.1923
0.2	0.3200	0.3284	0.3294	0.3306
0.3	0.4200	0.4234	0.4236	0.4238
0.4	0.4800	0.4789	0.4784	0.4777
0.5	0.5000	0.4972	0.4964	0.4953
0.6	0.4800	0.4789	0.4784	0.4777
0.7	0.4200	0.4234	0.4236	0.4238
0.8	0.3200	0.3284	0.3294	0.3306
0.9	0.1800	0.1897	0.1909	0.1923

TABLE 4.4

Values of $\Delta_m S/R$ at Critical Temperature according to Several Approximations for Close-packed Lattice

<i>x</i>	<i>Zeroth</i>	<i>First (pairs)</i>	<i>Triplets</i>	<i>Quadruplets</i>
0.1	0.3251	0.3214	0.3212	0.3202
0.2	0.5004	0.4894	0.4881	0.4863
0.3	0.6109	0.5927	0.5903	0.5873
0.4	0.6730	0.6499	0.6467	0.6428
0.5	0.6931	0.6683	0.6648	0.6605
0.6	0.6730	0.6499	0.6467	0.6428
0.7	0.6109	0.5927	0.5903	0.5873
0.8	0.5004	0.4894	0.4881	0.4863
0.9	0.3251	0.3214	0.3212	0.3202

TABLE 4.5

Values of p_B/p_B^0 at Critical Temperature according to Several Approximations for Close-packed Lattice

x	Zeroth	First (pairs)	Triplets	Quadruplets
0.1	0.5053	0.5552	0.5612	0.5720
0.2	0.7193	0.7549	0.7596	0.7661
0.3	0.7993	0.8227	0.8257	0.8294
0.4	0.8218	0.8408	0.8430	0.8458
0.5	0.8244	0.8427	0.8450	0.8477
0.6	0.8263	0.8444	0.8464	0.8491
0.7	0.8381	0.8535	0.8555	0.8577
0.8	0.8666	0.8774	0.8784	0.8798
0.9	0.9182	0.9224	0.9228	0.9231

TABLE 4.6

Values of p_B/p_B^0 at Temperature $T = \frac{3}{2}T_c$ according to Several Approximations for Close-packed Lattice

x	Zeroth	First (pairs)	Triplets	Quadruplets
0.1	0.2945	0.3178	0.3208	0.3250
0.2	0.4695	0.4926	0.4957	0.4995
0.3	0.5766	0.5960	0.5985	0.6017
0.4	0.6464	0.6628	0.6649	0.6675
0.5	0.6978	0.7121	0.7138	0.7160
0.6	0.7427	0.7548	0.7563	0.7581
0.7	0.7893	0.7991	0.7999	0.8011
0.8	0.8438	0.8498	0.8505	0.8512
0.9	0.9121	0.9143	0.9144	0.9146

TABLE 4.7

Values of p_B/p_B^0 at Temperature $T = 0.9T_c$ according to Several Approximations for Close-packed Lattice

x	Zeroth	First (pairs)	Triplets	Quadruplets
0.1	0.6050	0.6667	0.6750	0.6850
0.2	0.8293	0.8672	0.8722	0.8784
0.8	0.8744	0.8868	0.8882	0.8899
0.9	0.9202	0.9251	0.9255	0.9260
	0.237	0.218	0.215	0.212

Values of x , or $1-x$, in coexisting phases at $T = 0.9T_c$

TABLE 4.8

Values of T'/T_c at which Compositions x and $1-x$ of Two Coexisting Phases have Specified Values, according to Several Approximations for Close-packed Lattice

x or $1-x$	Zeroth	Quasi-chemical		
		Pairs	Triplets	Quadruplets
0.5	1	1	1	1
0.4	0.9865	0.9887	0.9890	0.9894
0.3	0.9442	0.9527	0.9540	0.9555
0.2	0.8656	0.8844	0.8871	0.8904
0.1	0.7282	0.7598	0.7640	0.7691
0.05	0.6113	0.6484	0.6529	0.6585
0.02	0.4933	0.5307	0.5350	0.5403
0.01	0.4265	0.4619	0.4657	0.4704

4.23. Expansions as power series in w/zkT

It was pointed out by Kirkwood† that it is in principle possible to evaluate $\ln \Omega$ to any desired degree of accuracy as a power series in w/zkT . We rewrite formula (4.04.1) as

$$\ln \Omega - \frac{N_A \chi_A + N_B \chi_B}{kT} = \ln \sum e^{-W/kT}, \quad (4.23.1)$$

where $W = Xw$ is the excess potential energy of a particular configuration over that of the unmixed pure components. We now denote the total number of distinguishable configurations, regardless of energy values, by $g(N_A, N_B)$, so that

$$g(N_A, N_B) = \frac{N!}{N_A! N_B!}. \quad (4.23.2)$$

Subtracting $\ln g$ from both sides of (1) we have

$$\ln \Omega - \ln g - \frac{N_A \chi_A + N_B \chi_B}{kT} = \ln \left\{ \frac{1}{g} \sum e^{-W/kT} \right\}. \quad (4.23.3)$$

If we now introduce an auxiliary quantity h defined by

$$h = 1 - \frac{1}{g} \sum e^{-W/kT}, \quad (4.23.4)$$

we can rewrite (3) as

$$\ln \Omega - \ln g - \frac{N_A \chi_A + N_B \chi_B}{kT} = \ln(1-h) = -h - \frac{1}{2}h^2 - \frac{1}{3}h^3 - \frac{1}{4}h^4 - \dots \quad (4.23.5)$$

† Kirkwood (1938), *J. Chem. Phys.* 6, 70.

If we expand the exponential in (4) in powers of W/kT we obtain

$$h = \frac{W_{Av}}{kT} - \frac{(W^2)_{Av}}{\Sigma!(kT)^2} + \frac{(W^3)_{Av}}{3!(kT)^3} - \dots \quad (4.23.6)$$

where W_{Av} denotes the unweighted average over all configurations, so that

$$W_{Av} = Nz(1-x)w, \quad (4.23.7)$$

and similarly $(W^i)_{Av}$ denotes the unweighted average of W^i over all configurations. If we now substitute (6) into (5) and collect powers of kT we obtain another power series in $1/kT$, namely

$$\begin{aligned} \ln \Omega - \ln g - \frac{N_A \chi_A + N_B \chi_B}{kT} &= -\frac{W_{Av}}{kT} - \frac{(W_{Av})^2 - (W^2)_{Av}}{2!(kT)^2} - \\ &\quad - \frac{(W^3)_{Av} - 3(W^2)_{Av} W_{Av} + 2(W_{Av})^3}{3!(kT)^3} - \dots, \quad (4.23.8) \end{aligned}$$

where the higher terms can be written down immediately if required. Since $W = Xw$ it follows that $(W^2)_{Av}$ and $(W_{Av})^2$ are each of the order N^2w^2 , but it turns out that their difference is of order only Nw^3 . Owing to similar cancellations of leading terms one finds that all the numerators in (8) are of first order in N . It is accordingly convenient to rewrite (8) as

$$\begin{aligned} \ln \Omega - \ln g - \frac{N_A \chi_A + N_B \chi_B}{kT} &= -Nx(1-x) \frac{w}{kT} + \\ &\quad + \frac{1}{2} N^2 \left\{ \frac{l_2}{2!} \left(\frac{2w}{zkT} \right)^2 + \frac{l_3}{3!} \left(\frac{2w}{zkT} \right)^3 + \frac{l_4}{4!} \left(\frac{2w}{zkT} \right)^4 + \dots \right\}, \quad (4.23.9) \end{aligned}$$

where l_2, l_3 are defined by

$$\frac{2}{z} N l_2 = (W^2)_{Av} - (W_{Av})^2, \quad (4.23.10)$$

$$\left(\frac{2}{z} \right)^2 N l_3 = -(W^3)_{Av} + 3(W^2)_{Av} W_{Av} - 2(W_{Av})^3. \quad (4.23.11)$$

Similar definitions of l_4, l_5, \dots can be written down immediately. Thus defined all l 's are of order zero in N .

Substituting the value of g from (2) into (9) we obtain for the configurational free energy F_c

$$\begin{aligned} \frac{F_c}{kT} &= -\frac{N_A \chi_A + N_B \chi_B}{kT} + N\{(1-x)\ln(1-x) + x \ln x\} + Nx(1-x) \frac{w}{kT} - \\ &\quad - \frac{1}{2} z N \left\{ \frac{l_2}{2!} \left(\frac{2w}{zkT} \right)^2 + \frac{l_3}{3!} \left(\frac{2w}{zkT} \right)^3 + \frac{l_4}{4!} \left(\frac{2w}{zkT} \right)^4 + \dots \right\}. \quad (4.23.12) \end{aligned}$$

Consequently the molar free energy of mixing is given by

$$\frac{\Delta_m F}{RT} = (1-x)\ln(1-x) + x \ln x + x(1-x) \frac{w}{kT} - \\ - \frac{1}{2}z \left\{ \frac{l_2}{2!} \left(\frac{2w}{zkT} \right)^2 + \frac{l_3}{3!} \left(\frac{2w}{zkT} \right)^3 + \frac{l_4}{4!} \left(\frac{2w}{zkT} \right)^4 + \dots \right\}. \quad (4.23.13)$$

The evaluation of the series of coefficients l_2, l_3, \dots is in principle a straightforward counting operation which is, however, increasingly tedious and complicated as the series is ascended. Kirkwood† evaluated l_2 and l_3 finding

$$l_2 = x^2(1-x)^2, \quad (4.23.14)$$

$$l_3 = x^2(1-x)^2(1-2x)^2. \quad (4.23.15)$$

Bethe and Kirkwood‡ evaluated l_4 finding

$$l_4 = x^2(1-x)^2(1-6x+6x^2)^2 + 6 \left(\frac{y}{z} - 1 \right) x^4(1-x)^4, \quad (4.23.16)$$

where for the first time we meet a new parameter y depending on the lattice. Let us denote alternate sites of the lattice by a and b and denote by $z_{aa'}$ the number of b sites which are first neighbours common to the sites a and a' both on the a lattice. If we now form the sum $\sum_{a'} z_{aa'}^2$ over all positions of a' for given a , then y is defined by

$$y = \sum_a z_{aa'}^2 - z(z-1). \quad (4.23.17)$$

In a simple cubic lattice we have $z = 6$ and

$$\sum_{a'} z_{aa'}^2 = (12 \times 2^2) + (6 \times 1^2) = 54,$$

so that $y = 54 - 30 = 24$ and $y/z = 4$. In a body-centred cubic lattice we have $z = 8$ and

$$\sum_{a'} z_{aa'}^2 = (6 \times 4^2) + (12 \times 2^2) + (8 \times 1^2) = 152,$$

so that $y = 152 - 56 = 96$ and $y/z = 12$.

Chang§ evaluated l_5 finding

$$l_5 = x^2(1-x)^2(1-2x)^2(1-12x+12x^2)^2 + 60 \left(\frac{y}{z} - 1 \right) x^4(1-x)^4(1-2x)^2. \quad (4.23.18)$$

Chang also evaluated l_6 obtaining a formula involving as well as z, y two new parameters γ_1, γ_2 depending on the lattice.

† Kirkwood (1938), *J. Chem. Phys.* **6**, 70; (1939), *J. Phys. Chem.* **43**, 97.

‡ Bethe and Kirkwood (1939), *J. Chem. Phys.* **7**, 578.

§ Chang (1941), *J. Chem. Phys.* **9**, 169.

When $x = \frac{1}{2}$ the odd l 's vanish. For this value of x Wakefield† has evaluated the even l 's up to l_{12} for a simple cubic lattice. He finds

$$\begin{aligned} \frac{\Delta_m F}{RT} = & -\ln 2 + \frac{1}{4} \frac{w}{kT} - \frac{3}{8} \left(\frac{w}{6kT} \right)^2 - \frac{11}{64} \left(\frac{w}{6kT} \right)^4 - \frac{271}{960} \left(\frac{w}{6kT} \right)^6 - \\ & - \frac{123547}{215040} \left(\frac{w}{6kT} \right)^8 - \frac{7350121}{4838400} \left(\frac{w}{6kT} \right)^{10} - \frac{5671422011}{1277337600} \left(\frac{w}{6kT} \right)^{12} - \dots \\ & (x = \frac{1}{2}, z = 6). \quad (4.23.19) \end{aligned}$$

From (13) we deduce for the molar total energy of mixing

$$\frac{\Delta_m U}{RT} = x(1-x) \frac{w}{kT} - \frac{1}{2} z \left\{ l_2 \left(\frac{2w}{zkT} \right)^2 + \frac{l_3}{2!} \left(\frac{2w}{zkT} \right)^3 + \frac{l_4}{3!} \left(\frac{2w}{zkT} \right)^4 + \dots \right\}. \quad (4.23.20)$$

4.24. Power series from quasi-chemical approximation

It is of interest to compare the formulae of the quasi-chemical approximation with the accurate formulae of the previous section. This we can do by expanding the quasi-chemical formulae in powers of w/zkT . We begin by rewriting formula (4.10.3) as

$$\beta = (1+q\phi)^{\frac{1}{2}}, \quad (4.24.1)$$

where

$$q = 4x(1-x) \leq 1, \quad (4.24.2)$$

$$\phi = \eta^2 - 1 = e^{2w/zkT} - 1. \quad (4.24.3)$$

We assume that $q\phi < 1$, which is true for all values of q if

$$2w/zkT < \ln 2.$$

At the critical temperature $w/kT \simeq 2$, so that if $z = 6$ we have

$$2w/zkT \simeq \frac{2}{3}$$

which is just less than $\ln 2$. Hence the condition $q\phi < 1$ is satisfied above the critical temperature. It may well also be satisfied at temperatures below the critical for stable phases since for these q is usually appreciably less than 1.

Using the binomial theorem twice we can expand $2/(\beta+1)$ in powers of $q\phi$ and substitute the result in (4.10.4). We thus obtain eventually

$$\begin{aligned} \Delta_m U = & x(1-x)Nw \left\{ 1 - \frac{1}{2} \left(\frac{q\phi}{2} \right) + \frac{1}{2} \left(\frac{q\phi}{2} \right)^2 - \frac{5}{8} \left(\frac{q\phi}{2} \right)^3 + \frac{7}{8} \left(\frac{q\phi}{2} \right)^4 - \right. \\ & \left. - \frac{21}{16} \left(\frac{q\phi}{2} \right)^5 + \frac{33}{16} \left(\frac{q\phi}{2} \right)^6 - \dots \right\}, \quad (4.24.4) \end{aligned}$$

† Wakefield (1951), *Proc. Camb. Phil. Soc.* **47**, 419.

To obtain the free energy of mixing we use the relation

$$\Delta_m F = T \int_{1/T}^0 \Delta_m U d\left(\frac{1}{T}\right), \quad (4.24.5)$$

with adjustment of the integration constant to give the correct behaviour at high temperatures. Using the definition (3) of ϕ in (4) and substituting into (5) we obtain eventually, using as an abbreviation α defined by

$$\alpha = \frac{2w}{zkT}, \quad (4.24.6)$$

$$\begin{aligned} \frac{\Delta_m F}{RT} = & (1-x)\ln(1-x) + x \ln x + x(1-x) \frac{w}{kT} \times \\ & \times \left[1 - \frac{1}{2} \left(\frac{q}{2} \right) \left\{ \frac{1}{\alpha} (e^\alpha - 1) - 1 \right\} + \frac{1}{2} \left(\frac{q}{2} \right)^2 \left\{ \frac{1}{2\alpha} (e^{2\alpha} - 1) - \frac{2}{\alpha} (e^\alpha - 1) + 1 \right\} - \right. \\ & - \frac{5}{8} \left(\frac{q}{2} \right)^3 \left\{ \frac{1}{3\alpha} (e^{3\alpha} - 1) - \frac{3}{2\alpha} (e^{2\alpha} - 1) + \frac{3}{\alpha} (e^\alpha - 1) - 1 \right\} + \\ & + \frac{7}{8} \left(\frac{q}{2} \right)^4 \left\{ \frac{1}{4\alpha} (e^{4\alpha} - 1) - \frac{4}{3\alpha} (e^{3\alpha} - 1) + \frac{6}{2\alpha} (e^{2\alpha} - 1) - \frac{4}{\alpha} (e^\alpha - 1) + 1 \right\} - \\ & - \frac{21}{16} \left(\frac{q}{2} \right)^5 \left\{ \frac{1}{5\alpha} (e^{5\alpha} - 1) - \frac{5}{4\alpha} (e^{4\alpha} - 1) + \right. \\ & \quad \left. + \frac{10}{3\alpha} (e^{3\alpha} - 1) - \frac{10}{2\alpha} (e^{2\alpha} - 1) + \frac{5}{\alpha} (e^\alpha - 1) - 1 \right\} + \\ & + \frac{33}{16} \left(\frac{q}{2} \right)^6 \left\{ \frac{1}{6\alpha} (e^{6\alpha} - 1) - \frac{6}{5\alpha} (e^{5\alpha} - 1) + \frac{15}{4\alpha} (e^{4\alpha} - 1) - \frac{20}{3\alpha} (e^{3\alpha} - 1) + \right. \\ & \quad \left. + \frac{15}{2\alpha} (e^{2\alpha} - 1) - \frac{6}{\alpha} (e^\alpha - 1) + 1 \right\} - \dots \Big]. \quad (4.24.7) \end{aligned}$$

When we expand the exponentials in (7) and retain powers of α up to α^6 we obtain eventually

$$\begin{aligned} \frac{\Delta_m F}{RT} = & (1-x)\ln(1-x) + x \ln x + \\ & + x(1-x) \frac{w}{kT} \left[1 - \frac{1}{2} \frac{q}{2\alpha} \left\{ \frac{\alpha^2}{2!} + \frac{\alpha^3}{3!} + \frac{\alpha^4}{4!} + \frac{\alpha^5}{5!} + \frac{\alpha^6}{6!} \right\} + \right. \\ & + \frac{1}{2\alpha} \left(\frac{q}{2} \right)^2 \left\{ \frac{2\alpha^3}{3!} + \frac{6\alpha^4}{4!} + \frac{14\alpha^5}{5!} + \frac{30\alpha^6}{6!} \right\} - \\ & - \frac{5}{8\alpha} \left(\frac{q}{2} \right)^3 \left\{ \frac{6\alpha^4}{4!} + \frac{36\alpha^5}{5!} + \frac{150\alpha^6}{6!} \right\} + \\ & \quad \left. + \frac{7}{8\alpha} \left(\frac{q}{2} \right)^4 \left\{ \frac{24\alpha^5}{5!} + \frac{240\alpha^6}{6!} \right\} - \frac{21}{16\alpha} \left(\frac{q}{2} \right)^5 \frac{120\alpha^6}{6!} \right]. \quad (4.24.8) \end{aligned}$$

Before passing on, we may remark that at temperatures below that of critical mixing, where α is near to 1, formula (7) may be more useful than (8). The convergence of the power series in α may then be rather slow, but the convergence of the power series in q will still be rapid because q will be small in both stable phases except in the immediate neighbourhood of the critical temperature.

When we collect powers of α and write $2w/zkT$ for α we obtain

$$\begin{aligned} \frac{\Delta_m F}{RT} = & (1-x)\ln(1-x) + x\ln x + x(1-x)\frac{w}{kT} - \\ & - \frac{1}{2}z\left\{ \frac{1}{16} \frac{q^2}{2!} \left(\frac{2w}{zkT}\right)^2 + \frac{1}{16} \frac{q^2(1-q)}{3!} \left(\frac{2w}{zkT}\right)^3 + \frac{1}{16} \frac{q^2(1-3q+\frac{15}{8}q^2)}{4!} \left(\frac{2w}{zkT}\right)^4 + \right. \\ & + \frac{1}{16} \frac{q^2(1-7q+\frac{45}{4}q^2-\frac{21}{4}q^3)}{5!} \left(\frac{2w}{zkT}\right)^5 + \\ & \left. + \frac{1}{16} \frac{q^2(1-15q+\frac{375}{8}q^2-\frac{105}{2}q^3+\frac{915}{16}q^4)}{6!} \left(\frac{2w}{zkT}\right)^6 \right\}. \quad (4.24.9) \end{aligned}$$

When we substitute for q its value given by (2) we obtain

$$\begin{aligned} \frac{\Delta_m F}{RT} = & (1-x)\ln(1-x) + x\ln x + x(1-x)\frac{w}{kT} - \\ & - \frac{1}{2}z\left\{ \frac{x^2(1-x)^2}{2!} \left(\frac{2w}{zkT}\right)^2 + \frac{x^2(1-x)^2(1-2x)^2}{3!} \left(\frac{2w}{zkT}\right)^3 + \right. \\ & + \frac{x^2(1-x)^2}{4!} (1-12x+42x^2-60x^3+30x^4) \left(\frac{2w}{zkT}\right)^4 + \\ & + \frac{x^2(1-x)^2(1-2x)^2}{5!} (1-24x+108x^2-168x^3+84x^4) \left(\frac{2w}{zkT}\right)^5 + \\ & + \frac{x^2(1-x)^2}{6!} (1-60x+810x^2-4860x^3+15870x^4-30249x^5+ \\ & \left. + 33600x^6-20160x^7+5040x^8) \left(\frac{2w}{zkT}\right)^6 + \dots \right\}. \quad (4.24.10) \end{aligned}$$

When formula (10) is compared with the accurate formula (4.23.13), with Kirkwood's and Chang's values for the l 's, it is found that there is agreement as far as the terms in $(2w/zkT)^3$ but not in the higher terms. It is also found that the next two terms in (10) can be obtained from Chang's accurate formula by putting $y = 0$. Chang† has moreover

† Chang (1941), *J. Chem. Phys.* 9, 169.

shown that the quasi-chemical approximation is equivalent to setting such quantities as y , γ_1 , γ_2 equal to zero.

We conclude from this that the usefulness of the quasi-chemical approximation depends on the rapidity of convergence of the power series in $2w/zkT$. We have already seen that smallness of q produces rapid convergence. We shall accordingly investigate the worst case of $q = 1$ corresponding to $x = \frac{1}{2}$. We accordingly set $q = 1$ in (9), obtaining

$$\frac{\Delta_m F}{RT} = -\ln 2 + \frac{1}{4} \frac{w}{kT} - \frac{1}{2} z \left\{ \frac{1}{8} \left(\frac{w}{zkT} \right)^2 - \frac{1}{192} \left(\frac{w}{zkT} \right)^4 + \dots \right\} \quad (x = \frac{1}{2}). \quad (4.24.11)$$

For a simple cubic lattice with $z = 6$ this becomes

$$\frac{\Delta_m F}{RT} = -\ln 2 + \frac{1}{4} \frac{w}{kT} - \frac{3}{8} \left(\frac{w}{6kT} \right)^2 + \frac{1}{64} \left(\frac{w}{6kT} \right)^4 - \dots \quad (x = \frac{1}{2}, z = 6). \quad (4.24.12)$$

Comparing (12) with the accurate expansion (4.23.19) we find a difference

$$\frac{12}{64} \left(\frac{w}{6kT} \right)^4.$$

If we set $w/kT = 2$, corresponding roughly to the critical temperature, this difference is less than $1/400$. We conclude that the quasi-chemical formulae should give a useful approximation for the free energy at temperatures above that of critical mixing.

4.25. Temperature of critical mixing

It is of some interest to compare the formulae giving the temperature of critical mixing according to several approximations. This temperature T_c is according to (4.08.11) determined by

$$\frac{\partial^2 \Delta_m F}{\partial x^2} = 0 \quad (x = \frac{1}{2}). \quad (4.25.1)$$

Differentiating the l 's, given by formulae (4.23.14) to (4.23.18), twice with respect to x and then putting $x = \frac{1}{2}$ we find

$$\begin{aligned} l''_2 &= -1 & (x = \frac{1}{2}), \\ l''_3 &= \frac{1}{2} & (x = \frac{1}{2}), \\ l''_4 &= -\frac{1}{4} - \frac{3y}{4z} & (x = \frac{1}{2}), \\ l''_5 &= \frac{1}{8} + \frac{15y}{8z} & (x = \frac{1}{2}). \end{aligned} \quad (4.25.2)$$

Using the values given by (2) in (4.23.13) we find

$$\begin{aligned} \frac{1}{RT} \frac{\partial^2 \Delta_m F}{\partial x^2} = 4 - 2 \frac{w}{kT} - \frac{1}{2} z \left\{ -\frac{1}{2!} \left(\frac{2w}{zkT} \right)^2 + \frac{1}{2} \frac{1}{3!} \left(\frac{2w}{zkT} \right)^3 - \right. \\ \left. - \left(\frac{1}{4} + \frac{3}{4} \frac{y}{z} \right) \frac{1}{4!} \left(\frac{2w}{zkT} \right)^4 + \left(\frac{1}{8} + \frac{15}{8} \frac{y}{z} \right) \frac{1}{5!} \left(\frac{2w}{zkT} \right)^5 - \dots \right\} \quad (x = \frac{1}{2}). \end{aligned} \quad (4.25.3)$$

Using (3) in (1) we obtain the equation determining the critical temperature T_c

$$\begin{aligned} \frac{4}{z} = \frac{2w}{zkT_c} - \frac{1}{4} \left(\frac{2w}{zkT_c} \right)^2 + \frac{1}{24} \left(\frac{2w}{zkT_c} \right)^3 - \left(1 + \frac{3y}{z} \right) \frac{1}{192} \left(\frac{2w}{zkT_c} \right)^4 + \\ + \left(1 + \frac{15y}{z} \right) \frac{1}{1920} \left(\frac{2w}{zkT_c} \right)^5 - \dots \quad (4.25.4) \end{aligned}$$

This expression for $1/z$ as a power series in $2w/zkT_c$ can be inverted into an expression for $2w/zkT_c$ as a power series in $1/z$. We obtain eventually

$$\frac{w}{kT_c} = 2 \left\{ 1 + \frac{1}{z} + \frac{4}{3} \frac{1}{z^2} + \left(2 + \frac{y}{z} \right) \frac{1}{z^3} + \left(\frac{16}{5} + 4 \frac{y}{z} \right) \frac{1}{z^4} + \dots \right\}. \quad (4.25.5)$$

If we make $z \rightarrow \infty$ the expression in brackets becomes unity and we recover the zeroth approximation. If in (5) we omit the terms in y/z we obtain an expansion agreeing with the first (quasi-chemical) approximation. In Table 4.9 are given values of w/kT_c obtained from (5) using one, two, three, four, or five terms; also values including the sixth term, calculated by Chang. Finally values obtained by the quasi-chemical approximation are included. The calculations have been done for the simple cubic lattice with $z = 6$, $y = 24$ and for the body-centred cubic lattice with $z = 8$, $y = 96$.

TABLE 4.9
Calculated Values of w/kT_c according to Several Approximations

Number of terms in formula (5)	Simple cubic $z = 6, y = 24$	Body-centred cubic $z = 8, y = 96$
1	2	2
2	2.333	2.250
3	2.407	2.292
4	2.463	2.346
5	2.493	2.371
6	2.514	2.392
Quasi-chemical	2.433	2.301

Study of Table 4.9 leads to two conclusions. Firstly, the convergence of the series expansion in powers of $1/z$ is too slow to lead to a precise

value of T_c . Secondly, whatever the true value may be, the quasi-chemical approximation appears to be considerably more accurate than the zeroth approximation.

4.26. Next-nearest neighbours

In all our approximations we have hitherto tacitly ignored all interactions between pairs of molecules which are not nearest neighbours. We shall now show† that when this restriction is removed by including the interaction between next-nearest neighbours in a quasi-chemical treatment the effect on the calculated values of typical measurable quantities is negligible.

We now denote the number of nearest neighbours of each site by z_1 and the number of next-nearest neighbours by z_2 . Thus in the simple cubic lattice $z_1 = 6$, $z_2 = 12$, and in the body-centred cubic lattice $z_1 = 8$, $z_2 = 6$. For both lattices we consider a group of 4 sites denoted by a, b, c, d . For both these lattices this group of 4 sites contains 4 pairs of nearest neighbours, namely ab, bc, cd, da , and 2 pairs of next-nearest neighbours, namely ac, bd . Thanks to this fact most of our formulae are applicable to both lattices only with different values of z_1, z_2 . In the simple cubic lattice $abcd$ is a square having ac and bd as diagonals. In the body-centred cubic lattice $abcd$ is a tetrahedron having 4 equal short edges ab, bc, ca, da , and 2 equal long edges ac, bd whose directions are at right angles to each other. The ratio of the lengths ac/ab is $\sqrt{2}$ in the simple cubic lattice and $2/\sqrt{3}$ in the body-centred cubic lattice. These geometrical details are, however, irrelevant to the derivation of our formulae.

We shall, in this section, measure all energies relative to those of the two pure substances A and B . This achieves brevity without in any way affecting the formulae obtained for the thermodynamic functions relating to the mixing process. With this convention we ignore interactions between pairs of like molecules and attribute an energy difference term to each interaction between two unlike molecules. We denote this term for a pair of unlike nearest neighbours by w_1/z_1 and for a pair of unlike next-nearest neighbours by w_2/z_2 . If now we consider a completely random arrangement of $N(1-x)$ molecules A and Nx molecules B , the energy of the mixture, in excess of that of the unmixed pure substances, is found to be $Nx(1-x)(w_1+w_2)$. Consequently in the zeroth approximation w_1+w_2 plays the part of the energy of interchange hitherto denoted by w . We now construct an

† Guggenheim and McGlashan (1951), *Trans. Faraday Soc.* **47**, 929.

approximate partition function for a mixture of $N_A = N(1-x)$ molecules A and $N_B = Nx$ molecules B . Since the procedure follows closely that of §§ 4.19–4.21 we need only sketch it briefly. The essential quantities required for the construction of the partition function are collected in the following table.

	Number of manners of same type	Number of sets of 4 sites so occupied	Boltzmann's factor in partition function
AA	1	$\frac{1}{8}z_1 N\alpha$	1
AA	1	$\frac{1}{8}z_1 N\alpha$	1
BA	4	$\frac{1}{8}z_1 N4\zeta$	$\eta^{-2}\phi^{-1}$
AA	4	$\frac{1}{8}z_1 N4v$	$\eta^{-2}\phi^{-2}$
BB	4	$\frac{1}{8}z_1 N4v'$	$\eta^{-2}\phi^{-2}$
AB	2	$\frac{1}{8}z_1 N2v'$	η^{-4}
BB	4	$\frac{1}{8}z_1 N4\xi$	$\eta^{-2}\phi^{-1}$
BA	1	$\frac{1}{8}z_1 N\beta$	1
BB	1	$\frac{1}{8}z_1 N\beta$	1
BB	1	$\frac{1}{8}z_1 N\beta$	1

The first column gives several manners of occupation of the group of 4 sites and the second column gives the number of such manners which are equivalent, differing from one another only in orientation. The third column defines parameters α , ζ , v , v' , ξ , β proportional to the numbers of groups of 4 sites occupied in the several ways. Of these parameters ζ , v , v' , ξ are to be considered as independent, but α , β are to be considered as convenient abbreviations defined by

$$\alpha = 1 - x - 3\zeta - 2v - v' - \xi, \quad (4.26.1)$$

$$\beta = x - \zeta - 2v - v' - 3\xi. \quad (4.26.2)$$

These relations ensure that the total numbers of A and B atoms are in the correct ratio $(1-x) : x$ and that the total number of sets of 4 sites being considered is $\frac{1}{8}z_1 N$. As each set of 4 sites contains 4 pairs of nearest neighbours, this means that we are considering in all $\frac{1}{8}z_1 N$ pairs of nearest neighbours, that is to say the correct number. The last column of the table gives Boltzmann's factor to be included in the partition function for each set of 4 sites occupied in the specified manner. Here η is defined by

$$\eta = e^{\nu_1 z_1 kT}, \quad (4.26.3)$$

while ϕ is an analogous quantity relating to a pair of unlike next-nearest neighbours.

We have already mentioned that we are considering a system of $\frac{1}{2}Nz_1$ sets of 4 sites containing in all the correct number $\frac{1}{2}Nz_1$ of pairs of nearest neighbours. This system then contains $\frac{1}{4}Nz_1$ pairs of next-nearest neighbours, whereas the correct number in the real system is $\frac{1}{2}Nz_2$. Since $z_2 \neq \frac{1}{2}z_1$ there is an inherent contradiction in the treatment which cannot be eliminated. This contradiction was first pointed out by Hill,[†] who at the same time suggested an antidote equivalent to writing

$$\phi = e^{2w_2/z_2 kT}, \quad (4.26.4)$$

instead of the more intuitive

$$\phi = e^{w_2/z_2 kT}. \quad (4.26.5)$$

It is doubtful whether such *ad hoc* treatment of Boltzmann's factor produces the desired improvement. Fortunately we can proceed with the development of all the formulae without detailed specification of ϕ which we may define as the *most appropriate* Boltzmann factor. It is only when we come to insert numerical values that we need to choose between (4) and (5); we shall in fact use (5) as being the more natural form for Boltzmann's factor since the energy term per pair is by definition w_2/z_2 .

From the above table we now write down an approximate configurational partition function Ω exactly according to the rules prescribed in § 4.14. The formula so obtained is

$$\begin{aligned} \Omega = & \frac{N!}{\{N(1-x)\}!\{Nx\}!} \times \\ & \times \frac{(\frac{1}{2}z_1 N\alpha^*)! \{(\frac{1}{2}z_1 N\zeta^*)!\}^4 \{(\frac{1}{2}z_1 Nv^*)!\}^4 \{(\frac{1}{2}z_1 Nv'^*)!\}^2 \{(\frac{1}{2}z_1 N\xi^*)!\}^4 \{(\frac{1}{2}z_1 N\beta^*)!\}}{(\frac{1}{2}z_1 N\alpha)! \{(\frac{1}{2}z_1 N\zeta)\}!^4 \{(\frac{1}{2}z_1 Nv)\}!^4 \{(\frac{1}{2}z_1 Nv')\}^3 \{(\frac{1}{2}z_1 N\xi)\}!^4 \{(\frac{1}{2}z_1 N\beta)\}!} \times \\ & \times \eta^{-z_1 N(\zeta + v + v' + \xi)} \phi^{-\frac{1}{2}z_1 N(\zeta + 2v + \beta)}, \end{aligned} \quad (4.26.6)$$

where α^* , ζ^* , v^* , v'^* , ξ^* , β^* denote the values of α , ζ , v , v' , ξ , β in a completely random arrangement of the $N(1-x)$ molecules *A* and Nx molecules *B*. According to this definition their values are

$$\alpha^* = (1-x)^4, \quad (4.26.7)$$

$$\zeta^* = (1-x)^3 x, \quad (4.26.8)$$

$$v^* = v'^* = (1-x)^2 x^2, \quad (4.26.9)$$

$$\xi^* = (1-x)x^3, \quad (4.26.10)$$

$$\beta^* = x^4. \quad (4.26.11)$$

[†] Hill (1950), *J. Chem. Phys.* 18, 988.

The partition function Ω defined by (6) is that for prescribed values of x, ζ, v, v', ξ . The complete partition function for given x is obtained by summation over all possible values of ζ, v, v', ξ . As usual we may replace the sum over all possible values of ζ, v, v', ξ by the maximum term in the sum. We may thus use formula (6) for Ω without any summation provided the values of $\alpha, \zeta, v, v', \xi, \beta$ in the denominator are such as to make the expression a maximum. These values are determined by the conditions

$$\frac{\partial \ln \Omega}{\partial \zeta} = 0, \quad \frac{\partial \ln \Omega}{\partial v} = 0, \quad \frac{\partial \ln \Omega}{\partial v'} = 0, \quad \frac{\partial \ln \Omega}{\partial \xi} = 0. \quad (4.26.12)$$

In performing these differentiations we must remember that α, β are not independent variables but are defined by (1) and (2) respectively. When we substitute (6) into (12) we obtain four equations of quasi-chemical equilibrium which together can be reduced to the set

$$\frac{v'}{v} = \eta^{-2}\phi^2, \quad (4.26.13)$$

$$\frac{\zeta \xi}{v^2} = \phi^2, \quad (4.26.14)$$

$$\frac{\alpha v}{\zeta^2} = \eta^2, \quad (4.26.15)$$

$$\frac{\beta v}{\xi^2} = \eta^2. \quad (4.26.16)$$

We have to solve these four equations together with (1) and (2) for the six quantities $\alpha, \zeta, v, v', \xi, \beta$. To do this it is convenient to introduce an auxiliary quantity κ defined by $\kappa^2 = \xi/\zeta$. We have then

$$\zeta = \kappa^{-1}v\phi, \quad (4.26.17)$$

$$\xi = \kappa v\phi, \quad (4.26.18)$$

$$\alpha = \kappa^{-2}v\eta^2\phi^2, \quad (4.26.19)$$

$$\beta = \kappa^2v\eta^2\phi^2. \quad (4.26.20)$$

Substituting (13), (17), (18), (19), (20) into (1), (2) in turn we obtain

$$1-x = v(\kappa^{-2}\eta^2\phi^2 + 3\kappa^{-1}\phi + 2 + \eta^{-2}\phi^2 + \kappa\phi), \quad (4.26.21)$$

$$x = v(\kappa^2\eta^2\phi^2 + 3\kappa\phi + 2 + \eta^{-2}\phi^2 + \kappa^{-1}\phi). \quad (4.26.22)$$

Now dividing (22) by (21) we obtain

$$\frac{x}{1-x} = \frac{\kappa^2\eta^2\phi^2 + 3\kappa\phi + 2 + \eta^{-2}\phi^2 + \kappa^{-1}\phi}{\kappa^{-2}\eta^2\phi^2 + 3\kappa^{-1}\phi + 2 + \eta^{-2}\phi^2 + \kappa\phi}. \quad (4.26.23)$$

This quartic in κ can be solved numerically for given x, η, ϕ . Substitution of the value of κ so obtained into (21) or (22) gives v and then $v', \zeta, \xi, \alpha, \beta$ are given by (13), (17), (18), (19), (20) respectively.

All the thermodynamic properties relating to mixing are determined by the configurational partition function Ω . In particular the molar free energy of mixing $\Delta_m F$ is given by

$$\Delta_m F = -\frac{RT}{N} \ln \Omega. \quad (4.26.24)$$

From (24) we can obtain the chemical potentials and thence the absolute activities, fugacities, and activity coefficients by differentiation with respect to $N_A = N(1-x)$ and $N_B = Nx$. In performing these differentiations we must not forget that such quantities as ζ, v, v', ξ depend on N_A, N_B . However, the fact that Ω is maximized with respect to all these quantities ensures that all terms coming from differentiation with respect to them cancel. It also follows from the definitions of $\zeta^*, v^*, v'^*, \xi^*$ that all terms coming from differentiation with respect to these also cancel. We may, therefore, in differentiating omit all such terms and this greatly reduces the work. In view of these simplifications formula (6) is in a particularly convenient form for differentiation with respect to N_A or N_B . We must remember that α, β are defined by (1), (2) respectively and that similar definitions apply to α^*, β^* . Performing these differentiations we obtain

$$\frac{\partial \Delta_m F}{\partial N_A} = kT \left\{ \ln \frac{N_A}{N_A + N_B} + \frac{1}{2} z_1 \ln \frac{N\alpha}{N\alpha^*} \right\} = kT \left\{ \ln(1-x) + \frac{1}{2} z_1 \ln \frac{\alpha}{\alpha^*} \right\}, \quad (4.26.25)$$

$$\frac{\partial \Delta_m F}{\partial N_B} = kT \left\{ \ln \frac{N_B}{N_A + N_B} + \frac{1}{2} z_1 \ln \frac{N\beta}{N\beta^*} \right\} = kT \left\{ \ln x + \frac{1}{2} z_1 \ln \frac{\beta}{\beta^*} \right\}. \quad (4.26.26)$$

Consequently the absolute activities λ , the fugacities p , and the activity coefficients f are determined by

$$\frac{\lambda_A}{\lambda_A^0(1-x)} = \frac{p_A}{p_A^0(1-x)} = f_A = \left(\frac{\alpha}{\alpha^*} \right)^{\frac{1}{2} z_1} = \left(\frac{\alpha}{(1-x)^4} \right)^{\frac{1}{2} z_1}, \quad (4.26.27)$$

$$\frac{\lambda_B}{\lambda_B^0 x} = \frac{p_B}{p_B^0 x} = f_B = \left(\frac{\beta}{\beta^*} \right)^{\frac{1}{2} z_1} = \left(\frac{\beta}{x^4} \right)^{\frac{1}{2} z_1}, \quad (4.26.28)$$

where the superscript 0 denotes values for the pure substance *A* or *B*. The values of α and β to be inserted into (27) and (28) have to be determined numerically as described above.

At temperatures below the temperature of critical mixing the co-existing phases have to satisfy the relation

$$\frac{\lambda_A}{\lambda_A^0} = \frac{\lambda_B}{\lambda_B^0}. \quad (4.26.29)$$

If we substitute (27) and (28) into (29) we obtain

$$\frac{x}{1-x} = \left\{ \frac{\alpha x^4}{\beta(1-x)^4} \right\}^{\frac{1}{z_1}}. \quad (4.26.30)$$

But from (19) and (20) we have

$$\frac{\alpha}{\beta} = \kappa^{-4}, \quad (4.26.31)$$

so that (30) reduces to $\kappa = r^{1-2/z_1}$, (4.26.32)

where r denotes the mole ratio defined by

$$r = \frac{x}{1-x}. \quad (4.26.33)$$

We now substitute (32) into equation (23) and so obtain

$$r = \frac{r^{2(1-2/z_1)} \eta^2 \phi^2 + 3r^{1-2/z_1} \phi + 2 + \eta^{-2} \phi^2 + r^{-(1-2/z_1)} \phi}{r^{-2(1-2/z_1)} \eta^2 \phi^2 + 3r^{-(1-2/z_1)} \phi + 2 + \eta^{-2} \phi^2 + r^{1-2/z_1} \phi}. \quad (4.26.34)$$

This equation in r always has one root $r = 1$; at low temperatures it has two other real roots which determine the compositions of the two coexisting phases. At the temperature of critical mixing T_c equation (34) has three coincident roots at $r = 1$. We therefore obtain the critical conditions by putting $r = 1 + \delta$ in (34) and making δ tend to zero. In this way we obtain at the critical temperature

$$\left(3 - \frac{8}{z_1}\right) \eta_c^2 - 2 \left(\frac{4}{z_1} \phi_c^{-1} + \phi_c^{-2}\right) - \eta_c^{-2} = 0, \quad (4.26.35)$$

where the subscript c denotes the critical value. If we ignore the interaction between next-nearest neighbours, w_2 is zero and ϕ is unity. The more important the interaction between next-nearest neighbours the more ϕ will deviate from unity. Since our object is to obtain a general idea of the effect of the interaction between next-nearest neighbours, there is no need to make calculations for numerous alternative values of ϕ . It will suffice to consider the greatest deviation from unity likely to be of physical interest.

To obtain a rough estimate of how ϕ is related to η let us consider

the simple case where the interaction energy ϵ between two molecules at a distance r is of the form

$$\begin{aligned} \epsilon &= \infty, \quad r < D, \\ \epsilon &= -\frac{\epsilon^*}{r^6}, \quad r > D \quad (\epsilon^*, D \text{ const.}), \end{aligned} \quad (4.26.36)$$

and where D has the same value, but ϵ^* has different values for AA , BB , and AB interactions. Under these conditions the interaction energy difference w_2/z_2 for a pair of next-nearest neighbours will be related to the interaction energy difference w_1/z_1 for a pair of nearest neighbours as the inverse sixth power of the distances. Under these conditions the relations will be

$$\frac{w_2}{z_2} = \frac{1}{8} \frac{w_1}{z_1} \quad (\text{simple cubic}), \quad (4.26.37)$$

$$\frac{w_2}{z_2} = \frac{27}{64} \frac{w_1}{z_1} \quad (\text{body-centred cubic}). \quad (4.26.38)$$

We may accordingly take $\phi = \eta^{\frac{1}{3}}$ as reasonably representative for the simple cubic lattice and $\phi = \eta^{\frac{1}{4}}$ similarly representative for the body-centred cubic lattice. These values have been used in comparisons with the opposite assumption $\phi = 1$ corresponding to neglect of the interaction between next-nearest neighbours. We here give results of such comparisons only for the body-centred cubic lattice. We shall find that the effect on all measurable properties of including the interaction between next-nearest neighbours is extremely small. It will suffice to mention that the effect in the case of the simple cubic lattice is even smaller.

Since in our present state of knowledge we have no *a priori* information concerning the magnitude of w_1 or w_2 , we must regard these as adjustable parameters, whose values we fix by the theoretical relation between them and the temperature of critical mixing. Having thus fixed the values of w_1/kT_c and w_2/kT_c we use these values to compare the calculated values of several measurable quantities according as the interaction between next-nearest neighbours is included in the theory or neglected. We shall also make the comparison with values calculated according to the quasi-chemical treatment in its simplest form applied to pairs of nearest neighbours. We shall confine ourselves to the body-centred cubic lattice so that $z_1 = 8$, $z_2 = 6$. The relations between w_1 , w_2 , and kT_c according to the several approximations are as follows:

(a) The quasi-chemical approximation in its simplest form applied

to pairs of nearest neighbours, neglecting interactions between more distant pairs, leads to the formula (4.12.13) which in our present notation becomes

$$\frac{w_1}{kT_c} = z_1 \ln \frac{z_1}{z_1 - 2} = 8 \ln \frac{8}{6} = 2.3015, \quad w_2 = 0. \quad (4.26.39)$$

(b) In the quasi-chemical treatment applied to a quadruplet of sites but neglecting the interaction between all pairs of molecules which are not nearest neighbours we have formula (35) with $\phi_c = 1$. Using this value of ϕ_c and putting $z_1 = 8$ the equation becomes

$$2\eta_c^4 - 3\eta_c^2 - 1 = 0 \quad (4.26.40)$$

having the solution $\eta_c = 1.2512$, so that

$$\frac{w_1}{kT_c} = 2, \quad w_2 = 0. \quad (4.26.41)$$

(c) In the quasi-chemical treatment applied to a quadruplet of sites we take account of interaction between next-nearest neighbours by putting $\phi_c = \eta_c^{\frac{1}{2}}$. Using this value in (35) and putting $z_1 = 3$ we have

$$2\eta_c^4 - \eta_c^{\frac{1}{2}} - 2\eta_c - 1 = 0, \quad (4.26.42)$$

having the solution $\eta_c = 1.2512$, so that

$$\frac{w_1}{kT_c} = 1.7930, \quad \frac{w_2}{kT_c} = \frac{3}{8} \frac{w_1}{kT_c} = 0.6724. \quad (4.26.43)$$

Having fixed the values of w_1/kT_c and w_2/kT_c according to the several approximations, we now use these to compare calculated values of several typical measurable properties of the mixture. We begin by comparing values of $\Delta_m H/RT_c$ for an equimolecular mixture at the temperature of critical mixing. The comparison is shown in the first line of Table 4.10. We next compare calculated values of the activity coefficient f_B for several values of x and of T/T_c . These are also shown in Table 4.10. There is no need to quote values of f_A since by symmetry f_A is the same function of $1-x$ as f_B is of x .

Finally Table 4.11 shows a comparison according to the three approximations of calculated values of T/T_c at which the compositions of two coexisting phases have given values.

From Tables 4.10 and 4.11 we see that the differences between all the calculated observable quantities according to the three approximations are exceedingly small. They are much smaller than the differences between any of these quasi-chemical approximations and the zeroth approximation, which differences are themselves usually unimportant.

We thus conclude that the effect on measurable properties of the mixture of taking account of interaction between next-nearest neighbours is entirely negligible.

TABLE 4.10

Comparison of Three Quasi-chemical Treatments for a Body-centred Cubic Lattice, $z_1 = 8, z_2 = 6$

(a) Pairs. (b) Quadruplets with $w_3 = 0$. (c) Quadruplets with $w_3 = \frac{1}{3}w_1$.

	a	b	c
$\Delta_m H/RT$ for $x = 0.5$ at $T = T_c$	0.4931	0.4927	0.4948
f_B for $x = 0.2$ at $T = T_c$	3.8691	3.8800	3.8354
$x = 0.5$, , ,	1.7060	1.7077	1.6974
$x = 0.8$, , ,	1.1045	1.1050	1.1006
f_B for $x = 0.2$ at $T = 1.5T_c$	2.5325	2.5376	2.5033
$x = 0.5$, , ,	1.4408	1.4422	1.4335
$x = 0.8$, , ,	1.0670	1.0672	1.0645
f_B for $x = 0.2$ at $T = 0.9T_c$	4.4324	4.4424	4.3930
$x = 0.8$, , ,	1.1176	1.1182	1.1133

TABLE 4.11

Values of T/T_c at which Compositions x and $1-x$ of two Coexisting Phases have Specified Values, according to Several Approximations for Body-centred Cubic Lattice, $z_1 = 8, z_2 = 6$

(a) Pairs. (b) Quadruplets with $w_3 = 0$. (c) Quadruplets with $w_3 = \frac{1}{3}w_1$.

x or $1-x$	a	b	c
0.6	1.0	1.0	1.0
0.4	0.9897	0.9892	0.9855
0.3	0.9569	0.9574	0.9558
0.2	0.8938	0.8950	0.8911
0.1	0.7762	0.7779	0.7704
0.05	0.6684	0.6702	0.6633
0.02	0.5518	0.5534	0.5422
0.01	0.4822	0.4836	0.4724

4.27. Dependence of w on temperature

We have throughout tacitly assumed that w is independent of the temperature and we must now consider whether such an assumption is either justifiable or necessary.† One possible manner of investigation is to regard the quasi-chemical equation as defining w . Thus defined w is a complicated average energy. In fact $2w$ is the energy

† Guggenheim (1948), *Trans. Faraday Soc.* **44**, 1007; (1949), *Supp. Nuovo Cimento*, **6**, 181.

required to decrease by one the number of AA pairs and of BB pairs while increasing by two the number of AB pairs, averaged over all accessible states of the remainder of the system, each such state being weighted with the relevant Boltzmann factor. Thus $2w$ is in a sense the free energy increase of the whole system when an AA pair and a BB pair are converted into two AB pairs. The value of w thus defined may be expected to depend on the relative numbers of AA , BB , AB pairs in each configuration of the whole system. Such a quantity as w may be called a *co-operative free energy*.

Having thus redefined w , let us consider some of its properties. The equation of quasi-chemical equilibrium is essentially an isothermal distribution law containing the parameter w/kT . Its usefulness depends on knowledge, either accurate or approximate, of how w depends at a given temperature on the configuration of the remainder of the system. The essence of the quasi-chemical treatment consists in the approximation that w is independent of the configuration of the remainder of the system. It is not essential to the quasi-chemical treatment to assume that w is independent of temperature and we shall accordingly consider briefly the effect of removing this unwarranted restriction.

All our formulae for the configurational free energy F_c , the molar free energy of mixing $\Delta_m F$, the chemical potentials μ_A , μ_B , the absolute activities λ_A , λ_B , and the activity coefficients f_A , f_B contain w in the form of the ratio w/kT or in particular $\eta = e^{w/kT}$. We may regard either of these quantities as a single parameter whose value determines all the above-mentioned thermodynamic properties at a given temperature. None of the formulae for any of these quantities is affected by removing the restriction that w should be independent of the temperature. Nor are the formulae for the compositions of the two coexisting phases nor those for critical mixing affected.

The formulae for the configurational total energy or heat function and for the molar energy or heat of mixing are obtained from the formulae for the free energy by operations including differentiation with respect to T . The formulae for these quantities are therefore affected by the dependence of w on the temperature. The effect of such temperature dependence is that in all formulae for total energies or heat functions w becomes replaced by u , defined by

$$u = w - T \frac{dw}{dT}. \quad (4.27.1)$$

We may call u the *co-operative total energy* corresponding to the *co-operative free energy* w .

In particular when we substitute into the relation

$$\Delta_m H = \Delta_m U = \frac{d(\Delta_m F/T)}{d(1/T)}, \quad (4.27.2)$$

the zeroth approximation (4.04.12) for $\Delta_m F$ we obtain immediately

$$\Delta_m H = x(1-x)N\left(w - T\frac{dw}{dT}\right) = x(1-x)Nu. \quad (4.27.3)$$

In the first approximation the algebra is not so simple. From (4.10.9) we have

$$\begin{aligned} \frac{\Delta_m F}{RT} &= (1-x)\ln(1-x) + x \ln x + \\ &\quad + \frac{1}{2}z\left\{(1-x)\ln\frac{\beta+1-2x}{(1-x)(\beta+1)} + x \ln\frac{\beta-1+2x}{x(\beta+1)}\right\}. \end{aligned} \quad (4.27.4)$$

Substituting (4) into (2) we have

$$\begin{aligned} \frac{\Delta_m U}{N} &= \frac{1}{2}z\left\{(1-x)\left(\frac{1}{\beta+1-2x} - \frac{1}{\beta+1}\right) + x\left(\frac{1}{\beta-1+2x} - \frac{1}{\beta+1}\right)\right\}\frac{d\beta}{d(1/kT)} \\ &= \frac{zx(1-x)}{\beta+1}\left\{\frac{1}{\beta+1-2x} + \frac{1}{\beta-1+2x}\right\}\frac{d\beta}{d(1/kT)} \\ &= \frac{zx(1-x)}{\beta+1}\frac{2\beta}{\beta^2-(1-2x)^2}\frac{d\beta}{d(1/kT)}. \end{aligned} \quad (4.27.5)$$

From the definition (4.10.2) of β we have

$$\beta^2 = (1-2x)^2 + 4x(1-x)\eta^2 = (1-2x)^2 + 4x(1-x)e^{2w/zkT}, \quad (4.27.6)$$

so that

$$2\beta\frac{d\beta}{d(1/kT)} = 4x(1-x)e^{2w/zkT}\frac{2}{z}\left(w - T\frac{dw}{dT}\right) = \frac{2u}{z}\{\beta^2 - (1-2x)^2\}. \quad (4.27.7)$$

Substituting (7) into (5) we find

$$\frac{\Delta_m U}{N} = \frac{2}{\beta+1}x(1-x)u, \quad (4.27.8)$$

which is the same as (4.10.4) except that w is now replaced by u .

Let us now assume tentatively that w can be expressed as a linear function of T . We then write

$$w = u^0 - s^0 T \quad (u^0, s^0 \text{ constants}). \quad (4.27.9)$$

We deduce $u = w - T\frac{dw}{dT} = u^0.$ (4.27.10)

Hence in the zeroth approximation given by (3) we have

$$\Delta_m H = x(1-x)Nu^0 \quad (u^0 \text{ constant}). \quad (4.27.11)$$

We thus see that the assumption that w depends on the temperature does not necessarily imply that the heat of mixing varies with the temperature. With the same assumptions the molar entropy of mixing is given in the zeroth approximation by

$$\frac{\Delta_m S}{R} = -(1-x)\ln(1-x) - x \ln x + x(1-x) \frac{s^0}{k} \quad (s^0 \text{ constant}). \quad (4.27.12)$$

4.28. Comparison with experiment

Any adequate comparison of the theories and formulae of this chapter with experiment requires the experimental determination of partial vapour pressures of suitable binary mixtures over the whole range of composition and for several temperatures. Unfortunately there are exceedingly few systems for which such measurements have been made.

As examples of older measurements we may mention the systems ether/acetone and chloroform/acetone. It was shown by Porter† many years ago that the experimental partial vapour pressures in ether/acetone mixtures at 30° C. can be expressed approximately by formulae (4.05.5) and (4.05.6) of the zeroth approximation if w/kT is given the value 0.74. These data are not of sufficient accuracy to warrant any more refined analysis. The system chloroform/acetone provides an example of w negative. The vapour-pressure measurements of von Zawidzki‡ at 35° C. can be represented only roughly, but not within the probable experimental accuracy, by formulae (4.05.5) and (4.05.6) of the zeroth approximation with $w/kT = -0.9$.

When we turn to modern measurements we find that those of Scatchard and his collaborators are conspicuous for their outstanding precision. By comparison no other measurements are worth consideration. Of the mixtures studied by Scatchard several contain an alcohol and are therefore quite unsuitable for comparison with the theory of regular solutions. Only three of the mixtures consist of two non-polar substances, namely benzene/cyclohexane,§ carbon tetrachloride/benzene,|| and carbon tetrachloride/cyclohexane.†† The molecular volumes of the three substances are as follows:

Benzene	89 ml./mole
Cyclohexane	109 ml./mole
Carbon tetrachloride	97 ml./mole.

† Porter (1920), *Trans. Faraday Soc.* **16**, 339.

‡ von Zawidzki (1900), *Z. Physikal. Chem.* **35**, 123.

§ Scatchard, Wood, and Mochel (1939), *J. Phys. Chem.* **43**, 119.

|| Scatchard, Wood, and Mochel (1940), *J. Am. Chem. Soc.* **62**, 712.

†† Scatchard, Wood, and Mochel (1939), *J. Am. Chem. Soc.* **61**, 3206.

Owing to the 20 per cent. difference in volume between benzene and cyclohexane we can hardly expect their mixture to behave as *s*-regular. In the mixtures of carbon tetrachloride with each of the hydrocarbons the ratio of the sizes of the molecules is probably near enough to unity, but the shapes of the molecules are entirely different. Nevertheless these two mixtures are undoubtedly more suitable for comparison with the theory than any other for which there are any precision measurements. We shall accordingly use these.

Scatchard measured the total pressure and the composition of both liquid and vapour phases at a given temperature. From these he calculated the two partial vapour pressures and corrected these for the imperfection of the vapour. He thus obtained the activity coefficients f_A and f_B of the two components. The quantity tabulated by Scatchard, suitable for comparison with the theory, is the excess of the molar Gibbs function of mixing over its value for an ideal mixture; that is to say the quantity

$$\Delta_m G - RT(1-x)\ln(1-x) - RTx\ln x = RT\{(1-x)\ln f_A + x\ln f_B\}. \quad (4.28.1)$$

For both mixtures the value of w/kT is about $\frac{1}{2}$ or less, and consequently the error introduced into the calculation of the quantity (1) by using the zeroth approximation is always less than 1 per cent. We shall therefore use only the zeroth approximation. The theoretical value of the experimental quantity (1) is then

$$Nwx(1-x). \quad (4.28.2)$$

The comparison between the theoretical quantity (2) and the experimental quantity (1) involves two questions. First, can the experimental data over the whole concentration range at a given temperature be represented by the theoretical formula by a suitable choice of w ? Second, if a value of w can be found to fit over the whole range of concentration, is this value of w independent of the temperature?

We find that for both mixtures agreement can be obtained between experiment and theory by assuming a temperature dependent w , but not by means of a temperature independent w . The comparison for the system carbon tetrachloride/benzene is shown in Table 4.12. The values of w used at the several temperatures are given at the top of the columns. We see that with few exceptions the agreement between experimental and calculated values is better than 0.1 cal./mole. A discrepancy of 0.1 cal./mole in the quantity tabulated is equivalent to an inaccuracy of only about one part in five thousand in the pressure.

The agreement between calculated and experimental values is about as good as the experimental accuracy. No such agreement could be obtained by assuming a temperature independent w . In other words,

TABLE 4.12

Experimental Values in calories of the Excess Molar Gibbs Function of mixing over its Ideal Value compared with the Theoretical Value $Nx(1-x)w$ for Carbon Tetrachloride/Benzene

Temperature $w/\text{cal. mole}^{-1}$	30° C.		40° C.		50° C.		60° C.		70° C.	
x (approx.)	exp.	calc.								
0.14	9.11	9.18	8.86	8.79
0.24	13.85	13.83	13.13	13.07
0.37	17.78	17.85	16.98	16.90
0.49	19.46	19.44	19.06	19.07	18.74	18.70	18.35	18.33	17.63	17.95
0.50	18.99	19.07
0.62	17.82	17.97	16.76	16.87
0.76	13.86	13.98	12.93	13.01
0.87	8.06	8.53	7.80	7.85

there is agreement with the modified theory described in § 4.27 but not with the simpler theory considered earlier in this chapter.

According to the values of w used the temperature derivative dw/dT has the constant value $-0.15 \text{ cal./deg. mole}$. The molar heat of mixing is then given by

$$\Delta_m H = Nx(1-x)u = Nx(1-x)\left(w - T \frac{dw}{dT}\right). \quad (4.28.3)$$

The calculated value of $u = w - T dw/dT$ is 123 cal./mole, so that the calculated value of $\Delta_m H$ for an equimolar mixture is 31 cal./mole. The directly measured value† of this quantity obtained at 25° C. is 26 cal./mole. The agreement is not striking, but may be regarded as moderate.

In Table 4.13 a similar comparison is shown for the system carbon tetrachloride/cyclohexane. Again excellent agreement between experimental and calculated values is obtained by assuming a temperature dependent w . The assumed value for the temperature coefficient is $dw/dT = -0.23 \text{ cal./deg. mole}$. The calculated value of $u = w - T dw/dT$ is 135 cal./mole, so that the molar heat of mixing of an equimolar mixture should be 34 cal./mole. There is no direct experimental measurement with which to compare this.

In conclusion we should mention that Scatchard‡ has developed a

† Hirobe (1925), *J. Fac. Sci. Imp. Univ. Tokyo*, 1, 155; Cheesman and Whitaker (1952), *Proc. Roy. Soc. A.*

‡ Scatchard (1937), *Trans. Faraday Soc.* 33, 160.

theory relating the temperature dependence of w to the volume change occurring on mixing the two components. As this theory lies outside our field we refer the interested reader to the original exposition.

TABLE 4.13

Experimental Values in calories of the Excess Molar Gibbs Function of mixing over its Ideal Value compared with the Theoretical Value $Nx(1-x)w$ for Carbon Tetrachloride/Cyclohexane

Temperature $w/\text{cal. mole}^{-1}$	30° C.		40° C.		50° C.		60° C.		70° C.	
x (approx.)	exp.	calc.								
0.125	6.77	6.97	5.98	6.15
0.25	11.50	11.70	10.19	10.47
0.37	14.62	14.68	13.03	13.03
0.47	13.38	16.33	15.61	15.76
0.48	15.65	15.76	15.23	15.21	14.57	14.63	13.92	14.05
0.51	15.90	15.79	13.90	14.06
0.61	15.16	15.09	13.48	13.43
0.75	12.01	11.72	10.79	10.46
0.87	7.10	6.88	6.50	6.13

So much for vapour pressures. We must now consider briefly the use of solubility measurements. According to formula (1.07.9) the activity coefficient f_B of the solute B in a solution saturated with respect to the pure solid phase of B at a temperature T is given by

$$\ln f_B = \ln \frac{1}{x} - \frac{\Delta_f H_B^0}{R} \left(\frac{1}{T} - \frac{1}{T_B^0} \right), \quad (4.28.4)$$

where x denotes the mole fraction of B in the saturated solution, $\Delta_f H_B^0$ is the molar heat of fusion of the pure substance B , and T_B^0 is the freezing-point of the pure liquid B . If then one determines T_B^0 , $\Delta_f H_B^0$ and then measures the solubility x at several temperatures T , one can calculate the activity coefficient in the saturated solution at each temperature T . The value of f_B thus calculated can then be compared with a theoretical formula so as to determine the value of the interchange energy w which fits best. It must be stressed that in this method there is at each temperature only one composition at which the comparison can be made and so at each temperature only one determination of the value of w which fits. Thus all that can be done is to find out whether the same value of w fits the saturated solution at several temperatures. This is essentially the method of comparison proposed by Hildebrand† and applied by him to a vast variety of binary

† Hildebrand and Scott (1950), *Solubility of Non-electrolytes*, Reinhold.

mixtures. It was in the course of such comparisons that Hildebrand[†] invented the name *regular solutions* to denote those mixtures whose behaviour showed a certain kind of regularity. The class of regular mixtures with the theory of which we have been concerned is somewhat more restricted than accords with Hildebrand's original definition. When necessary we emphasize the distinction by using the name *strictly regular* or *s-regular* to denote the more restricted class of mixtures of which we may hope that our theoretical models may be more or less representative. In particular for a mixture to be *s*-regular the two kinds of molecules must be sufficiently similar in size to be interchangeable on the lattice postulated in the model. It is only with *s*-regular mixtures that we are here concerned, and it is for these only that we describe comparison between theory and experiment. The procedure, as already mentioned, is to calculate the activity in the saturated solution from (4) and compare this value with a theoretical one. In particular if we use the zeroth approximation we have according to (4.06.4)

$$\ln f_B = (1-x)^2 \frac{w}{kT} = (1-x)^2 \frac{Nw}{RT}. \quad (4.28.5)$$

Comparing (5) with (4) we have for the determination of *w* the equation

$$(1-x)^2 Nw = RT \ln \frac{1}{x} - \Delta_f H_B^0 \left(1 - \frac{T}{T_B^0} \right). \quad (4.28.6)$$

At this stage we recall that $\Delta_f H_B^0$ strictly denotes the value of the heat of fusion, not at the temperature T_B^0 , at which alone it can be directly measured, but an average value over the temperature range T to T_B^0 . In practice it is rarely if ever possible to do better than use the value at the temperature T_B^0 . This necessitates a certain error in $\Delta_f H_B^0$ which introduces a comparable error in Nw . Since, however, Nw is usually much smaller than $\Delta_f H_B^0$, the fractional error in *w* is usually greater than that in $\Delta_f H_B^0$. Consequently this method of comparison cannot lead to precise values of *w*, and for this reason there is no point in using any approximation better than the zeroth, the more so as we have seen that the difference between the zeroth and the first approximation is never very important. Hildebrand has applied this method of comparison to numerous binary mixtures, and it can be said that for such mixtures as may reasonably be expected to be *s*-regular the value of *w* obtained by formula (6) is within the accuracy of the estimate, usually independent of temperature. It is, however, only fair

[†] Hildebrand (1929), *J. Am. Chem. Soc.* 51, 66.

to say that accurate comparisons are difficult and correspondingly scarce. Some of the many mixtures considered by Hildebrand consist of two kinds of molecules differing too much in size for the mixture to be *s*-regular, though it may still be regular according to Hildebrand's criterion.

4.29 Exact treatment in two dimensions

All the treatments described hitherto, except the series expansions in powers of w/zkT are only approximations. The series expansions are presumably exact provided the series converge, but we have seen that some of the series converge only slowly, if at all. The analogous problem in two dimensions has been investigated by more powerful, but much more elaborate, mathematical techniques.[†] These lead to a closed formula for the temperature of critical mixing T_c . For the simple square lattice with $z = 4$ this takes the form

$$\sinh \frac{w}{4kT_c} = 1, \quad (4.29.1)$$

which gives $w/kT_c = 3.5255$.

It is interesting to compare this closed solution with that obtained from the series expansion (4.25.5)

$$\frac{w}{kT_c} = 2 \left\{ 1 + \frac{1}{z} + \frac{4}{3} \frac{1}{z^2} + \left(2 + \frac{y}{z} \right) \frac{1}{z^3} + \left(\frac{16}{5} + 4 \frac{y}{z} \right) \frac{1}{z^4} + \dots \right\}. \quad (4.29.2)$$

For the simple square lattice $z = 4$, $y/z = 2$ so that (2) becomes

$$\frac{w}{kT_c} = 2 \left\{ 1 + \frac{1}{4} + \frac{1}{12} + \frac{1}{16} + \frac{7}{160} + \dots \right\}. \quad (4.29.3)$$

In Table 4.14 the second column gives the several values of w/kT_c obtained from formula (3) according to the number of terms retained as compared with the exact value given by (1). It is evident that the series converges to the exact value extremely slowly.

The quasi-chemical approximation for a simple square lattice takes the form

$$\begin{aligned} \frac{w}{kT_c} &= z \ln \frac{z}{z-2} = 2 \left\{ 1 + \frac{1}{2} \frac{2}{z} + \frac{1}{3} \left(\frac{2}{z} \right)^2 + \frac{1}{4} \left(\frac{2}{z} \right)^3 + \frac{1}{5} \left(\frac{2}{z} \right)^4 + \dots \right\} \\ &= 2 \left\{ 1 + \frac{1}{4} + \frac{1}{12} + \frac{1}{32} + \frac{1}{80} + \dots \right\}. \end{aligned} \quad (4.29.4)$$

[†] Kramers and Wannier (1941), *Phys. Rev.* **60**, 263. Onsager (1944), *Phys. Rev.* **65**, 117. Wannier (1945), *Rev. Mod. Phys.* **17**, 50.

Formula (4) differs from formula (2) by the omission of the terms in y/z . As a result of this omission formula (4), in contrast to formulae (2) and (3), converges quite fast, as can be seen from the last column of Table 4.14.

TABLE 4.14

Values of w/kT_c for square lattice, $z = 4$

No. of terms	Accurate	Quasi-chemical
1	2	2
2	2.5	2.5
3	2.6667	2.6667
4	2.7917	2.7292
5	2.8792	2.7542
closed formula	3.5255	2.7726

DILUTE SOLUTIONS

5.01. Definition of diluteness

We call a solution, whether liquid or solid, *dilute* when one species called the *solvent* is present in large excess compared with the other species called *solute*. The characteristic of a dilute solution is that the mutual interactions of solute molecules should be negligible. If, as in the two previous chapters, we suppose that each molecule has z nearest neighbours and we neglect interactions between pairs of molecules not nearest neighbours, then the condition for a binary solution to be dilute is $zx \ll 1$, which means roughly speaking $x < 0.01$.

5.02. Dilute regular solutions

We begin our study of dilute solutions by examining the behaviour of a regular solution when the condition for diluteness is satisfied. The configurational free energy of a binary regular solution is given by (4.04.4) with \bar{X} related to \bar{X} by (4.04.7) and \bar{X} in turn given by (4.10.1). We now assume $N_B \ll N_A$ so that zN_B^2/N_A^2 may be neglected. We may then replace the right side of (4.10.1) by its leading term and so have

$$\bar{X} \simeq \frac{N_A N_B}{N_A + N_B} \simeq N_B. \quad (5.02.1)$$

Consequently with sufficient accuracy

$$\bar{X} = \bar{X} = N_B. \quad (5.02.2)$$

The physical meaning of (2) is simple: there are so few B molecules present compared with A molecules that practically every B molecule is entirely surrounded by A molecules and there are practically no BB pairs of nearest neighbours. In other words, the solution is so dilute that mutual interactions between solute molecules are negligible. Thus (2) follows immediately from our definition of diluteness.

Substituting the value of \bar{X} given by (2) into (4.04.4) we obtain for the configurational free energy

$$F_c = -N_A \chi_A - N_B \chi_B + N_A kT \ln \frac{N_A}{N_A + N_B} + N_B kT \ln \frac{N_B}{N_A + N_B} + N_B w. \quad (5.02.3)$$

By differentiation of (3) with respect to N_A , N_B we obtain for the chemical potentials (per molecule) and for the absolute activities

$$\mu_A - \mu_A^0 = kT \ln \frac{\lambda_A}{\lambda_A^0} = kT \ln \frac{N_A}{N_A + N_B} = kT \ln(1-x), \quad (5.02.4)$$

$$\mu_B - \mu_B^0 = kT \ln \frac{\lambda_B}{\lambda_B^0} = kT \ln \frac{N_B}{N_A + N_B} + w = kT \ln x + w. \quad (5.02.5)$$

5.03. Raoult's law and Henry's law

From (5.02.4) and (5.02.5) we obtain immediately for the partial vapour pressures

$$\frac{p_A}{p_A^0} = \frac{\lambda_A}{\lambda_A^0} = (1-x), \quad (5.03.1)$$

$$\frac{p_B}{p_B^0} = \frac{\lambda_B}{\lambda_B^0} = xe^{w/kT}. \quad (5.03.2)$$

We observe that formula (1) for the vapour pressure of the solvent is identical with (3.03.9). In other words, *Raoult's law* is valid for the solvent species A . On the other hand, formula (2) differs from Raoult's law by the presence of the factor $e^{w/kT}$. Formula (2) is an example of the isothermal relation

$$p_B = hx \quad (h = \text{const.} \neq p_B^0), \quad (5.03.3)$$

known as *Henry's law*.

5.04. More general treatment

We have derived the properties of dilute solutions by regarding them as a special class of regular solutions. Actually the laws of dilute solutions are more general, being independent of the assumption that all the molecules have comparable volumes and similar manners of packing. We shall therefore give an alternative derivation of these laws, starting with a different method of approximation. At the same time we extend the treatment to cover the case of several solute species s .

For sufficiently dilute solutions of non-electrolytes we may ignore all mutual interactions between solute molecules. In this respect the solute molecules behave like the molecules in a perfect gas. We accordingly treat the solute molecules s as a perfect quasi-gas moving freely in a region of constant potential energy $-\chi_s$ depending on the nature of s , on the nature of the solvent, and on the temperature. The molecular partition function of a molecule in a perfect gas is directly proportional

to the total volume V . We accordingly ascribe to each solute molecule a partition function of the form

$$\phi_s V e^{\chi_s/kT}, \quad (5.04.1)$$

where the factor, $e^{\chi_s/kT}$ takes account of the average interaction between a single solute molecule of type s and the surrounding solvent while $\phi_s V$ is the partition function for the translational, rotational, and all internal degrees of freedom of the molecule. The important property of ϕ_s , as of χ_s , is its independence of the number of solute molecules of any kind in the solution.

The partition function Q of the whole solution is then of the form

$$Q = Q^0 \prod_s \frac{(\phi_s V e^{\chi_s/kT})^{N_s}}{N_s!}, \quad (5.04.2)$$

where Q^0 is the value of Q when all the N_s are zero. The factor $N_s!$ in the denominator takes care of the indistinguishability of molecules of the same species, as explained in the discussion of gases in Chapter VIII.

The free energy F of the mixture is then given by

$$F = -kT \ln Q^0 - \sum_s N_s \chi_s - kT \sum_s N_s \ln \frac{\phi_s V e}{N_s}, \quad (5.04.3)$$

when Stirling's approximation is used for $N_s!$. By differentiating (3) with respect to N_s we obtain for the chemical potential μ_s ,

$$\mu_s = -\chi_s - kT \ln \phi_s + kT \ln \frac{N_s}{V}. \quad (5.04.4)$$

The volume V of the whole solution is related to the partial molar volumes V_1 , V_s by

$$V = N_1 V_1 + \sum_s N_s V_s, \quad (5.04.5)$$

but since the solution is dilute we shall assume that $\sum_s N_s V_s \ll N_1 V_1$ and shall replace (5) by the approximation

$$V = (N_1 + \sum_s N_s) V_1. \quad (5.04.6)$$

Substituting (3) into (4) we obtain finally

$$\mu_s = -\chi_s - kT \ln \phi_s V_1 + kT \ln x_s. \quad (5.04.7)$$

Since χ_s , ϕ_s , and V_1 are assumed independent of x_s it follows that

$$\lambda_c = e^{-\mu_s/kT} \propto x_s. \quad (5.04.8)$$

Owing to the unsymmetrical nature of our approximation, which treats the solvent as a medium in which the solute molecules are immersed, we shall not expect to obtain useful information concerning

μ_1 from formula (3). By using the Gibbs–Duhem relation, however, we can show that formula (7) leads to the formula for the solvent

$$\mu_1 = \mu_1^0 + kT \ln x_1. \quad (5.04.9)$$

We do not give details because in § 5.06 we shall give an equivalent formula for the vapour pressure of the solvent by using the Duhem–Margules relation.

5.05. Henry's law and Nernst's law

From (5.04.8) we immediately derive for the vapour pressure, or strictly fugacity, of each solute species s

$$p_s = h_s x_s, \quad (5.05.1)$$

where h_s depends on the nature of the solvent, the nature of the solute, and the temperature, but not on the mole fractions x_s . This relation is called *Henry's law*.

If we apply formula (1) to solutions of the same solute s in two immiscible solvents in mutual equilibrium, we have

$$p_s = h'_s x'_s = h''_s x''_s, \quad (5.05.2)$$

where the two solvents are denoted by single and double dashes respectively. Formula (2) represents the relation known as *Nernst's distribution law*.

5.06. Raoult's law

We have seen that in a dilute solution of several solute species, each solute s obeys Henry's law (5.05.1), which we can also write in the differential form

$$d \ln p_s = d \ln x_s. \quad (5.06.1)$$

We can now obtain a formula for the partial vapour pressure of the solvent by using the Duhem–Margules relation. Denoting the solvent species by the subscript 1, the Duhem–Margules relation can be written in the form

$$x_1 d \ln p_1 + \sum_s x_s d \ln p_s = 0. \quad (5.06.2)$$

Substituting (1) into (2), we obtain

$$\begin{aligned} x_1 d \ln p_1 &= - \sum_s x_s d \ln x_s \\ &= - \sum_s dx_s \\ &= dx_1, \end{aligned} \quad (5.06.3)$$

of which the integrated form is

$$\ln p_1 = \ln x_1 + \text{const.} \quad (5.06.4)$$

The integration constant is determined by the condition that when $x_1 = 1$ the vapour pressure p_1 becomes that of the pure solvent denoted as usual by p_1^0 . Consequently (4) becomes

$$p_1 = p_1^0 x_1 = p_1^0 \left(1 - \sum_s x_s\right), \quad (5.06.5)$$

which is Raoult's law.

We have thus reached the important conclusion that in any sufficiently dilute solution of any number of (non-electrolyte) solute species the solvent obeys Raoult's law. A solution sufficiently dilute for Raoult's law to be obeyed is usually called *ideally dilute*. As long as electrolyte solutions are excluded there is no danger in using the simpler epithet *dilute*.

5.07. Osmotic pressure

The osmotic pressure Π_1 for the osmotic equilibrium of the solvent species 1 is related to its partial vapour pressure by the thermodynamic relation (1.06.5)

$$\Pi_1 = \frac{RT}{V_1} \ln \frac{p_1^0}{p_1}. \quad (5.07.1)$$

Substituting (5.06.5) into (1) we obtain

$$\Pi_1 = -\frac{RT}{V_1} \ln \left(1 - \sum_s x_s\right). \quad (5.07.2)$$

Since from the definition of a dilute solution $\sum_s x_s \ll 1$, we may replace (2) by

$$\Pi_1 = RT \frac{\sum_s x_s}{V_1} \simeq RT \sum_s c_s, \quad (5.07.3)$$

where c_s denotes the concentration of the solute species s in moles per unit volume. Formula (3) is known as *van't Hoff's law* for the osmotic pressure of a dilute solution.

5.08. Heat of dilution

From formula (5.02.3) we obtain for the configurational energy and heat function of a binary dilute solution

$$H_c = U_c = F_c - T \frac{\partial F_c}{\partial T} = -N_A \chi_A - N_B (\chi_B - w). \quad (5.08.1)$$

Consequently the partial molar heat functions are related to the molar heat functions of the pure substances by

$$H_A - H_A^0 = 0, \quad (5.08.2)$$

$$H_B - H_B^0 = w. \quad (5.08.3)$$

Formula (2) tells us that the *heat of dilution*, i.e. of adding more solvent, is zero. Formula (3) tells us that the molar *heat of dissolution*, i.e. of adding more solute, is w .

Similar formulae apply when there are several solute species.

5.09. Use of mole ratios. Molality scale

Formula (5.04.4) can be abbreviated to

$$\lambda_s \propto c_s, \quad (5.09.1)$$

where c_s denotes the concentration of s on a scale of molecules per unit volume; the proportionality factor depends on the nature of the solvent, on the nature of the solute s , and on the temperature, but is independent of the concentration of any of the solutes. Formula (5.04.8) has the similar form

$$\lambda_s \propto x_s, \quad (5.09.2)$$

where again the proportionality factor depends on the nature of the solvent, on the nature of the solute s , and on the temperature, but not on the concentration of any of the solutes. It is clear from § 5.04 that for the dilute solutions with which we are concerned in this chapter the relations (1) and (2) are equivalent. They are of course not equivalent for more concentrated solutions.

The relations (1) and (2) are not the only possible ones describing Henry's law for a dilute solution. Another such relation of practical importance is

$$\lambda_s \propto \frac{N_s}{N_1} \propto m_s, \quad (5.09.3)$$

where m_s , called the *molality*, denotes the number of moles of s in a quantity of solution containing one kilogram of solvent. The relation (3) is equivalent to (1) and (2) for the dilute solutions with which alone we are concerned in this chapter, but would not be equivalent for more concentrated solutions. The relations (2) and (3) have the advantage over (1) that x_s , m_s do not change when the temperature of a mixture is altered. Formula (3) has the further practical advantage over (2) that m_s for a particular species s can be accurately measured even if there are in the mixture other solute species of unknown kinds or of unknown amounts, as may well occur if some of these other species are capable of associating or dissociating or reacting chemically with one another. Moreover, the determination of the molality m_s does not require any knowledge of the molecular weight or even the chemical nature of the solvent. From a practical point of view it is generally recognized that the molality scale is the most convenient for dilute

solutions and the relation (3) is then the appropriate formulation of Henry's law.

Since, as we have already stressed, formulae (1), (2), and (3) are mutually equivalent for dilute solutions, it follows that each of them must be consistent with Raoult's law for the solvent. The precise form of Raoult's law will, however, be slightly different in the three cases. We already know that if we substitute (2) into the Gibbs-Duhem relation we obtain Raoult's law in the form

$$\frac{p_1}{p_1^0} = \frac{\lambda_1}{\lambda_1^0} = 1 - \sum_s x_s. \quad (5.09.4)$$

Let us now see what we obtain when we start from (3) instead of from (2). For this purpose it is convenient to use the *mole ratio* r_s defined by

$$r_s = \frac{N_s}{N_1}, \quad (5.09.5)$$

and rewrite (3) as $\lambda_s \propto r_s$. (5.09.6)

We can write the Duhem-Margules relation in the form

$$-d \ln \lambda_1 = \sum_s r_s d \ln \lambda_s. \quad (5.09.7)$$

Differentiating (6) logarithmically and substituting into (7) we obtain

$$-d \ln \lambda_1 = \sum_s r_s d \ln r_s = \sum_s dr_s = d \sum_s r_s. \quad (5.09.8)$$

Integrating (8) we obtain $\ln \frac{\lambda_1^0}{\lambda_1} = \sum_s r_s$, (5.09.9)

or, in terms of the fugacity p_1 ,

$$\ln \frac{p_1^0}{p_1} = \sum_s r_s. \quad (5.09.10)$$

Formula (4) can be rewritten as

$$\frac{p_1^0 - p_1}{p_1^0} = \sum_s x_s = \frac{\sum_s r_s}{1 + \sum_s r_s}, \quad (5.09.11)$$

so that

$$\frac{p_1^0 - p_1}{p_1} = \sum_s r_s. \quad (5.09.12)$$

It is evident that for solutions so dilute that $\sum_s r_s \ll 1$ formulae (10) and (12) are equivalent.

VI

LATTICE IMPERFECTIONS

6.01. Nature of imperfections

By lattice imperfections in a crystal we mean any deviations from the regular arrangement of atoms or molecules on the lattice of a crystal. For the sake of brevity we shall speak of atoms, although much of what is said could in principle apply also to a crystal of molecules. The most obvious and most important kinds of imperfections are (*a*) a *hole*, that is an unoccupied lattice site; (*b*) an *interstitial atom*, that is an atom located somewhere between the lattice sites; (*c*) a *wrong atom*, that is an atom located on a lattice site appropriate to a different kind of atom; and (*d*) an *impurity*, that is an atom of a different kind from those forming the bulk of the crystal.

The existence of imperfections such as those mentioned is important in various transport phenomena† in solids, in particular diffusion, electrolytic conduction, photoconductivity, and semiconductivity. It is outside the province of this book to discuss any of these phenomena. We shall confine ourselves to a discussion of the equilibrium numbers of several kinds of lattice imperfections.

The simplest system susceptible to lattice imperfections is a crystalline element, such as a pure metal, which may contain holes and interstitial atoms. Since an element is in no sense of the word a mixture, the discussion of this example is not in our field of study. We shall, however, consider imperfections in a binary salt such as NaCl or AgBr, not only because this is the simplest example of a system containing two kinds of atoms but also because imperfections in such a substance, especially AgBr, are in fact important in connexion with some of the transport phenomena mentioned above.

It is well known that the density and energy of formation of a salt such as NaCl can be quantitatively accounted for by regarding it as composed of Na^+ ions and Cl^- ions. Such a description of NaCl is accordingly useful and legitimate, but there is no ground for the opinion sometimes expressed that it is obligatory. We are equally at liberty to regard NaCl as built of atoms Na and Cl. In fact if one asks the question whether NaCl is composed of the ions Na^+ and Cl^- or of the

† For accounts of this field see Jost (1937), *Diffusion und chemische Reaktion in festen Stoffen*, Dresden; Mott and Gurney (1940), *Electronic Processes in Ionic Crystals*, Oxford University Press.

atoms Na and Cl the answer evidently depends on an arbitrary assignment of a geometrical boundary separating Na from Cl. For our present purpose it is convenient to describe the salt as composed of atoms.

6.02. Imperfections in a single salt

We consider a crystalline salt, such as AgBr, which for brevity we denote by AB . In principle it is possible in such a crystal to have two kinds of holes, namely on A sites and B sites; two kinds of interstitial atoms, namely A and B ; two kinds of wrong atoms, namely A atoms on B sites and B atoms on A sites. Actually wrong atoms do not occur to any detectable extent in salts and we shall not consider them here; they are important in the case where A , B denote two metal atoms such as Cu, Zn, but such systems will be described in Chapter VII. In many salts the atoms of one kind are much more firmly held to their lattice sites than those of the other kind, so that some kinds of imperfections are much rarer than others. For example in AgBr imperfections associated with bromine atoms or bromine sites are extremely infrequent compared with those associated with Ag atoms or Ag sites. If then for the sake of brevity and simplicity we restrict ourselves to the consideration of only holes on A sites and interstitial A atoms, we shall still be dealing with a typical real example.

We accordingly consider a crystal AB containing N sites of type B all occupied by B atoms and N sites of type A of which N_h are unoccupied (holes) while the remaining $N - N_h$ are occupied by A atoms. We denote the number of possible positions for interstitial A atoms by αN and the actual number of interstitial A atoms by N_i . In the case of a simple cubic lattice with alternate lattice sites of types A and B , the only likely place for an interstitial atom is in the middle of a cube formed by eight lattice sites. In this case $\alpha = 2$, but in more complicated lattices α may have some other value comparable to unity. We denote by χ_h the work required to remove an A atom from an A site inside the crystal, thereby creating a hole, and take it to rest at infinite distance from the crystal. We denote by χ_i the work required to remove an A atom from an interstitial position and take it to rest at infinite distance from the crystal. We denote by Q^0 the partition function for the perfect crystal having $N_h = 0$ and $N_i = 0$. We denote by q_A the contribution of each A atom to the partition function for the acoustic modes, and we assume as an approximation that q is the same for an interstitial atom as for an atom on a lattice site. As usual we denote the absolute activity of A by λ_A .

We now construct the semi-grand partition function as defined in § 2.09 in terms of the independent variables T, N_B, λ_A . When we take as energy zero of the atoms a state of rest at infinite separation, the semi-grand partition function has the form

$$\Xi(T, N_B, \lambda_A) = Q^0 \lambda_A^N \sum_{N_h, N_i} \frac{N!}{N_h!(N-N_h)!} \frac{(\alpha N)!}{N_i!(\alpha N - N_i)!} \times \\ \times (\lambda_A q_A)^{N_i - N_h} \exp\{-(N_h \chi_h - N_i \chi_i)/kT\}. \quad (6.02.1)$$

In this formula the first factor under the summation is the number of possible arrangements of N_h holes on the lattice; the next factor is the number of possible arrangements of N_i interstitial atoms; the next factor is a contribution from the extra number $N_i - N_h$ of A atoms above the number N in a perfect crystal. In the exponential factor $N_h \chi_h$ is the extra energy due to the N_h holes and $-N_i \chi_i$ the decrease of energy due to the interstitial A atoms, all relative to an energy zero of a state of rest at infinity.

As usual the equilibrium values of N_h, N_i are those in the maximum term of Ξ . They are therefore determined by

$$\frac{N_h}{N - N_h} = (\lambda_A q_A)^{-1} e^{-\chi_h/kT}, \quad (6.02.2)$$

$$\frac{N_i}{\alpha N - N_i} = \lambda_A q_A e^{\chi_i/kT}. \quad (6.02.3)$$

Since in practical applications N_h and N_i are extremely small compared with N , we may replace (2) and (3) by

$$N_h = N(\lambda_A q_A)^{-1} e^{-\chi_h/kT}, \quad (6.02.4)$$

$$N_i = \alpha N \lambda_A q_A e^{\chi_i/kT}. \quad (6.02.5)$$

If we multiply (4) by (5) we obtain

$$N_h N_i = \alpha N^2 e^{-(\chi_h - \chi_i)/kT} = \alpha N^2 e^{-w_i/kT}, \quad (6.02.6)$$

where w_i denotes the work required to move an A atom from an A site to an interstitial position. We can also write (6) as

$$N_h N_i = N_0^2, \quad (6.02.7)$$

where N_0 denotes the equilibrium value of N_h and of N_i in the special case when the number of A atoms is exactly equal to the number of B atoms. If we now denote the number of A atoms by $N + \Delta N$, where ΔN may be positive or negative, we have

$$N_i - N_h = \Delta N. \quad (6.02.8)$$

Solving (7) and (8) we find

$$N_h = \{N_0 + (\frac{1}{2}\Delta N)^2\}^{\frac{1}{2}} - \frac{1}{2}\Delta N, \quad (6.02.9)$$

$$N_i = \{N_0 + (\frac{1}{2}\Delta N)^2\}^{\frac{1}{2}} + \frac{1}{2}\Delta N. \quad (6.02.10)$$

Formulae (9) and (10) tell us how the numbers of holes and of interstitial atoms are related to the excess of *A* atoms over *B* atoms.

In principle there is no difficulty in extending the above kind of treatment to the more general case where both *A* and *B* sites can be empty and both *A* and *B* atoms can occupy interstitial positions. We have only to construct the grand partition function $\Xi(T, \lambda_A, \lambda_B)$ which with an obvious extension of notation has the form

$$\begin{aligned} \Xi(T, \lambda_A, \lambda_B) = Q^0(\lambda_A \lambda_B)^N \sum_{N_{Ah}, N_{Bh}, N_{Ai}, N_{Bi}} & \frac{N!}{N_{Ah}!(N-N_{Ah})!} \frac{N!}{N_{Bh}!(N-N_{Bh})!} \times \\ & \times \frac{(\alpha N)!}{N_{Ai}! N_{Bi}! (\alpha N - N_{Ai} - N_{Bi})!} (\lambda_A q_A)^{N_{Ai}-N_{Ah}} (\lambda_B q_B)^{N_{Bi}-N_{Bh}} \times \\ & \times \exp\{(-N_{Ah} \chi_{Ah} - N_{Bh} \chi_{Bh} + N_{Ai} \chi_{Ai} + N_{Bi} \chi_{Bi})/kT\}, \end{aligned} \quad (6.02.11)$$

where Q^0 denotes the partition function for a perfect crystal having $2N$ sites, N of each kind. The equilibrium values of N_{Ah} , N_{Bh} , N_{Ai} , N_{Bi} are obtained by selecting the maximum term in the quadruple summation. We leave it to the interested reader to complete the details.

6.03. Impurities

We turn now to a brief study of a crystal assumed to be without imperfections, except for containing small quantities of foreign atoms as impurities. We consider the simplest case of a crystal composed of atoms *A* containing a small number of atoms *B* as an impurity. These *B* atoms may be situated either on a lattice site, so displacing *A* atoms, or in interstitial positions. We denote the total number of sites by N and the total number of interstitial positions by αN , where α is either one or some simple rational number comparable to one. We denote the number of *B* atoms on lattice sites by N_w and the number in interstitial positions by N_i . We refer all energies to the energy zero of infinite separation of the atoms. We denote by χ_{Ah} the work required to remove an *A* atom from an *A* site inside the crystal, thereby creating a hole, and to take it to rest at infinite distance from the crystal. We denote by χ_{Bh} the work required to remove a *B* atom from an *A* site inside the crystal, thereby creating a hole, and to take it to rest at infinite distance from the crystal. We denote by χ_{Bi} the work required to remove a *B* atom from an interstitial position and take it to rest at infinite

distance from the crystal. We denote by Q^0 the partition function for the perfect crystal having $N_w = 0$ and $N_i = 0$. We denote by q_A and q_B the contributions of each A and B atom respectively to the acoustic modes; we assume as usual that q_A, q_B may be taken to be independent of N_w, N_i .

We now construct the grand partition function $\Xi(T, \lambda_A, \lambda_B)$ having the form

$$\begin{aligned} \Xi(T, \lambda_A, \lambda_B) = Q^0 \lambda_A^N \sum_{N_w, N_i} & \frac{N!}{N_w!(N-N_w)!} \frac{(\alpha N)!}{N_i!(\alpha N-N_i)!} \times \\ & \times (\lambda_A q_A)^{-N_w} (\lambda_B q_B)^{N_w+N_i} \exp\{(-N_w \chi_{Ah} + N_w \chi_{Bh} + N_i \chi_{Bi})/kT\}. \end{aligned} \quad (6.03.1)$$

Formula (1) can be transformed by using the following properties of the perfect pure crystal of A . The free energy F_A per atom of A in the pure crystal has the form

$$F_A = -\chi_A - kT \ln q_A, \quad (6.03.2)$$

where $N\chi_A$ denotes the energy required to separate the crystal of N atoms in its lowest quantal state into N separate A atoms at rest at infinity. In so far as we may neglect interactions between all pairs of atoms other than nearest neighbours $\chi_A = \frac{1}{2}\chi_{Ah}$, but we shall not use this relation. As usual, for a non-gaseous phase ignoring the distinction between F and G , we may replace (2) by

$$\mu_A = kT \ln \lambda_A = -\chi_A - kT \ln q_A, \quad (6.03.3)$$

whence

$$\lambda_A q_A = e^{-\chi_A/kT}. \quad (6.03.4)$$

Using (4) in (1) we obtain

$$\begin{aligned} \Xi(T, \lambda_A, \lambda_B) = Q^0 \lambda_A^N \sum_{N_w, N_i} & \frac{N!}{N_w!(N-N_w)!} \frac{(\alpha N)!}{N_i!(\alpha N-N_i)!} \times \\ & \times (\lambda_B q_B)^{N_w+N_i} \exp\{(N_w \chi_A - N_w \chi_{Ah} + N_w \chi_{Bh} + N_i \chi_{Bi})/kT\}. \end{aligned} \quad (6.03.5)$$

The equilibrium values of N_w, N_i are then determined by the maximum term of the double sum. We find

$$\frac{N_w}{N-N_w} = \lambda_B q_B e^{(\chi_{Bh}-\chi_{Ah}+\chi_A)/kT}, \quad (6.03.6)$$

$$\frac{N_i}{\alpha N-N_i} = \lambda_B q_B e^{\chi_{Bh}/kT}. \quad (6.03.7)$$

We note that the quantity $\chi_{Bh}-\chi_{Ah}+\chi_A$ occurring in the exponent of (6) is the energy required to remove to infinity an atom B from a lattice site and to 'seal' the hole by rearrangement of the remaining atoms.

Since N_u , N_i are always much smaller than N , we may replace (6) and (7) by

$$\frac{N_w}{N} = \lambda_B q_B e^{(\chi_{Bh} - \chi_{Bi} + \chi_A)/kT}, \quad (6.03.8)$$

$$\frac{N_i}{\alpha N} = \lambda_B q_B e^{\chi_{Bi}/kT}. \quad (6.03.9)$$

We may regard (8) and (9) as determining N_w , N_i in terms of λ_B or conversely as means of calculating λ_B from N_w or N_i . We may describe the crystal as supersaturated, saturated, or unsaturated with respect to a phase of pure B according as λ_B is greater than, equal to, or less than its value in the pure phase of B .

From (8) and (9) we deduce for the ratio of N_i to N_w

$$\frac{N_i}{N_w} = \alpha e^{(\chi_{Bi} - \chi_{Bh} + \chi_{Ah} - \chi_A)/kT}. \quad (6.03.10)$$

We note that the quantity $\chi_{Bi} - \chi_{Bh} + \chi_{Ah} - \chi_A$ occurring in the exponent in (10) is equal to the energy required to create a hole by moving an A atom to the surface of the crystal and moving an impurity atom B into the hole from an interstitial position.

VII

SUPERLATTICE

7.01. Qualitative description

We have studied in Chapter IV the phenomenon of critical mixing. We saw that when the mixing of two kinds of molecules *A* and *B* is *endothermic* (*w* positive) they can mix in all proportions only at temperatures above a critical temperature T_c . Below the temperature T_c the mutual solubility of the two kinds of molecules is limited and it decreases as the temperature decreases, eventually approaching complete mutual insolubility at very low temperatures. This is due to the tendency to avoid the formation of *AB* pairs: a tendency which becomes stronger as w/kT increases. In this chapter we shall study the converse situation when the mixing of *A* and *B* atoms is *exothermic*. As the temperature decreases we may expect an increasingly strong tendency to form *AB* pairs. At low temperatures this tendency may be so strong as to suggest the formation of a chemical compound *AB*, at least in the particular case of equal numbers of *A* and *B* atoms. We shall not discuss the general phenomenon of the formation of exothermic molecular compounds at low temperatures. This subject is of considerable interest to chemists, but too complicated to be amenable to a general quantitative theory. We shall confine ourselves primarily to the simplest possible case of a system containing equal numbers of two kinds of atoms *A* and *B* assumed to be sufficiently similar in size to be interchangeable on a crystal lattice. In the limit of high temperatures we know that the two kinds of atoms will be arranged nearly at random, forming a regular solution. In the limit of low temperatures we may expect the *A* and *B* atoms to alternate on the lattice. It is entirely a matter of convention whether or not we call such a structure a chemical compound *AB*. The subject of this chapter is the investigation of the change, as the temperature is decreased, from the disordered mixture of *A* and *B* atoms at high temperatures to the completely ordered arrangement of alternating *A* and *B* atoms at low temperatures.

It will have been noticed that we have spoken of *A* and *B* atoms rather than molecules. This is because the formation of the ordered structure requires great similarity in both size and shape of the two species *A* and *B*. The only important case where this condition is fulfilled in practice is for a mixture of two kinds of metallic atoms. The best studied example is the mixture of equal or nearly equal

numbers of copper and zinc atoms, this mixture being known as β -brass.

Before passing to the discussion of the equilibrium conditions for the phenomena in question, we may mention briefly one of several methods by which the ordered structure can be distinguished from the disordered, namely the study of reflection of X-rays. In the state of complete disorder all lattice sites concerned are occupied at random by either of the two kinds of atoms and the crystal reflects X-rays just as if all were occupied in the same average manner. The X-ray photograph shows all sites to be equivalent. But in the ordered or partially ordered state one set of sites is occupied predominantly by *A* atoms and the other set by *B* atoms, scattering the X-rays differently. Consequently, the X-rays distinguish between the two sorts of sites and new X-ray reflections appear because, when lattice sites previously identical become different, the average crystal pattern no longer repeats so frequently. Thus a lattice of larger spacing (*superlattice*) is formed, and the new X-ray reflections correspondingly are called *superlattice lines*.†

It should be fairly obvious that the formation of a superlattice is possible only in a true crystal. No analogous phenomenon can occur in a liquid. We have previously made considerable use of the quasi-crystalline model for a liquid, and indeed this was justifiable as long as we were concerned only with the short range interactions between closest neighbours. The formation of a superlattice, however, implies a regular alternation of sites extending right across the crystal. Such an alternation is ruled out by the disordered structure of a liquid. This chapter is accordingly devoted to crystalline binary alloys of simple composition, in particular β -brass.

It is not an essential condition for the formation of a superlattice that the ratio of the numbers of atoms of the two kinds should be one to one. Other simple ratios are possible. For example copper and gold form a superlattice having a ratio of three copper atoms to one gold atom. This example will be discussed at the end of the chapter. Initially we shall confine ourselves to the simplest case where the ratio of the two kinds of atoms is one to one.

As we have already emphasized, superlattice formation occurs only when the mixing energy *w* is negative. Instead of this negative quantity it will be convenient to use an energy of separation $w_s = -w$. We recall

† A useful review of all aspects of superlattices is given by Nix and Shockley (1938), *Rev. Mod. Phys.* 10, 1.

that in Chapter IV we used η as an abbreviation for $e^{w_{jk}kT}$. We shall again have occasion to use this same abbreviation, which in our new notation denotes $e^{-w_{jk}kT}$.

7.02. Classification of configurations

We consider a lattice of $2N$ sites which we regard as two interpenetrating lattices each of N sites denoted by a and b respectively. We restrict ourselves to structures such that every a site has z closest neighbours all b sites, and that every b site has z closest neighbours all a sites. We may illustrate such arrangements by mentioning some familiar crystal structures. In CsCl the Cs atoms form a simple cubic lattice and the Cl atoms form another simple cubic lattice. These two simple cubic lattices interpenetrate in such a way that each Cs atom is surrounded by 8 Cl atoms and each Cl atom by 8 Cs atoms. Thus in this case $z = 8$. Incidentally the two lattices together form a body-centred cubic lattice. In NaCl the Na atoms form a face-centred cubic lattice and the Cl atoms form a face-centred cubic lattice. These two face-centred cubic lattices interpenetrate in such a way that each Na atom is surrounded by 6 Cl atoms and each Cl atom by 6 Na atoms. Thus in this case $z = 6$. Incidentally the two lattices together form a simple cubic lattice. In ZnS the Zn atoms form a face-centred cubic lattice and the S atoms another face-centred cubic lattice. These two face-centred cubic lattices interpenetrate in such a way that each Zn atom is surrounded by 4 S atoms and each S atom by 4 Zn atoms. Thus in this case $z = 4$.

The structure of the completely ordered crystal of CuZn, called β -brass, is actually analogous to that of CsCl so that for β -brass $z = 8$.

We now consider the arrangement of N atoms A and N atoms B on the lattice. Let us denote the number of A atoms on a sites by Nr . Then the remaining $N(1-r)$ atoms A will be on b sites. It follows immediately that the number of B atoms on b sites is Nr and on a sites is $N(1-r)$. We may without loss of generality define the lattice of a sites as the one containing not fewer atoms A than the other lattice. With this convention $r \geq \frac{1}{2}$.

The state of complete randomness is characterized by $r = \frac{1}{2}$ and the state of complete order by $r = 1$.

We now consider the numbers of pairs of neighbouring sites occupied in the four possible ways. We denote the number of pairs of neighbouring sites both occupied by A atoms by $zN\xi$. Since the total number of A atoms on a sites is Nr and each has z neighbours, it follows that

the number of pairs of sites such that the a site is occupied by an A and the b site by a B must be $zN(r-\xi)$. Similarly, since the total number of A atoms on b sites is $N(1-r)$ and each has z neighbours, it follows that the number of pairs of sites such that the a site is occupied by a B atom and the b site by an A atom must be $zN(1-r-\xi)$. Finally, since the total number of pairs of sites is zN , the number of pairs of sites both occupied by B atoms must be $zN\xi$. We can accordingly construct Table 7.1.

TABLE 7.1

Distribution of N Atoms A and N Atoms B on Pairs of Neighbouring Sites, one a and one b

A on a , B on b :	$zN(r-\xi)$	B on a , A on b :	$zN(1-r-\xi)$
A on a , A on b :	$zN\xi$	B on a , B on b :	$zN\xi$

We shall denote the number of configurations of given N , r , ξ by $g(N, r, \xi)$.

7.03. Configurational energy

As explained in § 2.05, we continue to assume as an approximation that the configurational and acoustic energies are independent. We accordingly need consider only the configurational energy. We assume as in Chapters III and IV that the configurational energy may be expressed as a sum of contributions from pairs of neighbouring atoms. We continue to denote such contributions from each AA and BB pair by $-2\chi_A/z$ and $-2\chi_B/z$ respectively. We shall denote the contribution of each AB pair by $(-\chi_A - \chi_B - w_s)/z$ so that w_s is the same as the quantity previously denoted by $-w$. We shall be concerned only with positive values of w_s .

Using these definitions and Table 7.1 we now construct Table 7.2 showing the contributions of the several kinds of pairs to the configurational energy E_c .

TABLE 7.2

Contributions of Several Kinds of Pairs to the Configurational Energy

A on a , B on b :	$N(r-\xi)(-\chi_A - \chi_B - w_s)$
A on a , A on b :	$-N\xi^2\chi_A$
B on a , A on b :	$N(1-r-\xi)(-\chi_A - \chi_B - w_s)$
B on a , B on b :	$-N\xi^2\chi_B$
All	$N(-\chi_A - \chi_B - w_s) + 2N\xi w_s$

Part of our problem is to determine, either accurately or approximately, the average or equilibrium value ξ of ξ . The equilibrium value of the configurational energy is then given by

$$U_c = \bar{E}_c = N(-\chi_A - \chi_B - w_s) + 2N\xi w_s, \quad (7.03.1)$$

where we assume that w_s is independent of temperature.

7.04. Determination of equilibrium properties

All relevant equilibrium properties are determined by the configurational partition function

$$\Omega = \sum_{r,\xi} g(N, r, \xi) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\xi w_s\}/kT]. \quad (7.04.1)$$

To make progress we group together all states having the same value of r and write

$$\Omega = \sum_r \Omega_r, \quad (7.04.2)$$

$$\Omega_r = \sum_\xi g(N, r, \xi) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\xi w_s\}/kT]. \quad (7.04.3)$$

As in other similar cases we may for the purpose of constructing thermodynamic functions replace Ω by its maximum term in (2). When we use this procedure the problem of determining the equilibrium properties has two stages, namely:

- (a) to evaluate Ω_r and so the free energy for arbitrary r ;
- (b) to find the value of r which maximizes Ω_r or minimizes the free energy.

We shall for stage (b) use straightforward classical thermodynamics. We have first to solve accurately or approximately the problem of stage (a).

We now consider the evaluation of (3). We denote by $g(N, r)$ the total number of configurations of given N, r regardless of ξ , so that by definition

$$g(N, r) = \sum_\xi g(N, r, \xi). \quad (7.04.4)$$

Then $g(N, r)$ is the product of the number of ways of dividing the N sites a into two groups of Nr occupied by A atoms and $N(1-r)$ by B atoms and the number of ways of dividing the N sites b into two groups of Nr occupied by B and $N(1-r)$ occupied by A atoms. Consequently

$$g(N, r) = \left[\frac{N!}{\{Nr\}! \{N(1-r)\}!} \right]^2, \quad (7.04.5)$$

or, by use of Stirling's theorem,

$$\ln g(N, r) = -2N\{r \ln r + (1-r) \ln (1-r)\}. \quad (7.04.6)$$

We may note in passing that when $r = \frac{1}{2}$, (5) becomes for large N

$$g(N, \frac{1}{2}) = \left[\frac{N!}{(\frac{1}{2}N)! (\frac{1}{2}N)!} \right]^2 \simeq \frac{(2N)!}{N! N!} = \sum_r g(N, r). \quad (7.04.7)$$

This means that the total number of configurations when half the A atoms are on the a lattice and half on the b lattice is not significantly different from the total number of configurations when we no longer distinguish between the a and b lattices. In other words, when $r = \frac{1}{2}$ the system becomes a regular mixture with equal numbers of the two kinds of atoms.

We now introduce a formalism resembling that used in § 4.04 for regular mixtures. We define $\bar{\xi}$ by the relation

$$\begin{aligned}\Omega_r &= \sum_{\bar{\xi}} g(N, r, \xi) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\xi w_s\}/kT] \\ &= g(N, r) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\bar{\xi} w_s\}/kT].\end{aligned}\quad (7.04.8)$$

It follows immediately that the configurational free energy F_c is, in this notation,

$$F_c = -N(\chi_A + \chi_B + w_s) - kT \ln g(N, r) + 2N\bar{\xi} w_s,\quad (7.04.9)$$

or, when we use (6),

$$F_c = -N(\chi_A + \chi_B + w_s) + 2NkT\{r \ln r + (1-r) \ln(1-r)\} + 2N\bar{\xi} w_s.\quad (7.04.10)$$

The configurational total energy U_c is then given by

$$U_c = F_c - T \frac{\partial F_c}{\partial T} = -N(\chi_A + \chi_B + w_s) + 2N\left(\bar{\xi} - T \frac{\partial \bar{\xi}}{\partial T}\right)w_s.\quad (7.04.11)$$

Comparison of (11) with (7.03.1) shows that $\bar{\xi}$ is related to ξ by

$$\begin{aligned}\xi &= \bar{\xi} - T \frac{\partial \bar{\xi}}{\partial T}, \\ \text{or} \quad \bar{\xi} &= T \int_0^{1/T} \xi d\left(\frac{1}{T}\right),\end{aligned}\quad (7.04.12)$$

the lower limit of integration being determined by the condition that as $w_s/kT \rightarrow 0$ the formulae should approach those corresponding to complete randomness, that is to say those for an ideal mixture.

We have by no means solved the problem of determining the equilibrium properties. We have merely translated it into the problem of evaluating ξ or $\bar{\xi}$ in terms of r .

7.05. Crude treatment (zeroth approximation)

We begin by describing the most crude treatment of the problem because this treatment, which we call the zeroth approximation, has been much used† and is a useful approximation to the more refined

† Gorsky (1928), *Z. Phys.* **50**, 64. Bragg and Williams (1934), *Proc. Roy. Soc. A* **145**, 699; (1935), **151**, 540.

treatment, which we call the first approximation, described in later sections.

The zeroth approximation is the analogue of the zeroth approximation in the treatment of regular solutions. This approximation consists in replacing ξ for each configuration of given r by the simple (unweighted) average ξ_{Av} for all states of given r . Since for given r this ξ_{Av} is independent of the temperature, we have according to this approximation

$$\bar{\xi} = \xi = \xi_{Av}. \quad (7.05.1)$$

This approximation is equivalent to assuming a purely random arrangement of the Nr atoms A and $N(1-r)$ atoms B on the lattice a and a purely random arrangement of the Nr atoms B and $N(1-r)$ atoms A on the lattice b . Such a random arrangement will contain numbers of pairs of sites occupied in the four possible ways as shown in Table 7.3.

TABLE 7.3

Random Distribution of Nr Atoms A and $N(1-r)$ Atoms B on the a Lattice together with Nr Atoms B and $N(1-r)$ Atoms A on the b Lattice

A on a , B on b :	zNr^2	B on a , A on b :	$zN(1-r)^2$
A on a , A on b :	$zNr(1-r)$	B on a , B on b :	$zNr(1-r)$

By comparison of Tables 7.3 and 7.1 we see that

$$\xi_{Av} = r(1-r). \quad (7.05.2)$$

Substituting (1) and (2) into (7.04.10) we obtain as the zeroth approximation to the configurational free energy for a given r

$$F_c = -N(\chi_A + \chi_B + w_s) + 2NkT\{r \ln r + (1-r) \ln (1-r)\} + 2Nr(1-r)w_s. \quad (7.05.3)$$

It will be found convenient to rewrite (3) in the form

$$\frac{F_c(r) - F_c(\frac{1}{2})}{2NkT} = r \ln r + (1-r) \ln (1-r) + \ln 2 - (r - \frac{1}{2})^2 \frac{w_s}{kT}. \quad (7.05.4)$$

7.06. Equilibrium state

As explained in § 7.04, the equilibrium value of r is the value which minimizes the configurational free energy. Using the zeroth approximation (7.05.3) for F_c , we have

$$\frac{\partial F_c}{\partial r} = 2NkT \ln \frac{r}{1-r} + 2N(1-2r)w_s. \quad (7.06.1)$$

The equilibrium value of r must therefore satisfy the condition

$$\frac{1}{2r-1} \ln \frac{r}{1-r} = \frac{w_s}{kT}. \quad (7.06.2)$$

For all values of w_s/kT one solution of (2) is $r = \frac{1}{2}$. It is, however, necessary to explore whether this is the only real solution and also whether this solution gives a minimum or a maximum. This is readily investigated by plotting the expression in (7.05.4) against r for various values of w_s/kT as in Fig. 7.1. This shows that for small values of w_s/kT , that is high temperatures, the root $r = \frac{1}{2}$ is the only root and it corresponds to a minimum of $F_c(r)$. There is then no distinction

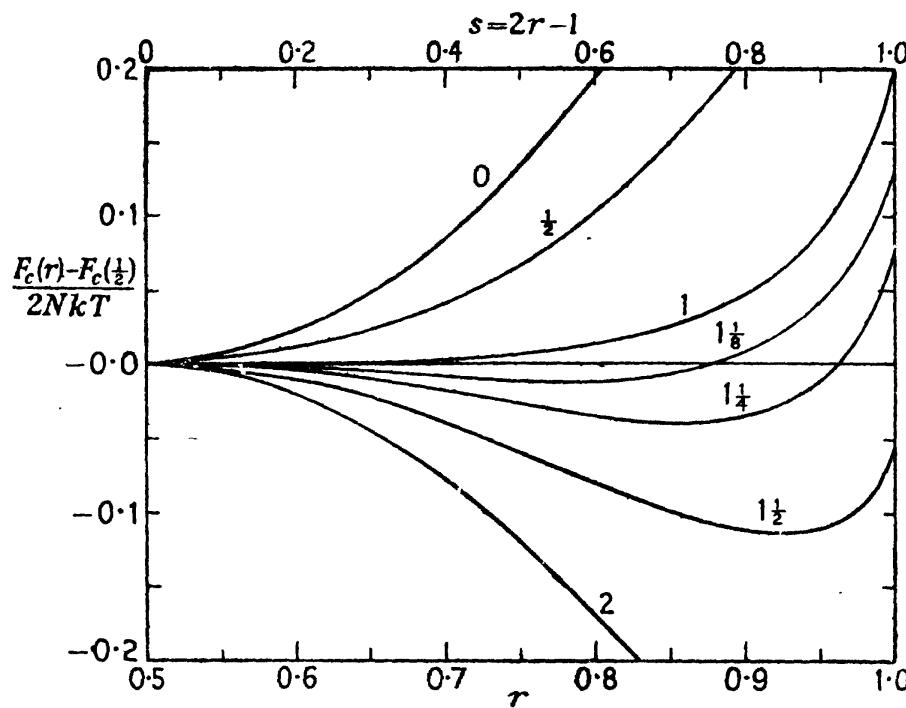


FIG. 7.1. Dependence of the configurational free energy $F_c(r)$ on r , and on the degree of order $s = 2r - 1$, for alloy of composition AB according to the zeroth approximation at various temperatures. The numbers attached to the curves are values of $\frac{1}{2}w_s/kT = T_\lambda/T$.

- between the a and b lattices and so the alloy behaves as a regular mixture. At low enough temperatures, that is large values of w/kT , there is another root $\frac{1}{2} \leq r \leq 1$ and this root corresponds to a minimum of $F_c(r)$ while the root $r = \frac{1}{2}$ now corresponds to a maximum. There exists a temperature T_λ such that at temperatures below T_λ the equilibrium value of r is greater than $\frac{1}{2}$ and increases as the temperature decreases. The equilibrium value of r becomes $\frac{1}{2}$ at the temperature T_λ and remains $\frac{1}{2}$ at all higher temperatures. For reasons given later this temperature is called a *lambda point*. It is also sometimes called a Curie point owing to its similarity to the ferromagnetic Curie point discovered by Curie.

7.07. Lambda point

By definition the lambda point is the temperature at which the maximum in $F_c(r)$ at $r = \frac{1}{2}$ changes into a minimum. In other words, it is the temperature at which $F_c(r)$ has a point of horizontal inflection at $r = \frac{1}{2}$. Consequently T_λ is determined by

$$r = \frac{1}{2}, \quad \partial F_c / \partial r = 0, \quad \partial^2 F_c / \partial r^2 = 0. \quad (7.07.1)$$

Differentiating formula (7.06.1) with respect to r , we obtain

$$\frac{\partial^2 F_c}{\partial r^2} = \frac{2NkT}{r(1-r)} - 4Nw_s. \quad (7.07.2)$$

Using (2) in (1) we obtain for the lambda point

$$kT_\lambda = \frac{1}{2}w_s. \quad (7.07.3)$$

7.08. Degree of order

In virtue of (7.07.3) we can rewrite (7.06.2) as

$$\frac{T_\lambda}{T} = \frac{1}{2(2r-1)} \ln \frac{r}{1-r}. \quad (7.08.1)$$

Although we cannot express r as an explicit function of T , we can by means of (1) calculate at what temperature r has any equilibrium value between $\frac{1}{2}$ and 1. We thus have a numerical relation between T and the equilibrium value of r which is shown as curve *A* in Fig. 7.2. At each temperature the equilibrium value of r determines the free energy according to (7.05.4) and thence all other thermodynamic properties. Before proceeding further we shall, however, make some remarks concerning nomenclature and notation.

The fundamental formula (7.06.2) which determines the equilibrium value of r is due to Gorsky,[†] who called r the *degree of order*. Gorsky's treatment was extended by Bragg and Williams[‡] to alloys in which the ratio of *A* atoms to *B* atoms differed somewhat from the ideal ratio one to one. We shall not here pursue this extension of the theory. At the same time Bragg and Williams considered it desirable that the *degree of order* should be so defined as to have the value zero when the lattices *a* and *b* become indistinguishable and the value unity when all the *A* atoms are on the *a* lattice. With this object Bragg and Williams redefined the *degree of order* as a quantity s related to r by

$$r = \frac{1}{2}(1+s), \quad s = 2r-1. \quad (7.08.2)$$

[†] Gorsky (1928), *Z. Phys.* **50**, 64, formula (11).

[‡] Bragg and Williams (1934), *Proc. Roy. Soc. A* **145**, 699; (1935), **151**, 540.

This definition of degree of order is now generally accepted and we shall therefore use it.

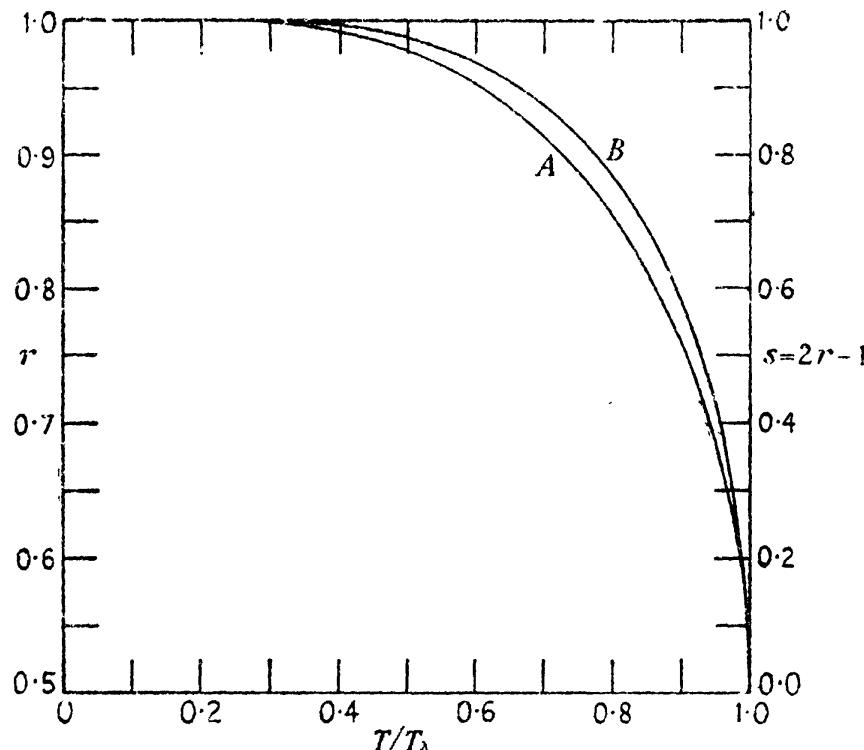


FIG. 7.2. Equilibrium degree of order as function of temperature for alloy of composition AB . Curve A: zeroth approximation. Curve B: first approximation, $z = 8$.

This quantity $s = 2r - 1$ is not the only one having a value zero at the lambda point and increasing towards unity at low temperatures. Another quantity which obviously shares this property is $s^2 = (2r - 1)^2$. We may mention in passing that Borelius† used the name *degree of disorder* for the quantity $1 - s^2 = 4r(1 - r)$. Since the definition of Bragg and Williams is the best known, we follow them in using the name *degree of order* for s defined by (2).

Substituting (2) into (1) we obtain

$$\frac{T_\lambda}{T} = \frac{1}{2s} \ln \frac{1+s}{1-s}, \quad (7.08.3)$$

which can be written in the more convenient form

$$\frac{T_\lambda}{T} = \frac{\tanh^{-1}s}{s}. \quad (7.08.4)$$

7.09. Total energy

Using the zeroth approximation for ξ , namely (7.05.2) in (7.03.1), we have

$$U_c = N(-\chi_A - \chi_B - w_s) + 2Nr(1-r)w_s, \quad (7.09.1)$$

† Borelius (1934), *Ann. d. Phys.* 20, 57.

which could equally well be obtained from (7.05.3) with

$$U_c = F_c - T \frac{dF_c}{dT}. \quad (7.09.2)$$

Using the substitution (7.08.2) in (1) we have

$$U_c = N(-\chi_A - \chi_B - w_s) + \frac{1}{2}N(1-s^2)w_s. \quad (7.09.3)$$

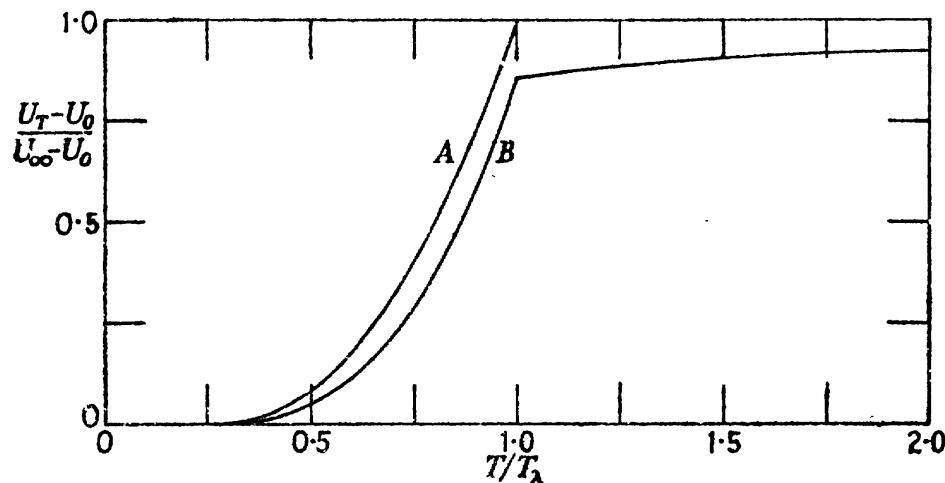


FIG. 7.3. Equilibrium configurational energy as function of temperature for alloy of composition AB. Curve A: zeroth approximation. Curve B: first approximation, $z = 8$.

It is convenient to rewrite (3) as

$$U(s) - U(1) = \frac{1}{2}N(1-s^2)w_s, \quad (7.09.4)$$

or as

$$\frac{U(s) - U(1)}{U(\infty) - U(1)} = 1 - s^2. \quad (7.09.5)$$

Formulae (5) and (7.08.4) together completely determine the dependence of the configurational energy on the temperature, when the temperature is less than T_λ . At temperatures above T_λ the configurational energy has the constant value corresponding to $s = 0$. Formula (5) can be rewritten using subscripts to denote the temperature

$$\frac{U_T - U_0}{U_\infty - U_0} = 1 - s^2(T) \quad (7.09.6)$$

with s determined by (7.08.4). Fig. 7.3 shows the quantity (6) plotted against T/T_λ as the curve marked A. The other curve, marked B, is obtained by a better approximation to be described later.

7.10. Correlation between superlattices and regular mixtures

We observe the formal resemblance between formula (7.06.2) determining the equilibrium value of r for a given temperature T below T_λ and formula (4.07.3) determining the mole fractions x and $1-x$ of the

two coexisting regular solutions at a given temperature T below T_c . We also notice the formal resemblance between formula (7.07.3) determining the lambda point and formula (4.08.10) determining the temperature of critical mixing T_c . Such formal resemblance not only exists in the zeroth approximation but persists at every degree of accuracy, being inherent in the nature of the two classes of system. We now give a general explanation of this resemblance.

We continue to consider two interpenetrating sub-lattices a and b such that each a site has z closest neighbours all b sites and each b site has z closest neighbours all a sites. We consider, however, a more general distribution of A and B atoms over the N sites a and N sites b , namely that shown in Table 7.4. For the moment we regard the two fractions θ and θ' as independent. The following argument is simplified without affecting the conclusion, by a particular choice of new energy zeros for A and B atoms. We accordingly define these such that the energy of a pure phase of N atoms of A is $-\frac{1}{2}Nw$ and the energy of a pure phase of N atoms of B is also $-\frac{1}{2}Nw$. The energy of a perfectly ordered phase of N atoms A and N atoms B is then $\frac{1}{2}Nw = -\frac{1}{2}Nw_s$.

TABLE 7.4

Distribution of A and B Atoms over 2N Sites

A on a : $N\theta$	A on b : $N\theta'$
B on a : $N(1-\theta)$	B on b : $N(1-\theta')$

Consider now what happens if we change every A atom on the b lattice into a B atom and every B atom on the b lattice into an A atom, without altering the composition of the a lattice. That is to say, interchange θ' and $1-\theta'$ without altering θ . For any chosen configuration the potential energy, relative to the chosen zeros, becomes changed in sign but not in magnitude. In other words, w has to be changed to w_s or conversely. Moreover, the new number of configurations with an energy W will be equal to the previous number of configurations with an energy $-W$. The effect on the configurational partition function is expressed by

$$\Omega(N, \theta, \theta', w) = \Omega(N, \theta, 1-\theta', w_s). \quad (7.10.1)$$

Likewise the effect on the configurational free energy F_c , with the chosen convention relating to energy zeros, is expressed by

$$F_c(N, \theta, \theta', w) = F_c(N, \theta, 1-\theta', w_s). \quad (7.10.2)$$

Thus far we have treated θ , θ' as independent fractions. We now investigate the two special cases $\theta' = \theta$ and $\theta' = 1-\theta$. When $\theta = \theta'$

there are equal numbers of A atoms on each sub-lattice and consequently equal numbers of B atoms on each sub-lattice. The two sub-lattices are indistinguishable as regards manner of occupation, and as already explained in § 7.04 the system has degenerated to a regular mixture with $x = 1 - \theta$. On the other hand, when $\theta' = 1 - \theta$, the numbers of A atoms on the two sub-lattices are not equal, but the total number of A atoms is N and the total number of B atoms is likewise N . We have then precisely the kind of system which we have been discussing in this chapter with $r = \theta$. It follows from (2) that the configurational free energy of a superlattice, having equal numbers of atoms of the two kinds, depends on r, w_s in precisely the same manner as the configurational free energy of a regular mixture depends on x, w .

To prevent confusion we may mention that in discussing regular mixtures in Chapter IV we considered altogether N sites whereas in discussing superlattices here we consider altogether $2N$ sites. This difference in the treatment in no way affects the above argument. We saw in § 4.07 that the condition for the mutual equilibrium of two phases is

$$\partial F_c / \partial x = 0 \quad (x \neq \frac{1}{2}), \quad (7.10.3)$$

while in § 7.04 we saw that the equilibrium value of r in a superlattice is determined by

$$\partial F_c / \partial r = 0 \quad (r \neq \frac{1}{2}). \quad (7.10.4)$$

From the preceding argument it follows that the equilibrium value of r will be related to w_s/kT in the same manner as x , for one of the coexisting phases, is related to w/kT . This mathematical resemblance can be given the following physical interpretation. Consider an alloy containing equal numbers of A and B atoms initially at a temperature above T_λ and suppose it to be cooled to a temperature below T_λ . We know that the atoms will rearrange themselves into a state determined by the equilibrium value of r at the particular temperature. There will then be a fraction r of A atoms on the a lattice and a fraction $1-r$ on the b lattice. Alternatively there might be a fraction r of A atoms on the b lattice and a fraction $1-r$ on the a lattice. The difference is of course physically non-significant. There is a third manner of describing the situation, whose difference is also physically non-significant, but which brings to light the analogy with a regular mixture. Let us artificially impose the condition that as the alloy is cooled atoms may rearrange themselves on either sub-lattice but may not move from one sub-lattice to the other. The alloy can still preserve equilibrium by splitting into two equal parts one having a fraction r of A atoms

on the a sub-lattice and the other having a fraction r of A atoms on the b sub-lattice. This interpretation of the appearance of order is the analogue of the splitting of a regular mixture into two phases with mole fractions x and $1-x$ of B molecules.

At each temperature below the lambda point the equation $\partial F_c / \partial r = 0$ has three real roots, one giving an equilibrium value of r , another giving the physically indistinguishable value $1-r$, and the third lying at $r = \frac{1}{2}$. The lambda point is the temperature at which these three roots coincide; it is therefore determined by

$$\frac{\partial F_c}{\partial r} = 0, \quad \frac{\partial^2 F_c}{\partial r^2} = 0, \quad \frac{\partial^3 F_c}{\partial r^3} = 0 \quad (r = \frac{1}{2}). \quad (7.10.5)$$

These are precisely analogous to the conditions for critical mixing, namely

$$\frac{\partial F_c}{\partial x} = 0, \quad \frac{\partial^2 F_c}{\partial x^2} = 0, \quad \frac{\partial^3 F_c}{\partial x^3} = 0 \quad (x = \frac{1}{2}). \quad (7.10.6)$$

Now that we have a clear picture of the close resemblance between the equilibrium conditions for superlattices on the one hand and regular mixtures on the other, we can readily transcribe formulae derived for one kind of system into formulae appropriate to the other kind. We thereby save considerable repetition. We shall now transcribe two of the treatments of regular mixtures, namely the quasi-chemical treatment or first approximation and the expansion in powers of w/kT .

7.11. First approximation. Combinatory formula

We now construct† an approximate formula for $g(N, r, \xi)$ defined in § 7.02 using reasoning precisely analogous to that used in § 4.14 to obtain an approximate formula for $g(N_A, N_B, X)$. We call this the first approximation. If there were no mutual interference between the various types of pairs of nearest neighbours the number of configurations of specified N, r, ξ would, according to Table 7.1, be

$$\frac{\{zN\}!}{\{zN(r-\xi)\}! \{zN\xi\}! \{zN\xi\}! \{zN(1-r-\xi)\}!}. \quad (7.11.1)$$

This expression when summed over all values of ξ would not lead to the correct value given by (7.04.5), namely

$$\sum_{\xi} g(N, r, \xi) = g(N, r) = \left[\frac{N!}{\{Nr\}! \{N(1-r)\}!} \right]^2. \quad (7.11.2)$$

† Fowler and Guggenheim (1940), *Proc. Roy. Soc. A* 174, 189.

We remove this defect, as described in § 4.14, by inserting the appropriate normalizing factor. By this procedure we are led to the approximate combinatory formula

$$g(N, r, \xi) = \left[\frac{N!}{\{Nr\}! \{N(1-r)\}!} \right]^2 \times \\ \times \frac{\{zN(r-\xi^*)\}! \{zN\xi^*\}! \{zN\xi^*\}! \{zN(1-r-\xi^*)\}!}{\{zN(r-\xi)\}! \{zN\xi\}! \{zN\xi\}! \{zN(1-r-\xi)\}!}, \quad (7.11.3)$$

where ξ^* denotes the random value of ξ which maximizes the expression (1). ξ^* is accordingly given by

$$\xi^* = r(1-r). \quad (7.11.4)$$

7.12. Maximization. Quasi-chemical equation

According to (7.04.8) the configurational partition function for given r is

$$\Omega_r = \sum_{\xi} g(N, r, \xi) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\xi w_s\}/kT], \quad (7.12.1)$$

in which we now use the approximation (7.11.3) for $g(N, r, \xi)$.

As usual we may replace the sum by its maximum term. Denoting the value of ξ in the maximum term by $\bar{\xi}$, we have

$$\Omega_r = g(N, r, \bar{\xi}) \exp[\{N(\chi_A + \chi_B + w_s) - 2N\bar{\xi}w_s\}/kT], \quad (7.12.2)$$

where $\bar{\xi}$ is determined by

$$\partial \ln \Omega_r / \partial \xi = 0 \quad (\xi = \bar{\xi}). \quad (7.12.3)$$

When we use formula (7.11.3) for $g(N, r, \xi)$, equation (3) becomes

$$zN \ln(r-\bar{\xi}) - 2zN \ln \bar{\xi} + zN \ln(1-r-\bar{\xi}) = 2N \frac{w_s}{kT}, \quad (7.12.4)$$

or $\bar{\xi}^2 = (r-\bar{\xi})(1-r-\bar{\xi})e^{-2w_s/kT}, \quad (7.12.5)$

which is a quasi-chemical equation in the sense defined in § 4.09.

All the equilibrium properties according to this approximation, which we call the first approximation, are obtainable by substituting the value $\bar{\xi}$ of ξ determined by the quasi-chemical equation (5) into formula (7.11.3) for $g(N, r, \xi)$ and using this value of $g(N, r, \xi)$ in (2).

7.13. Free energy and equilibrium state

The configurational free energy for given N, r is

$$F_c(N, r) = -kT \ln \Omega_r = -kT \ln g(N, r, \bar{\xi}) - N(\chi_A + \chi_B + w_s) + 2N\bar{\xi}w_s, \quad (7.13.1)$$

with $g(N, r, \xi)$ given by (7.11.3) with $\xi = \bar{\xi}$ determined by (7.12.5). The

formula for $F_c(N, r)$ can be obtained in a simpler form by changing the variables from N and r to $N_a = Nr$ and $N_b = N(1-r)$. At the same time we write X for $N\xi$ and X^* for $N\xi^*$. We accordingly rewrite (7.11.3) as

$$g(N_a, N_b, X) = \left\{ \frac{(N_a + N_b)!}{N_a! N_b!} \right\}^2 \left\{ \frac{\{z(N_a - X^*)\}! \{zX^*\}! \{zX^*\}! \{z(N_b - X^*)\}!}{\{z(N_a - X)\}! \{zX\}! \{zX\}! \{z(N_b - X)\}!} \right\}. \quad (7.13.2)$$

Since in these variables $F_c(N_a, N_b)$ is homogeneous of the first degree in N_a and N_b , we have by Euler's theorem

$$F_c(N_a, N_b) = N_a \frac{\partial F_c}{\partial N_a} + N_b \frac{\partial F_c}{\partial N_b}. \quad (7.13.3)$$

The advantage of using (3) is that the expressions for $\partial F_c / \partial N_a$ and $\partial F_c / \partial N_b$ are comparatively simple. When we differentiate F_c with respect to N_a or N_b we must remember that \bar{X} is a function of N_a, N_b , but since by definition of ξ we know that $\partial F_c / \partial \bar{X} = 0$ it follows that all terms coming from differentiation with respect to \bar{X} cancel. We may thus ignore such terms. We can also readily verify that $\partial \ln g / \partial X^*$ vanishes so that the terms in $\partial X^* / \partial N_a$ or $\partial X^* / \partial N_b$ also cancel. Noting these simplifications we obtain immediately from (1) and (2), using Stirling's theorem for factorials,

$$\frac{1}{kT} \frac{\partial F_c}{\partial N_a} = 2 \ln \frac{N_a}{N_a + N_b} + z \ln \frac{N_a - \bar{X}}{N_a - X^*} - \frac{\chi_A + \chi_B + w_s}{kT}, \quad (7.13.4)$$

$$\frac{1}{kT} \frac{\partial F_c}{\partial N_b} = 2 \ln \frac{N_b}{N_a + N_b} + z \ln \frac{N_b - \bar{X}}{N_b - X^*} - \frac{\chi_A + \chi_B + w_s}{kT}. \quad (7.13.5)$$

Substituting (4) and (5) into (3) and changing the variables back from N_a, N_b to N, r we have

$$\begin{aligned} \frac{F_c(r)}{2NkT} &= -\frac{\chi_A + \chi_B + w_s}{2kT} + r \ln r + (1-r) \ln (1-r) + \\ &\quad + \frac{1}{2} z \left\{ r \ln \frac{r - \xi}{r - \xi^*} + (1-r) \ln \frac{1-r - \xi}{1-r - \xi^*} \right\} \\ &= -\frac{\chi_A + \chi_B + w_s}{2kT} + r \ln r + (1-r) \ln (1-r) + \\ &\quad + \frac{1}{2} z \left\{ r \ln \frac{r - \xi}{r^2} + (1-r) \ln \frac{1-r - \xi}{(1-r)^2} \right\}, \end{aligned} \quad (7.13.6)$$

when we insert the value of ξ^* defined by (7.11.4). We have to substitute into (6) the value of ξ determined by (7.12.5).

At this stage we can verify that the zeroth approximation of § 7.05 is obtained by making z tend to infinity. We solve the quasi-chemical formula (7.12.5) obtaining

$$\xi = \frac{2r(1-r)}{1 + \{1 + 4r(1-r)(e^{2w_s/zkT} - 1)\}^{\frac{1}{2}}}. \quad (7.13.7)$$

We expand in powers of w_s/zkT , neglecting all powers higher than the first, and obtain

$$\xi = r(1-r) \left\{ 1 - r(1-r) \frac{2w_s}{zkT} \right\}, \quad (7.13.8)$$

so that

$$\frac{r-\xi}{r^2} = 1 + (1-r)^2 \frac{2w_s}{zkT}, \quad (7.13.9)$$

$$\frac{1-r-\xi}{(1-r)^2} = 1 + r^2 \frac{2w_s}{zkT}. \quad (7.13.10)$$

When we substitute (9) and (10) into (6), expand the last two logarithms, and then make $z \rightarrow \infty$, we obtain

$$\frac{F_c(r)}{2NkT} = -\frac{\chi_A + \chi_B + w_s}{2kT} + r \ln r + (1-r) \ln(1-r) + r(1-r) \frac{w_s}{kT}, \quad (7.13.11)$$

in agreement with the zeroth approximation (7.05.3).

The equilibrium value of r is determined by minimizing $F_c(r)$ with respect to r , so that

$$\frac{\partial F_c(r)}{\partial r} = 0. \quad (7.13.12)$$

If we use formula (1) for $F_c(r)$ with $g(N, r, \xi)$ given by (7.11.3), then all terms in $d\xi/dr$ may be ignored because $\partial F_c/\partial \xi = 0$, and all terms in $d\xi^*/dr$ may also be ignored because $\partial \ln g/\partial \xi^*$ vanishes from the definition (7.11.4) of ξ^* . We thus obtain immediately

$$\frac{1}{2NkT} \frac{\partial F_c}{\partial r} = \ln \frac{r}{1-r} + \frac{1}{2} z \left\{ \ln \frac{r-\xi}{r^2} - \ln \frac{1-r-\xi}{(1-r)^2} \right\}. \quad (7.13.13)$$

Substituting (13) into (12) we obtain for the value of r at which $\partial F_c/\partial r$ vanishes, the equation

$$\frac{r-\xi}{1-r-\xi} = \left\{ \frac{r}{1-r} \right\}^{2(z-1)/z}. \quad (7.13.14)$$

Evidently equation (14) is always satisfied by $r = \frac{1}{2}$, but we shall also be concerned with other solutions of (14). It is convenient for the sake of brevity to introduce the quantity ρ defined by

$$\frac{r-\xi}{1-r-\xi} = \rho^2, \quad (7.13.15)$$

from which it follows that

$$1-r-\xi = \frac{1-2r}{1-\rho^2} \quad (\rho \neq 1); \quad (7.13.16)$$

$$\xi = \frac{r-\rho^2(1-r)}{1-\rho^2} \quad (\rho \neq 1). \quad (7.13.17)$$

Using (15) we can rewrite the quasi-chemical equation (7.12.5) as

$$\xi = (1-r-\xi)\rho e^{-w_s/zkT}. \quad (7.13.18)$$

Substituting (16) and (17) into (18) we obtain

$$e^{w_s/zkT} = \frac{2r-1}{\rho(1-r)-\rho^{-1}r} \quad (\rho \neq 1). \quad (7.13.19)$$

Using (15) we can rewrite the condition for $\partial F_c/\partial r$ to vanish as

$$\rho = \left\{ \frac{r}{1-r} \right\}^{(z-1)/z}. \quad (7.13.20)$$

Substituting (20) into (19) we obtain

$$e^{w_s/zkT} = \frac{2r-1}{r^{1-1/z}(1-r)^{1/z}-(1-r)^{1-1/z}r^{1/z}} \quad (r \neq \frac{1}{2}). \quad (7.13.21)$$

Equation (21) determines the temperature at which $\partial F_c/\partial r$ vanishes† for a given value of r other than $\frac{1}{2}$. We have already noted that $\partial F_c/\partial r$ also vanishes at $r = \frac{1}{2}$ for all values of T . It can be verified that at high temperatures (21) has no real root, so that the only stationary value of $F_c(r)$ is at $r = \frac{1}{2}$ and this is a minimum of F_c . Thus at high temperatures the equilibrium state is one in which the two sub-lattices are equivalent and there is no long range order. It can also be verified that at low temperatures the solution $r = \frac{1}{2}$ is a maximum of F_c , while there is another solution $r > \frac{1}{2}$ determined by equation (21) which gives a minimum. It is this minimum which corresponds to the equilibrium state. The equilibrium value of r as a function of T/T_λ is shown as curve *B* in Fig. 7.2.

The configurational total energy can be derived from the configurational free energy by using the thermodynamic relation

$$U_c = -T^2 \frac{d}{dT} \left(\frac{F_c}{T} \right). \quad (7.13.22)$$

† This relation derived by McGlashan has not previously been published.

We use formula (1) for F_c and, remembering that $\partial F_c / \partial \xi = 0$ so that all terms in $d\xi/dT$ cancel, we obtain immediately

$$\frac{U_c}{N} = -(\chi_A + \chi_B + w_s) + 2\xi w_s, \quad (7.13.23)$$

which indeed is physically obvious from the meaning of ξ .

In the limit for low temperatures $r \rightarrow 1$ so that $\xi \rightarrow 0$ and

$$\frac{U_c}{N} \rightarrow -(\chi_A + \chi_B + w_s) \quad (T \rightarrow 0). \quad (7.13.24)$$

In the limit of high temperatures $e^{w_s/zkT} \rightarrow 1$ and $r \rightarrow \frac{1}{2}$ so that $\xi \rightarrow \frac{1}{2}$ and

$$\frac{U_c}{N} \rightarrow -(\chi_A + \chi_B + \frac{1}{2}w_s) \quad (T \rightarrow \infty). \quad (7.13.25)$$

Using subscripts to denote the temperature we may then rewrite (23) as

$$\frac{U_T - U_0}{U_\infty - U_0} = \frac{U_T - U_0}{\frac{1}{2}Nw_s} = 4\xi, \quad (7.13.26)$$

whereas according to the zeroth approximation the right side of (26) would be $4\xi^*$ or $4r(1-r)$ instead of 4ξ .

At each temperature less than T_λ the equilibrium value of r is determined by equation (21) and that of ξ by equation (14). At temperatures above T_λ , on the other hand, $r = \frac{1}{2}$ and the quasi-chemical quadratic equation (7.12.5) reduces to the simple equation

$$\xi = (\frac{1}{2} - \xi)e^{-w_s/zkT} \quad (T \geq T_\lambda), \quad (7.13.27)$$

with the solution

$$2\xi = \frac{1}{e^{w_s/zkT} + 1} \quad (T \geq T_\lambda). \quad (7.13.28)$$

Formula (26) then becomes

$$\frac{U_T - U_0}{U_\infty - U_0} = \frac{U_T - U_0}{\frac{1}{2}Nw_s} = \frac{2}{e^{w_s/zkT} + 1} \quad (T \geq T_\lambda). \quad (7.13.29)$$

The configurational energy given by formulae (26) and (29) is plotted as curve *B* in Fig. 7.3.

7.14. Lambda point

The lambda point is defined as the temperature T_λ such that when $T > T_\lambda$ the equilibrium value of r is $\frac{1}{2}$, whereas when $T < T_\lambda$ the equilibrium value of r is greater than $\frac{1}{2}$. At the lambda point itself the minimum in F_c at $r = \frac{1}{2}$ changes to a maximum. If then F_c is

plotted against r there is a point of horizontal inflexion at $r = \frac{1}{2}$. Thus at the lambda point we have

$$\frac{\partial F_c}{\partial r} = 0, \quad \frac{\partial^2 F_c}{\partial r^2} = 0 \quad (r = \frac{1}{2}, T = T_\lambda). \quad (7.14.1)$$

The equations (1) can be used to determine T_λ , but we can more conveniently determine T_λ from equation (7.13.21), which relates T to r at all temperatures below T_λ , by making $r \rightarrow \frac{1}{2}$. We accordingly write

$$r = \frac{1}{2}(1+\delta), \quad 1-r = \frac{1}{2}(1-\delta). \quad (7.14.2)$$

Substituting (2) into (7.13.21) and then making $\delta \rightarrow 0$ we obtain

$$e^{w_s/zkT_\lambda} = \frac{z}{z-2}, \quad (7.14.3)$$

which can also be written as

$$\frac{w_s}{kT_\lambda} = z \ln \frac{z}{z-2}. \quad (7.14.4)$$

If we expand the logarithm in powers of z^{-1} and then make $z \rightarrow \infty$ we recover the zeroth approximation:

$$\frac{w_s}{kT_\lambda} = 2, \quad (7.14.5)$$

which is the same as (7.07.3).

7.15. Expansion in powers of w_s/zkT

It was pointed out by Kirkwood† that it is in principle possible to evaluate $\ln \Omega_r$ and so $F_c(r)$ as a power series in w_s/zkT . The technique is precisely the same as that described in § 4.23. Since we have seen in § 7.10 that there is complete formal resemblance between the formulae for superlattices and for regular mixtures, we can immediately transcribe any of the formulae of § 4.23. In particular formula (4.23.12) for the configurational free energy becomes

$$\begin{aligned} \frac{F_c}{2NkT} = & -\frac{\chi_A + \chi_B + w_s}{2kT} + (1-r)\ln(1-r) + r \ln r + r(1-r)\frac{w_s}{kT} - \\ & - \frac{1}{2}z \left\{ \frac{l_2}{2!} \left(\frac{2w_s}{zkT} \right)^2 + \frac{l_3}{3!} \left(\frac{2w_s}{zkT} \right)^3 + \frac{l_4}{4!} \left(\frac{2w_s}{zkT} \right)^4 + \dots \right\}. \end{aligned} \quad (7.15.1)$$

We need comment only on the differences between this formula and (4.23.12). The two obvious changes are from x to r and from w to w_s . There is also a change from N to $2N$ which is a mere formality due to our considering altogether $N = N_A + N_B$ sites for a regular mixture,

† Kirkwood (1938), *J. Chem. Phys.* **6**, 70.

but altogether $2N$ sites, N on each sub-lattice, in the present discussion of superlattices. The remaining change is from $(1-x)\chi_A + x\chi_B$ to $\chi_A + \chi_B + w_s$. This is required because $x = 1$ or 0 implies no AB pairs, whereas $r = 1$ or 0 implies all AB pairs and no AA or BB pairs.

The coefficients l_2 and l_3 are defined by (4.23.10) and (4.23.11) respectively. Similar definitions of l_4 , l_5 , ... can be written down immediately. Thus defined all l 's are of order zero in N . The evaluation of the series of coefficients l_2 , l_3 , ... is in principle a straightforward counting operation which is, however, increasingly tedious and complicated as the series is ascended. Kirkwood evaluated l_2 and l_3 finding

$$l_2 = r^2(1-r)^2, \quad (7.15.2)$$

$$l_3 = r^2(1-r)^2(1-2r)^2. \quad (7.15.3)$$

Bethe and Kirkwood† evaluated l_4 finding

$$l_4 = r^2(1-r)^2(1-6r+6r^2)^2 + 6\left(\frac{y}{z}-1\right)r^4(1-r)^4, \quad (7.15.4)$$

where y is a parameter depending on the lattice. Let us denote by $z_{aa'}$ the number of b sites which are nearest neighbours common to two sites a and a' both on the a lattice. If we now form the sum $\sum_{a'} z_{aa'}^2$ over all positions of a' for a given a , then y is defined by

$$y = \sum_a z_{aa'}^2 - z(z-1). \quad (7.15.5)$$

In the CsCl lattice, which is the same as that in β -brass, we have $z = 8$ and

$$\sum_a z_{aa'}^2 = (6 \times 4^2) + (12 \times 2^2) + (8 \times 1^2) = 152,$$

so that $y = 152 - 56 = 96$ and $y/z = 12$.

Chang‡ evaluated l_5 finding

$$l_5 = r^2(1-r)^2(1-2r)^2(1-12r+12r^2)^2 + 60\left(\frac{y}{z}-1\right)r^4(1-r)^4(1-2r)^2. \quad (7.15.6)$$

Chang also evaluated l_6 obtaining a formula involving as well as z , y two new parameters γ_1 , γ_2 depending on the lattice. For the CsCl lattice, the formula becomes

$$l_6 = r^2(1-r)^2\{1-60r(1-r)(1-2r)^2\} + 5190r^4(1-r)^4 - 44400r^5(1-r)^5 + 118080r^6(1-r)^6. \quad (7.15.7)$$

The quasi-chemical approximation is in agreement with formula

† Bethe and Kirkwood (1941), *J. Chem. Phys.* **7**, 578.

‡ Chang (1941), *J. Chem. Phys.* **9**, 169.

(7.15.1) as far as terms in $(w/zkT)^3$. Chang has further shown that the quasi-chemical approximation is equivalent to setting such quantities as y , γ_1 , γ_2 equal to zero.

7.16. Bethe's method

In § 4.17 we described the treatment of regular mixtures by a technique due to Bethe† and generally known as Bethe's method. In § 7.10 we stressed the mathematical equivalence between the problem of regular mixtures and that of superlattices. As a consequence of this equivalence any method of treatment suitable for the one problem is equally applicable to the other and leads to parallel formulae. We may therefore be sure that Bethe's method is equally applicable to superlattices and to regular mixtures and will lead to similar formulae. We therefore need not expound Bethe's method of treating superlattices in any detail. We shall rather describe quite briefly what comes out of its application.

We recall that Bethe's method is the construction of a grand partition function for a sample group of sites. In its original form the chosen group of sites consisted of a central a site together with its z closest neighbours all b sites. The grand partition function could then be written in the form recalling (4.17.1)

$$\Xi_{z+1} = q_A \lambda_A (\epsilon_A \eta + \epsilon_B)^z + q_B \lambda_B (\epsilon_A + \epsilon_B \eta)^z. \quad (7.16.1)$$

However, all the conclusions reached by the use of such a grand partition function can be reached equally well and rather more simply by constructing instead a grand partition function for a single pair of sites one a and the other b . Such a grand partition function Ξ_2 has the form recalling (4.17.10)

$$\Xi_2 = q_A \lambda_A (\zeta_A \eta + \zeta_B) + q_B \lambda_B (\zeta_A + \zeta_B \eta). \quad (7.16.2)$$

The several terms in Ξ_{z+1} or in Ξ_2 are proportional to the several possible manners of occupation of the group of sites. Thus in (2) the relative probabilities are as follows:

- A on a , A on b : $q_A \lambda_A \zeta_A \eta$,
- A on a , B on b : $q_A \lambda_A \zeta_B$,
- B on a , A on b : $q_B \lambda_B \zeta_A$,
- B on a , B on b : $q_B \lambda_B \zeta_B \eta$.

In the original use of Bethe's treatment the method of procedure was to deduce an equation between ϵ_B/ϵ_A and $q_B \lambda_B/q_A \lambda_A$ from the obvious fact that all physically significant conclusions must be the same whether

† Bethe (1935), *Proc. Roy. Soc. A* 150, 552.

the chosen group of sites consists of a central a with z neighbours b or a central b with z neighbours a . There is, however, available, precisely as described in § 4.17, a much simpler procedure, namely the direct elimination of ϵ_B/ϵ_A from (1) or of ζ_B/ζ_A from (2). Let us use the symbol $[A/a, A/b]$ to denote the probability that there is an A atom on the a site and an A atom on a neighbouring b site, and analogous symbols for analogous probabilities. Then we have immediately

$$\frac{[A/a, A/b]}{[B/a, A/b]} = \frac{q_A \lambda_A \eta}{q_B \lambda_B}, \quad (7.16.3)$$

$$\frac{[B/a, B/b]}{[A/a, B/b]} = \frac{q_B \lambda_B \eta}{q_A \lambda_A}. \quad (7.16.4)$$

If we now multiply (3) by (4) we obtain

$$\frac{[A/a, A/b][B/a, B/b]}{[A/a, B/b][B/a, A/b]} = \eta^z, \quad (7.16.5)$$

which is nothing other than the familiar equation of quasi-chemical equilibrium.

We see then that for superlattices as for regular mixtures Bethe's method is mathematically equivalent to the quasi-chemical method. All results derivable from Bethe's method can be obtained more directly by the quasi-chemical method. It might be thought that Bethe's method could be regarded as a basis for the quasi-chemical treatment. In fact the analysis in § 4.18 shows that the converse is true. The essential assumption underlying Bethe's method is that the relative probabilities for a pair of neighbouring sites to be occupied in the several possible ways are independent of the manner of occupation of all other sites. This assumption, when one writes $\eta = \exp(-w_s/zkT)$, is precisely that of the quasi-chemical treatment.

There is one significant difference between the treatments of superlattices on the one hand and regular solutions on the other, namely an historical one. The quasi-chemical treatment was invented† in its most primitive form for regular solutions in 1935. In the same year Bethe‡ first applied his method to superlattices. In 1938 Rushbrooke§ showed that both methods correctly applied to regular mixtures are mathematically equivalent to each other. In 1939 Fowler and Guggenheim|| proved the equivalence of the two methods when applied to

† Guggenheim (1935), *Proc. Roy. Soc. A* 148, 304.

‡ Bethe (1935), *ibid. Proc. Roy. Soc. A* 150, 552.

§ Rushbrooke (1938), *Proc. Roy. Soc. A* 166, 296.

|| Fowler and Guggenheim (1940), *Proc. Roy. Soc. A* 174, 189.

superlattices. The proof that the two methods actually depend on the same assumption was given its most general form† in 1944.

7.17. Intercomparison of methods

It is of some interest to compare the numerical results obtained by the several methods of treatment already described. We have seen that the method of expansion in power series of w_s/kT is, in principle, accurate, but its usefulness must depend on the rapidity of convergence. We shall see that, although the series for the free energy may converge fairly well, the derived series determining the lambda point converges rather slowly if at all. The quasi-chemical treatment, or the mathematically equivalent method of Bethe, has the advantage of giving closed formulae, but the disadvantage that it is difficult to assess the degree of inaccuracy. The zeroth approximation is obtainable from either of the more accurate treatments by making z tend to infinity.

We shall compare the values of the lambda point temperature given by the several approximations. This inevitably involves some repetition of the comparison already made in § 4.25 for the temperature of critical mixing of regular solutions. We shall here confine ourselves to the CsCl structure, which is the structure of β -brass. We then have $z = 8$, $y/z = 12$. The formula for $\partial^2 F_c / \partial r^2$ derived from (7.15.1) becomes when we insert the values of the l 's for $r = \frac{1}{2}$

$$\begin{aligned} \frac{1}{2NkT} \frac{\partial^2 F_c}{\partial r^2} = 4 - 2 \frac{w_s}{kT} - \frac{1}{2} z \left\{ -\frac{1}{2!} \left(\frac{2w_s}{zkT} \right)^2 + \frac{1}{2} \frac{1}{3!} \left(\frac{2w_s}{zkT} \right)^3 - \right. \\ \left. - \left(\frac{1}{4} + \frac{3}{4} \frac{y}{z} \right) \frac{1}{4!} \left(\frac{2w_s}{zkT} \right)^4 + \left(\frac{1}{8} + \frac{15}{8} \frac{y}{z} \right) \frac{1}{5!} \left(\frac{2w_s}{zkT} \right)^5 - \dots \right\}. \quad (7.17.1) \end{aligned}$$

Hence the equation determining the lambda point temperature is

$$\begin{aligned} \frac{4}{z} = \frac{2w_s}{zkT_\lambda} - \frac{1}{4} \left(\frac{2w_s}{zkT_\lambda} \right)^2 + \frac{1}{24} \left(\frac{2w_s}{zkT_\lambda} \right)^3 - \left(1 + \frac{3y}{z} \right) \frac{1}{192} \left(\frac{2w_s}{zkT_\lambda} \right)^4 + \\ + \left(1 + 15 \frac{y}{z} \right) \frac{1}{1920} \left(\frac{2w_s}{zkT_\lambda} \right)^5 - \dots. \quad (7.17.2) \end{aligned}$$

The expression for $1/z$ as a power series in $2w_s/zkT_\lambda$ can be inverted into an expression for $2w_s/zkT_\lambda$ as a power series in $1/z$. We obtain eventually

$$\frac{w_s}{kT_\lambda} = 2 \left\{ 1 + \frac{1}{z} + \frac{4}{3} \frac{1}{z^2} + \left(2 + \frac{y}{z} \right) \frac{1}{z^3} + \left(\frac{16}{5} + \frac{4y}{z} \right) \frac{1}{z^4} + \dots \right\}. \quad (7.17.3)$$

The zeroth approximation obtained by making $z \rightarrow \infty$ is $w_s/kT_\lambda = 2$. The expansion obtainable from the quasi-chemical treatment is

† Guggenheim (1944), *Proc. Roy. Soc. A* 183, 221.

obtained by putting $y/z = 0$. We now insert the values $z = 8$, $y/z = 12$ appropriate to β -brass and (3) becomes

$$\frac{w_s}{kT_\lambda} = 2 \left\{ 1 + \frac{1}{8} + \frac{4}{3} \frac{1}{8^2} + 14 \frac{1}{8^3} + \frac{256}{5} \frac{1}{8^4} + \dots \right\}. \quad (7.17.4)$$

From (4) we construct Table 7.5 showing the values obtained for w_s/kT_λ according to the number of terms in (4) which we use. The value is also given including the sixth term calculated by Chang.

TABLE 7.5

Calculated Values of w_s/kT_λ and of 4ξ at the Lambda point according to Several Approximations for the β -brass Lattice with $z = 8$, $y/z = 12$

Highest l retained	Number of terms in formula (4)	$\frac{w_s}{kT_\lambda}$	Number of terms in formula (8)	4ξ at $T = T_\lambda$
l_1	1	2	1	1
l_2	2	2.250	2	0.859
l_3	3	2.292	2	0.857
l_4	4	2.346	3	0.817
l_5	5	2.371	3	0.814
l_6	6	2.392	4	—
Quasi-chemical		2.301	—	0.857

Study of Table 7.5 leads to two conclusions. The convergence of the series expansion in powers of z^{-1} is too slow to lead to a precise value of T_λ . Whatever the true value may be, the quasi-chemical approximation appears to be considerably more accurate than the zeroth approximation.

Another quantity, whose values obtained by the several methods can readily be compared, is the equilibrium value of ξ at the lambda point. We recall that the configurational total energy per atom is

$$-\frac{\chi_A + \chi_B + w_s}{2} + \xi w_s. \quad (7.17.5)$$

Since in the limit of very low temperatures ξ tends to zero, it follows that ξw_s is the excess configurational total energy at any temperature over its value in the limit $T \rightarrow 0$. To obtain a formula for ξ as a power series in w_s/zkT , we accordingly require the series for U_c . From formula (7.15.1) and the relation (7.13.22) we obtain immediately

$$\begin{aligned} \frac{U_c}{2NkT} &= -\frac{\chi_A + \chi_B + w_s}{2kT} + r(1-r) \frac{w_s}{kT} - \\ &- \frac{1}{2} z \left\{ \frac{l_2}{1!} \left(\frac{2w_s}{zkT} \right)^2 + \frac{l_3}{2!} \left(\frac{2w_s}{zkT} \right)^3 + \frac{l_4}{3!} \left(\frac{2w_s}{zkT} \right)^4 + \frac{l_5}{4!} \left(\frac{2w_s}{zkT} \right)^5 + \dots \right\}, \quad (7.17.6) \end{aligned}$$

so that according to (5) the equilibrium value of ξ is given by

$$\xi = r(1-r) - \left\{ l_2 \left(\frac{2w_s}{zkT} \right) + \frac{l_3}{2!} \left(\frac{2w_s}{zkT} \right)^2 + \frac{l_4}{3!} \left(\frac{2w_s}{zkT} \right)^3 + \frac{l_5}{4!} \left(\frac{2w_s}{zkT} \right)^4 + \dots \right\}. \quad (7.17.7)$$

Inserting the values of the l 's given in § 7.15 for $r = \frac{1}{2}$, when all the odd l 's vanish, we obtain

$$4\xi = 1 - \frac{1}{4} \frac{2w_s}{zkT} - \frac{1}{192} \left(3 \frac{y}{z} - 1 \right) \left(\frac{2w_s}{zkT} \right)^3 - \dots = 1 - \frac{1}{4} \frac{w_s}{4kT} - \frac{35}{192} \left(\frac{w_s}{4kT} \right)^3 - \dots \quad (7.17.8)$$

using the values $z = 8$, $y/z = 12$ appropriate to β -brass. In Table 7.5 the last column gives the values calculated for 4ξ when using for w_s/kT the value calculated for w_s/kT_λ by using the series (3) and cutting off at the same l as in (8). Included in the table is the value given by the quasi-chemical treatment, namely by use of (7.13.7) and (7.14.3),

$$4\xi = \frac{2}{1 + e^{w_s/zkT_\lambda}} = \frac{z-2}{z-1} = \frac{6}{7} \quad (r = \frac{1}{2}, T = T_\lambda). \quad (7.17.9)$$

The figures in the last column of Table 7.5 strongly suggest that formula (8) converges too slowly to be useful, if indeed it converges at all.

7.18. Anomalous heat capacity

When the configurational total energy is plotted against the temperature as in Fig. 7.3 we see that the slope of the curve is discontinuous at the lambda point. This slope is proportional to the heat capacity. If we plot the heat capacity per atom against the temperature we obtain a curve gradually rising up to the lambda point where it suddenly falls. The shape of this curve resembles a Greek capital letter lambda, whence the name *lambda point* suggested by Ehrenfest.[†] In Fig. 7.4 C/k is plotted against T/T_λ where C denotes the configurational contribution to the heat capacity per atom. The two curves represent the zeroth approximation and the first (quasi-chemical) approximation for the β -brass structure with $z = 8$.

Although it is not possible to obtain any simple formula for C as a function of temperature it is possible to obtain formulae valid in the immediate neighbourhood of the lambda point, both above and below. In particular one can obtain formulae for the discontinuity $-\Delta C$ at the lambda point. The algebra required[‡] for obtaining such formulae is tedious and we shall only quote the results obtained.

[†] See Keesom (1942), *Helium*, p. 216, Elsevier.

[‡] Fowler and Guggenheim (1939), *Statistical Thermodynamics*, § 1319, Cambridge University Press.

The quasi-chemical approximation leads to the closed formula

$$-\frac{\Delta C}{\frac{1}{2}k} = \left(\frac{w_s}{2kT_\lambda} \right)^2 \frac{z-2}{z-1}. \quad (7.18.1)$$

The corresponding zeroth approximation obtained by making z tend to infinity is

$$-\frac{\Delta C}{\frac{1}{2}k} = 1. \quad (7.18.2)$$

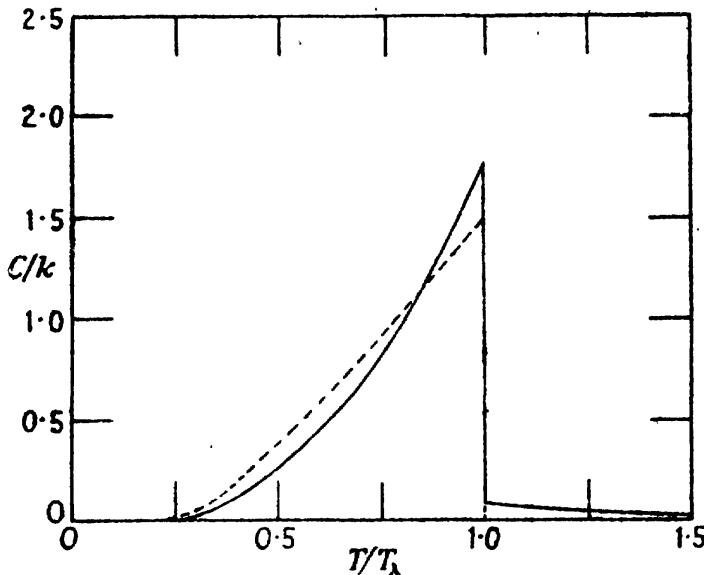


FIG. 7.4. Configurational atomic heat capacity as function of temperature for alloy of composition *AB*. —— zeroth approximation. —— first approximation, $z = 8$.

Using (7.14.4) we can rewrite (1) as

$$-\frac{\Delta C}{\frac{1}{2}k} = \left(\frac{1}{2}z \ln \frac{z}{z-2} \right)^2 \left(\frac{z-2}{z-1} \right). \quad (7.18.3)$$

When the right side of (3) is expanded as a power series in $1/z$ we obtain

$$-\frac{\Delta C}{\frac{1}{2}k} = 1 + \frac{1}{z} + \frac{2}{3} \frac{1}{z^2} - \frac{52}{45} \frac{1}{z^4} - \frac{28}{9} \frac{1}{z^5} + \dots, \quad (7.18.4)$$

in which we notice that there is no term in $1/z^3$.

It is interesting to compare this with the similar series obtained† from the accurate expansion of the free energy in powers of w_s/zkT , namely,

$$\begin{aligned} -\frac{\Delta C}{\frac{1}{2}k} = 1 + \frac{1}{z} + \frac{2}{3} \frac{1}{z^2} + & \left(3 \frac{y}{z} \right) \frac{1}{z^3} + \left(6 \frac{y}{z} - \frac{52}{45} \right) \frac{1}{z^4} + \\ & + \left(5 \frac{\gamma_2}{z} - 40 \frac{\gamma_1}{z} - \frac{26}{3} \frac{y}{z} - \frac{28}{9} \right) \frac{1}{z^5} + \dots. \end{aligned} \quad (7.18.5)$$

It will be noticed that if the terms in (5) containing y , γ_1 , and γ_2 are ignored this formula reduces to (4).

† Chang (1941), *J. Chem. Phys.* 9, 169.

For β -brass $z = 8$ and the other structural constants have the values

$$\frac{y}{z} = 12, \quad \frac{\gamma_1}{z} = 18, \quad \frac{\gamma_2}{z} = 222.$$

Whereas the series (4) converges rapidly, the series (5) converges slowly, if at all. This may be seen from the following table which shows the values of $-\Delta C/\frac{3}{2}k$ obtained for β -brass when various numbers of terms are included.

Number of terms	1	2	3	4	5	6	∞
Formula (4)	1	1.1250	1.1354	1.1354	1.1351	1.1350	1.1350
Formula (5)	1	1.1250	1.1354	1.2057	1.2230	1.2463	?

The author's personal view is complete distrust of this series expansion in the absence of any investigation of its convergence.

7.19. Comparison with experiment

We shall now consider briefly the comparison between the theoretical predictions of the foregoing sections and what is found experimentally. In making such a comparison it is important that the experimental conditions should be free from hysteresis so that the measurements are really made under equilibrium conditions. The alloy of Cu and Zn known as β -brass is suitable for comparison between theory and experiment because in the neighbourhood of the lambda point equilibrium is attained rapidly. This is proved by the fact that the observed values of the heat capacity with rising and with falling temperatures agree with each other. The phase range of β -brass extends only between the atomic fractions 0.458 and 0.489 of Zn. Thus the ideal composition CuZn is just outside the range, but the deviation from the ideal ratio will be neglected. The superlattice structure of this alloy has been established by X-ray measurements. In the ordered state the structure is analogous to that of CsCl with $z = 8$. The lambda point is at 742° K.

Accurate measurements of the heat capacity have been made by Sykes and Wilkinson† and independently by Moser.‡ The two sets of measurements are in strikingly good agreement with each other. The drop in the heat capacity per atom at the lambda point is about $5k$ as compared with the theoretical values given in § 7.18, namely $\frac{3}{2}k$ according to the zeroth approximation and $1.70k$ according to the first approximation with $z = 8$.

There is thus a serious discrepancy between the theory and experiment which may be due to any of several causes such as

- (1) neglect of interactions between atoms not nearest neighbours;

† Sykes and Wilkinson (1937), *J. Inst. Metals*, **61**, 223.

‡ Moser (1936), *Physikal. Z.* **37**, 737.

- (2) neglect of dependence of w on the interatomic distance which alters with temperature;
- (3) neglect of the electronic structure which may be quite different in an alloy from that in the simple metals.

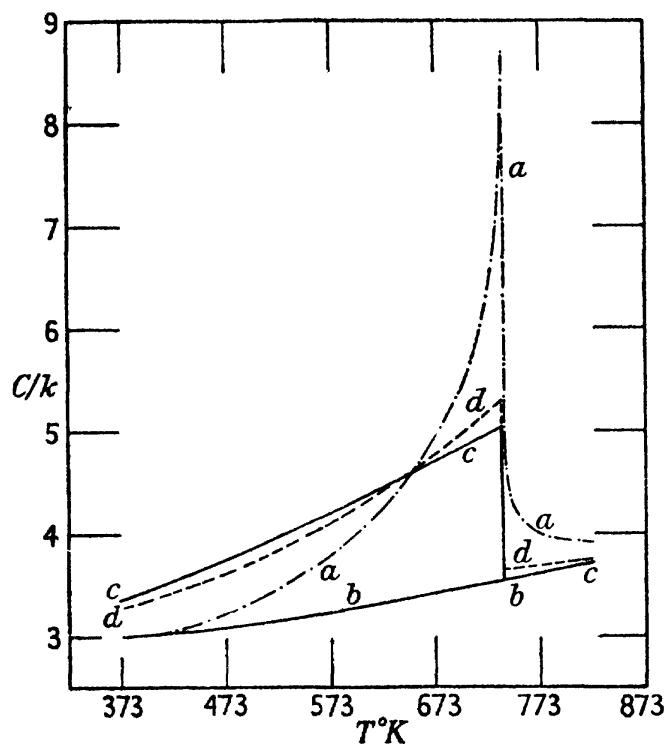


FIG. 7.5. Atomic heat capacity of CuZn. a , experimental for CuZn (Sykes and Wilkinson; Moser). b , mean of experimental curves for pure Cu and pure Zn. c , calculated, zeroth approximation. d , calculated, first approximation with $z = 8$.

The discrepancy between theory and experiment is less obvious if instead of comparing heat capacities we compare the energy change over a wide temperature range. That is to say we compare the integral of the configurational heat capacity, computed as the excess heat capacity of the alloy over the mean of the heat capacities of the two pure metals. The most suitable temperature range for the comparison is from a temperature so low that the structure is completely ordered up to the lambda point. According to formula (7.13.29) the configurational total energy at any temperature not less than the lambda point is given by

$$\frac{U(T) - U(0)}{2N} = \frac{\frac{1}{2}w_s}{e^{w_s/zkT} + 1} \quad (T \geq T_\lambda). \quad (7.19.1)$$

In particular at the lambda point, using (7.14.4) we have

$$\frac{U(T_\lambda) - U(0)}{2NkT_\lambda} = \frac{z(z-2)}{4(z-1)} \ln \frac{z}{z-2}, \quad (7.19.2)$$

which for $z = 8$ becomes

$$\frac{U(T_\lambda) - U(0)}{2NkT_\lambda} = 0.493, \quad (7.19.3)$$

while the zeroth approximation gives the value 0.50. The experimental value given by the area between the curves a and b in Fig. 7.5 to the left of $T = T_\lambda$ is 0.43. Even with this method of comparison the extent of agreement is not impressive.

The strongest point of the theory is the qualitative prediction of a lambda point, and in this respect the first approximation is no better than the zeroth.

7.20. AuCu₃ superlattice

We turn now to a different type of superlattice of which the best known example is the alloy AuCu₃. Its behaviour is so strikingly different from that of CuZn as to warrant rather detailed consideration. We begin by describing the lattice.

A face-centred cubic lattice may be regarded as composed of four interpenetrating simple cubic lattices, which we shall call sub-lattices a , c_1 , c_2 , c_3 respectively. Every lattice site has $z = 12$ nearest neighbours of which $\frac{1}{2}z = 4$ are on each of the other three sub-lattices. A lattice site has no nearest neighbours on its own sub-lattice. We now describe the structure of AuCu₃ and for brevity we denote Au atoms by A and Cu atoms by C . We consider a crystal containing N atoms A and $3N$ atoms C , that is $4N$ atoms in all. At very high temperatures these atoms are distributed completely at random, so that the four sub-lattices are indistinguishable. At very low temperatures on the contrary all the A atoms are on the sub-lattice a and all the C atoms on the three sub-lattices c_1 , c_2 , c_3 . Our problem is to study the change from the completely disordered structure at high temperatures to the completely ordered structure at low temperatures. Instead of the lambda point, which occurs in the case of CuZn, we shall find an ordinary phase change with a discontinuity in the energy.

7.21. Zeroth approximation

We shall initially study the system by using an approximation† analogous to that described in § 7.05 which we call the zeroth approximation. We denote by r the fraction of A atoms on the sub-lattice a . When r is specified, the zeroth approximation consists in assuming a purely random arrangement of the Nr atoms A and $N(1-r)$ atoms C

† Bragg and Williams (1935), *Proc. Roy. Soc. A* **151**, 540.

on the sub-lattice a and a purely random arrangement of the $N(1-r)$ atoms A and $N(2+r)$ atoms C on the three sub-lattices c_1, c_2, c_3 .

TABLE 7.6

Distribution of Atoms A and C over Four Sub-lattices

A on a :	Nr	C on a :	$N(1-r)$
A on c_1 :	$N\frac{1}{3}(1-r)$	C on c_1 :	$N\frac{1}{3}(2+r)$
A on c_2 :	$N\frac{1}{3}(1-r)$	C on c_2 :	$N\frac{1}{3}(2+r)$
A on c_3 :	$N\frac{1}{3}(1-r)$	C on c_3 :	$N\frac{1}{3}(2+r)$

Table 7.6 shows the distribution of the two kinds of atoms over the four sub-lattices. From this we can, assuming randomness on each sub-lattice, count the number of pairs of nearest neighbours of each kind. The total number of pairs of nearest neighbours is $\frac{1}{2}zN$, where $z = 12$, but there is no advantage in using the numerical value of z at this stage. One sixth of these is of each of the types $ac_1, ac_2, ac_3, c_1c_2, c_1c_3, c_2c_3$. Thus there are zN pairs of the type ac , where c may be c_1 or c_2 or c_3 , and zN pairs of the type cc' , where c and c' denote two different c 's. Let us now count the number of AC pairs of closest neighbours. These can be of three kinds and their numbers are as follows

$$\begin{aligned}A \text{ on } a, C \text{ on } c: & zNr\frac{1}{3}(2+r), \\A \text{ on } c, C \text{ on } a: & zN\frac{1}{3}(1-r)(1-r), \\A \text{ on } c, C \text{ on } c': & 2zN\frac{1}{3}(1-r)\frac{1}{3}(2+r).\end{aligned}$$

By addition we find for the total number of AC pairs of nearest neighbours $zN - zN\frac{1}{3}(1+r-2r^2)$. The numbers of AA and of CC pairs are counted similarly and we then construct Table 7.7. As previously we

TABLE 7.7

Distribution of Pairs and their Contributions to the Configurational Energy

Kind of pair	Number of pairs	Contribution to configurational energy
AA	$zN\frac{1}{3}(1+r-2r^2)$	$-N\frac{1}{3}(1+r-2r^2)\chi_A$
CC	$zN + zN\frac{1}{3}(1+r-2r^2)$	$-N2\chi_C - N\frac{1}{3}(1+r-2r^2)\chi_C$
AC	$zN - zN\frac{1}{3}(1+r-2r^2)$	$-N(\chi_A + \chi_C + w_s) + N\frac{1}{3}(1+r-2r^2)(\chi_A + \chi_C + w_s)$

denote the contributions of AA , CC , and AC pairs to the configurational energy by $-2\chi_A/z$, $-2\chi_C/z$ and $-(\chi_A + \chi_C + w_s)/z$ respectively. Multiplying the number of pairs of each kind by their contributions to the configurational energy we obtain the expressions in the last column of

Table 7.7. By addition we obtain for the configurational energy E_c for given r

$$\frac{E_c}{N} = -\chi_A - 3\chi_C - w_s + \frac{3}{2}(1-r)(1+2r)w_s. \quad (7.21.1)$$

We note the two extreme cases of complete order

$$\frac{E_c}{N} = -\chi_A - 3\chi_C - w_s \quad (r = 1), \quad (7.21.2)$$

and of complete disorder

$$\frac{E_c}{N} = -\chi_A - 3\chi_C - \frac{3}{4}w_s \quad (r = \frac{1}{2}). \quad (7.21.3)$$

We now require an expression for $g(r)$, the number of distinguishable configurations of given r . This is equal to the product of the number of ways of distributing Nr atoms A on the sub-lattice a and the number of ways of distributing $N(1-r)$ atoms A over the remaining three sub-lattices. Hence

$$g(r) = \frac{N!}{\{Nr\}! \{N(1-r)\}!} \left[\frac{N!}{\{N\frac{1}{3}(1-r)\}! \{N\frac{1}{3}(2+r)\}!} \right]^3, \quad (7.21.4)$$

or alternatively

$$g(r) = \frac{N!}{\{Nr\}! \{N(1-r)\}!} \frac{\{3N\}!}{\{N(1-r)\}! \{N(2+r)\}!}. \quad (7.21.5)$$

Formula (4) is obtained by considering how to distribute $\frac{1}{3}N(1-r)$ atoms A over each of three sub-lattices, while formula (5) is obtained by considering how to distribute $N(1-r)$ atoms A over the $3N$ lattice sites of the three sub-lattices together. For large values of N the two formulae are equivalent.

The configurational free energy $F_c(r)$ for given r is given by

$$F_c(r) = -kT \ln g(r) + E_c(r). \quad (7.21.6)$$

Substituting (1) and (4) into (6) and using Stirling's theorem for the factorials we obtain

$$\begin{aligned} \frac{F_c(r)}{NkT} &= r \ln r + (1-r) \ln (1-r) + (1-r) \ln \frac{(1-r)}{3} + (2+r) \ln \frac{(2+r)}{3} - \\ &- \frac{\chi_A}{kT} - \frac{3\chi_C}{kT} - \frac{w_s}{kT} + \frac{3}{2}(1-r)(1+2r) \frac{w_s}{kT}. \end{aligned} \quad (7.21.7)$$

7.22. Equilibrium conditions

The equilibrium value of r , and thence all equilibrium properties, can be obtained by minimizing the configurational free energy. Differentiating (7.21.7) with respect to r we have

$$\frac{1}{NkT} \frac{\partial F_c}{\partial r} = \ln \frac{r(2+r)}{(1-r)^2} - \frac{2(4r-1)}{kT} \frac{w_s}{kT}, \quad (7.22.1)$$

so that stationary values of $F_c(r)$ are determined by

$$\ln \frac{r(2+r)}{(1-r)^2} = \frac{2(4r-1)}{kT} \frac{w_s}{kT}. \quad (7.22.2)$$

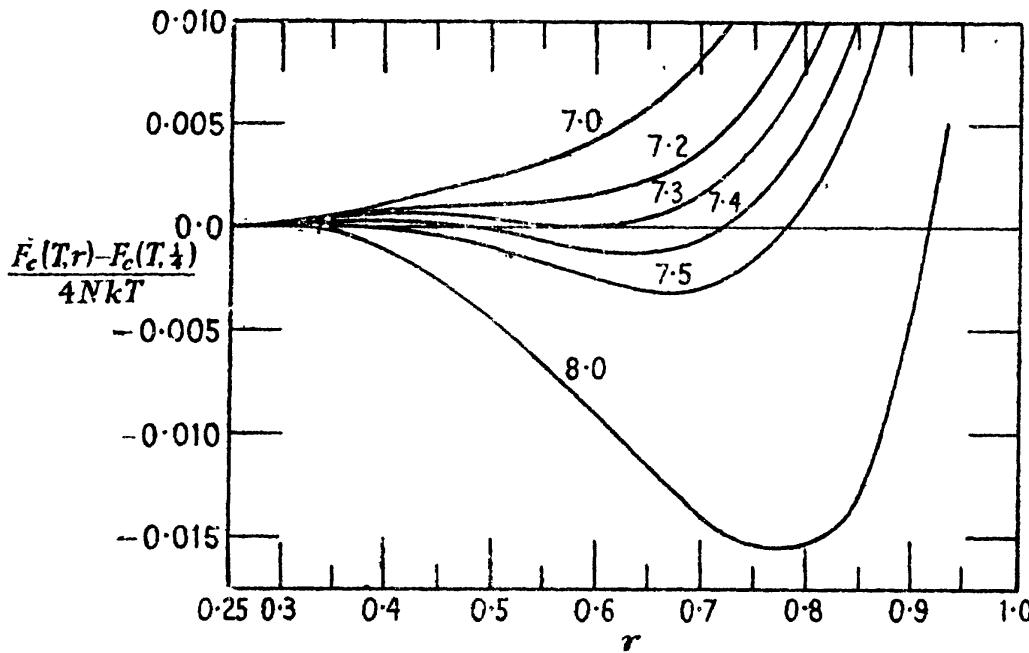


FIG. 7.6. Dependence of the configurational free energy $F_c(T, r)$ on r for alloy of composition AC_3 according to the zeroth approximation for various temperatures. The numbers attached to the curves are values of w_s/kT .

Equation (2) is always satisfied by $r = \frac{1}{2}$ corresponding to complete disorder, but it does not follow that this is a minimum rather than a maximum; even if it is a minimum it may or may not be the lowest minimum. We must therefore study $F_c(r)$ more thoroughly. This has been done in Fig. 7.6, where $\{F_c(T, r) - F_c(T, \frac{1}{2})\}/4NkT$ has been plotted against r for several values of w_s/kT . We see that at high temperatures, the only stationary value of $F_c(r)$ is a minimum at $r = \frac{1}{2}$ and the stable state is that of complete disorder. As the temperature is lowered a second minimum appears but is initially higher than that at $r = \frac{1}{2}$; the stable state is still that of complete disorder, the second minimum being metastable. At still lower temperatures the second minimum becomes lower than that at $r = \frac{1}{2}$ and so the stable state is the other

minimum which we denote by $r = r^*$. When the temperature is lowered still further the minimum at $r = \frac{1}{2}$ changes into a maximum, as in the system CuZn. Our main interest is in the transition of the stable phase from $r = \frac{1}{2}$ to $r = r^*$. This is determined by the simultaneous equations

$$F_c(r^*) - F_c\left(\frac{1}{2}\right) = 0, \quad (7.22.3)$$

$$\frac{\partial F_c}{\partial r} = 0 \quad (r = r^*). \quad (7.22.4)$$

Putting $r = \frac{1}{2}$ into (7.21.7) and subtracting the result from the original equation we find

$$\begin{aligned} \frac{1}{NkT} \{F(r) - F\left(\frac{1}{2}\right)\} &= r \ln r + (1-r) \ln(1-r) + (1-r) \ln \frac{(1-r)}{3} + \\ &+ (2+r) \ln \frac{(2+r)}{3} - 3 \ln 3 + 4 \ln 4 - \frac{1}{2}(r-\frac{1}{2})^2 \frac{w_s}{kT}. \end{aligned} \quad (7.22.5)$$

Substituting (5) into (3) and (1) into (4) we obtain the simultaneous equations for the transition temperature T_t

$$\begin{aligned} \frac{1}{2}(r-\frac{1}{2})^2 \frac{w_s}{kT_t} &= \frac{1}{2}(r-\frac{1}{2}) \ln \frac{r(2+r)}{(1-r)^2} \\ &= r \ln r + (1-r) \ln(1-r) + (1-r) \ln \frac{(1-r)}{3} + \\ &+ (2+r) \ln \frac{(2+r)}{3} - 3 \ln 3 + 4 \ln 4. \end{aligned} \quad (7.22.6)$$

Solving the second equation by successive approximations we find that the equilibrium value r_t of the ordered phase at the transition temperature T_t is $r_t = 0.597$. Then using this in the first equation we obtain $w_s/kT_t = 7.32$ or $kT_t/w_s = 0.137$.

7.23. Total energy

Using the Gibbs–Helmholtz relation we obtain from (7.22.5) for the configurational total energy

$$\frac{1}{4N} \{U\left(\frac{1}{2}\right) - U(r)\} = \frac{1}{2}(r-\frac{1}{2})^2 w_s. \quad (7.23.1)$$

Alternatively, either from (7.21.7) or more directly from (7.21.1) and (7.21.2) we have

$$\frac{1}{4N} \{U(r) - U(1)\} = \frac{1}{2}(1-r)(r+\frac{1}{2})w_s. \quad (7.23.2)$$

Formula (1) gives the difference between the value of U in the limit $T \rightarrow \infty$ ($r \rightarrow \frac{1}{2}$) and its value at an intermediate temperature; formula

(2) gives the difference between the value of U at an intermediate temperature and its value in the limit $T \rightarrow 0$ ($r \rightarrow 1$). In either formula r is related to the temperature by (7.22.2). From this formula we can calculate directly the temperature T at which r has an equilibrium value in the range $r_t \leq r \leq 1$. The result is shown plotted as the broken curve in Fig. 7.7.

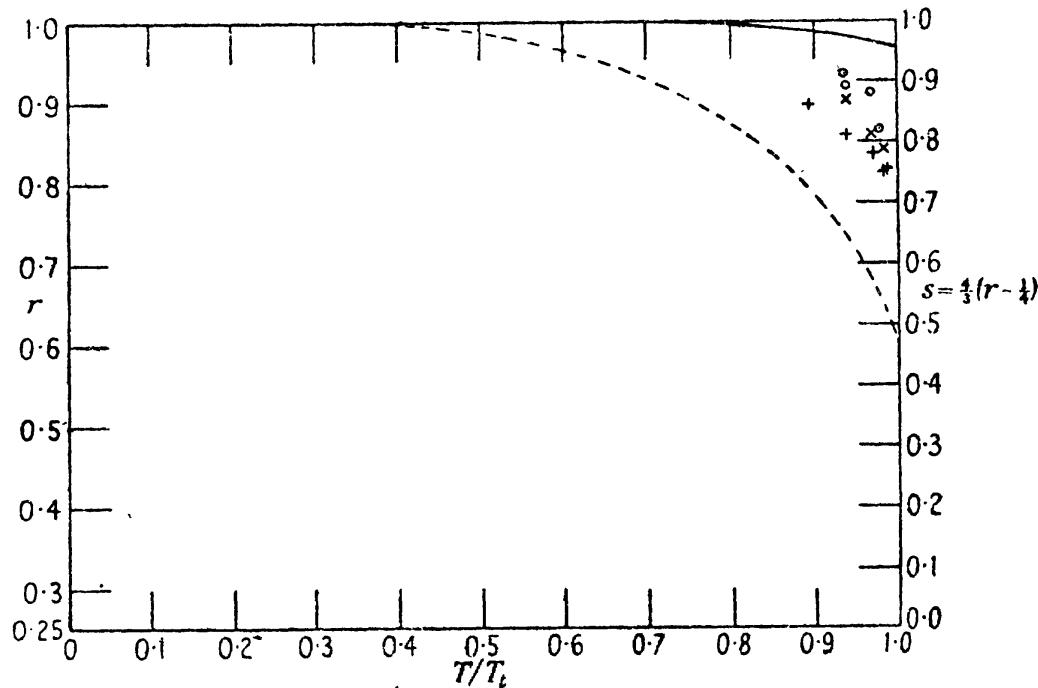


FIG. 7.7. Equilibrium degree of order as function of temperature for alloy of composition AC_3 . —— zeroth approximation. —— first approximation, $z = 12$. \times experimental data of Wilchinsky for $AuCu_3$. \odot , + experimental data of Cowley for $AuCu_3$ (two series).

Since in the transition at T_t the equilibrium value of r changes suddenly from r_t to $\frac{1}{2}$, it follows from (1) that the energy of the transition is given by

$$\frac{\Delta U}{4N} = \frac{1}{2}(r_t - \frac{1}{2})^2 w_s = \frac{1}{2}(0.347)^2 w_s, \quad (7.23.3)$$

or by
$$\frac{\Delta U}{4NkT_t} = \frac{1}{2}(0.347)^2 \times 7.32 = 0.098. \quad (7.23.4)$$

7.24. Degree of order

We have seen that at temperatures above the transition temperature the equilibrium value of r is $\frac{1}{2}$ whereas at temperatures below the transition temperature r has values between 0.597 at T_t and 1 as $T \rightarrow 0$. It is sometimes considered† convenient to use instead of r a linear function of r having the value zero in the limit $T \rightarrow \infty$ and the value

† Bragg and Williams (1934), *Proc. Roy. Soc. A* 145, 702.

unity in the limit $T \rightarrow 0$. This linear function is called the *degree of order* and is denoted by s . The relation defining s is

$$s = \frac{1}{2}(r - \frac{1}{4}). \quad (7.24.1)$$

Any of our formulae involving r can by means of (1) be transcribed into formulae involving s . In particular the formulae (7.23.1) and (7.23.2) for the total energy can be rewritten as

$$\frac{1}{4N} \{U(0) - U(s)\} = \frac{1}{16}s^2 w_s, \quad (7.24.2)$$

$$\frac{1}{4N} \{U(s) - U(1)\} = \frac{1}{16}(1 - s^2) w_s. \quad (7.24.3)$$

We can transcribe (7.22.2) into an equation determining the equilibrium value of s , namely

$$\frac{w_s}{kT} = \frac{3}{2s} \ln \left\{ 1 + \frac{16s}{3(1-s)^2} \right\} \quad (T \leq T_i). \quad (7.24.4)$$

The value s_i of s of the ordered phase at the transition temperature is 0.463.

7.25. First approximation

We shall now consider a better approximation which, in accordance with the terminology already used for regular mixtures in Chapter IV and for β -brass in §§ 7.11–7.14, we call the first approximation or the quasi-chemical approximation. It is mathematically equivalent to Bethe's method in its usual form.

It was first stated by Peierls† that this method, applied in its usual and simplest form, predicts wrongly that in the system AuCu_3 a superlattice is never stable however low the temperature. By extending the application of Bethe's method to a group of thirteen sites on a close-packed lattice Peierls was able to deduce a transition to a superlattice at low temperatures, but the algebra required is so cumbrous and complicated that only incomplete and approximate numerical results were obtained. As we shall see, these algebraic difficulties can be avoided by confining our attention to suitably chosen groups of only four sites instead of the thirteen sites considered by Peierls.

Li‡ has made the statement, recalling that of Peierls, that a stable superlattice in AuCu_3 cannot be explained by the quasi-chemical approximation applied to pairs of neighbouring sites. Yang and Li§ have, however, shown that a stable superlattice at low temperatures

† Peierls (1936), *Proc. Roy. Soc. A* 154, 207. ‡ Li (1949), *Phys. Rev.* 76, 972.
§ Yang (1945), *J. Chem. Phys.* 13, 66. Yang and Li (1947), *Chinese J. Phys.* 7, 59.

and a phase change to a disordered structure at a transition temperature can be accounted for by applying the quasi-chemical approximation to tetrahedral quadruplets of sites. Such a group contains one site on each of the four sublattices a, c_1, c_2, c_3 and may therefore be regarded† in a sense as the smallest and simplest group of sites capable of representing the superlattice. This may well be the reason why the quasi-chemical approximation applied to such groups of sites leads to physically correct results in contrast to the application of the same approximation to pairs of sites. We shall now describe the quasi-chemical approximation applied to a tetrahedral group of sites. Our treatment will follow closely that used in § 4.21 for regular mixtures. This treatment‡ differs in details of algebra from that of Yang and Li, but the conclusions are identical.

We consider a system of $\frac{1}{z}N = 4N$ tetrahedral quadruplets of sites in order that the total number of pairs of neighbouring sites shall have the correct value $\frac{1}{2}z4N = 24N$ for a crystal consisting of $4N$ sites, N on each of the four sublattices a, c_1, c_2, c_3 . We begin by constructing Table 7.8 specifying the various manners of occupation of the group of four sites

TABLE 7.8
Distribution of Quadruplets

<i>Manner of occupation of group</i>	<i>Number of groups so occupied</i>	<i>Energy of all groups so occupied</i>
$a \quad c \ c \ c$		
$A \quad AAA$	$\frac{1}{z}Na$	$-\frac{2}{z}\chi_A 6Na$
$A \quad AAC$	$\frac{1}{z}N3b$	$-\frac{2}{z}\{\frac{1}{2}\chi_A + \frac{1}{2}\chi_C + \frac{1}{2}w_s\}3Nb$
$A \quad ACC$	$\frac{1}{z}N3c$	$-\frac{2}{z}\{3\chi_A + 3\chi_C + 2w_s\}3Nc$
$A \quad CCC$	$\frac{1}{z}Nd$	$-\frac{2}{z}\{\frac{3}{2}\chi_A + \frac{3}{2}\chi_C + \frac{3}{2}w_s\}Nd$
$C \quad AAA$	$\frac{1}{z}Ne$	$-\frac{2}{z}\{\frac{1}{2}\chi_A + \frac{1}{2}\chi_C + \frac{1}{2}w_s\}Ne$
$C \quad AAC$	$\frac{1}{z}N3f$	$-\frac{2}{z}\{3\chi_A + 3\chi_C + 2w_s\}3Nf$
$C \quad ACC$	$\frac{1}{z}N3g$	$-\frac{2}{z}\{\frac{3}{2}\chi_A + \frac{3}{2}\chi_C + \frac{3}{2}w_s\}3Ng$
$C \quad CCC$	$\frac{1}{z}Nh$	$-\frac{2}{z}\chi 6Nh$

with their numbers and energies. The second column of the table defines parameters a, b, c, d, e, f, g, h proportional to the numbers of groups occupied in the several manners. The factors 3 occurring in some places take account of the distinguishability of the three sub-lattices c_1, c_2 , and c_3 . The energies given in the third column follow immediately from the definitions of χ_A , χ_C , and w_s namely that the contributions of AA , CC , and AC pairs to the configurational energy are denoted by $-2\chi_A/z$, $-2\chi_C/z$, and $-(\chi_A + \chi_C + w_s)/z$ respectively.

† Yang (1945), *J. Chem. Phys.* 13, 66. Yang and Li (1947), *Chinese J. Phys.* 7, 59.

‡ McGlashan (1951), Thesis, Reading University.

The eight parameters a, b, c, d, e, f, g, h are not all independent. The conditions that the total number of groups of four sites considered is $\frac{1}{3}zN$ and that the fraction of a sites occupied by A atoms is r can together be expressed as

$$a = r - 3b - 3c - d, \quad (7.25.1)$$

$$h = 1 - r - 3g - 3f - e. \quad (7.25.2)$$

We accordingly regard a and h as abbreviations for the quantities defined by the equations (1) and (2) respectively.

There is also the condition that the number of A atoms is equal to the number of a sites. When we use (1) and (2), this condition can be expressed as

$$r - b - 2c - d = \frac{1}{3}(1 - r) - g - 2f - e. \quad (7.25.3)$$

From the third column of Table 7.8 using (1), (2), and (3) we can obtain various equivalent formulae for the configurational energy E_c . One such formula is

$$E_c = -N\{\chi_A + 3\chi_C + (1 - a + c + f - h)w_s\}. \quad (7.25.4)$$

From the second column of Table 7.8, using the principles prescribed in § 4.14, we now write down as in § 4.21 an approximate formula for the number of configurations for given N, r and given a, b, c, d, e, f, g, h subject to (1), (2), and (3). The expression† so obtained is

$$\begin{aligned} g(N, r, a, \dots, h) &= \frac{N!}{\{Nr\}! \{N(1-r)\}!} \frac{(3N)!}{\{N(1-r)\}! \{N(2+r)\}!} \frac{(\frac{1}{3}zNa^*)!}{(\frac{1}{3}zNa)!} \times \\ &\times \frac{\{(\frac{1}{3}zNb^*)!\}^3 \{(\frac{1}{3}zNc^*)!\}^3 \{(\frac{1}{3}zNd^*)!\}^3 \{(\frac{1}{3}Ne^*)!\}^3 \{(\frac{1}{3}Nf^*)!\}^3 \{(\frac{1}{3}Ng^*)!\}^3 \{(\frac{1}{3}Nh^*)!\}}{((\frac{1}{3}Nb)!)^3 ((\frac{1}{3}Nc)!)^3 ((\frac{1}{3}Nd)!)^3 ((\frac{1}{3}Ne)!)^3 ((\frac{1}{3}Nf)!)^3 ((\frac{1}{3}Ng)!)^3 ((\frac{1}{3}Nh)!)}, \end{aligned} \quad (7.25.5)$$

where a^*, \dots, h^* denotes the values of a, \dots, h in a completely random arrangement. According to this definition their values are given by

$$\begin{aligned} a^* &= r(1-r)^3/27, \\ b^* &= r(1-r)^2(2+r)/27, \\ c^* &= r(1-r)(2+r)^2/27, \\ d^* &= r(2+r)^3/27, \\ e^* &= (1-r)^4/27, \\ f^* &= (1-r)^3(2+r)/27, \\ g^* &= (1-r)^2(2+r)^2/27, \\ h^* &= (1-r)(2+r)^3/27. \end{aligned} \quad (7.25.6)$$

† The function $g()$ will not be confused with the parameter g .

The configurational partition function $\Omega(T, N, r)$ for the system is obtained by substituting from (4) and (5) into the general formula

$$\Omega(T, N, r) = \sum g(N, r, a, \dots, h) \exp\{-E_c(N, r, a, \dots, h)/kT\}, \quad (7.25.7)$$

where the summation extends over all values of a, b, c, d, e, f, g, h consistent with the conditions (1), (2), and (3).

As usual we may replace the sum in (7) by its maximum term. We accordingly write

$$\Omega(T, N, r) = g(N, r, a, \dots, h) \exp\{-E_c(N, r, a, \dots, h)/kT\}, \quad (7.25.8)$$

where the values of a, b, c, d, e, f, g, h are such as to maximize the expression subject to the conditions (1), (2), and (3). These conditions of maximization are satisfied when

$$\frac{a}{\epsilon^3} = \frac{b\eta^3}{\epsilon^2} = \frac{c\eta^4}{\epsilon} = d\eta^3, \quad (7.25.9)$$

$$\frac{e\eta^3}{\epsilon^3} = \frac{f\eta^4}{\epsilon^2} = \frac{g\eta^3}{\epsilon} = h, \quad (7.25.10)$$

where η denotes as previously $e^{-w_e/kT}$ and ϵ is a parameter, whose value has to satisfy the conditions (1), (2), and (3).

At this stage we may remark that if, instead of starting from the combinatory formula (5), we had applied Bethe's method to tetrahedral groups of sites we should have written down equations (9) and (10) or their equivalent *ab initio*. Such procedure would thus appear at first sight to provide a useful short cut, but it would still leave unsolved the problem of constructing a formula for the free energy, whereas in the procedure adopted this follows, as we shall see, directly from formula (8). By eliminating ϵ from the equations (9) and (10) we can, of course, obtain a number of quasi-chemical equations which it is not necessary to write down.

Substituting from (9) and (10) into (1), (2), and (3) we obtain eventually

$$\frac{3r}{1-r} = \frac{(1-3\epsilon^2\eta^{-4}-2\epsilon^3\eta^{-3})(1+3\epsilon^{-1}\eta^{-3}+3\epsilon^{-2}\eta^{-4}+\epsilon^{-3}\eta^{-5})}{(1+2\epsilon^{-1}\eta^{-3}+\epsilon^{-2}\eta^{-4})(1+3\epsilon\eta^{-3}+3\epsilon^2\eta^{-4}+\epsilon^3\eta^{-5})}. \quad (7.25.11)$$

This equation determines the value of ϵ and hence all the parameters a, b, c, d, e, f, g, h for given r and η .

The configurational free energy for any values of T, r is given by

$$\begin{aligned} F_c(T, r) &= -kT \ln \Omega(T, r) \\ &= -kT \ln g(T, r) + E_c(T, r). \end{aligned} \quad (7.25.12)$$

Substituting (4) and (5) into (12) and using formulae (6), (9), and (10) to simplify the expression we obtain eventually for $z = 12$,

$$\begin{aligned} \frac{F_c(T, r)}{NkT} = & r \ln r + 2(1-r) \ln(1-r) + (2+r) \ln(2+r) - 3 \ln 3 + \\ & + \ln \frac{a}{a^*} + 3 \ln \frac{h}{h^*} + (4r-1) \ln \frac{cf^*}{c^*f} - \frac{\chi_A + 3\chi_C}{kT}. \end{aligned} \quad (7.25.13)$$

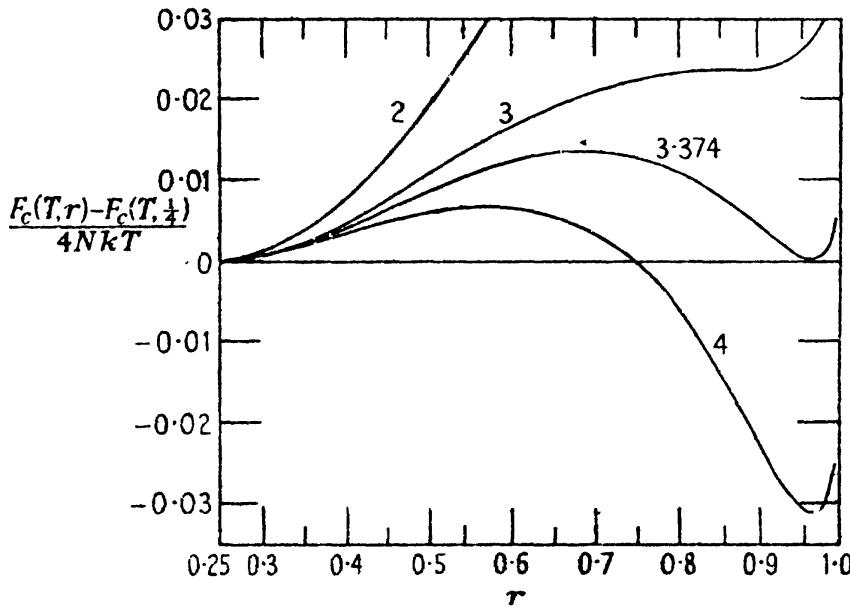


FIG. 7.8. Dependence of the configurational free energy $F_c(T, r)$ on r for alloy AC_3 according to the first approximation for several temperatures. The numbers attached to the curves are values of $\eta^{-1} = \exp(w_s/12kT)$.

The formula for $\partial F_c/\partial r$, which will also be required, can similarly be reduced for $z = 12$ to the form

$$\frac{1}{NkT} \frac{\partial F_c(T, r)}{\partial r} = -3 \ln \frac{r(2+r)}{(1-r)^2} + 4 \ln \frac{c}{f}. \quad (7.25.14)$$

7.26. Numerical results

By means of the formulae of the previous section the value of the configurational free energy $F_c(T, r)$ can be calculated for any given values of T or η and of r . This has been done for several temperatures and the result is shown in Fig. 7.8 where $\{F_c(T, r) - F_c(T, \frac{1}{2})\}/4NkT$ has been plotted against r for several values of $\eta^{-1} = e^{w_s/12kT}$. By comparison with Fig. 7.6 we see immediately that the predictions of the present treatment are qualitatively similar to those of the zeroth approximation. At high temperatures the only stationary value of $F_c(r)$ is at $r = \frac{1}{2}$ and the stable state is that of complete disorder. As the temperature

is lowered a second minimum appears, but is initially higher than that at $r = \frac{1}{2}$; the stable state is still that of complete disorder, the second minimum being metastable. At still lower temperatures the second minimum becomes lower than that at $r = \frac{1}{2}$ and so the stable state is the other minimum which we denote by $r = r^*$. Of particular interest is the transition temperature T_t where the stable phase changes suddenly from $r = \frac{1}{2}$ to $r = r^*$. This is determined by the simultaneous equations

$$F_c(T_t, r^*) - F_c(T_t, \frac{1}{2}) = 0, \quad (7.26.1)$$

$$\frac{\partial F_c}{\partial r} = 0 \quad (r = r^*, T = T_t). \quad (7.26.2)$$

These equations have been solved numerically and the results obtained are

$$\eta_t^{-1} = \exp(w_s/12kT_t) = 3.3740, \quad w_s/kT_t = 14.593,$$

$$r^* = 0.9663 \quad (T = T_t).$$

At temperatures below T_t the equilibrium value r^* of r is determined by equation (2). This has been solved numerically and the result is shown as the full curve in Fig. 7.7. Having determined the equilibrium value of r at each temperature we obtain the configurational total energy $U_c(T)$ by substituting this value of r into formula (7.25.4) for $E_c(T, r)$. The result is shown in Fig. 7.9 where $\{U_c(T, r) - U_c(T_t, \frac{1}{2})\}/4NkT_t$ is plotted against T/T_t . The broken curve in Fig. 7.9 is that calculated according to the zeroth approximation from formula (7.23.1). The single point calculated approximately by Peierls[†] is also shown on the diagram.

7.27. Comparison with experiment

We shall now briefly compare the theory with the experimental results for the alloy AuCu₃. This alloy has been thoroughly investigated by Sykes and Jones.[‡] They established a sharp phase change at 664° K. with a heat of transition of 1.26 ± 0.13 cal./g.

Rough estimates of the degree of order can be obtained from the intensities of the superlattice lines in the X-ray spectrum of the alloy AuCu₃. The estimates thus obtained by Wilchinsky[§] and by Cowley^{||} are shown in Fig. 7.7. The agreement between experiment and theory, either zeroth or first approximation, is rather poor.

[†] Peierls (1936), *Proc. Roy. Soc. A* 154, 207.

[‡] Sykes and Jones (1936), *Proc. Roy. Soc. A* 157, 213.

[§] Wilchinsky (1944), *J. App. Phys.* 15, 806.

^{||} Cowley (1950), *J. App. Phys.* 21, 24.

For a further comparison between theory and experiment we use the calorimetric measurements of Sykes and Jones† on AuCu_3 . These are shown‡ plotted in Fig. 7.9. We have arbitrarily chosen to superpose the experimental points on the theoretical curves so that they agree for the disordered state $r = \frac{1}{2}$ at the transition temperature $T = T_t$. The experimental points below the transition temperature and one point above the transition temperature were determined by

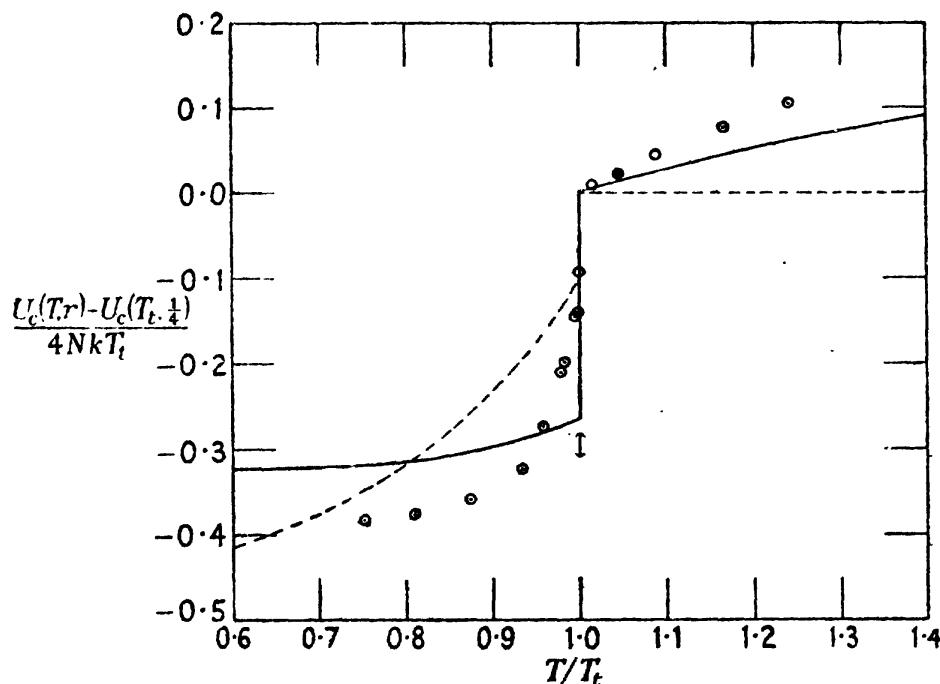


FIG. 7.9. Equilibrium configurational energy as function of temperature for alloy of composition AC_3 . — zeroth approximation. — first approximation, $z = 12$. \downarrow Peierls's approximation. \circ calorimetric measurements of Sykes and Jones for AuCu_3 .

direct measurements of the energy of transformation. The remaining points above the transition temperature have been estimated by rough integration between the observed specific heat curve and the estimated curve for an ideal mixture of gold and copper in the proportion 1:3.

Qualitatively both the zeroth and the first approximations successfully predict the formation of a superlattice at low temperatures and

† Sykes and Jones (1936), *Proc. Roy. Soc. A* **157**, 213.

‡ The theoretical curve for the zeroth approximation is given correctly by Bragg and Williams (1935), *Proc. Roy. Soc. A* **151**, 561, Fig. 8. Unfortunately the curve given by Sykes and Jones (1936), *Proc. Roy. Soc. A* **157**, 219, Fig. 3, curve *b*, is based on Bragg and Williams (1934), *Proc. Roy. Soc. A* **145**, 711, Fig. 7, which is wrongly drawn. Nix and Shockley (1938), *Rev. Mod. Phys.* **10**, 1 in Fig. 37, copy the incorrect curve, but give the correct curve in Fig. 12.

its sudden disappearance at a transition temperature with a discontinuity in the energy. Quantitatively the agreement between theory and experiment is far from good and this agreement is hardly improved when the zeroth approximation of Bragg and Williams is replaced by the quasi-chemical approximation. It appears that the theory does not go deep enough to give more than a semi-quantitative account of the actual behaviour of the alloy. This is accentuated by recent experimental work† on the alloy Au_3Cu . This alloy, like AuCu_3 , has been shown to undergo a phase change from an ordered to a disordered structure, but the transition temperature is reported to be 516°K . which is considerably lower than the 664°K . of AuCu_3 . According to the present theory, or any modification of it which treats the system as composed of structureless atoms, the two alloys should have the same transition temperature. The asymmetry between the two components is evidently related to the electronic structure of the alloys which has here been ignored.

7.28. AuCu superlattice

See Appendix, p. 259.

7.29. First approximation

See Appendix, p. 260.

7.30. Numerical results

See Appendix, p. 262.

† Hirabayashi (1951), *J. Phys. Soc. Japan*, 6, 129.

VIII

GASEOUS MIXTURES

8.01. Introduction

GASES are strikingly different from liquids or solids in that the molecules are mostly far apart. In liquids and solids the molecules are in close contact so that the volume of the whole phase is determined mainly by the number of molecules of each kind and this volume is only slightly affected by changes of pressure. It is therefore convenient for liquids and solids to choose the pressure as independent variable and then, for many purposes, to ignore it. In gases, on the contrary, the volume is determined by the containing vessel and is, at least initially, a natural choice for an independent variable.

The most important thermodynamic potential for a gas is the free energy $F(T, V)$ rather than $G(T, P)$. We must also remember that for a gas the difference between the values of G and F is not trivial, as it usually is for liquids or solids; we must not treat G and F as equal to each other, as we have been doing for liquids and solids.

Owing to the wide separation of the molecules of a gas the interactions between the molecules play a minor part except at very high pressures. At ordinary and lower pressures the interactions between molecules may often be entirely neglected. When they are neglected the gas is said to be a *perfect gas*. We must, however, emphasize that a perfect gas is not a reality but an abstraction corresponding to an approximate model.

8.02. Mixture of perfect gases

We begin by considering a mixture of N_A molecules A and N_B molecules B in a volume V and initially we neglect all interactions between molecules. The degrees of freedom of any two different molecules are, to this approximation, completely separable and so the partition function is a product of factors for individual molecules. We accordingly write

$$Q = \frac{(Q_A)^{N_A}}{N_A!} \frac{(Q_B)^{N_B}}{N_B!}, \quad (8.02.1)$$

where Q_A , Q_B are molecular partition functions independent of N_A , N_B . The factors $N_A!$ and $N_B!$ in the denominator are required to take care of the indistinguishability of identical molecules.

The molecular partition function Q_A is itself separable into a factor

proportional to V for the translational degrees of freedom and a factor independent of V for the remaining degrees of freedom. We accordingly write

$$Q_A = \phi_A V, \quad (8.02.2)$$

where ϕ_A is independent of V , N_A , N_B and similarly

$$Q_B = \phi_B V. \quad (8.02.3)$$

Substituting (2) and (3) into (1) we have

$$Q = \frac{(\phi_A V)^{N_A}}{N_A!} \frac{(\phi_B V)^{N_B}}{N_B!}. \quad (8.02.4)$$

The free energy F is accordingly given by

$$F = -kT \ln Q = N_A kT \left(\ln \frac{N_A}{\phi_A V} - 1 \right) + N_B kT \left(\ln \frac{N_B}{\phi_B V} - 1 \right). \quad (8.02.5)$$

From (5) we see that for a given volume V the free energies of the two component gases are additive. It follows immediately by differentiating with respect to T that for a given volume V the entropies and the energies are also additive.

By differentiating (5) with respect to V we obtain for the pressure P

$$P = -\frac{\partial F}{\partial V} = (N_A + N_B) \frac{kT}{V}, \quad (8.02.6)$$

so that for a given volume V the pressures are also additive. The component terms $N_A kT/V$ and $N_B kT/V$ are called the *partial pressures* and are denoted by p_A and p_B respectively.

The chemical potentials μ_A , μ_B are obtained from (5) by differentiating with respect to N_A , N_B respectively. Thus

$$\mu_A = \left(\frac{\partial F}{\partial N_A} \right)_V = kT \ln \frac{N_A}{\phi_A V}, \quad (8.02.7)$$

$$\mu_B = \left(\frac{\partial F}{\partial N_B} \right)_V = kT \ln \frac{N_B}{\phi_B V}. \quad (8.02.8)$$

We thus see that the chemical potential of each gas is determined by its concentration and is independent of the presence of the other gas.

This is all we need to say about a mixture of perfect gases when the independent variables are T , V , N_A , N_B . Let us now examine what happens when we change the independent variables to T , P , N_A , N_B . Using (6) in (5) we obtain

$$G = F + PV = N_A kT \ln \frac{N_A P}{(N_A + N_B) \phi_A kT} + N_B kT \ln \frac{N_B P}{(N_A + N_B) \phi_B kT}. \quad (8.02.9)$$

From (9) we see that for a given pressure P , in contrast to a given volume V , the value of G for the mixture is less than that of the separate gases each at the pressure P by the amount

$$-\Delta G = N_A kT \ln \frac{N_A + N_B}{N_A} + N_B kT \ln \frac{N_A + N_B}{N_B}. \quad (8.02.10)$$

By differentiation with respect to T it follows that the entropy of the mixture at the pressure P exceeds that of the separate gases each at the pressure P by the amount

$$\Delta S = N_A k \ln \frac{N_A + N_B}{N_A} + N_B k \ln \frac{N_A + N_B}{N_B}. \quad (8.02.11)$$

We thus see that the entropy of mixing at given pressure is given by the same expression as for an ideal liquid mixture, whereas the entropy of mixing at given volume is zero.

We can obtain the chemical potentials by differentiating (9) with respect to N_A , N_B respectively. Thus

$$\mu_A = \left(\frac{\partial G}{\partial N_A} \right)_P = kT \ln \frac{N_A P}{(N_A + N_B) \phi_A kT}, \quad (8.02.12)$$

$$\mu_B = \left(\frac{\partial G}{\partial N_B} \right)_P = kT \ln \frac{N_B P}{(N_A + N_B) \phi_B kT}, \quad (8.02.13)$$

in agreement with (7), (8) respectively. If we introduce the partial pressures p_A , p_B we can rewrite (12), (13) as

$$\mu_A = kT \ln \frac{p_A}{\phi_A kT}, \quad (8.02.14)$$

$$\mu_B = kT \ln \frac{p_B}{\phi_B kT}, \quad (8.02.15)$$

and the absolute activities λ_A , λ_B are given by

$$\lambda_A = p_A / \phi_A kT, \quad (8.02.16)$$

$$\lambda_B = p_B / \phi_B kT. \quad (8.02.17)$$

This proportionality between absolute activity and partial vapour pressure in a perfect gas has been frequently assumed in previous chapters.

8.03. Single pair of interacting molecules

We turn now to the more serious study of real gases, bearing in mind that their resemblances to perfect gases are more striking than their differences from perfect gases. As a first step towards the study of real gases it is profitable to consider the behaviour of a single pair of

molecules, which we denote by i, k respectively and which at this stage we treat as distinguishable.

If there were no interaction at all between the two molecules i and k , the partition function for the pair of molecules, treated as distinguishable, would be the simple product of the partition functions for the two isolated molecules, namely $\phi_i \phi_k V^2$. We now study how this partition function is altered by the interaction between the two molecules.[†] If we denote the interaction energy for a particular configuration of each molecule by w_{ik} , then we have to replace the factor V^2 by the integral of $e^{-w_{ik}kT}$ over all positions of both molecules. If we choose as independent coordinates one set describing the position of the centre of mass of the pair of molecules and the other describing the position of the molecule k relative to that of i , the integral becomes a product of V and a factor depending only on the relative position of the two molecules. In particular if we assume that the interaction energy depends only on the distance r between the two molecules, the partition function Q for the pair of molecules regarded as distinguishable has the form

$$Q = \phi_i \phi_k V \int e^{-w_{ik}kT} 4\pi r^2 dr, \quad (8.03.1)$$

where the integration extends over all possible values of r when the two molecules are both inside the volume V . If the forces between the molecules are not central the integral will be more complicated but the main ensuing argument will be unaffected. Since two molecules interact appreciably with each other only when they are rather close together, $e^{-w_{ik}kT}$ is unity for all values of r except those comparable with the dimensions of the molecule, say five or ten diameters. It is expedient to rewrite (1) in the form

$$Q = \phi_i \phi_k V (V + 2b_{ik}), \quad (8.03.2)$$

where b_{ik} is defined by

$$b_{ik} = \frac{1}{2} \int_0^R (e^{-w_{ik}kT} - 1) 4\pi r^2 dr \quad (8.03.3)$$

and R is a distance beyond which w_{ik} becomes negligible. The important property of b_{ik} is that it is independent of V . Even if the intermolecular forces are not central, it is still possible to write Q in the form (2) with b_{ik} independent of V .

We shall refer to two molecules within a distance R of each other,

[†] See Mayer and Mayer (1940), *Statistical Mechanics*, chap. xiii, Wiley; Rushbrooke (1949), *Statistical Mechanics*, chap. xvi, Oxford University Press.

where R is the distance beyond which w_{ik} becomes negligible, as an *interacting pair*. We may regard the term $\phi_i \phi_k V 2b_{ik}$ in (2) as the contribution of the interacting pair to the complete partition function of the two molecules.

8.04. Slightly imperfect real gas

We now consider a mixture containing N_A molecules of A and N_B molecules of B . We denote the interaction energies of two A molecules by w_{AA} , of two B molecules by w_{BB} , and of an A molecule with a B molecule by w_{AB} . We have seen that when we ignore interactions the partition function of the gaseous mixture is according to (8.02.4)

$$\frac{(\phi_A V)^{N_A}}{N_A!} \frac{(\phi_B V)^{N_B}}{N_B!}. \quad (8.04.1)$$

When we take into account the molecular interactions we have to replace the factors $V^{N_A+N_B}$ by the integral of $e^{-W/kT}$ over all positions of all the molecules, where W denotes the total mutual interaction energy for a particular configuration. In general W will contain not only terms due to pairs of molecules near enough to each other to contribute, but also terms due to triplets of molecules close to one another as well as to quadruplets and larger clusters. The problem of evaluating the partition function is then rather complicated, but it is considerably simplified if we restrict ourselves to sufficiently low pressures so that we may ignore the simultaneous proximity of any molecule to more than one other. We call a gas subject to this restriction *slightly imperfect*. For the common gases this gives a useful approximation for pressures up to a few atmospheres.

Let us denote the number of interacting pairs of the three kinds AA , AB , BB in a given configuration by n_{AA} , n_{AB} , n_{BB} respectively. We now group together all configurations having the same values of n_{AA} , n_{AB} , n_{BB} . By an extension of the reasoning and notation of § 8.03 it can be shown that the contribution of each such group of configurations to the partition function is

$$g(n_{AA}, n_{AB}, n_{BB}) \frac{(\phi_A V)^{N_A}}{N_A!} \frac{(\phi_B V)^{N_B}}{N_B!} \left(\frac{2b_{AA}}{V} \right)^{n_{AA}} \left(\frac{2b_{AB}}{V} \right)^{n_{AB}} \left(\frac{2b_{BB}}{V} \right)^{n_{BB}}, \quad (8.04.2)$$

where b_{AA} , b_{AB} , b_{BB} are related to w_{AA} , w_{AB} , w_{BB} by definitions of the form (8.03.3) and where $g(n_{AA}, n_{AB}, n_{BB})$ denotes the number of possible

ways of choosing n_{AA} pairs AA , n_{AB} pairs AB , and n_{BB} pairs BB out of N_A molecules A and N_B molecules B . Its value is given by

$$g(n_{AA}, n_{AB}, n_{BB}) = \frac{N_A! N_B!}{(N_A - 2n_{AA} - n_{AB})! (N_B - 2n_{BB} - n_{AB})!} \times \\ \times \frac{1}{n_{AA}! n_{AB}! n_{BB}! 2^{n_{AA}} 2^{n_{BB}}} \quad (8.04.3)$$

Substituting (3) into (2) and then forming the sum for all possible values of n_{AA} , n_{AB} , n_{BB} we obtain the partition function

$$Q = \sum_{n_{AA}, n_{AB}, n_{BB}} \frac{(\phi_A V)^{N_A} (\phi_B V)^{N_B} (b_{AA}/V)^{n_{AA}} (2b_{AB}/V)^{n_{AB}} (b_{BB}/V)^{n_{BB}}}{(N_A - 2n_{AA} - n_{AB})! (N_B - 2n_{BB} - n_{AB})! n_{AA}! n_{AB}! n_{BB}!} \quad (8.04.4)$$

We may with sufficient accuracy replace Q by its greatest term, which is determined by

$$\frac{n_{AA}}{(N_A - 2n_{AA} - n_{AB})^2} = \frac{b_{AA}}{V}, \quad (8.04.5)$$

$$\frac{n_{AB}}{(N_A - 2n_{AA} - n_{AB})(N_B - 2n_{BB} - n_{AB})} = 2 \frac{b_{AB}}{V}, \quad (8.04.6)$$

$$\frac{n_{BB}}{(N_B - 2n_{BB} - n_{AB})^2} = \frac{b_{BB}}{V}. \quad (8.04.7)$$

When we substitute (5), (6), and (7) into a single term of (4), we obtain using Stirling's theorem

$$\ln Q = N_A (\ln \phi_A V + 1) + N_B (\ln \phi_B V + 1) - N_A \ln (N_A - 2n_{AA} - n_{AB}) - \\ - N_B \ln (N_B - 2n_{BB} - n_{AB}) - (n_{AA} + n_{AB} + n_{BB}), \quad (8.04.8)$$

other terms cancelling. Our assumption that the gas is only slightly imperfect implies that n_{AA} , n_{AB} are much smaller than N_A and that n_{AB} , n_{BB} are much smaller than N_B . We therefore expand the logarithms and neglect terms like n_{AA}^2/N_A . The expression for $\ln Q$ then reduces to

$$\ln Q = N_A \left(\ln \frac{\phi_A V}{N_A} + 1 \right) + N_B \left(\ln \frac{\phi_B V}{N_B} + 1 \right) + (n_{AA} + n_{AB} + n_{BB}). \quad (8.04.9)$$

Now substituting for n_{AA} , n_{AB} , n_{BB} from (5), (6), (7) respectively, neglecting terms small compared with n_{AA} , n_{AB} , n_{BB} , we obtain finally

$$\ln Q = N_A \left(\ln \frac{\phi_A V}{N_A} + 1 \right) + N_B \left(\ln \frac{\phi_B V}{N_B} + 1 \right) + \\ + \frac{1}{V} (N_A^2 b_{AA} + 2N_A N_B b_{AB} + N_B^2 b_{BB}). \quad (8.04.10)$$

The free energy F of the gaseous mixture may then be written

$$F = N_A kT \left(\ln \frac{N_A}{\phi_A V} - 1 \right) + N_B kT \left(\ln \frac{N_B}{\phi_B V} - 1 \right) + \\ + \frac{kT}{NV} (N_A^2 B_{AA} + 2N_A N_B B_{AB} + N_B^2 B_{BB}), \quad (8.04.11)$$

where B_{AA} , B_{AB} , B_{BB} are defined by

$$B_{AA} = -Nb_{AA}, \quad B_{AB} = -Nb_{AB}, \quad B_{BB} = -Nb_{BB}. \quad (8.04.12)$$

8.05. Virial coefficients

If the relation between the pressure P and volume per mole V_m of a gas is written empirically as

$$PV_m = RT \left\{ 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right\}, \quad (8.05.1)$$

B is called the *second virial coefficient* and C the *third virial coefficient*. In a perfect gas the second and all higher virial coefficients are ignored. When we regard a gas as slightly imperfect, we neglect the third and higher virial coefficients but take account of the second.

By differentiating (8.04.11) with respect to V we obtain for the pressure of a slightly imperfect gaseous mixture

$$P = -\frac{\partial F}{\partial V} = (N_A + N_B) \frac{kT}{V} + \frac{kT}{NV^2} (N_A^2 B_{AA} + 2N_A N_B B_{AB} + N_B^2 B_{BB}). \quad (8.05.2)$$

If we denote the total number of molecules by N and introduce the mole fraction x by the definition

$$N_A = (1-x)N, \quad N_B = xN, \quad (8.05.3)$$

we can rewrite (2) as

$$P = \frac{NkT}{V} + \frac{N^2 kT}{NV^2} \{(1-x)^2 B_{AA} + 2x(1-x) B_{AB} + x^2 B_{BB}\}, \quad (8.05.4)$$

or introducing the molar volume $V_m = NV/N$

$$PV_m = RT + \frac{RT}{V_m} \{(1-x)^2 B_{AA} + 2x(1-x) B_{AB} + x^2 B_{BB}\}. \quad (8.05.5)$$

Comparing (5) with (1) we see that the second virial coefficient B is given by

$$B = (1-x)^2 B_{AA} + 2x(1-x) B_{AB} + x^2 B_{BB}. \quad (8.05.6)$$

From (6) we conclude that the second virial coefficient B is a quadratic function of the mole fraction x .

8.06. Entropy, total energy, and chemical potentials

By differentiating formula (8.04.11) with respect to T we obtain for the entropy

$$\begin{aligned} S = - \left(\frac{\partial F}{\partial T} \right)_V &= -N_A k \left(\ln \frac{N_A}{\phi_A V} - 1 - T \frac{d \ln \phi_A}{dT} \right) - \\ &- N_B k \left(\ln \frac{N_B}{\phi_B V} - 1 - T \frac{d \ln \phi_B}{dT} \right) - \frac{k}{NV} \left\{ N_A^2 \left(B_{AA} + T \frac{dB_{AA}}{dT} \right) + \right. \\ &\quad \left. + 2N_A N_B \left(B_{AB} + T \frac{dB_{AB}}{dT} \right) + N_B^2 \left(B_{BB} + T \frac{dB_{BB}}{dT} \right) \right\}, \quad (8.06.1) \end{aligned}$$

and for the total energy U

$$\begin{aligned} U = F - T \left(\frac{\partial F}{\partial T} \right)_V &= F + TS \\ &= N_A k T^2 \frac{d \ln \phi_A}{dT} + N_B k T^2 \frac{d \ln \phi_B}{dT} - \\ &- \frac{k T^2}{NV} \left(N_A^2 \frac{dB_{AA}}{dT} + 2N_A N_B \frac{dB_{AB}}{dT} + N_B^2 \frac{dB_{BB}}{dT} \right). \quad (8.06.2) \end{aligned}$$

We obtain the chemical potentials μ_A , μ_B by differentiation of (8.04.11) with respect to N_A , N_B respectively. Thus

$$\mu_A = \left(\frac{\partial F}{\partial N_A} \right)_V = kT \ln \frac{N_A}{\phi_A V} + 2 \frac{kT}{NV} (N_A B_{AA} + N_B B_{AB}), \quad (8.06.3)$$

$$\mu_B = \left(\frac{\partial F}{\partial N_B} \right)_V = kT \ln \frac{N_B}{\phi_B V} + 2 \frac{kT}{NV} (N_B B_{BB} + N_A B_{AB}). \quad (8.06.4)$$

8.07. Change of variable from V to P

In case it is desired to use the pressure instead of the volume as independent variable, this is a convenient stage for making the change. We shall do this for a slightly imperfect gas. That is to say we shall retain the second virial coefficient, but neglect small terms of higher order in N/V .

Formula (8.05.2) expresses P as a power series in V^{-1} . We can invert this into a formula for V as a power series in P and obtain to the same degree of accuracy

$$\frac{V}{N_A + N_B} = \frac{kT}{P} + \frac{N_A^2 B_{AA} + 2N_A N_B B_{AB} + N_B^2 B_{BB}}{N(N_A + N_B)^2}. \quad (8.07.1)$$

Substituting (1) into (8.06.3) we obtain to the same degree of accuracy

$$\begin{aligned}\mu_A &= kT \ln \frac{N_A P}{(N_A + N_B)\phi_A kT} + \frac{P}{N} \left\{ B_{AA} + \left(\frac{N_B}{N_A + N_B} \right)^2 (2B_{AB} - B_{AA} - B_{BB}) \right\} \\ &= kT \ln \frac{(1-x)P}{\phi_A kT} + \frac{P}{N} \{ B_{AA} + x^2 (2B_{AB} - B_{AA} - B_{BB}) \},\end{aligned}\quad (8.07.2)$$

$$\begin{aligned}\mu_B &= kT \ln \frac{N_B P}{(N_A + N_B)\phi_B kT} + \frac{P}{N} \left\{ B_{BB} + \left(\frac{N_A}{N_A + N_B} \right)^2 (2B_{AB} - B_{AA} - B_{BB}) \right\} \\ &= kT \ln \frac{xP}{\phi_B kT} + \frac{P}{N} \{ B_{BB} + (1-x)^2 (2B_{AB} - B_{AA} - B_{BB}) \}.\end{aligned}\quad (8.07.3)$$

The Gibbs function G is given by

$$\begin{aligned}G &= F + PV = N_A \mu_A + N_B \mu_B \\ &= N_A kT \ln \frac{N_A P}{(N_A + N_B)\phi_A kT} + N_B kT \ln \frac{N_B P}{(N_A + N_B)\phi_B kT} + \\ &\quad + \frac{P}{N} \left\{ N_A B_{AA} + N_B B_{BB} + \frac{N_A N_B}{N_A + N_B} (2B_{AB} - B_{AA} - B_{BB}) \right\}.\end{aligned}\quad (8.07.4)$$

By differentiation of (4) with respect to T we obtain for the entropy

$$\begin{aligned}S &= -\frac{\partial G}{\partial T} = -N_A k \left\{ \ln \frac{N_A P}{(N_A + N_B)\phi_A kT} - 1 - T \frac{d \ln \phi_A}{dT} \right\} - \\ &\quad - N_B k \left\{ \ln \frac{N_B P}{(N_A + N_B)\phi_B kT} - 1 - T \frac{d \ln \phi_B}{dT} \right\} - \\ &\quad - \frac{P}{N} \left\{ N_A \frac{dB_{AA}}{dT} + N_B \frac{dB_{BB}}{dT} + \frac{N_A N_B}{N_A + N_B} \frac{d}{dT} (2B_{AB} - B_{AA} - B_{BB}) \right\},\end{aligned}\quad (8.07.5)$$

and for the heat function

$$\begin{aligned}H &= G - T \frac{\partial G}{\partial T} = G + TS \\ &= N_A kT \left(T \frac{d \ln \phi_A}{dT} + 1 \right) + N_B kT \left(T \frac{d \ln \phi_B}{dT} + 1 \right) + \\ &\quad + \frac{PN_A}{N} \left(B_{AA} - T \frac{dB_{AA}}{dT} \right) + \frac{PN_B}{N} \left(B_{BB} - T \frac{dB_{BB}}{dT} \right) + \\ &\quad + \frac{PN_A N_B}{N(N_A + N_B)} \left(1 - T \frac{d}{dT} \right) (2B_{AB} - B_{AA} - B_{BB}).\end{aligned}\quad (8.07.6)$$

8.08. Comparison with perfect gas. Fugacity

It is sometimes stated that as the pressure is indefinitely diminished the difference between the properties of a real and a perfect gas tends to zero. Actually it is easy to see that this statement is true of some

properties but false of others. Let us use the superscript Id to denote the value for a perfect gas at the same pressure. Then evidently

$$PV_m - (PV_m)^{\text{Id}} = PB \rightarrow 0 \quad \text{as } P \rightarrow 0. \quad (8.08.1)$$

Equally evidently $V_m - V_m^{\text{Id}} = B$, (8.08.2)

which remains non-zero when $P \rightarrow 0$. Again it is evident from (8.07.6) that $H - H^{\text{Id}}$ tends to zero with P , but that $\partial H / \partial P$, a quantity closely related to the Joule-Thomson effect, remains a non-zero constant.

Among the quantities which do tend to zero with P are $\mu - \mu^{\text{Id}}$ and $\ln(\lambda / \lambda^{\text{Id}})$. According to (8.07.2) we have

$$\lambda_A = \frac{(1-x)P}{\phi_A kT} \exp \left[\frac{P}{RT} \{ B_{AA} + x^2 (2B_{AB} - B_{AA} - B_{BB}) \} \right], \quad (8.08.3)$$

and a similar formula for λ_B . We see that as the pressure tends to zero, we have

$$\frac{\lambda_A}{(1-x)P} = \frac{\lambda_A}{p_A} \rightarrow \frac{1}{\phi_A kT} \quad (P \rightarrow 0), \quad (8.08.4)$$

where p_A denotes the partial pressure of A .

We can then define a quantity p_A^* , called the *fugacity*† of A , by

$$p_A^* = \phi_A kT \lambda_A, \quad (8.08.5)$$

or alternatively by the two conditions

$$p_A^* / \lambda_A = \text{const.} \quad (T \text{ const.}), \quad (8.08.6)$$

$$p_A^* / (1-x)P \rightarrow 1, \quad \text{as } P \rightarrow 0. \quad (8.08.7)$$

By using the fugacity, thus defined, many of the thermodynamic functions and equilibrium conditions for a real gas can be given the same simple form as for a perfect gas, except that the fugacity takes the place of the partial pressure. This simplification is purely formal and leads nowhere unless we are able to express the fugacity in terms of the pressure and the composition; when we do this we are back where we were before the fugacity was introduced. According to (3) the fugacity of A in a slightly imperfect binary gaseous mixture is given by

$$p_A^* = (1-x)P \exp \left[\frac{P}{RT} \{ B_{AA} + x^2 (2B_{AB} - B_{AA} - B_{BB}) \} \right], \quad (8.08.8)$$

$$p_B^* = xP \exp \left[\frac{P}{RT} \{ B_{BB} + (1-x)^2 (2B_{AB} - B_{AA} - B_{BB}) \} \right]. \quad (8.08.9)$$

† Lewis (1901), *Proc. Am. Acad. Sci.* 37, 49; (1901), *Z. Physikal. Chem.* 38, 205.

8.09. A naïve approximation

A glance over the formulae obtained for binary gaseous mixtures shows that many of them would simplify considerably if the quantity

$$B_{AB} - \frac{1}{2}(B_{AA} + B_{BB}) \quad (8.09.1)$$

were to vanish. In particular the fugacity of each component would be equal to the product of its mole fraction and the fugacity of the pure gas at the same total pressure. This would be an extremely convenient state of affairs.

Since it is often assumed† tacitly or explicitly that the quantity (1) does vanish, it may be said at once that there is no theoretical or experimental basis for such an assumption. We shall in the following sections show how for simple substances B_{AB} can be computed from a knowledge of B_{AA} and B_{BB} . We shall see that the naïve suggestion that the quantity (1) vanishes is completely disproved. The most that can be said is that the quantity (1) is often numerically much smaller than either B_{AA} or B_{BB} .

8.10. Corresponding states for mixed gases

We shall show how B_{AB} can be computed from a knowledge of B_{AA} and B_{BB} for mixtures of such substances as obey the principle of corresponding states. In general the more accurately the substances conform to this principle the more reliably one can predict the properties of the gaseous mixture. No attention whatever will be paid to polar substances, nor to substances which for chemical reasons cannot be expected to conform to the principle of corresponding states.

We must of necessity begin with a short digression on the principle of corresponding states for single substances. Whereas the principle of corresponding states had its historical origin in van der Waals's equation, the principle properly formulated‡ makes no reference to any particular equation of state, least of all to one known to be grossly inaccurate. The conditions for substances to conform to the principle have been clearly prescribed by Pitzer. In order that a substance shall conform to the principle of corresponding states it is necessary to use the assumption, amongst others, that the interaction energy w of two molecules distant r apart can be adequately represented by a relation of the form

$$\frac{w}{\epsilon^*} = u\left(\frac{r}{r^*}\right), \quad (8.10.1)$$

† Lewis and Randall (1923), *Thermodynamics and the Free Energy of Chemical Substances*, p. 225, McGraw-Hill; Beattie (1949), *Chem. Rev.* **44**, 178.

‡ Pitzer (1939), *J. Chem. Phys.* **7**, 583; Guggenheim (1945), *J. Chem. Phys.* **13**, 253.

where ϵ^* is an energy and r^* is a length both characteristic of the molecule, while u is the same function for all the molecules concerned. From (1) it can be shown by simple dimensional analysis that the relation between the second virial coefficient B and the temperature T is of the form

$$\frac{B}{V^*} = \phi\left(\frac{T}{T^*}\right), \quad (8.10.2)$$

where ϕ is the same function for all the substances concerned, V^* is a characteristic volume proportional to r^{*3} , and T^* is a characteristic temperature proportional to ϵ^*/k . Except for the lightest molecules V^* and T^* may be identified with the molar critical volume V_c and with the critical temperature T_c respectively. Owing to quantal effects† hydrogen does not conform to the principle of corresponding states at its critical temperature, but it does conform at higher temperatures. For hydrogen then V^* , T^* must not be equated to V_c , T_c but instead to the values which V_c , T_c would have in the absence of the quantal deviations. Such values can be estimated approximately by extrapolation from the values for H_2 through those for D_2 .

The verification of formula (2) for several substances, including hydrogen but excluding helium, is shown in Fig. 8.1, where B/V^* is plotted against T/T^* . The values of T^* , V^* and the sources of the experimental data for the virial coefficients are given in Table 8.1. It is seen that all these substances, except perhaps ethane, conform rather well to formula (2). The curve has been drawn empirically through the experimental points and will be further used in our treatment of mixtures.

We turn now to the extension of the principle of corresponding states to mixtures.‡ We use subscripts AA , BB , AB to denote the several kinds of molecule-pairs. For the sake of precision we rewrite equation (1) for the two kinds of molecules A , B as

$$\frac{w_{AA}}{\epsilon_{AA}^*} = u\left(\frac{r_{AA}}{r_{AA}^*}\right), \quad (8.10.3)$$

$$\frac{w_{BB}}{\epsilon_{BB}^*} = u\left(\frac{r_{BB}}{r_{BB}^*}\right). \quad (8.10.4)$$

The manner of extending the principle of corresponding states to a mixture of A and B is now evident. We assume that the interaction

† De Boer (1948), *Physica*, 14, 129.

‡ Guggenheim and M. Glashan (1951), *Proc. Roy. Soc. A* 206, 448; Lennard-Jones and Cook (1927), *Proc. Roy. Soc. A* 115, 334.

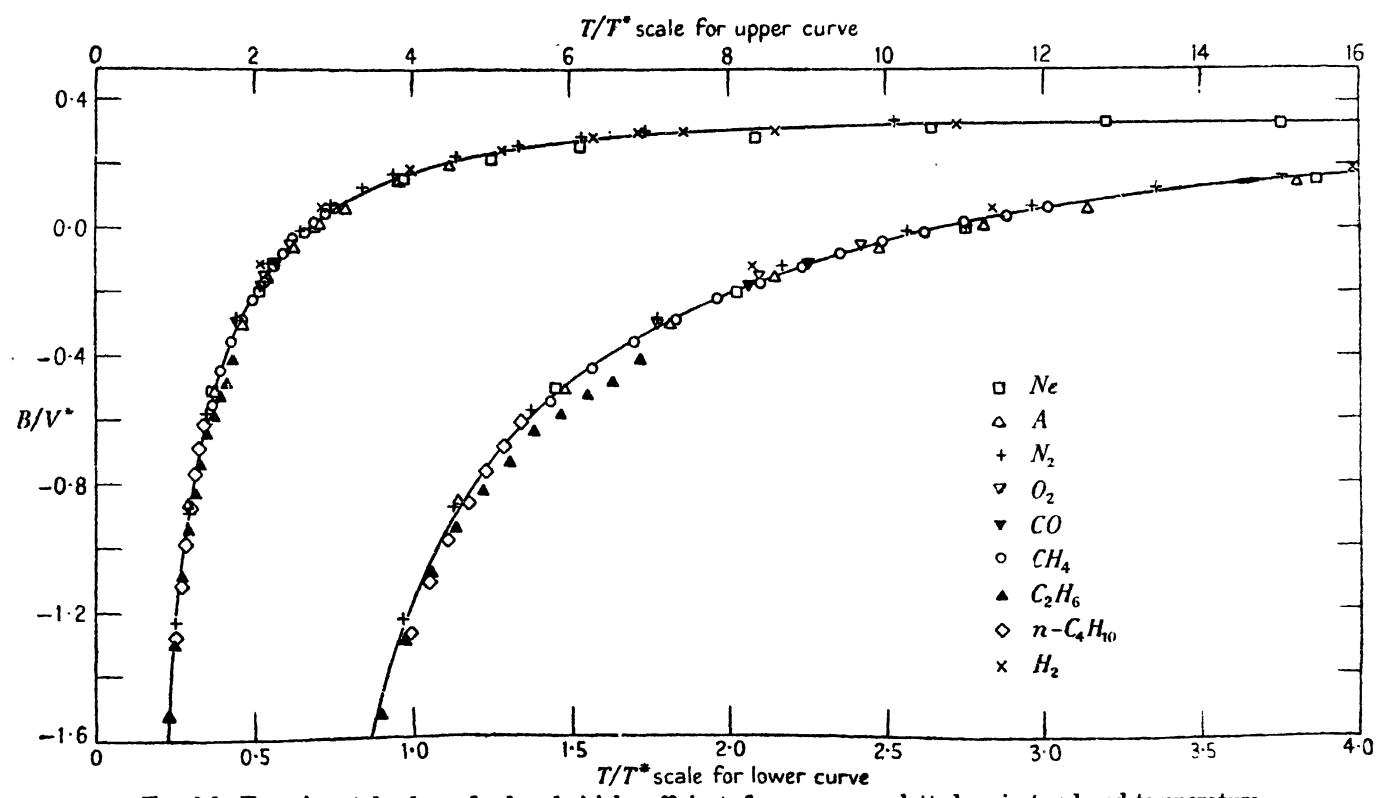


FIG. 8.1. Experimental values of reduced virial coefficients for pure gases plotted against reduced temperature.

TABLE 8.1

Characteristic Temperatures and Volumes for Single Substances

Substance	T^* deg. K.	V^* cm. ³ /mole	Source of virial coefficient data
Ne	44.8	41.7	1
A	150.7	75.3	1
N ₂	126.0	90.2	1, 2
O ₂	154.3	74.5	1
CO	133.0	93.2	3
CH ₄	190.3	98.8	4, 5, 6
C ₂ H ₆	305.3	148.2	7, 8
n-C ₄ H ₁₀	425.0	258.1	4, 8
H ₂	43.4	50	1, 2

1. Holborn and Otto (1925), *Z. Physik*, **33**, 1.
2. Keyes (1941), *Temperature*, p. 45, Reinhold.
3. Townend and Bhatt (1932), *Proc. Roy. Soc. A* **134**, 502.
4. Beattie and Stockmayer (1942), *J. Chem. Phys.* **10**, 473.
5. Michels and Nederbragt (1935), *Physica*, **2**, 1001.
6. Michels and Nederbragt (1936), *Physica*, **3**, 589.
7. Michels and Nederbragt (1939), *Physica*, **6**, 656.
8. Hirschfelder, McClure, and Weeks (1942), *J. Chem. Phys.* **10**, 201.

energy w_{AB} between the molecules of different kinds depends on their distance apart r_{AB} by the relation

$$\frac{w_{AB}}{\epsilon_{AB}^*} = u\left(\frac{r_{AB}^*}{r_{AB}^*}\right), \quad (8.10.5)$$

where ϵ_{AB}^* , r_{AB}^* are characteristic of the pair of molecular species while u is the same function as in (3) and (4). We now define a characteristic temperature T_{AB}^* and a characteristic volume V_{AB}^* by the equations

$$\frac{T_{AB}^*}{\epsilon_{AB}^*} = \frac{T_{AA}^*}{\epsilon_{AA}^*} = \frac{T_{BB}^*}{\epsilon_{BB}^*}, \quad (8.10.6)$$

$$\frac{V_{AB}^*}{(r_{AB}^*)^3} = \frac{V_{AA}^*}{(r_{AA}^*)^3} = \frac{V_{BB}^*}{(r_{BB}^*)^3}. \quad (8.10.7)$$

We recall that for the substances considered, other than hydrogen, T_{AA}^* , T_{BB}^* are equal to the critical temperatures and V_{AA}^* , V_{BB}^* are equal to the critical molar volumes. It then follows by an immediate extension of the argument for single substances that

$$\frac{B_{AB}}{V_{AB}^*} = \phi\left(\frac{T}{T_{AB}^*}\right), \quad (8.10.8)$$

where ϕ is the same function as in (2), or in other words the function represented by the curve in Fig. 8.1.

8.11. Averaging rules

We must now consider how we may expect r_{AB}^* to be related to r_{AA}^* , r_{BB}^* and how we may expect ϵ_{AB}^* to be related to ϵ_{AA}^* , ϵ_{BB}^* . Questions similar to these have often been formulated and the answers usually suggested† as most reasonable are

$$r_{AB}^* = \frac{1}{2}(r_{AA}^* + r_{BB}^*), \quad (8.11.1)$$

$$\epsilon_{AB}^* = (\epsilon_{AA}^* \epsilon_{BB}^*)^{\frac{1}{2}}. \quad (8.11.2)$$

Formula (1) would be true if the two kinds of molecules behaved as spheres with diameters proportional to r_{AA}^* and r_{BB}^* . Formula (2) would be approximately true if the most important contribution to the energy of interaction were of the kind called dispersion energy. We shall accept formulae (1) and (2) as semi-empirical relations without attempt at further justification.

Combining equations (8.10.7) and (1) we derive

$$(V_{AB}^*)^{\frac{1}{2}} = \frac{1}{2}(V_{AA}^*)^{\frac{1}{2}} + \frac{1}{2}(V_{BB}^*)^{\frac{1}{2}}. \quad (8.11.3)$$

Combining equations (8.10.6) and (2) we derive

$$T_{AB}^* = (T_{AA}^* T_{BB}^*)^{\frac{1}{2}}. \quad (8.11.4)$$

We shall find that formulae (3) and (4) combined with formula (8.10.8) lead to useful agreement with experiment in striking contrast with the naive assumption $B_{AB} = \frac{1}{2}B_{AA} + \frac{1}{2}B_{BB}$.

8.12. Comparison with experiment

We are now ready to compare our formulae with experimental data. Suitable data on second virial coefficients of mixtures are rather scarce. Many researches covering wide ranges of pressure are not suited to providing accurate values of the second virial coefficient. The six mixtures for which the experimental data seem most suitable are collected in Table 8.2. The first column gives the nature of the two components of the mixture, the second column gives the value of T_{AB}^* calculated by equation (8.11.4), and the third column gives the value of V_{AB}^* calculated from (8.11.3). The values of T^* , V^* for the single substances were taken from Table 8.1. The fourth column gives the source of the experimental values of the virial coefficients. Fig. 8.2 shows the experimental values of B_{AB}/V_{AB}^* for all these mixtures plotted against T/T_{AB}^* . The curve drawn is identical with the curve in Fig. 8.1. It is immediately clear that the agreement between the

† See Lorentz (1881), *Ann. Phys.* 12, 127; Berthelot (1898), *C.R. Acad. Sci. Paris*, 126, 1703, 1857.

TABLE 8.2

Characteristic Temperatures and Volumes for Pairs of Substances

Mixture	T_{AB}^* deg. K.	V_{AB}^* cm. ³ /mole	Source of virial coefficient data
N ₂ /O ₂	139.4	82.1	1
N ₂ /H ₂	73.9	67.8	2
A/H ₂	80.9	61.5	3
H ₂ /CO	76.0	69.1	4
CH ₄ /C ₂ H ₆	241.0	121.9	5
CH ₄ /n-C ₄ H ₁₀	284.4	165.9	6

1. Holborn and Otto (1925), *Z. Physik*, **33**, 1.
2. Verschoyle (1926), *Proc. Roy. Soc. A* **111**, 552.
3. Tanner and Masson (1930), *Proc. Roy. Soc. A* **126**, 268.
4. Townend and Bhatt (1932), *Proc. Roy. Soc. A* **134**, 502.
5. Michels and Nederbragt (1939), *Physica*, **6**, 656.
6. Beattie and Stockmayer (1942), *J. Chem. Phys.* **10**, 473.

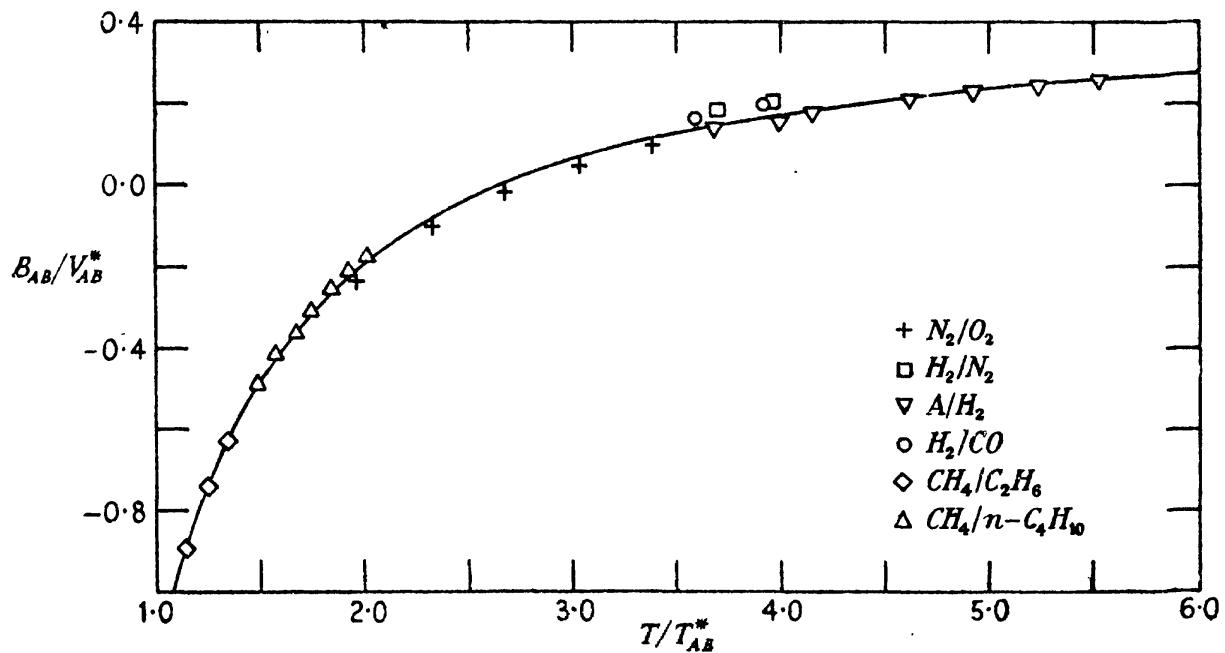


FIG. 8.2. Experimental values of reduced virial coefficient of binary mixtures plotted against reduced temperature. Curve identical with that of Fig. 8.1.

calculated and experimental values is at least good enough to merit further discussion. We accordingly give in Table 8.3 a more detailed comparison for the six mixtures. The first column gives the temperature T , the second column the reduced temperature T/T_{AB}^* , the third column the value of the reduced virial coefficient B_{AB}/V_{AB}^* read from the curve. The fourth column gives the calculated value of B_{AB} , and the fifth column gives the experimental value of B_{AB} . The last column gives the value of B_{AB} calculated from the naive assumption

$$B_{AB} = \frac{1}{2}B_{AA} + \frac{1}{2}B_{BB}.$$

TABLE 8.3

Comparison between Theory and Experiment for Mixtures

T deg. K.	T/T_{AB}^*	B_{AB}/V_{AB}^* calc.	B_{AB} calc. $\text{cm.}^3/\text{mole}$	B_{AB} exp. $\text{cm.}^3/\text{mole}$	B_{AB} naive $\text{cm.}^3/\text{mole}$
Air (N_2/O_2)					
473	3.39	0.115	9.4	7.7	9.8
423	3.03	0.065	5.3	3.4	6.4
373	2.68	0.000	0.0	-1.5	1.3
323	2.32	-0.090	-7.4	-8.1	-5.5
273	1.96	-0.220	-18.1	-19.5	-16.2
H_2/N_2					
273	3.69	0.152	10.3	12.3	1.8
293	3.97	0.178	12.1	13.7	4.3
A/H_2					
298	3.58	0.150	9.2	8.2	-1.3
323	3.99	0.180	11.1	9.3	2.1
343	4.30	0.202	12.4	11.0	4.0
373	4.61	0.222	13.7	12.5	5.6
398	4.92	0.230	14.1	13.8	7.2
423	5.23	0.245	15.1	14.8	8.4
447	5.53	0.255	15.7	15.8	9.4
H_2/CO					
273	3.59	0.140	9.6	11.2	-0.9
298	3.92	0.175	12.1	13.7	+2.0
$\text{CH}_4/\text{C}_2\text{H}_6$					
273	1.13	-0.910	-111	-109	-140
298	1.24	-0.755	-92	-90	-116
323	1.34	-0.640	-78	-77	-97
$\text{CH}_4/n\text{-C}_4\text{H}_{10}$					
573	2.02	-0.187	-31	-29	-75
548	1.93	-0.225	-37	-35	-86
523	1.84	-0.270	-45	-42	-98
498	1.75	-0.320	-53	-51	-113
473	1.66	-0.375	-62	-60	-129
448	1.58	-0.430	-71	-69	-148
423	1.49	-0.500	-83	-82	-170

We see from Table 8.3 that the agreement between our calculated values of B_{AB} and the experimental values is almost always better than $2 \text{ cm.}^3/\text{mole}$ and often considerably better. This implies an agreement better than $1 \text{ cm.}^3/\text{mole}$ in B itself. The mixtures are given in approximately chronological order. On the whole the agreement is better with the later experiments than with the earlier ones. This suggests that at least part of the discrepancies may be due to experimental error.

There is, on the contrary, no similarity whatever, except in the case of air, between the values predicted by the naïve assumption and the experimental values. In some cases even the sign of B_{AB} is predicted wrongly by this assumption which was proposed many years ago when experimental data were almost non-existent. It was then as good a guess as any alternative, but we now know it to be a wrong guess.

8.13. Form of molecular interactions

In describing how B_{AB} can be calculated, at least approximately, from a knowledge of B_{AA} , B_{BB} we have expressly avoided the assumption of any particular analytical form either for the interaction energy w or for the second virial coefficient. We wish to emphasize that the analytical form of these quantities is irrelevant to the treatment described above. We may now, however, profitably consider what analytical form of the interaction energy leads to a relation between second virial coefficients and temperature in accord with experiment.

The exact form of the relation between interaction energy w and distance r is probably quite complicated even for the simplest monoatomic atoms. For simple non-polar molecules a useful approximation to the exact relation is given by the formula

$$w = 4\epsilon^* \left\{ \left(\frac{D}{r}\right)^{12} - \left(\frac{D}{r}\right)^6 \right\}. \quad (8.13.1)$$

Here D is the distance at which the repulsive and attractive terms in the energy just cancel each other, so that D may be regarded as a molecular diameter. The interaction energy w has a minimum $-\epsilon^*$ at the distance $r = 2^{1/2}D = 1.123D$. Formula (1) is a special case of (8.10.1) with D playing the part of r^* . Lennard-Jones† deduced from (1) the formula for the second virial coefficient B

$$\frac{B}{N} = \frac{2\pi D^3}{3} \sqrt{2} \left(\frac{\epsilon^*}{kT} \right)^{1/2} \left\{ \Gamma\left(\frac{5}{4}\right) - \sum_{n=1}^{\infty} \frac{2^{n-2}}{n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{\epsilon^*}{kT} \right)^{1/2n} \right\}. \quad (8.13.2)$$

In comparing (2) with experiment we can assign arbitrary values to ϵ^*/kT^* and to ND^3/V^* . We recall that except for hydrogen and helium, T^* and V^* are the same as T_c and V_c respectively. If we choose the values determined by

$$\frac{\epsilon^*}{kT^*} = 0.780, \quad (8.13.3)$$

$$\frac{2\pi D^3}{3} = \frac{V^*}{1.355N} = 0.738 \frac{V^*}{N}, \quad (8.13.4)$$

† Lennard-Jones (1924), *Proc. Roy. Soc. A* **106**, 463; (1937), *Physica*, **4**, 941.

we obtain the curve a of Fig. 8.3. The parameters given by (3) and (4) have been chosen so that the curve should fit the experimental data at the critical temperature T^* and at the Boyle point $\frac{1}{2}T^*$. We see that with the parameters thus adjusted the theoretical formula (2) of Lennard-Jones is a useful representation of the experimental data over the whole temperature range.

Except possibly at very high values of T/T^* an equally good fit of the second virial coefficients can be obtained by assuming the simpler form for the interaction energy w

$$\begin{aligned} w &= +\infty \quad (r < D), \\ w &= -\epsilon^* \left(\frac{D}{r} \right)^6 \quad (r > D). \end{aligned} \quad (8.13.5)$$

This two-parameter formula is a special case of (8.10.1) in which the molecular diameter D plays the part of r^* . It was shown by Keesom† that when (5) is substituted into (8.03.3) one obtains, observing (8.04.12),

$$\frac{B}{N} = \frac{2}{3}\pi D^3 \left\{ 1 - \sum_{n=1}^{\infty} \frac{1}{n!(2n-1)} \left(\frac{\epsilon^*}{kT} \right)^n \right\}. \quad (8.13.6)$$

In comparing (6) with experiment we can assign arbitrary values to ϵ^*/kT^* and to ND^3/V^* . If we choose the values determined by

$$\frac{\epsilon^*}{kT^*} = 2.277, \quad (8.13.7)$$

$$\frac{2\pi D^3}{3} = 0.4324 \frac{V^*}{N}, \quad (8.13.8)$$

we obtain curve b of Fig. 8.3. The parameters given by (7) and (8) have again been chosen so that the curve should fit the experimental data at the critical temperature T^* and at the Boyle point $\frac{1}{2}T^*$. The only notable difference between curves a and b is that the former has a flat maximum in the neighbourhood of $T/T^* = 30$ while the latter rises steadily.

We can obtain a much simpler formula for the second virial coefficient without much loss of accuracy by assuming an interaction energy of the form

$$\begin{aligned} w &= +\infty \quad (r < D), \\ w &= -\epsilon^* \quad (D < r < R), \\ w &= 0 \quad (r > R). \end{aligned} \quad (8.13.9)$$

† Keesom (1912), *Comm. Phys. Lab. Leiden supp.* 24b, 32.

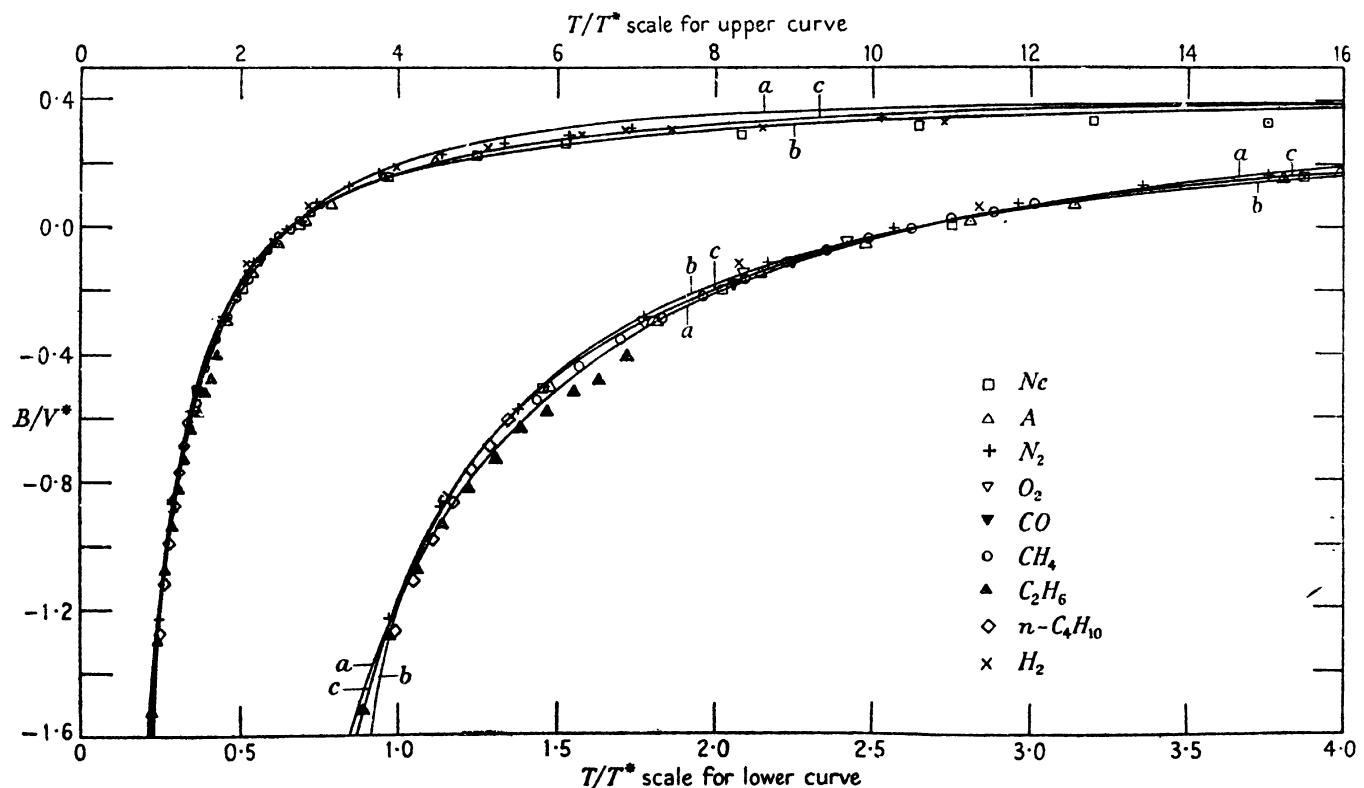


FIG. 8.3. Calculated values of B/V^* according to three equations of state plotted against T/T^* and compared with experiment.
 a, Lennard-Jones's formula (8.13.2); b, Keesom's formula (8.13.6); c, square well formula (8.13.10).

When we substitute from (9) into (8.03.3), observing (8.04.12), we obtain immediately

$$\frac{B}{N} = \frac{2}{3}\pi D^3 \left\{ 1 + \left(\frac{R^3}{D^3} - 1 \right) \left(1 - e^{\epsilon^*/kT} \right) \right\}. \quad (8.13.10)$$

In comparing (10) with experiment we have three independently adjustable parameters which we may take to be ϵ^*/kT^* , ND^3/V^* , and R^3/D^3 . To obtain a fit between the formula and the experimental data we have to choose for R^3/D^3 a value between 3 and 4. In particular if we choose the values determined by

$$\frac{R^3}{D^3} = 3.380, \quad (8.13.11)$$

$$\frac{\epsilon^*}{kT^*} = 0.936, \quad (8.13.12)$$

$$\frac{2\pi D^3}{3} = 0.447 \frac{V^*}{N}, \quad (8.13.13)$$

formula (10) becomes

$$\frac{B}{V^*} = 0.447 \{ 1 + 2.380(1 - e^{0.936T^*/T}) \}, \quad (8.13.14)$$

and we obtain curve *c* in Fig. 8.3. The parameters given by (11), (12), and (13) have been chosen so that the curve should fit the experimental data at the critical temperature T^* , at the Boyle point $\frac{4}{3}T^*$, and at the temperature $8T^*$.

We see from Fig. 8.3 that any of the theoretical formulae (2), (6), (10) with suitable choice of parameters is a useful representation of the experimental data over the temperature range $T/T^* = 1$ to $T/T^* = 12$. Values of B_{AB} calculated from any one of these formulae using (8.11.3) and (8.11.4) are in good agreement with the experimental values given in Table 8.3.

It should be pointed out that the three curves shown in Fig. 8.3 diverge at temperatures below T^* . An analysis of second virial coefficients of simple non-polar molecules at temperatures below the critical should provide interesting information concerning the true form of the interaction energy. Unfortunately such experimental data are still scanty and not as accurate as desirable.

For some purposes it may be convenient to express the theoretical formulae (1), (5), and (9) in terms of a parameter r^* defined by

$$\frac{4}{3}\pi r^{*3} = \frac{V^*}{N}. \quad (8.13.15)$$

The formula (1) becomes in this notation when we use (3) and (4)

$$\frac{w}{kT^*} = 6.797 \left(2.179 \left(\frac{r^*}{r} \right)^{12} - \left(\frac{r^*}{r} \right)^6 \right). \quad (8.13.16)$$

Formula (5) becomes similarly when we use (7) and (8)

$$\begin{aligned} \frac{w}{kT^*} &= +\infty & \left(\frac{r}{r^*} < 0.953 \right), \\ \frac{w}{kT^*} &= -1.703 \left(\frac{r^*}{r} \right)^3 & \left(\frac{r}{r^*} > 0.953 \right). \end{aligned} \quad (8.13.17)$$

Formula (9) becomes similarly when we use (11), (12), and (13)

$$\begin{aligned} \frac{w}{kT^*} &= +\infty & \left(\frac{r}{r^*} < 0.963 \right), \\ \frac{w}{kT^*} &= -0.933 & \left(0.963 < \frac{r}{r^*} < 1.445 \right), \\ \frac{w}{kT^*} &= 0 & \left(\frac{r}{r^*} > 1.445 \right). \end{aligned} \quad (8.13.18)$$

Formulae (16), (17), and (18) are shown as curves in Fig. 8.4.

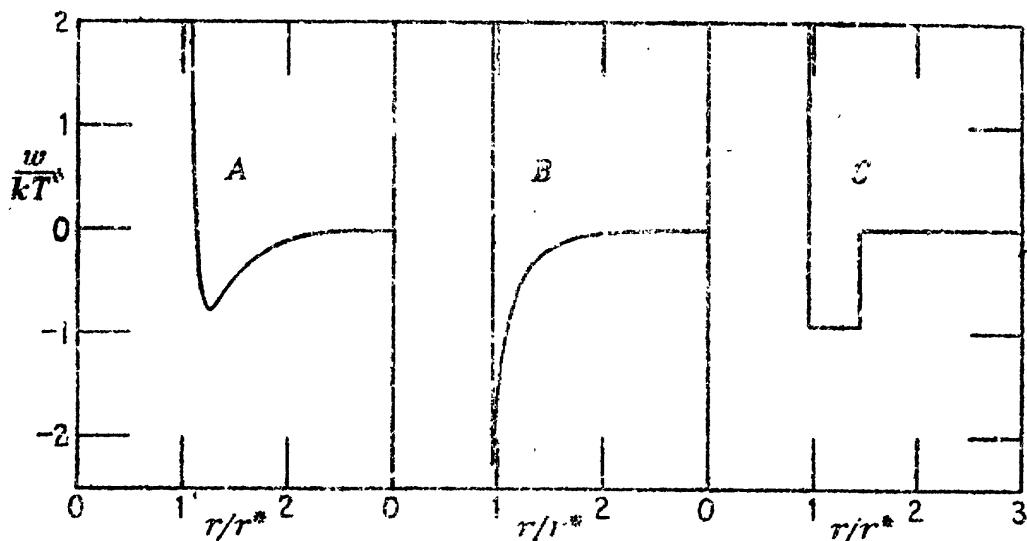


FIG. 8.4. Comparison of potential functions. *A*, Lennard-Jones's formula (8.13.16); *B*, Keesom's formula (8.13.17); *C*, square well formula (8.13.18).

IX

SURFACES OF SIMPLE LIQUID MIXTURES

9.01. Thermodynamics of surface phases

A SURFACE phase must strictly be regarded as all that volume of material surrounding an interface between two bulk phases in which the properties of the material differ appreciably from those of the bulk phases on either side. When the two bulk phases consist of the same pure substance the surface layer can differ only in structural arrangement. When the bulk phases contain more than one component the surface layer in general contains these components in changed proportions.

Our first task is briefly to extend the summary of thermodynamic formulae given in Chapter I so as to include surface phases. We shall use the method[†] of approach proposed by van der Waals junior and Bakker. For the sake of simplicity and brevity we assume the interface to be planar. Fig. 9.1a shows schematically a planar interface,

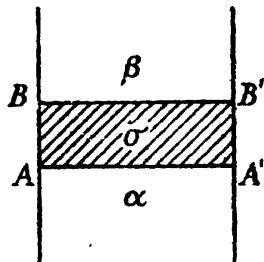


FIG. 9.1 a. Surface phase between two bulk phases.

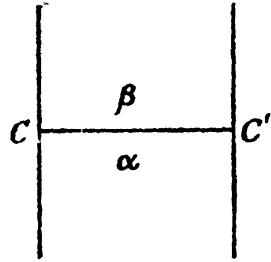


FIG. 9.1 b. Gibbs's surface separating two bulk phases.

whose properties are all uniform in directions parallel to AA' , but not in the direction normal to AA' . This surface layer, shown shaded in the diagram, is completely contained between the two parallel planes AA' and BB' . We call the bulk phase extending up to AA' the phase α and the bulk phase extending down to BB' the phase β . We call all the material between the geometrical planes AA' and BB' the *surface phase* σ .

Since the surface phase σ , defined in this manner, is a material system with a well-defined volume and material content, its thermodynamic properties require no special definition. We may speak of its

[†] van der Waals and Bakker (1928), *Handb. Experimentalphysik*, 6; Guggenheim (1940), *Trans. Faraday Soc.* 36, 397; (1949), *Thermodynamics*, North-Holland Publishing Company, §§ 1.51–1.55 and 5.55–5.60.

temperature, free energy, composition, volume, and so on just as for an isotropic bulk phase. In addition it has an area A and a surface tension γ . Whereas the free energy F^α of a bulk phase α containing two components 1 and 2 varies in a manner given by the fundamental equation

$$dF^\alpha = -S^\alpha dT - P dV^\alpha + \mu_1 dn_1^\alpha + \mu_2 dn_2^\alpha, \quad (9.01.1)$$

the corresponding formula for variations of the free energy F^σ of the surface phase σ is

$$dF^\sigma = -S^\sigma dT - P dV^\sigma + \gamma dA + \mu_1 dn_1^\sigma + \mu_2 dn_2^\sigma. \quad (9.01.2)$$

In (1) and (2) we have used superscripts α and σ to relate to the bulk phase and the surface phase respectively. The superscripts have been omitted from the intensive properties T , P , μ_1 , μ_2 which have the same values in all phases in mutual equilibrium. They have also been omitted from γ and A since these are relevant to the surface phase only.

Before proceeding further it is as well to emphasize certain points relating to this method of treatment and particularly to formula (2). The placing of the two geometrical surfaces AA' and BB' is arbitrary provided only that the inhomogeneous layer is completely contained between them. If either or both the boundaries AA' and BB' be shifted, then the content of the surface phase becomes changed and so, of course, do the values of its extensive properties such as F^σ , S^σ , V^σ , n_1^σ , n_2^σ . Nevertheless it can readily be verified that formula (2) remains invariant, the value of γ being also unaffected.

An alternative method of treatment of the thermodynamics of surfaces due to Gibbs is shown schematically in Fig. 9.1b. Instead of two geometrical surfaces enclosing the inhomogeneous layer, we now have a single geometrical surface CC' within the layer. Gibbs defined each thermodynamic extensive property of the surface as the excess of its value for the whole system over an imaginary value it would have if the bulk phases α and β both remained completely homogeneous as far as CC' . In this method of approach the variations of the free energy obey a relation similar to (2), but with the term $-P dV^\sigma$ omitted since now the surface is represented by a geometrical boundary occupying no volume. Gibbs's method of approach, being more abstract, is more difficult to visualize. In common with the method of approach described above, the values of the extensive properties F^σ , S^σ , n_1^σ , n_2^σ depend on the precise position of the geometrical surface, but the relation (2) without the term $-P dV^\sigma$ remains invariant. The only advantage of Gibbs's method is such simplification as may come from the disappearance of the term $-P dV^\sigma$. We shall, however, find that in

our preferred method of treatment the two geometrical surfaces AA' and BB' can usually be so placed that PV^σ is entirely negligible and so the term $-P dV^\sigma$ may be omitted anyway.

Formula (2) being the fundamental equation for the independent variables T , V^σ , A , n_1^σ , n_2^σ , it is possible by simple algebra, just as for bulk phases, to transform it to other forms, to integrate it, and to derive related formulae. We shall not here give details of these operations, but merely quote some of the most important results.

$$F^\sigma + PV^\sigma - \gamma A = \mu_1 n_1^\sigma + \mu_2 n_2^\sigma, \quad (9.01.3)$$

$$S^\sigma dT - V^\sigma dP + A d\gamma + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2 = 0, \quad (9.01.4)$$

$$d(PV^\sigma - \gamma A) = S^\sigma dT + P dV^\sigma - \gamma dA + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2, \quad (9.01.5)$$

$$d\left(\frac{PV^\sigma}{RT} - \frac{\gamma A}{RT}\right) = \frac{U^\sigma}{RT^2} dT + \frac{P}{RT} dV^\sigma - \frac{\gamma}{RT} dA + n_1^\sigma d\ln\lambda_1 + n_2^\sigma d\ln\lambda_2. \quad (9.01.6)$$

We shall be concerned only with interfaces between a liquid phase and the vapour phase in equilibrium with it. We shall assume that the inhomogeneous layer has a thickness not greater than a few times the distance between two neighbouring molecules in the liquid phase, and a density comparable to that of the liquid phase. We may then so place the two geometrical surfaces AA' and BB' that the ratio of V^σ to $(n_1^\sigma + n_2^\sigma)$ is comparable to a molar volume in a liquid phase, so that at all ordinary pressures $PV^\sigma/(n_1^\sigma + n_2^\sigma) \ll RT$. All terms in PV^σ then become negligible and we shall henceforth neglect them just as we have always done for non-gaseous bulk phases. The above formulae may now be written more simply as follows:

$$dF^\sigma = -S^\sigma dT + \gamma dA + \mu_1 dn_1^\sigma + \mu_2 dn_2^\sigma, \quad (9.01.7)$$

$$F^\sigma - \gamma A = \mu_1 n_1^\sigma + \mu_2 n_2^\sigma, \quad (9.01.8)$$

$$S^\sigma dT + A d\gamma + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2 = 0, \quad (9.01.9)$$

$$-d(\gamma A) = S^\sigma dT - \gamma dA + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2, \quad (9.01.10)$$

$$-d\left(\frac{\gamma A}{RT}\right) = \frac{U^\sigma}{RT^2} dT - \frac{\gamma}{RT} dA + n_1^\sigma d\ln\lambda_1 + n_2^\sigma d\ln\lambda_2. \quad (9.01.11)$$

These simplified formulae are formally the same as those obtainable by Gibbs's method of approach without the need for using any approximation. Nevertheless we prefer the alternative method of approach, whose advantage will become apparent when we come to consider molecular models.

All the above formulae relate to a surface of area A . It is often more

useful to have formulae relating to unit area of surface. We shall use the subscript σ instead of the superscript to denote quantities per unit area of surface. We also denote the values of n_1^σ and n_2^σ per unit area by Γ_1 and Γ_2 respectively, and we call these quantities surface concentrations. With this notation we have according to (8)

$$\gamma = F_\sigma - \Gamma_1 \mu_1 - \Gamma_2 \mu_2. \quad (9.01.12)$$

It should be emphasized that γ is not equal to F_σ . We also have according to (10)

$$-d\gamma = S_\sigma dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2. \quad (9.01.13)$$

In particular at constant temperature we have

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (T \text{ const.}), \quad (9.01.14)$$

which is commonly known as *Gibbs's adsorption formula*. It can conveniently be rewritten in terms of absolute activities λ or fugacities p as

$$-\frac{1}{RT} d\gamma = \Gamma_1 d \ln \lambda_1 + \Gamma_2 d \ln \lambda_2 = \Gamma_1 d \ln p_1 + \Gamma_2 d \ln p_2 \quad (T \text{ const.}). \quad (9.01.15)$$

In a bulk liquid phase we have by the Gibbs-Duhem relation

$$(1-x) d \ln \lambda_1 + x d \ln \lambda_2 = 0 \quad (T \text{ const.}), \quad (9.01.16)$$

or by the Duhem-Margules relation

$$(1-x) d \ln p_1 + x d \ln p_2 = 0 \quad (T \text{ const.}), \quad (9.01.17)$$

where x denotes the mole fraction of the substance 2 in the bulk liquid phase. Using (16) or (17) in (15) we obtain

$$-\frac{1}{RT} d\gamma = \left(\Gamma_2 - \frac{x}{1-x} \Gamma_1 \right) d \ln \lambda_2 = \left(\Gamma_2 - \frac{x}{1-x} \Gamma_1 \right) d \ln p_2 \quad (T \text{ const.}). \quad (9.01.18)$$

Whereas the values of Γ_1 and Γ_2 depend on the arbitrary placing of the geometrical surface AA' (and to a much less extent BB'), it is readily verified† that the quantity

$$\Gamma_2 - \frac{x}{1-x} \Gamma_1, \quad (9.01.19)$$

denoted by Gibbs as $\Gamma_{2(1)}$, remains invariant. We may regard this quantity as a measure of the adsorption of the substance 2 per unit area relative to the substance 1.

9.02. Example of water and ethyl alcohol

Before leaving the field of classical thermodynamics and entering that of statistical mechanics it may be useful to illustrate by an example

† Guggenheim and Adam (1933), *Proc. Roy. Soc. A* 139, 218.

the use of Gibbs's adsorption formula for estimating the preferential adsorption of either component at the interface between a liquid mixture and its vapour. We choose as our example† mixtures of water and ethyl alcohol, for which satisfactory experimental data are available at 25° C. over the whole range of composition. The experimental data are given in the first four columns of Table 9.1. The subscript 1 relates to

TABLE 9.1
Water/Alcohol Mixtures at 25° C.

$$\text{Determination of } \Gamma_2 - \frac{x}{1-x} \Gamma_1$$

x	p_1	p_2	γ	$\frac{\partial \gamma}{\partial \ln p_2}$	$\Gamma_2 - \frac{x}{1-x} \Gamma_1$	$\Gamma_2 - \frac{x}{1-x} \Gamma_1$
	mm. Hg	mm. Hg	erg cm. ⁻²	erg cm. ⁻²	10^{-10} moles cm. ⁻²	10^{-2} molecules Å ⁻²
0.0	23.75	0.0	72.2	0.0	0.0	0.0
0.1	21.7	17.8	36.4	15.6	6.3	3.8
0.2	20.4	26.8	29.7	16.0	6.45	3.9
0.3	19.4	31.2	27.6	14.6	5.9	3.6
0.4	18.35	34.2	26.35	12.6	5.1	3.1
0.5	17.3	36.9	25.4	10.5	4.25	2.6
0.6	15.8	40.1	24.6	8.45	3.4	2.06
0.7	13.3	43.9	23.85	7.15	2.9	1.75
0.8	10.0	48.3	23.2	6.2	2.5	1.5
0.9	5.5	53.3	22.6	5.45	2.2	1.33
1.0	0.0	59.0	22.0	5.2	2.1	1.27

water and the subscript 2 to the alcohol. The first column gives the mole fraction x of alcohol. The second and third columns give the partial vapour pressures p_1 and p_2 of the water and the alcohol respectively. It has been verified that these experimental values are in satisfactory agreement with the Duhem-Margules relation. The fourth column gives the experimental values of the surface tension γ . Values of $-\partial\gamma/\partial\ln p_2$ are obtained by plotting γ against p_2 and the fifth column gives the values so obtained for $-\partial\gamma/\partial\ln p_2$. We rewrite formula (9.01.18) as

$$\Gamma_2 - \frac{x}{1-x} \Gamma_1 = -\frac{1}{RT} \frac{\partial \gamma}{\partial \ln p_2}, \quad (9.02.1)$$

and we see that values of

$$\Gamma_2 - \frac{x}{1-x} \Gamma_1 \quad (9.02.2)$$

are obtainable from those of $-\partial\gamma/\partial\ln p_2$ merely by division by RT . The values so obtained for the expression (2) are given in the sixth

† Guggenheim and Adam (1933), *Proc. Roy. Soc. A* 139, 218.

column expressed in moles/cm.² and again in the last column expressed in molecules/Å².

As already mentioned, the quantity (2) may be regarded as a measure of the adsorption per unit area of alcohol relative to the water. We emphasize that this is as far as pure thermodynamics can take us. It can give us no information concerning the separate values of Γ_1 and Γ_2 , which in any case depend on the position assigned to the geometrical surface AA' (and to a much less extent the surface BB'). If we wish to assign values to Γ_1 , Γ_2 separately we must make some non-thermodynamic assumption concerning the structure of the interface and then define the positions to be assigned to the bounding surfaces AA' and BB' relative to this assumed structure. The simplest conceivable assumption is that the interfacial layer is unimolecular and that each molecule of water occupies a constant area A_1 and each molecule of alcohol likewise occupies a constant area A_2 of the unimolecular layer. With this assumption it is natural to place the bounding surfaces AA' and BB' immediately below and immediately above the unimolecular layer. With this convention our assumption may be expressed by

$$A_1 \Gamma_1 + A_2 \Gamma_2 = 1 \quad (A_1, A_2 \text{ const.}) \quad (9.02.3)$$

We may, if we like, call A_1 , A_2 the partial molar areas of the water and alcohol respectively in the surface. The essence of our assumption is not the definition of these quantities but the assignment to them of definite constant values, which can neither be determined nor be verified by thermodynamics.

As an example we might assume arbitrarily

$$\begin{aligned} A_1 &= 0.04 \times 10^{10} \text{ cm.}^2/\text{mole} = 7 \text{ Å}^2/\text{molecule}, \\ A_2 &= 0.12 \times 10^{10} \text{ cm.}^2/\text{mole} = 20 \text{ Å}^2/\text{molecule}. \end{aligned} \quad (9.02.4)$$

The relation (3) with the values of A_1 , A_2 given by (4) is sufficient to determine values of Γ_1 , Γ_2 from the values of the expression (2) already given in Table 9.1. The results of the calculation are given in Table 9.2. The first column gives the mole fraction x of alcohol, the second the value of the expression (2) taken from the previous table, the third and fourth columns the values of Γ_1 and Γ_2 respectively calculated by means of (3). The fifth column gives values of $\Gamma_2/(\Gamma_1 + \Gamma_2)$ which we may call the mole fraction of alcohol in the unimolecular layer. Since the mole fraction, thus calculated, in the unimolecular layer steadily increases with the mole fraction x in the liquid, we may conclude that

although the model on which our assumptions were based is admittedly arbitrary, at least it does not lead to unreasonable or surprising results.

TABLE 9.2

Water/Alcohol Mixtures at 25°C.

Values of Γ in 10^{-10} moles/cm.² calculated from

$$A_1 \Gamma_1 + A_2 \Gamma_2 = 1$$

with

$$A_1 = 0.04 \times 10^{10} \text{ cm.}^2/\text{mole of water}, \quad A_2 = 0.12 \times 10^{10} \text{ cm.}^2/\text{mole of alcohol}$$

x	$\Gamma_2 - \frac{x}{1-x} \Gamma_1$	Γ_2	Γ_1	$\frac{\Gamma_2}{\Gamma_1 + \Gamma_2}$
0.0	0.0	0.0	25.0	0.00
0.05	5.85	6.2	6.4	0.49
0.1	6.3	6.8	4.6	0.60
0.2	6.45	7.25	3.25	0.69
0.3	5.9	7.25	3.25	0.69
0.4	5.1	7.25	3.25	0.69
0.5	4.25	7.3	3.1	0.70
0.6	3.4	7.45	2.65	0.74
0.7	2.9	7.85	2.0	0.79
0.8	2.5	7.9	1.3	0.86
0.9	2.2	8.1	0.7	0.94
1.0	2.1	8.35	0.0	1.00

9.03. Statistical mechanics of surface layers

We turn now to the application of statistical mechanics to the interface between a binary liquid mixture of A and B molecules and the vapour phase. First we have to choose a sufficiently simple model of the interfacial layer and then we have to specify where we place the lower and upper boundaries of the surface phase. For the most part we shall, as in the previous section, assume that the interfacial layer may be regarded as only one molecule thick and we then place the boundaries AA' and BB' immediately below and immediately above this unimolecular layer. Having completely defined the boundaries of our surface phase we denote quantities relating to this unimolecular layer by primed symbols. In particular we denote by N'_A and N'_B the number of molecules A and B respectively in the unimolecular layer.

Given a sufficiently simple model it is in principle possible to construct a partition function $Q'(T, A, N'_A, N'_B)$ for the surface phase. We could then deduce the free energy of the surface phase by means of the relation

$$F^\sigma = -kT \ln Q'(T, A, N'_A, N'_B). \quad (9.03.1)$$

Since, however, N'_A, N'_B are not known *a priori*, it would be necessary

to use a formula for F^α , the free energy of the bulk phase, and then determine N'_A , N'_B by minimizing $F^\alpha + F^\sigma$.

There is, however, a more direct route† for determining the equilibrium properties of the surface. We have merely to use the independent variables T , A , λ_A , λ_B instead of T , A , N'_A , N'_B and then use the fact that λ_A , λ_B in the surface must have values equal to the values in the liquid.

We accordingly construct the grand partition function Ξ' for the surface phase. This is defined by

$$\Xi' = \sum_{N'_A, N'_B} Q'(T, A, N'_A, N'_B) \lambda_A^{N'_A} \lambda_B^{N'_B}. \quad (9.03.2)$$

As usual we may replace the sum by its maximum term. The conditions of maximization determine N'_A , N'_B in terms of λ_A , λ_B which themselves have values determined by the composition of the bulk liquid. Finally we obtain the surface tension from the relation

$$-\gamma A = kT \ln \Xi', \quad (9.03.3)$$

which is the analogue of the relation for a bulk phase

$$PV = kT \ln \Xi. \quad (9.03.4)$$

The grand partition function thus affords a powerful tool for determining the equilibrium properties of a surface and we shall accordingly use it.

9.04. Quasi-crystalline model

We continue to use the quasi-crystalline model and assume that in the bulk phase every molecule whether A or B has the same number z of nearest neighbours. We assume, as previously, that the total intermolecular energy may be regarded as the sum of contributions from pairs of closest neighbours. We continue to make use of an energy of interchange w so defined that w/z is the excess potential energy of an AB pair of neighbours over the mean of the energies of an AA and a BB pair. For the sake of simplicity we shall confine ourselves to the zeroth approximation. The absolute activities λ_A , λ_B are then related to the mole fractions $1-x$, x in the bulk phase by

$$\ln \lambda_A = \ln(1-x)\lambda_A^0 + x^2 w/kT, \quad (9.04.1)$$

$$\ln \lambda_B = \ln x\lambda_B^0 + (1-x)^2 w/kT, \quad (9.04.2)$$

where the superscript 0 denotes the value for the pure liquid A or B .

We must now specify the model which we use of the surface phase. We shall assume firstly that the molecules in the surface are packed

† Guggenheim (1945), *Trans. Faraday Soc.*, 41, 150.

in the same manner as in the bulk making the same contribution per pair of neighbours to the configurational potential energy, and secondly that the difference in composition from that of the bulk liquid is confined to a single layer of molecules at the surface.

Consider now any molecule in the surface layer. Let the number of its neighbours in this layer be lz and the number of its neighbours in the next layer below be mz , its total number of neighbours being thus $(l+m)z$. It is clear that the corresponding total number of neighbours of an interior molecule will be $(l+2m)z$, but by definition this number is z . Consequently we have the identity

$$l+2m = 1. \quad (9.04.3)$$

In a simple cubic lattice $z = 6$, $l = \frac{1}{2}$, and $m = \frac{1}{3}$, while in a close packed lattice $z = 12$, $l = \frac{1}{2}$, $m = \frac{1}{4}$.

9.05. Formulae for pure liquids

Our main treatment of the surface of a mixture will be facilitated by a preliminary discussion of the surface of a single substance. This will help to clarify our definitions of certain molecular partition functions.

We accordingly consider a quantity of the pure liquid A containing N_A interior molecules and N'_A surface molecules. Molecular partition functions q_A and q'_A can be defined so that the free energy F of the whole system has the form

$$F = -N_A kT \ln q_A - N'_A kT \ln q'_A. \quad (9.05.1)$$

The molecular partition function q_A will contain the factor $\exp(\chi_A/kT)$, where χ_A denotes as usual the energy required to remove an A molecule in its lowest quantum state from the interior of the liquid and take it to rest at infinity. The molecular partition function q'_A will similarly contain the factor $\exp\{(l+m)\chi_A/kT\}$. There may also be differences between q_A and q'_A in the factors for some of the translational, rotational, or vibrational degrees of freedom.

Neglecting, as usual for a liquid, the difference between F and G we have for the chemical potential μ_A^0 of the pure liquid

$$\mu_A^0 = -kT \ln q_A, \quad (9.05.2)$$

and so for the absolute activity λ_A^0 of the pure liquid

$$\lambda_A^0 q_A = 1. \quad (9.05.3)$$

If the surface tension of the pure liquid A is γ_A^0 and the surface area is A , then

$$\begin{aligned}\gamma_A^0 A &= F - (N_A + N'_A) \mu_A^0 \\ &= F - (N_A + N'_A) kT \ln \lambda_A^0 \\ &= -N'_A kT \ln(\lambda_A^0 q'_A) \\ &= N'_A kT \ln(q_A/q'_A),\end{aligned}\tag{9.05.4}$$

or if a denotes the area per molecule in the surface layer

$$\gamma_A^0 a = -kT \ln(\lambda_A^0 q'_A) = kT \ln(q_A/q'_A).\tag{9.05.5}$$

An analogous set of relations holds for the pure liquid B .

Any one of the formulae (1), (4), or (5) may be regarded as defining the partition function q'_A of a molecule A in the surface of the pure liquid. The object of devoting so much space to the definition and properties of q'_A is to make it clear that, when we come to construct a partition function for a surface layer of a mixture, if a factor $\exp(-w/zkT)$ is used for each AB contact, then the contributions of AA and BB contacts are correctly taken care of by using one q'_A factor for each A molecule in the surface layer and one q'_B factor for each B molecule in the surface layer. We have thus adopted a notation such that all factors of the form $\exp(\chi/zkT)$ are absorbed into the q and q' factors.

9.06. Surface layer of mixture

Consider a mixture of A and B , of molecular fractions $1-x$ and x respectively, having the form of a cylinder or prism of cross-section $\frac{1}{2}A$. Imagine this to be sliced in two in a direction normal to its axis of symmetry, thus creating two new free surfaces each of area $\frac{1}{2}A$, the total area of the newly created surface thus being A . Let the number of molecules in a layer of area A be denoted by N' . Now imagine the whole of the new surface area A to be covered over with a fresh layer of N' molecules of which $N'_A = (1-x')N'$ are of type A and $N'_B = x'N'$ of type B .

Whenever we speak of a thermodynamic function of the surface layer, we shall mean the *excess of the function for the final system after covering with the new layer over that for the initial system before slicing in half*. We shall also denote by W the product of w/z and the excess number of AB contacts in the final system over the number in the initial system.

9.07. Grand partition function of surface layer

The ordinary partition function Q' of the surface layer defined in the preceding section is

$$Q' = \frac{N'!}{N'_A! N'_B!} (q'_A)^{N'_A} (q'_B)^{N'_B} e^{-W/kT}. \quad (9.07.1)$$

We recall that according to our definitions all contributions to the intermolecular energy from AA and BB contacts as well as AB contacts are correctly included in (1).

The corresponding grand partition function Ξ' is given by

$$\Xi' = \sum_{N'_A, N'_B} \frac{N'!}{N'_A! N'_B!} (\lambda_A q'_A)^{N'_A} (\lambda_B q'_B)^{N'_B} e^{-W/kT} \quad (9.07.2)$$

where the summation is over all values of N'_A , N'_B subject to

$$N'_A + N'_B = N'. \quad (9.07.3)$$

Alternatively we may write

$$\Xi' = \sum_{x'} \frac{N'!}{\{N'(1-x')\}! \{N'x'\}!} (\lambda_A q'_A)^{(1-x')N'} (\lambda_B q'_B)^{x'N'} e^{-W/kT}, \quad (9.07.4)$$

where the summation now extends over all values of x' between 0 and 1.

Using Stirling's approximation for factorials we may rewrite (4) as

$$\Xi' = \sum_{x'} \left(\frac{\lambda_A q'_A}{1-x'} \right)^{(1-x')N'} \left(\frac{\lambda_B q'_B}{x'} \right)^{x'N'} e^{-W/kT}, \quad (9.07.5)$$

where the summation extends over all possible values of x' .

9.08. Ideal solutions

Before going further with the general case we may conveniently consider the specially simple case of an ideal solution.† By the definition of an ideal solution $w = 0$ and consequently $W = 0$, so that the formula for Ξ' reduces to

$$\Xi' = \sum_{x'} \left(\frac{\lambda_A q'_A}{1-x'} \right)^{(1-x')N'} \left(\frac{\lambda_B q'_B}{x'} \right)^{x'N'}. \quad (9.08.1)$$

As usual we may, for the purpose of deriving thermodynamic properties, replace the sum by its maximum term. Thus

$$\Xi' = \left(\frac{\lambda_A q'_A}{1-x'} \right)^{(1-x')N'} \left(\frac{\lambda_B q'_B}{x'} \right)^{x'N'}, \quad (9.08.2)$$

where x' is determined by

$$\frac{\lambda_A q'_A}{1-x'} = \frac{\lambda_B q'_B}{x'} = \lambda_A q'_A + \lambda_B q'_B. \quad (9.08.3)$$

† Schuchowitzky (1944), *Acta Physicochemica U.R.S.S.* 19, 176; Belton and Evans (1945), *Trans. Faraday Soc.* 41, 1.

Using (3) we can rewrite (2) in the much simpler form

$$\Xi' = (\lambda_A q'_A + \lambda_B q'_B)^{N'}. \quad (9.08.4)$$

We recall that according to formula (9.03.3)

$$\Xi' = \exp\left(-\frac{\gamma A}{kT}\right) = \exp\left(-N' \frac{\gamma a}{kT}\right), \quad (9.08.5)$$

where $a = A/N'$ is the area of surface per molecule. From (4) and (5) we have

$$\exp\left(-\frac{\gamma a}{kT}\right) = \lambda_A q'_A + \lambda_B q'_B. \quad (9.08.6)$$

We now use the relations characteristic of an ideal solution

$$\lambda_A = \lambda_A^0(1-x), \quad \lambda_B = \lambda_B^0 x. \quad (9.08.7)$$

Substituting (7) into (6) we obtain

$$\exp\left(-\frac{\gamma a}{kT}\right) = (1-x)\lambda_A^0 q'_A + x\lambda_B^0 q'_B = (1-x)\frac{q'_A}{q_A} + x\frac{q'_B}{q_B}, \quad (9.08.8)$$

using (9.05.3). Finally comparing (8) with (9.05.5) we find

$$\exp\left(-\frac{\gamma a}{kT}\right) = (1-x)\exp\left(-\frac{\gamma_A^0 a}{kT}\right) + x\exp\left(-\frac{\gamma_B^0 a}{kT}\right). \quad (9.08.9)$$

We have thus derived an additive relation, not for γ^0 but for

$$\exp(-\gamma^0 a/kT).$$

This is the simplest and most symmetrical relation obtainable for the surface tension of an ideal mixture.

In particular for an equimolecular mixture of A and B , with $x = \frac{1}{2}$, formula (9) can be rewritten as

$$\gamma = \frac{\gamma_A^0 + \gamma_B^0}{2} - \frac{kT}{a} \ln \cosh \frac{(\gamma_B^0 - \gamma_A^0)a}{2kT} \quad (x = \frac{1}{2}). \quad (9.08.10)$$

It may generally be expected that for pairs of liquids forming ideal mixtures $(\gamma_B^0 - \gamma_A^0)/\frac{1}{2}(\gamma_A^0 + \gamma_B^0)$ is unlikely to exceed 0.1. We may then usually with sufficient accuracy replace $\ln \cosh$ by the first term of its expansion as a power series. We have then

$$\gamma = \frac{\gamma_A^0 + \gamma_B^0}{2} - \frac{(\gamma_B^0 - \gamma_A^0)^2 a}{8kT} \quad (x = \frac{1}{2}). \quad (9.08.11)$$

9.09. Regular solutions

We return now to the more general case of regular solutions, using the zeroth approximation. It is now necessary to express W in (9.07.5) as the correct multiple of w/z . Using the zeroth approximation we shall assume complete randomness in the surface layer as well as in the

bulk. In the slicing process described in § 9.06 the number of AB contacts destroyed, assuming complete randomness, would be

$$\frac{1}{2}mzN'\{(1-x)x+x(1-x)\}. \quad (9.09.1)$$

In covering the newly formed surface with a new layer of N' molecules, again assuming complete randomness, the number of AB contacts created within the new layer is

$$lxN'(1-x')x', \quad (9.09.2)$$

and the number created between the new layer and the next layer is

$$mzN'\{(1-x')x+x'(1-x)\}. \quad (9.09.3)$$

Adding (2) and (3) and subtracting (1) we thus obtain for the net increase in the number of AB contacts

$$zN'[l(1-x')x'+m\{(1-x')x+x'(1-x)-x(1-x)\}]. \quad (9.09.4)$$

Multiplying this by w/z we obtain for W

$$\begin{aligned} W &= N'w[l(1-x')x'+m\{(1-x')x+x'(1-x)-x(1-x)\}] \\ &= (1-x')N'w(lx'^2+mx^2)+x'N'w\{l(1-x')^2+m(1-x)^2\}. \end{aligned} \quad (9.09.5)$$

Substituting (5) into (9.07.5) we obtain finally for the grand partition function

$$\begin{aligned} \Xi' &= \sum_{x'} [\lambda_A q'_A \exp\{-(lx'^2+mx^2)w/kT\}/(1-x')]^{1-x'N'} \times \\ &\quad \times [\lambda_B q'_B \exp\{-(l[1-x']^2+m[1-x]^2)w/kT\}/x']^{x'N'}, \end{aligned} \quad (9.09.6)$$

where the summation extends over all possible values of x' .

As usual we replace the sum in (6) by its greatest term. Differentiating (6) with respect to x' and equating to zero, we obtain after some simplification

$$\begin{aligned} \Xi' &= [\lambda_A q'_A \exp\{-(lx'^2+mx^2)w/kT\}/(1-x')]^{N'} \\ &= [\lambda_B q'_B \exp\{-(l[1-x']^2+m[1-x]^2)w/kT\}/x']^{N'}. \end{aligned} \quad (9.09.7)$$

We can rewrite formula (9.03.5) in the form

$$\Xi' = \exp\left(-\frac{\gamma A}{kT}\right) = \left[\exp\left(-\frac{\gamma a}{kT}\right)\right]^{N'}, \quad (9.09.8)$$

where $a = A/N'$ is the mean area of surface per molecule. Comparing (8) with (7) we have

$$\begin{aligned} \gamma &= \frac{kT}{a} \ln \frac{1-x'}{\lambda_A q'_A} + (lx'^2+mx^2) \frac{w}{a} \\ &= \frac{kT}{a} \ln \frac{x'}{\lambda_B q'_B} + (l[1-x']^2+m[1-x]^2) \frac{w}{a}. \end{aligned} \quad (9.09.9)$$

Now using (9.04.3) and (9.05.3) we can rewrite formulae (9.04.1) and (9.04.2) respectively as

$$\ln \lambda_A = \ln \frac{1-x}{q_A} + lx^2 \frac{w}{kT} + 2mx^2 \frac{w}{kT}, \quad (9.09.10)$$

$$\ln \lambda_B = \ln \frac{x}{q_B} + l(1-x)^2 \frac{w}{kT} + 2m(1-x)^2 \frac{w}{kT}. \quad (9.09.11)$$

Substituting for λ_A , λ_B from (10) and (11) respectively into (9), we obtain

$$\begin{aligned} \gamma &= \frac{kT}{a} \ln \frac{(1-x')q_A}{(1-x)q'_A} + l(x'^2 - x^2) \frac{w}{a} - mx^2 \frac{w}{a} \\ &= \frac{kT}{a} \ln \frac{x'q_B}{xq'_B} + l([1-x']^2 - [1-x]^2) \frac{w}{a} - m[1-x]^2 \frac{w}{a}. \end{aligned} \quad (9.09.12)$$

Finally using the formula (9.05.5) for the pure liquid A and the analogous formula for the pure liquid B , we can rewrite (12) as

$$\begin{aligned} \gamma &= \gamma_A^0 + \frac{kT}{a} \ln \frac{1-x'}{1-x} + l(x'^2 - x^2) \frac{w}{a} - mx^2 \frac{w}{a} \\ &= \gamma_B^0 + \frac{kT}{a} \ln \frac{x'}{x} + l([1-x']^2 - [1-x]^2) \frac{w}{a} - m[1-x]^2 \frac{w}{a}. \end{aligned} \quad (9.09.13)$$

Formula (13) provides a pair of simultaneous equations for γ , x' in terms of γ_A^0 , γ_B^0 , x . The second equation has to be solved numerically for x' and the value so obtained substituted back to give the value of γ .

9.10. Gibbs's adsorption formula and further simplification

It is of interest to investigate whether our formulae satisfy Gibbs's adsorption formula as they should. For this purpose it is convenient to rewrite formula (9.09.9) in the form

$$\begin{aligned} \gamma &= -\frac{kT}{a} (1-x') \ln \frac{\lambda_A q'_A}{1-x'} + (1-x')(lx'^2 + mx^2) \frac{w}{a} - \\ &\quad - \frac{kT}{a} x' \ln \frac{\lambda_B q'_B}{x'} + x'(l[1-x']^2 + m[1-x]^2) \frac{w}{a}, \end{aligned} \quad (9.10.1)$$

where x' has the value such as to minimize this expression for γ . We now form the differential of (1) with respect to composition at constant

temperature. Since, as already noted, $\partial\gamma/\partial x' = 0$ all terms in dx' cancel and so may be ignored. We have then

$$-d\gamma = \frac{1-x'}{a} kT d\ln \lambda_A + \frac{x'}{a} kT d\ln \lambda_B + m \frac{w}{a} 2(x'-x) dx, \quad (9.10.2)$$

which would be equivalent to the thermodynamic relation (9.01.15) were it not for the presence of the term

$$m \frac{w}{a} 2(x'-x) dx. \quad (9.10.3)$$

We thus reach the unsatisfactory conclusion that our formulae must be thermodynamically inconsistent. Presumably we were not justified in assuming that the molecular layer adjacent to the outermost one has the same composition as the bulk phase. This suggests trying to improve the treatment by assuming that the outermost two layers have compositions different from the bulk. This improvement has been investigated† and the following conclusions are reached.

The second layer has at equilibrium a composition intermediate between that of the outermost layer and that of the bulk. The discrepancy between the formula obtained and the necessary thermodynamic formula is considerably reduced. There is a strong indication that this discrepancy rapidly disappears as the number of layers incorporated into the surface phase is increased. The calculated values for the surface tension are not greatly affected.

There is another way of looking at this thermodynamic inconsistency of our formulae. We have throughout used the zeroth approximation in assuming complete randomness both in the bulk and in the surface layer. We know that this is equivalent to ignoring terms of order $(w/zkT)^2$. Consequently our approximate treatment is unlikely to be useful, unless the terms in w are fairly small corrections to the formulae obtained by neglecting w . If this is the case we may perhaps with small loss of accuracy be even less careful about the terms in w than we have so far. Let us accordingly replace x' by x in the terms in w , assumed to be small. We then obtain instead of (9.09.13)

$$\gamma = \gamma_A^0 + \frac{kT}{a} \ln \frac{1-x'}{1-x} - mx^2 \frac{w}{a} = \gamma_B^0 + \frac{kT}{a} \ln \frac{x'}{x} - m(1-x)^2 \frac{w}{a}, \quad (9.10.4)$$

† Defay and Prigogine (1950), *Trans. Faraday Soc.* **46**, 199.

which can be rewritten as

$$\begin{aligned} e^{-\gamma a/kT} &= \frac{1-x}{1-x'} e^{-\gamma_A^0 a/kT} e^{mx^2 w/kT} = \frac{x}{x'} e^{-\gamma_B^0 a/kT} e^{m(1-x)^2 w/kT} \\ &= (1-x)e^{-\gamma_A^0 a/kT} e^{mx^2 w/kT} + xe^{-\gamma_B^0 a/kT} e^{m(1-x)^2 w/kT}. \quad (9.10.5) \end{aligned}$$

In particular for an equimolecular mixture of *A* and *B* formula (5) becomes

$$e^{-\gamma a/kT} = \frac{1}{2}\{e^{-\gamma_A^0 a/kT} + e^{-\gamma_B^0 a/kT}\}e^{\frac{1}{2}mw/kT} \quad (x = \frac{1}{2}), \quad (9.10.6)$$

which is in a particularly convenient form for comparison with experiment.

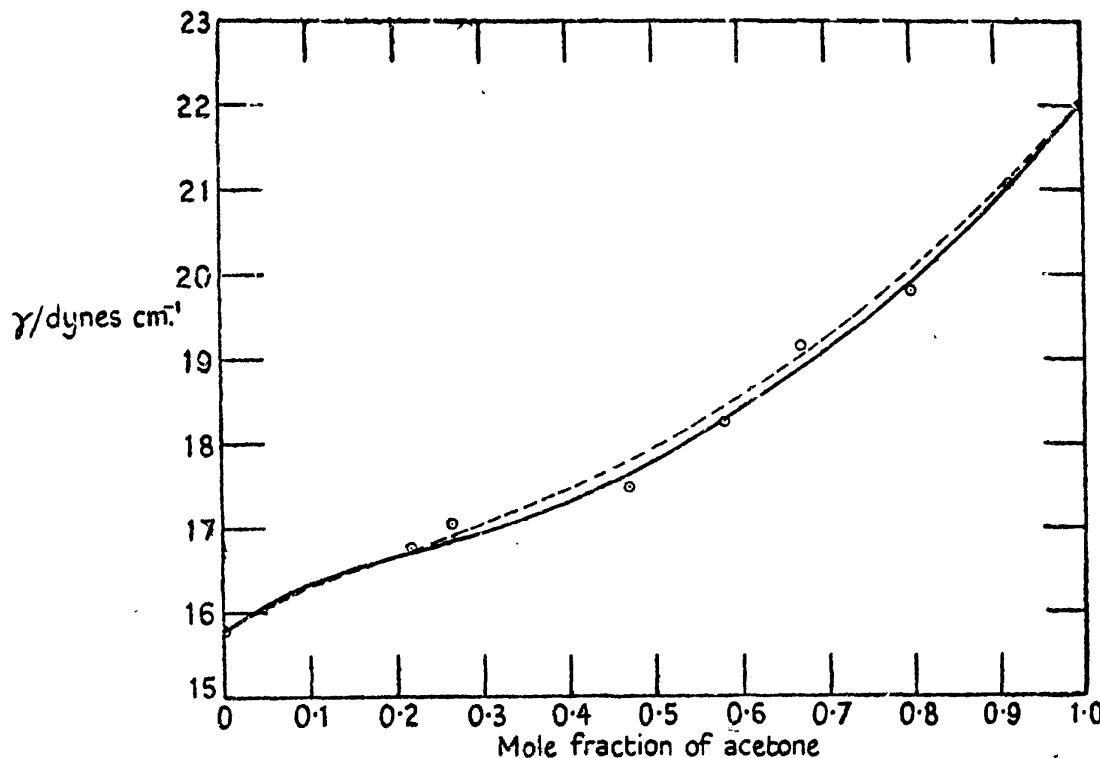


FIG. 9.2. Surface tension γ of mixtures of ether and acetone at 303° K. plotted against mole fraction of acetone. \odot experimental data of Narbond; — calculated for simple cubic lattice; - - - calculated for close packed lattice.

9.11. Comparison with experiment

We shall now compare our theoretical formulae with the experimental data for a typical ideal mixture and a typical regular mixture.

One of the best examples of an approximately ideal mixture is that of chlorobenzene and bromobenzene, which have surface tensions† 33.11 dyne/cm. and 36.60 dyne/cm. respectively at 20° C. The calculated surface tension of an equimolecular mixture by taking the arithmetic mean is 34.85 dyne/cm., and the value calculated by formula

† Experiments by Kremann and Meingast quoted by Belton and Evans (1945), *Trans. Faraday Soc.* 41, 1.

(9.08.10) is 34.72 dyne/cm. if we assume for the molecular area $a = 37 \text{ \AA}^2$. The observed value for the equimolecular mixture is 34.65 dyne/cm. The agreement may be considered satisfactory. Complete agreement could be forced by using for the molecular area the greater value 55 \AA^2 .

As an example of a regular mixture we use ethyl ether and acetone. The partial vapour pressures have been measured at 30° C . and were shown by Porter† to be well fitted by the zeroth approximation formulae (4.11.4) and (4.11.5) with $w/kT = 0.74$. The surface tension of mixtures of these two substances at 30° C . has been measured by Narbond.‡ Using Porter's value for w/kT and assuming $a = 30 \text{ \AA}^2$, the surface tension has been calculated§ as a function of mole fraction according to formula (9.09.13). The comparison was made assuming as alternatives $l = \frac{2}{3}$, $m = \frac{1}{6}$ corresponding to a simple cubic lattice and $l = \frac{1}{2}$, $m = \frac{1}{4}$ corresponding to a close packed lattice. The comparison is shown in Fig. 9.2. We see that whichever lattice is assumed there is excellent agreement between the observed and the calculated values over the whole range of composition.

† Porter (1920), *Trans. Faraday Soc.* **16**, 339.

‡ Narbond (1948), thesis, Brussels University.

§ Prigogine (1948), *Trans. Faraday Soc.* **44**, 626.

X

MOLECULES OF DIFFERENT SIZES: ATHERMAL MIXTURES

10.01. Historical introduction

WE have hitherto been concerned entirely with molecules sufficiently similar in size and shape as to be able to exchange places with one another. We have accordingly used the quasi-crystalline model of a lattice, each site of which is supposed to be occupied by one molecule. We now turn to the consideration of mixtures of two or more kinds of molecules differing from one another in size and shape. In the present chapter we shall be concerned with such mixtures as, in common with ideal mixtures, have zero energy of mixing. Such mixtures will be called *athermal mixtures* or *athermal solutions* in preference to an older name, semi-ideal solutions. The characteristic properties of athermal mixtures may then be summarized by the formulae

$$\Delta_m U = 0, \quad (10.01.1)$$

$$\Delta_m F = -T\Delta_m S, \quad (10.01.2)$$

where as previously the operator Δ_m refers to the increase in the value of a property when one mole of mixture is made isothermally from the requisite quantities of the pure components.

Until about fifteen years ago it was widely believed that the entropy of mixing of athermal solutions was independent of the sizes and shapes of the molecules. In other words, it was commonly believed that all athermal solutions should be ideal. This view was openly challenged† in a discussion held by the Faraday Society in 1936, at which Fowler then suggested that this view could be proved or disproved by a statistical analysis of a mixture of two kinds of molecules arranged on a lattice, each molecule of the one kind occupying two neighbouring sites of the lattice and each molecule of the other kind occupying one site. This problem was attacked by Fowler and Rushbrooke,‡ who showed that such a mixture would not be ideal. Fowler's idea of a lattice model has subsequently been widely used and has proved fruitful. It is the only model which leads to quantitative and explicit formulae

† Guggenheim (1937), *Trans. Faraday Soc.* **33**, 151.

‡ Fowler and Rushbrooke (1937), *Trans. Faraday Soc.* **33**, 1272.

without the introduction of arbitrary assumptions. This quasi-crystalline model will be used throughout our considerations of mixtures of molecules of different sizes.

We shall accordingly be considering molecules occupying various numbers of sites on a lattice or quasi-lattice. It will be convenient to use the following names:

- monomer: molecule occupying one site,
- dimer: molecule occupying two sites,
- trimer: molecule occupying three sites,
- tetramer: molecule occupying four sites,
- r -mer: molecule occupying r sites.

Closed formulae for the configurational free energy appropriate to a mixture of monomers and dimers were first obtained by Chang,[†] who used Bethe's method of constructing a grand partition function for a small group of sites. The same procedure was used by Miller[‡] to obtain closed formulae for a mixture of monomers and trimers. By analogy Miller also correctly guessed the formula for a mixture of monomers and any r -mer having the form of an open chain, i.e. without any closed rings. This formula was obtained independently by Huggins[§] and was later derived by a much simpler method^{||} than that used by Chang and extended to mixtures of any number of different kinds of open-chain r -mers. Chang's method has also been materially simplified by a reduction in the number of sites considered. Thus simplified the method has been applied to certain molecules containing closed rings, namely triangular trimers, tetrahedral tetramers, and square tetramers.

It is the main object of this chapter to describe the work mentioned above or at least such parts of it as have not become entirely superseded by simpler and more powerful techniques.

10.02. Terminology and notation

We shall be concerned almost entirely with mixtures of monomers with one kind of r -mer consisting of r elements each occupying one site. We shall denote the number of monomers by N_1 and the number of r -mers by N_r . We denote by $1-\phi$ the fraction of sites occupied by

[†] Chang (1939), *Proc. Roy. Soc. A* **169**, 512; (1939), *Proc. Cambridge Phil. Soc.* **35**, 265.

[‡] Miller (1942), *Proc. Cambridge Phil. Soc.* **38**, 109, (1943), **39**, 54.

[§] Huggins (1942), *Ann. New York Acad. Sci.* **43**, 9.

^{||} Guggenheim (1944), *Proc. Roy. Soc. A* **153**, 203.

the monomer and by ϕ the fraction occupied by the r -mer. We have thus the identities

$$1-\phi = \frac{N_1}{N_1+rN_r}, \quad \phi = \frac{rN_r}{N_1+rN_r}. \quad (10.02.1)$$

As long as we use the lattice model we may call $1-\phi$ and ϕ the *volume fractions*[†] of monomer and r -mer respectively.

As previously we denote by z the number of sites which are nearest neighbours of a given site. If then one element of an r -mer has been placed on a site there are z ways in which a second element, adjoining the one already placed, can be placed on the lattice.

We denote by ρ the number of ways in which the molecule as a whole can be placed after one of its end elements has been placed. Thus in the trivial case of a monomer $\rho = 1$. For dimers $\rho = z$. For trimers there are three distinct cases. If the trimers are linear and rigid $\rho = z$. If the trimers are non-linear and rigid $\rho = zz'$, where z' is the number of alternative sites for the third element when the first two elements have been placed. If the trimers are flexible $\rho = z(z-1)$.

For molecules occupying more than three sites there are numerous alternatives. The minimum value for ρ is z for rigid straight molecules. The maximum value for ρ is approximately $z(z-1)^{r-2}$ for entirely flexible molecules, but this is slightly inaccurate because it includes certain configurations in which the long molecule bends back on itself and two elements occupy the same site; such configurations should of course be excluded, but the error due to their inclusion is probably small. We shall find that a knowledge of ρ is not required for determining the free energy of mixing or for any of the thermodynamic properties derivable from it.

We now introduce[‡] an important quantity α defined as the ratio of the probability that a group of sites, congruent with the r -mer, be wholly occupied by a single r -mer to the probability that the group be entirely occupied by monomers. We stress the importance of α because it can be related independently and by quite different methods on the one hand to the thermodynamic functions such as the absolute activities or the configurational free energy and on the other to the composition of the mixture, that is to say to N_r/N_1 or to ϕ .

[†] The use of ϕ to denote a volume fraction is the notation of Hildebrand and Scott (1950), *Solubility of Nonelectrolytes*, Reinhold. It is hoped that it may be widely adopted. The use by some authors of the same letter v to denote both volume fraction and volume, even though in different formats, is deplorable.

[‡] Guggenheim and McGlashan (1950), *Proc. Roy. Soc. A* 203, 435.

We shall immediately obtain all required general relations between α and the important thermodynamic properties. We shall afterwards be concerned with the configurational problem of relating α to ϕ for various kinds of r -mers.

10.03. Relation of α to absolute activities

We recall the definition of α . We consider a group of r sites congruent with an r -mer. Such a group may be occupied in many distinguishable ways, among which two are outstandingly simple, namely:

- (a) occupation of the group by a single r -mer;
- (b) occupation of the group by r monomers.

It is the ratio of the probability of (a) to that of (b) which is denoted by α .

From the fundamental properties of grand partition functions and absolute activities it should be obvious that α is directly proportional to

$$\frac{\lambda_r q_r}{(\lambda_1 q_1)^r}, \quad (10.03.1)$$

where the λ 's denote as usual absolute activities and the q 's are partition functions. The only point which is not quite obvious is whether the proportionality factor is unity or some other simple factor depending on the shape and on the symmetry of the r -mer. The answer is that it depends on the precise definition of q_r , but that q_r can always be reasonably so defined as to absorb any such geometrical factor. Since any such factor as well as q_1 and q_r , will ultimately disappear from all formulae for the free energy of mixing and derived quantities, it is unnecessary to devote effort to detailed discussion of this point, which is really one of convention. We shall accordingly assume that by suitable definitions of q_1 , q_r we may write

$$\alpha = \frac{\lambda_r q_r}{(\lambda_1 q_1)^r}, \quad (10.03.2)$$

In case any reader is insufficiently familiar with the fundamental properties of the grand partition function to have confidence in (2), we may mention that the direct proportionality between α and the expression (1) can be simply derived† by applying the principle of detailed balancing to the two elementary processes:

- (a) the removal ('evaporation') of an r -mer from the selected group of r sites and its simultaneous replacement ('condensation') on these sites by r monomer molecules from the gas phase;

† Guggenheim (1944), *Proc. Roy. Soc. A* 183, 203.

(b) the inverse process of removal ('evaporation') of r monomer molecules from the same group of sites and their simultaneous replacement ('condensation') by an r -mer from the gas phase.

The sceptical reader can also readily verify that any constant proportionality factor may be absorbed into q_r , without affecting any of the essential conclusions.

10.04. Relation of α to free energy of mixing

We now require only straightforward thermodynamics[†] to relate α to the free energy of mixing. We begin with one of the fundamental relations, which for a binary mixture of N_1 monomers and N_r r -mers takes the form

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_r dN_r. \quad (10.04.1)$$

Since we are considering a non-gaseous phase at ordinary pressures the distinction between G and F is trivial; we accordingly as usual replace G by the more familiar F and omit the term in dP . As we shall be concerned only with variations of composition at given temperature, we also omit the term in dT , so that (1) reduces to

$$dF = \mu_1 dN_1 + \mu_r dN_r. \quad (10.04.2)$$

Using the relation between chemical potential μ and absolute activity λ

$$\mu = kT \ln \lambda, \quad (10.04.3)$$

we rewrite (2) as

$$\frac{1}{kT} dF = \ln \lambda_1 dN_1 + \ln \lambda_r dN_r. \quad (10.04.4)$$

We now take the important step of changing from the variables N_1 , N_r to the variables N_s , ϕ , where N_s denotes the total number of sites and ϕ the fraction of sites occupied by the r -mer, so that

$$N_s = N_1 + rN_r, \quad (10.04.5)$$

$$N_1 = (1-\phi)N_s, \quad N_r = \frac{\phi}{r}N_s. \quad (10.04.6)$$

Making this change of variables in (4) we have

$$\frac{1}{kT} dF = \left\{ (1-\phi) \ln \lambda_1 + \frac{\phi}{r} \ln \lambda_r \right\} dN_s + N_s \left\{ -\ln \lambda_1 + \frac{1}{r} \ln \lambda_r \right\} d\phi, \quad (10.04.7)$$

or for constant N_s $\frac{1}{N_s kT} dF = \frac{1}{r} \ln \frac{\lambda_r}{(\lambda_1)^r} d\phi. \quad (10.04.8)$

[†] Guggenheim (1944), *Proc. Roy. Soc. A* **183**, 208, § 5; Guggenheim and McGlashan (1950), *Proc. Roy. Soc. A* **203**, 446, § 9.

We now use formula (10.03.2) and obtain

$$\frac{1}{N_s kT} dF = \frac{1}{r} \ln \frac{\alpha (q_1)^r}{q_r} d\phi. \quad (10.04.9)$$

When we have obtained formulae relating α to ϕ , we have only to substitute for α into (9) and then integrate to obtain F . The question of the integration constant disappears when we consider the free energy of mixing. If we regard the free energy as a function of N_s and ϕ , then the free energy of mixing ΔF is given by

$$\Delta F = F(N_s, \phi) - (1-\phi)F(N_s, 0) - \phi F(N_s, 1). \quad (10.04.10)$$

Comparing (10) with (9) we see that ΔF takes the form

$$\frac{\Delta F}{N_s kT} = \frac{1}{r} \int_0^\phi \ln \alpha d\phi - \frac{\phi}{r} \int_0^1 \ln \alpha d\phi, \quad (10.04.11)$$

where, as predicted, all terms depending on q_1, q_r cancel.

Formula (11) gives the free energy of mixing of a mixture containing N_1 monomers and N_r r -mers, where N_1, N_r are related to N_s, ϕ by (6). To obtain the molar free energy of mixing $\Delta_m F$ we have to divide ΔF by the total number of molecules, namely $(1-\phi+\phi/r)N_s$ and multiply by Avogadro's number $N = R/k$. We thus obtain

$$\frac{\Delta_m F}{RT} = \frac{1}{r-(r-1)\phi} \left\{ \int_0^\phi \ln \alpha d\phi - \phi \int_0^1 \ln \alpha d\phi \right\}. \quad (10.04.12)$$

Whenever we have obtained a formula for α in terms of ϕ , formula (12) leads immediately to a closed expression for the molar free energy of mixing. Since the mixtures which we are discussing are athermal, we have by definition $\Delta_m U = 0$, and consequently

$$\frac{\Delta_m S}{R} = -\frac{\Delta_m F}{RT} = \frac{1}{r-(r-1)\phi} \left\{ - \int_0^\phi \ln \alpha d\phi + \phi \int_0^1 \ln \alpha d\phi \right\}. \quad (10.04.13)$$

10.05. Combinatory formula

If we denote by $g(N_1, N_r)$ the number of ways of arranging N_1 monomers and N_r r -mers on the lattice, then this quantity is related to the free energy F by

$$-\frac{F}{kT} = \ln g(N_1, N_r) + N_1 \ln q_1 + N_r \ln q_r. \quad (10.05.1)$$

If we now integrate (10.04.9) and compare with (1) we find

$$\ln \frac{g(N_1, N_r)}{g(N_s, 0)} = -\frac{N_s}{r} \int_0^\phi \ln \alpha d\phi. \quad (10.05.2)$$

But when $N_r = 0$ the lattice is completely covered with monomers so that evidently $g(N_s, 0) = 1$. Consequently (2) reduces to

$$\ln g(N_1, N_r) = -\frac{N_s}{r} \int_0^\phi \ln \alpha d\phi = -\left(\frac{N_1}{r} + N_r\right) \int_0^\phi \ln \alpha d\phi. \quad (10.05.3)$$

We should mention that $g(N_1, N_r)$ is here so defined that when we construct the complete partition function

$$g(N_1, N_r) q_1^{N_1} q_r^{N_r}, \quad (10.05.4)$$

for the system, the partition function q_r for a single r -mer contains a factor $1/\sigma_r$, where σ_r denotes the symmetry number of the r -mer. If we used the opposite convention omitting this factor $1/\sigma_r$ from q_r , then we should have to include an extra term $-N_r \ln \sigma_r$ in (3).

10.06. Dimers. Chang's method

We shall now obtain a formula for α in terms of ϕ for the simplest case of a mixture of dimers with monomers, disregarding the trivial case of an ideal mixture of monomers with monomers. We shall first use a method which is a considerably simplified modification of Chang's method. After obtaining the result we shall explain in what respect the modifications have simplified the treatment. We shall then give an entirely different and more direct derivation of the formula for α .

We are concerned with the possible arrangements of N_r dimers on N_s sites so that the fraction of sites occupied by dimers is $\phi = 2N_r/N_s$. As far as the enumeration of configurations is concerned it is quite immaterial whether the remaining $N_s(1-\phi)$ sites are occupied by monomers or are imagined to be vacant. The terminology of the following discussion and of later analogous discussions is simplified by calling a site *vacant* when we mean that it is not occupied by an r -mer, but is ultimately to be considered as occupied by a monomer.

We now consider a pair of sites a, b . Table 10.1 contains a list of the several possible manners of their occupation with their relative probabilities. The first column merely gives a number by which to refer to each type of configuration. The second column specifies the configuration

TABLE 10.1

Dimers

Reference number	Configuration	Relative probability
1	$a \quad b$ —	α
2	$X \quad X$	ϵ^2
3	$X \quad 0$	ϵ
3'	$0 \quad X$	ϵ
4	$0 \quad 0$	1

or type of configuration. The configuration 1, denoted by a line joining the two sites, is the one in which a dimer occupies the pair of sites. The symbol X denotes that a site is occupied by one element of a dimer, while its other element is on some site other than a or b . The symbol 0 denotes that a site is regarded as vacant, i.e. eventually to be occupied by a monomer. The third column gives ratios of probabilities for the several configurations or types of configuration, the value for configuration 4 with both sites empty being unity by convention. The two configurations 3 and 3' clearly have equal relative probabilities which are denoted by ϵ . The essential assumption or approximation of the treatment is that, if a and b are not occupied by the same dimer, then the relative probabilities of being occupied by an element of a dimer or vacant are independent for the two sites. This leads to a relative probability ϵ^2 for configuration 2.

We note that each factor ϵ represents $z-1$ orientations of a dimer. In others words, a single orientation of a dimer occupying a or b , but not both, is represented by a factor $\epsilon/(z-1)$. The probability, represented by α , that a dimer occupies the pair of sites ab must be equal to the probability that a dimer occupies the site a and some other specified neighbouring site. This condition is expressed by the equation

$$\alpha = \frac{\epsilon}{z-1} (\epsilon + 1). \quad (10.06.1)$$

Equations obtained by this kind of reasoning will be called *equivalence relations*.

As we have already mentioned, $\epsilon/(z-1)$ is the relative probability of occupation of a by a dimer having a specified orientation. Consequently $z\epsilon/(z-1)$ is equal to the relative probability of occupation of a by a dimer regardless of orientation. In other words, the probability that the site a , or any other chosen site, is occupied by a dimer is

$z\epsilon/(z-1)$ times the probability of its being vacant. But these two probabilities are evidently to one another in the ratio ϕ to $1-\phi$. Hence we have

$$\frac{z}{z-1}\epsilon = \frac{\phi}{1-\phi}. \quad (10.06.2)$$

Eliminating ϵ between (1) and (2) we obtain

$$\alpha = \frac{1}{z} \frac{\phi}{1-\phi} \frac{1-\phi/z}{1-\phi}, \quad (10.06.3)$$

which is the required relation between α and ϕ .

Formula (3) was first obtained by Chang,[†] but the derivation given here is much shorter and more direct than his. There are four contributory causes to the greater simplicity of the new derivation. In the first place Chang began by considering the more general and much more complicated problem in which the several configurations had different energies; he then treated the case of an athermal system, in which all configurations have equal energies, as a particular example. In the second place Chang considered a group of altogether $2z$ sites, whereas here we are considering only two sites. In the third place Chang distinguished between central sites and neighbouring sites, whereas here the two sites are treated on a par. In the fourth place if we had copied the technique used by Chang our derivation of formula (2) would have been as follows. We equate $\phi/(1-\phi)$ to the ratio of the sum of all relative probabilities for configurations in which a is occupied by a dimer to the sum of those for configurations in which a is vacant. This gives us

$$\frac{\phi}{1-\phi} = \frac{\alpha + \epsilon^2 + \epsilon}{\epsilon + 1}. \quad (10.06.4)$$

When we substitute from (1) into (4) we recover (2) by an unnecessarily circuitous route. This alternative derivation admittedly affords a useful check on the correctness and mutual consistency of (1) and (2).

These simplifications of Chang's treatment may seem unimportant here, but it is in fact their introduction which has made tractable the more complicated systems studied later in this chapter. Anticipating these it is convenient to introduce an abbreviation for use in tables of configurations. If we use the symbol U to denote either X or 0, then in place of Table 10.1 we have the abbreviated Table 10.2.

[†] Chang (1939), *Proc. Roy. Soc. A* **169**, 512; (1939), *Proc. Cambridge Phil. Soc.* **35**, 265.

TABLE 10.2

Dimers

Reference number	Configuration	Relative probability
1	$\begin{array}{c} a \\ \hline b \\ U \quad U \end{array}$	
2		$\frac{\alpha}{(\epsilon + 1)^2}$

10.07. Dimers. Direct method

We shall now leave Chang's method for the present and shall describe a more direct method of obtaining Chang's formula (10.06.3) for a mixture of N_1 monomers and N_2 dimers. We begin by noting that, whereas the number of sites which are neighbours of a monomer is z , the number of sites which are neighbours of a dimer is not $2z$, but only $2z - 2$.

Since all configurations are assumed to have the same energy it follows that the arrangement of the molecules will be completely random. A number of consequences follow immediately from this randomness, in particular the following.

The frequency of occupation of a chosen site by a monomer is $(1 - \phi) = N_1/(N_1 + 2N_2)$ and the frequency of its occupation by a dimer is $\phi = 2N_2/(N_1 + 2N_2)$.

If a site is occupied by a monomer, then the chances that a given neighbouring site is occupied by another monomer or by a dimer are as zN_1 to $(2z - 2)N_2$.

If a site is occupied by a dimer, then the chance that a given neighbouring site is occupied by the other element of the same dimer or by another molecule (dimer or monomer) are as 1 to $z - 1$.

If a site is occupied by a dimer, then the chances that a given neighbouring site is occupied by a monomer or by a different dimer are as zN_1 to $(2z - 2)N_2$.

These ratios uniquely determine the following expressions for the frequencies of occupation of a chosen pair of sites in alternative ways.

Both by monomers:
$$\frac{N_1}{N_1 + 2N_2} \frac{zN_1}{zN_1 + (2z - 2)N_2}; \quad (10.07.1)$$

First by monomer,
second by dimer:
$$\frac{N_1}{N_1 + 2N_2} \frac{(2z - 2)N_2}{zN_1 + (2z - 2)N_2}; \quad (10.07.2)$$

First by dimer,
second by monomer:
$$\frac{N_1}{N_1 + 2N_2} \frac{(2z - 2)N_2}{zN_1 + (2z - 2)N_2}; \quad (10.07.3)$$

Both by different dimers: $\frac{(2z-2)N_2}{z(N_1+2N_2)} \frac{(2z-2)N_2}{zN_1+(2z-2)N_2}; \quad (10.07.4)$

Both by same dimer: $\frac{2N_2}{z(N_1+2N_2)}. \quad (10.07.5)$

By definition α is equal to the ratio of the frequency of occupation of the two sites by the same dimer to the frequency of their occupation by two monomers. Hence from (1) and (5) we have immediately

$$\begin{aligned} \alpha &= \frac{2N_2}{z(N_1+2N_2)} \frac{N_1+2N_2}{N_1} \frac{zN_1+(2z-2)N_2}{zN_1} \\ &= \frac{1}{z} \frac{2N_2}{N_1+2N_2} \frac{N_1+2N_2}{N_1} \frac{N_1+(1-1/z)2N_2}{N_1} \\ &= \frac{1}{z} \frac{\phi}{1-\phi} \frac{1-\phi+(1-1/z)\phi}{1-\phi} \\ &= \frac{1}{z} \frac{\phi}{1-\phi} \frac{1-\phi/z}{1-\phi}, \end{aligned} \quad (10.07.6)$$

which is the same as formula (10.06.3).

10.08. Open chain r -mers

The method for obtaining α described in the previous section is so straightforward that it can immediately be extended to any r -mer provided only that it has the form of a simple chain or a branched chain without any closed rings.

We begin by defining a number q as follows. Consider a particular r -mer occupying a group of r sites. Each of these sites has z neighbouring sites some occupied by other elements of the same r -mer. We denote by zq the number of pairs of neighbouring sites of which one is a member of the group occupied by the given r -mer and the other is not. Then for a simple chain or branched chain r -mer q is related to r by

$$\frac{1}{2}z(r-q) = r-1. \quad (10.08.1)$$

Since all configurations are assumed to have the same energy, it follows that the arrangement of the molecules will be completely random. A number of consequences follow immediately from this randomness, in particular the following.

The frequency of occupation of a chosen site by a monomer is $N_1/(N_1+rN_r)$ and the frequency of its occupation by an r -mer is $rN_r/(N_1+rN_r)$.

† Guggenheim (1944), Proc. Roy. Soc. A 183, 203.

If a site is occupied by a monomer, then the chances that a given neighbouring site is occupied by another monomer or by an r -mer are as N_1 to qN_r .

If a site is occupied by an r -mer, then the chances that a given neighbouring site is occupied by another element of the same r -mer or by another molecule (r -mer or monomer) are as $r-q$ to q .

If a site is occupied by an r -mer, then the chances that a given neighbouring site is occupied by a monomer or by a different r -mer are as N_1 to qN_r .

These ratios determine uniquely the following expressions for the frequencies of occupation of a chosen pair of sites in alternative ways.

$$\text{Both by monomer: } \frac{N_1}{N_1+rN_r} \frac{N_1}{N_1+qN_r}; \quad (10.08.2)$$

$$\text{First by monomer, second by } r\text{-mer: } \frac{N_1}{N_1+rN_r} \frac{qN_r}{N_1+qN_r}; \quad (10.08.3)$$

$$\text{First by } r\text{-mer, second by monomer: } \frac{qN_r}{N_1+rN_r} \frac{N_1}{N_1+qN_r}; \quad (10.08.4)$$

$$\text{Both by different } r\text{-mers: } \frac{qN_r}{N_1+rN_r} \frac{qN_r}{N_1+qN_r}; \quad (10.08.5)$$

$$\text{Both by same } r\text{-mer: } \frac{(r-q)N_r}{N_r+rN_r}. \quad (10.08.6)$$

A thorough study of these expressions and their ratios is profitable, although we shall in fact require to use only (2).

Now consider a particular group of r sites so interrelated that it is possible for them to be occupied by an r -mer. If the r -mers are flexible, the group of r sites must be such that an r -mer occupying them is not bent back on itself. The frequency of occupation of a chosen one of these sites by any element of an r -mer is $\phi = rN_r/(N_1+rN_r)$, and the frequency of its occupation by a particular element of an r -mer (imagining the individual elements to be distinguishable) is $\phi/r = N_r/(N_1+rN_r)$. Consequently the frequency of occupation of the group by a single r -mer is

$$\frac{\sigma_g \phi}{\rho} = \frac{\sigma_g}{\rho} \frac{N_r}{N_1+rN_r}, \quad (10.08.7)$$

where ρ was defined in § 10.02 as the number of ways in which the r -mer as a whole can be placed after a particular one of its elements has been placed and σ_g denotes the symmetry number of the group of r sites being considered. We also require to know the frequency of occupation

of the whole group of r sites by monomers. By an obvious extension of (2) this frequency is

$$\frac{N_1}{N_1+rN_r} \left(\frac{N_1}{N_1+qN_r} \right)^{r-1}. \quad (10.08.8)$$

Now taking the ratio of (7) to (8) we obtain for α

$$\alpha = \frac{\sigma_g}{\rho} \frac{N_r}{N_1} \left(\frac{N_1+qN_r}{N_1} \right)^{r-1}, \quad (10.08.9)$$

or in terms of ϕ

$$\alpha = \frac{\sigma_g}{\rho r} \frac{\phi}{1-\phi} \left(\frac{1-\phi+q\phi/r}{1-\phi} \right)^{r-1} = \frac{\sigma_g}{\rho r} \frac{\phi}{1-\phi} \left(\frac{1-(r-q)\phi/r}{1-\phi} \right)^{r-1}. \quad (10.08.10)$$

In the simplest case of a dimer $r = 2$; $\sigma_g = 2$; $\rho = z$; $(r-q)/r = 1/z$ and formula (10) reduces to (10.06.3) or (10.07.6).

10.09. Thermodynamic properties

We now substitute for α from (10.08.10) into (10.04.12) and perform the integrations, thus obtaining

$$\begin{aligned} \frac{\Delta_m F}{RT} &= -\frac{\Delta_m S}{R} = \frac{r}{r-(r-1)\phi} \left\{ \frac{\phi}{r} \ln \phi + (1-\phi) \ln(1-\phi) - \right. \\ &\quad \left. - \frac{r-1}{r} \left(\frac{r}{r-q} - \phi \right) \ln \left(1 - \frac{r-q}{r} \phi \right) + \phi \frac{q(r-1)}{r(r-q)} \ln \frac{q}{r} \right\}. \end{aligned} \quad (10.09.1)$$

On reverting to the variables N_1 , N_r formula (1) can be written

$$(N_1+N_r) \frac{\Delta_m F}{RT} = \ln \frac{N_1!(rN_r)!}{(N_1+rN_r)!} + \frac{r-1}{r-q} \ln \frac{(N_1+rN_r)!(qN_r)!}{(N_1+qN_r)!(rN_r)!}. \quad (10.09.2)$$

By using (10.08.1) we can transform (2) to

$$\begin{aligned} (N_1+N_r) \frac{\Delta_m F}{RT} &= N_1 \ln \frac{N_1}{N_1+rN_r} + N_r \ln \frac{rN_r}{N_1+rN_r} + \\ &\quad + \frac{1}{2}z(N_1+qN_r) \ln \frac{N_1+rN_r}{N_1+qN_r} - \frac{1}{2}zqN_r \ln \frac{r}{q}. \end{aligned} \quad (10.09.3)$$

Formula (3) was first obtained by Huggins.[†] Actually Huggins's formula contains a complicated small quantity f_0 introduced to take account of flexible molecules bending back on themselves; if one sets $f_0 = 0$ in Huggins's formula it reduces to (3). Formula (3) was also

[†] Huggins (1942), *Ann. New York Acad. Sci.* **43**, 9.

tentatively proposed by Miller† as a generalization of the formulae already obtained by Chang for dimers and by himself for trimers.

By differentiation of (2) with respect to N_1 and N_r in turn we obtain for the absolute activities λ and the fugacities p

$$\frac{\lambda_1}{\lambda_1^0} = \frac{p_1}{p_1^0} = \frac{N_1}{N_1 + rN_r} \left(\frac{N_1 + rN_r}{N_1 + qN_r} \right)^{(r-1)/(r-q)} = \frac{N_1}{N_1 + rN_r} \left(\frac{N_1 + rN_r}{N_1 + qN_r} \right)^{\frac{1}{r}}, \quad (10.09.4)$$

$$\frac{\lambda_r}{\lambda_r^0} = \frac{p_r}{p_r^0} = \frac{N_r}{N_r + N_1/r} \left(\frac{N_r + N_1/r}{N_r + N_1/q} \right)^{q(r-1)/(r-q)} = \frac{N_r}{N_r + N_1/r} \left(\frac{N_r + N_1/r}{N_r + N_1/q} \right)^{\frac{q}{r}}, \quad (10.09.5)$$

where as usual the superscript 0 denotes the value of a quantity for the pure liquid.

By substituting for α from (10.08.9) into (10.05.3) and performing the integration we obtain for the number $g(N_1, N_r)$ of ways of arranging N_1 monomers and N_r r -mers on a lattice

$$g(N_1, N_r) = \left(\frac{\rho}{\sigma_g} \right)^{N_r} \frac{(N_1 + rN_r)!}{N_1! N_r!} \frac{((N_1 + qN_r)!)^{(r-1)/(r-q)}}{(N_1 + rN_r)!} \quad (10.09.6)$$

We have already noted that ρ and σ_g are irrelevant to the thermodynamic properties relating to the process of mixing. On the other hand, we note that formula (6) contains the symmetry number σ_g and we may mention that $g(N_1, N_r)$ is here so defined that, when the complete partition function of the system is formed, the internal partition function for each r -mer is assumed to contain as a factor the ratio σ_g/σ_r of the symmetry number σ_g of the group of sites to the symmetry number σ_r of the r -mer when occupying this group of sites.

10.10. More than two components

The formulae of the two preceding sections can readily be extended to a mixture of any number of kinds of r -mers, provided only that they all have the shape of open chains, which may or may not be branched. We shall merely quote some of the most interesting results‡ without proof.

Let the molecules of type i be N_i in number; let each such molecule occupy r_i sites; let the numbers of pairs of sites of which one is occupied by an extended molecule of type i and the other is not occupied by an

† Miller (1943), *Proc. Cambridge Phil. Soc.* 39, 54.

‡ Guggenheim (1944), *Proc. Roy. Soc. A* 183, 203.

element of the same molecule be zq_i . Then the q_i 's and r_i 's are related by

$$\frac{1}{2}z(r_i - q_i) = r_i - 1. \quad (10.10.1)$$

Let the number of alternative orientations of a molecule of type i be σ_i when one of its elements has been fixed. Let σ_i denote the symmetry number of the group of sites. If $g(N_i)$ denotes the total number of possible arrangements of molecules, then

$$g(N_i) = \left\{ \prod_i \left(\frac{\rho_i}{\sigma_i} \right)^{N_i} \right\} \frac{\left(\sum_i r_i N_i \right)!}{\prod_i N_i!} \left\{ \frac{\left(\sum_i q_i N_i \right)!}{\left(\sum_i r_i N_i \right)!} \right\}^{\frac{1}{2}z}, \quad (10.10.2)$$

$$\frac{\lambda_j}{\lambda_j^0} = \frac{p_j}{p_j^0} = \frac{r_j N_j}{\sum_i r_i N_i} \left(\frac{q_j \sum_i r_i N_i}{r_j \sum_i q_i N_i} \right)^{\frac{1}{2}zq_j}. \quad (10.10.3)$$

$$-\sum_i N_i \frac{\Delta_m S}{R} = \sum_j \left\{ N_j \ln \frac{r_j N_j}{\sum_i r_i N_i} + \frac{1}{2}zq_j N_j \ln \frac{q_j \sum_i r_i N_i}{r_j \sum_i q_i N_i} \right\}. \quad (10.10.4)$$

In particular for a binary mixture of molecules A and B neither of which are monomers we have the formulae

$$g(N_A, N_B) = \left(\frac{\rho_A}{\sigma_A} \right)^{N_A} \left(\frac{\rho_B}{\sigma_B} \right)^{N_B} \frac{(r_A N_A + r_B N_B)!}{N_A! N_B!} \left\{ \frac{(q_A N_A + q_B N_B)!}{(r_A N_A + r_B N_B)!} \right\}^{\frac{1}{2}z}, \quad (10.10.5)$$

$$\frac{\lambda_A}{\lambda_A^0} = \frac{p_A}{p_A^0} = \frac{r_A N_A}{r_A N_A + r_B N_B} \left(\frac{N_A + r_B N_B / r_A}{N_A + q_B N_B / q_A} \right)^{\frac{1}{2}zq_A}, \quad (10.10.6)$$

$$\frac{\lambda_B}{\lambda_B^0} = \frac{p_B}{p_B^0} = \frac{r_B N_B}{r_A N_A + r_B N_B} \left(\frac{N_B + r_A N_A / r_B}{N_B + q_A N_A / q_B} \right)^{\frac{1}{2}zq_B}, \quad (10.10.7)$$

$$\begin{aligned} & -(N_A + N_B) \frac{\Delta_m S}{R} \\ &= \ln \frac{(r_A N_A)! (r_B N_B)!}{(r_A N_A + r_B N_B)!} + \frac{1}{2}z \ln \frac{(q_A N_A)! (q_B N_B)! (r_A N_A + r_B N_B)!}{(r_A N_A)! (r_B N_B)! (q_A N_A + q_B N_B)!} \\ &= N_A \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2}zq_A N_A \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} + \\ & \quad + N_B \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2}zq_B N_B \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)}. \end{aligned} \quad (10.10.8)$$

We have mentioned these formulae not so much for their practical importance but rather to emphasize their existence. By contrast analogous formulae do not exist for mixtures of several kinds of r -mers when some of the r -mers contain closed rings.

10.11. Notation for triangles and tetrahedra

We shall now derive formulae† for a mixture of monomers either with trimers, which occupy three sites forming an equilateral triangle, or with tetramers, which occupy four sites forming a regular tetrahedron.

We assume that all the elements of a triangular or tetrahedral molecule are indistinguishable, so that $\sigma_r = \sigma_g = \sigma$. It will then be convenient to use a number ρ' defined as the number of *distinguishable* ways in which the molecule as a whole can be placed after one of its elements has been placed. When the first element has been placed the number of possible positions for a second element is z . We denote by z' the number of possible positions for the molecule as a whole after two elements have already been placed. Then ρ' is defined by

$$\rho' = \frac{r}{\sigma} z z', \quad (10.11.1)$$

being equal to $\frac{1}{2}zz'$ for triangles and equal to $\frac{1}{3}zz'$ for tetrahedra, where-as according to our previous usage

$$\rho = zz'. \quad (10.11.2)$$

We shall also use a quantity κ , related to ρ' and always smaller than ρ' , defined as follows. Consider a group of sites congruent with the r -mer and let one element of an r -mer be placed on one site of the group. Then κ denotes the number of distinguishable ways the r -mer as a whole can be placed without using any other sites of the given group. Take as a simple example equilateral triangular molecules on a plane triangular lattice: $z = 6$, $z' = 2$, $\rho' = \frac{1}{2}zz' = 6$, and $\kappa = 3$.

We shall as previously denote by α the ratio of the probability that a group of sites, congruent with the r -mer, be wholly occupied by one molecule to the probability that the group be completely vacant, i.e. eventually to be filled with monomers.

Our immediate problem then is to find a relation between α and ϕ , first for triangular molecules and then for tetrahedral molecules.

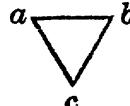
10.12. Triangular trimers

For mixtures of monomers with equilateral triangular trimers we revert to the simplified version of Chang's technique described in § 10.06. For brevity we shall refer to a site as vacant when we mean that it is not occupied by a trimer, but is eventually to be regarded as filled by a monomer. We consider a group of three sites a , b , c

† Guggenheim and McGlashan (1950), *Proc. Roy. Soc. A* 203, 435.

forming an equilateral triangle. The several possible manners of occupation together with their relative probabilities are summarized in Table 10.3. We use the abbreviated notation of Table 10.2 where U denotes

TABLE 10.3
Triangular Trimers

Reference number	Configuration	Relative probability
1		α
2	$U \quad U$ — U	$3(z' - 1)\zeta(\epsilon + 1)$
3	$U \quad U$ U	$(\epsilon + 1)^3$

either X (occupied by a trimer) or 0 (vacant). We continue to use the approximation of assuming that if two sites, say a and b , are not occupied by the same molecule, then the relative probabilities of being occupied or vacant are independent for the two sites. The fact that this is only an approximation is more obvious in the present example than in previous ones. Configurations 1 and 3 call for no further comment. In the set of configurations referred to as 2 two, and only two, of the three sites a , b , c are occupied by the same molecule. In the formula for the relative probability the factor 3 represents the three possible ways of choosing a pair of sites out of the three. The factor $z' - 1$ represents the number of possible configurations of a molecule specified as occupying two sites, say a , b , but not the third c . The factor $\epsilon + 1$ takes care of the third site. If then we completely specify the configuration of the trimer molecule occupying two of the sites, leaving unspecified whether the third site is empty or occupied, the relative probability is $\zeta(\epsilon + 1)$. This may be regarded as the definition of ζ . The parameter ϵ represents the occupation of one site, and one only, of the group of three by a trimer molecule and comprises a number κ of alternative configurations of this molecule. Hence any one of these alternative

configurations is represented by ϵ/κ . Evidently each completely specified configuration of a trimer molecule has the same probability whether this molecule occupies all three sites of the group or two of them or only one. This gives the equivalence relations

$$\alpha = \zeta(\epsilon + 1) = \frac{\epsilon}{\kappa} \{ (z' - 1)\zeta + (\epsilon + 1)^2 \}. \quad (10.12.1)$$

If we solve for ζ and α in terms of ϵ we obtain

$$\zeta = \frac{\epsilon}{\kappa} \frac{(\epsilon + 1)^2}{(z' - 1)\epsilon/\kappa + 1}, \quad (10.12.2)$$

$$\alpha = \frac{\epsilon}{\kappa} \frac{(\epsilon + 1)^3}{(z' - 1)\epsilon/\kappa + 1}. \quad (10.12.3)$$

Since, as already mentioned, ϵ/κ is the relative probability of occupation of a given site by a trimer molecule having a specified orientation, it follows that the total relative probability of occupation of a given site by a trimer is $\rho'\epsilon/\kappa$. Since this is true for any and every site we must have

$$\frac{\rho'}{\kappa} \epsilon = \frac{\phi}{1 - \phi}. \quad (10.12.4)$$

Substituting (4) into (3) we obtain

$$\alpha = \frac{\phi}{\rho'} \frac{\left(1 - \frac{\rho' - \kappa}{\rho'} \phi\right)^3}{(1 - \phi)^3 \left(1 - \frac{\rho' - \kappa + z' - 1}{\rho'} \phi\right)}. \quad (10.12.5)$$

According to the definitions of ρ' and κ their values for equilateral triangular molecules are

$$\rho' = \frac{1}{2}zz', \quad \kappa = \rho' - 2z' + 1. \quad (10.12.6)$$

Using (6) in (5) we obtain finally

$$\alpha = \frac{\phi}{\frac{1}{2}zz'} \frac{\left(1 - \frac{2z' - 1}{\frac{1}{2}zz'} \phi\right)^3}{(1 - \phi)^3 \left(1 - \frac{3z' - 2}{\frac{1}{2}zz'} \phi\right)}, \quad (10.12.7)$$

valid either for a planar triangular lattice with $z = 6$, $z' = 2$, or for a spatial close packed lattice with $z = 12$, $z' = 4$.

To obtain the thermodynamic properties of mixing we have to

substitute (7) into (10.04.13) and perform the integrations. We thus obtain

$$\begin{aligned} \frac{\Delta_m S}{R} = -\frac{\Delta_m F}{RT} &= (3-2\phi)^{-1} \left\{ -\phi \ln \phi - 3(1-\phi) \ln(1-\phi) + \right. \\ &+ 3 \left(\frac{\rho'}{2z'-1} - \phi \right) \ln \left(\frac{\rho'}{2z'-1} - \phi \right) - \left(\frac{\rho'}{3z'-2} - \phi \right) \ln \left(\frac{\rho'}{3z'-2} - \phi \right) - \\ &- (1-\phi) \left(\frac{3\rho'}{2z'-1} \ln \frac{\rho'}{2z'-1} - \frac{\rho'}{3z'-2} \ln \frac{\rho'}{3z'-2} \right) - \\ &\left. - \phi \left[3 \left(\frac{\rho'}{2z'-1} - 1 \right) \ln \left(\frac{\rho'}{2z'-1} - 1 \right) - \left(\frac{\rho'}{3z'-2} - 1 \right) \ln \left(\frac{\rho'}{3z'-2} - 1 \right) \right] \right\}, \end{aligned} \quad (10.12.8)$$

where $\rho' = \frac{1}{2}zz'$. On a close packed lattice $z = 12$, $z' = 4$, $\rho' = 24$. When we put these values into (8) we obtain

$$\begin{aligned} \frac{\Delta_m S}{R} = -\frac{\Delta_m F}{RT} &= (3-2\phi)^{-1} \left\{ -\phi \ln \phi - 3(1-\phi) \ln(1-\phi) + 3(\frac{24}{7}-\phi) \ln(\frac{24}{7}-\phi) - \right. \\ &- (\frac{12}{5}-\phi) \ln(\frac{12}{5}-\phi) - (1-\phi)(\frac{72}{7} \ln \frac{24}{7} - \frac{12}{5} \ln \frac{12}{5}) - \\ &\left. - \phi(\frac{51}{7} \ln \frac{17}{7} - \frac{7}{5} \ln \frac{7}{5}) \right\}. \quad (10.12.9) \end{aligned}$$

Transcription from the volume fraction ϕ to the mole fraction x is achieved by use of the relations

$$\phi = \frac{3x}{1+2x}, \quad 1-\phi = \frac{1-x}{1+2x}. \quad (10.12.10)$$

10.13. Tetrahedral tetramers

We now pass on to a mixture of monomers with tetrahedral tetramers on a face-centred cubic lattice for which $z = 12$, $z' = 2$.

We consider a group of four sites a , b , c , d forming a regular tetrahedron. Its several possible manners of occupation together with their relative probabilities are summarized in Table 10.4. The relative positions of the four sites a , b , c , d can be shown only schematically; the pairs ac and bd are in all respects equivalent to the pairs ab , bc , cd , and da . As previously the symbol U denotes either occupied by a tetrahedral molecule, which does not occupy any other sites of the group, or vacant, i.e. eventually filled by a monomer; these two alternatives have probabilities in the ratio ϵ to 1. The first and fourth configurations call for no comment. In the second set of configurations two molecules occupy opposite edges of the tetrahedron. The factor 3

TABLE 10.4

Tetrahedral Tetramers

<i>Reference number</i>	<i>Configuration</i>	<i>Relative probability</i>
1		α
2		$3(z'-1)^2\xi = 3\xi$
3	 U U	$3(z'-1)\zeta(\epsilon+1)^2 = 6\zeta(\epsilon+1)^2$
4	U U U U	$(\epsilon+1)^4$

in the relative probability represents the three pairs of opposite sides. Each of the factors $z'-1 = 1$ represents the number of ways a molecule can occupy a given pair of sites, say ab , without occupying either of the other two cd . Then ξ is by definition the probability that a molecule occupies a given pair of sites, say ab , with a specified orientation and simultaneously another molecule occupies the other pair of sites cd with a specified orientation. In the third set of configurations one molecule occupies two sites of the group while the other two sites may be occupied or vacant, but are not occupied by the same molecule. The factor 6 corresponds to the six edges of the tetrahedron. The factor $z'-1 = 1$ represents the number of ways a molecule can occupy two of the sites say a, b without occupying either of the other two c, d . The factor ζ is defined as the relative probability of a molecule occupying two given sites, say a and b , with a specified orientation when the other two sites c and d are empty. The two factors $(\epsilon+1)$ take care of the other two sites.

By considerations closely similar to those applying to triangular molecules we obtain the equivalence relations

$$\alpha = \xi + \zeta(\epsilon+1)^2 = \frac{\epsilon}{\kappa} \{3\zeta(\epsilon+1) + (\epsilon+1)^3\}. \quad (10.13.1)$$

There is also another independent equivalence relation

$$\xi = \frac{\epsilon^2}{\kappa^2} \{ \zeta + (\epsilon + 1)^2 \}, \quad (10.13.2)$$

expressing the fact that by using only two of the four sites a, b, c, d one can obtain configurations geometrically equivalent to those of the second set. When we solve (1) and (2) for ζ, ξ, α in terms of ϵ we obtain

$$\zeta = \frac{\epsilon}{\kappa} \frac{(\epsilon + 1)^2 \left(\epsilon + 1 - \frac{\epsilon}{\kappa} \right)}{(\epsilon + 1)^2 - 3 \frac{\epsilon}{\kappa} (\epsilon + 1) + \frac{\epsilon^2}{\kappa^2}}, \quad (10.13.3)$$

$$\xi = \frac{\epsilon^2}{\kappa^2} \frac{(\epsilon + 1)^3 \left(\epsilon + 1 - 2 \frac{\epsilon}{\kappa} \right)}{(\epsilon + 1)^2 - 3 \frac{\epsilon}{\kappa} (\epsilon + 1) + \frac{\epsilon^2}{\kappa^2}}, \quad (10.13.4)$$

$$\alpha = \frac{\epsilon}{\kappa} \frac{(\epsilon + 1)^3 \left((\epsilon + 1)^2 - 2 \frac{\epsilon^2}{\kappa^2} \right)}{(\epsilon + 1)^2 - 3 \frac{\epsilon}{\kappa} (\epsilon + 1) + \frac{\epsilon^2}{\kappa^2}}. \quad (10.13.5)$$

We have just as for triangles the relation between ϵ and ϕ

$$\epsilon = \frac{\kappa}{\rho'} \frac{\phi}{1 - \phi}, \quad (10.13.6)$$

with $\rho' = \frac{1}{3}zz'$, $\kappa = \rho' - 3z' + 2$. (10.13.7)

Substituting (6) and (7) into (5), we obtain

$$\alpha = \frac{\phi}{\rho'} \frac{\left(1 - \frac{3z' - 2}{\rho'} \phi \right)^3 \left(1 - \frac{6z' - 4}{\rho'} \phi + \frac{9z'^2 - 12z' + 2}{\rho'^2} \phi^2 \right)}{(1 - \phi)^4 \left(1 - \frac{6z' - 1}{\rho'} \phi + \frac{9z'^2 - 3z' - 1}{\rho'^2} \phi^2 \right)}. \quad (10.13.8)$$

When we put $z = 12$, $z' = 2$, $\rho' = 8$ corresponding to a close packed lattice, we obtain

$$\alpha = \frac{\phi}{8} \frac{(1 - \frac{1}{2}\phi)^3 (1 - \phi + \frac{7}{32}\phi^2)}{(1 - \phi)^4 (1 - \frac{11}{8}\phi + \frac{29}{64}\phi^2)}, \quad (10.13.9)$$

which is conveniently rewritten as

$$\alpha = \frac{\phi}{8} \frac{(1 - \frac{1}{2}\phi)^3 \left(1 - \frac{\phi}{a} \right) \left(1 - \frac{\phi}{b} \right)}{(1 - \phi)^4 \left(1 - \frac{\phi}{c} \right) \left(1 - \frac{\phi}{d} \right)}, \quad (10.13.10)$$

where

$$a = \frac{8}{4-\sqrt{2}}, \quad b = \frac{8}{4+\sqrt{2}}, \quad c = \frac{16}{11-\sqrt{5}}, \quad d = \frac{16}{11+\sqrt{5}}.$$

Substituting (10) into (10.04.13) and performing the integrations, we obtain

$$\begin{aligned} \frac{\Delta_m S}{R} &= -\frac{\Delta_m F}{RT} \\ &= (4-3\phi)^{-1} \{ -\phi \ln \phi - 4(1-\phi) \ln(1-\phi) + 3(2-\phi) \ln(2-\phi) + \\ &\quad + (a-\phi) \ln(a-\phi) + (b-\phi) \ln(b-\phi) - \\ &\quad - (c-\phi) \ln(c-\phi) - (d-\phi) \ln(d-\phi) - \\ &\quad - (1-\phi)[6 \ln 2 + a \ln a + b \ln b - c \ln c - d \ln d] - \\ &\quad - \phi[(a-1) \ln(a-1) + (b-1) \ln(b-1) - (c-1) \ln(c-1) - \\ &\quad - (d-1) \ln(d-1)] \}. \quad (10.13.11) \end{aligned}$$

Transcription from the volume fraction ϕ to the mole fraction x is achieved by use of the relations

$$\phi = \frac{4x}{1+3x}, \quad 1-\phi = \frac{1-x}{1+3x}. \quad (10.13.12)$$

10.14. Nature of approximation

As already mentioned the essential approximation in our treatment is the assumption that when two sites are not occupied by the same molecule the probabilities of being occupied or vacant are independent for the two sites. It is easy to see by an example that this assumption is at least sometimes false. Consider the triangular group of sites abc used in § 10.12. Let d denote another site forming an equilateral triangle with bc . Then when we state that a molecule occupies the site b , but not a or c , it may also occupy the site d . Likewise when we state that a molecule occupies the site c , but not a or b , it may also occupy the site d . When we state that two different molecules occupy the sites b and c , without occupying a , then either of them, but *not both*, may also occupy the site d . Hence the manners of occupation of sites b and c are not independent even when they are not occupied by the same molecule.

It is not easy to estimate the error due to this approximation. Its seriousness will almost certainly vary from one case to another. The best method of estimating the error is to modify the whole treatment in such a manner that the approximation is replaced by a less inaccurate one. This will be done for dimers in § 10.18.

10.15. Flory's approximation

Much simpler, though less accurate, formulae than those obtained above have been independently proposed by Flory.[†] These simpler formulae can be obtained formally by making $z \rightarrow \infty$. This means that in Huggins's formula (10.09.3) or the equivalent (10.09.1) we make $(r-q)/r \rightarrow 0$. When we do this (10.09.1) reduces to

$$\frac{\Delta_m F}{kT} = -\frac{\Delta_m S}{R} = \frac{r}{r-(r-1)\phi} \left\{ \frac{\phi}{r} \ln \phi + (1-\phi) \ln (1-\phi) \right\}. \quad (10.15.1)$$

Using the relation between volume fraction ϕ and mole fraction x

$$\phi = \frac{rx}{1-x+rx}, \quad x = \frac{\phi}{r-(r-1)\phi}, \quad (10.15.2)$$

we can rewrite (1) in the strikingly simple form

$$\frac{\Delta_m F}{RT} = -\frac{\Delta_m S}{R} = x \ln \phi + (1-x) \ln (1-\phi). \quad (10.15.3)$$

This is Flory's formula.

We can alternatively obtain Flory's formula by making $(r-q)/r \rightarrow 0$ in (10.08.10). We thus obtain

$$\alpha = \frac{\sigma_g}{\rho r} \frac{\phi}{(1-\phi)^r}. \quad (10.15.4)$$

When we substitute (4) into (10.04.13) and perform the integrations we recover (1).

Flory's approximation is also obtained formally from the formulae of § 10.12 for triangular trimers and those of § 10.13 for tetrahedral tetramers by making $z \rightarrow \infty$. We can readily prove this for triangles by considering formula (10.12.5). Using (10.12.6) we see that when $z \rightarrow \infty$ formula (10.12.5) becomes

$$\alpha = \frac{\phi}{\rho'(1-\phi)^3}, \quad (10.15.5)$$

which is equivalent to (4) with $r = 3$ and consequently leads to (3). Similarly for tetrahedra using (10.13.7) we see that when $z \rightarrow \infty$ formula (10.13.8) becomes

$$\alpha = \frac{\phi}{\rho'(1-\phi)^4}, \quad (10.15.6)$$

which is equivalent to (4) with $r = 4$ and consequently leads to (3).

[†] Flory (1942), *J. Chem. Phys.* **10**, 51.

10.16. Numerical values of entropies of mixing

The formulae of earlier sections have been used to calculate numerical values† for the molar entropy of mixing $\Delta_m S$. The results for trimers are given in Table 10.5. The first column gives the volume fraction ϕ of trimers, the second column the corresponding value of the mole

TABLE 10.5
Values of $\Delta_m S/R$ for Mixtures of Trimers with Monomers

ϕ	x	<i>Open chains z = 6</i>	<i>Triangles z = 12</i>	<i>Flory's approxima- tion z = ∞</i>	<i>Ideal solution</i>
0.05	0.01724	0.0981	0.0981	0.1021	0.0871
0.1	0.03571	0.1760	0.1760	0.1838	0.1541
0.2	0.07692	0.3147	0.3147	0.3298	0.2712
0.3	0.1250	0.4410	0.4411	0.4626	0.3768
0.4	0.1818	0.5575	0.5576	0.5846	0.4741
0.5	0.2500	0.6618	0.6621	0.6931	0.5623
0.6	0.3333	0.7475	0.7479	0.7811	0.6365
0.7	0.4375	0.7998	0.8004	0.8333	0.6853
0.8	0.5714	0.7879	0.7885	0.8173	0.6829
0.9	0.7500	0.6352	0.6357	0.6547	0.5823
0.95	0.8636	0.4416	0.4419	0.4528	0.3983
0.98	0.9423	0.2398	0.2400	0.2447	0.2206
0.99	0.9706	0.1427	0.1427	0.1452	0.1327

fraction x of trimers. The third column gives the values of $\Delta_m S/R$ for open-chain trimers on a simple cubic lattice calculated by means of formula (10.09.1) with $z = 6$, $r = 3$, $q = 7/3$. The fourth column gives the values of $\Delta_m S/R$ for triangular trimers on a spatial close packed lattice calculated from formula (10.12.9). The fifth column gives the values of $\Delta_m S/R$ calculated from Flory's formula (10.15.3) and the sixth column the values of $\Delta_m S/R$ for an ideal solution at the same value of the mole fraction x . It will be noticed that in spite of the quite different forms of equations (10.09.1) and (10.12.9) there is practically no difference in the numerical values of $\Delta_m S/R$ between triangles and open-chain trimers. It will also be noticed that Flory's formula gives a much closer approximation to these values than does the formula of an ideal solution.

The results for tetramers are given in Table 10.6. The first column gives the volume fraction ϕ of tetramer and the second column its mole fraction x . The third column gives the values of $\Delta_m S/R$ for open-chain tetramers on a simple cubic lattice calculated by means of formula

† Guggenheim and McGlashan (1950), *Proc. Roy. Soc. A* **203**, 451, § 12.

(10.09.1) with $z = 6$, $r = 4$, $q = 3$. The fourth column gives the values of $\Delta_m S$ for tetrahedra on a close packed lattice calculated by formula (10.13.11). The fifth column gives the values obtained from Flory's formula (10.15.3) and the sixth column the values in an ideal solution at the same value of the mole fraction x . The differences in the calcu-

TABLE 10.6

Values for $\Delta_m S/R$ for Mixtures of Tetramers with Monomers

ϕ	x	<i>Open chains $z = 6$</i>	<i>Tetrahedra $z = 12$</i>	<i>Flory's approxima- $z = \infty$</i>	<i>Ideal solution</i>
0.05	0.01299	0.0844	0.0823	0.0895	0.0693
0.1	0.02703	0.1547	0.1505	0.1647	0.1243
0.2	0.05882	0.2850	0.2770	0.3047	0.2237
0.3	0.09677	0.4071	0.3958	0.4357	0.3150
0.4	0.1429	0.5290	0.5152	0.5655	0.4068
0.5	0.2000	0.6502	0.6348	0.6931	0.5004
0.6	0.2727	0.7583	0.7429	0.8057	0.5860
0.7	0.3684	0.8434	0.8294	0.8918	0.6581
0.8	0.5000	0.8720	0.8617	0.9163	0.6931
0.9	0.6923	0.7505	0.7457	0.7814	0.6173
0.95	0.8261	0.5448	0.5430	0.5634	0.4620
0.98	0.9245	0.3056	0.3051	0.3139	0.2676
0.99	0.9612	0.1842	0.1840	0.1885	0.1642

lated values of $\Delta_m S/R$ between the two shapes of tetramers are small, but not so small as between the two kinds of trimers. Again it will be noticed that Flory's formula gives a considerably better approximation to these values than does the formula for ideal solutions.

10.17. Numerical values of activity coefficients

The molar entropy of mixing is a convenient quantity for comparing various approximations and was accordingly used for this purpose in the previous section. From this comparison we know that the formulae for open-chain trimers and tetramers are also useful approximations for triangular trimers and tetrahedral tetramers respectively. We shall therefore consider further formulae only for solutions of open-chain r -mers.

One of the most readily measurable equilibrium properties of a solution is the vapour pressure. At the temperatures at which such measurements can conveniently be made, the partial vapour pressure of the solute r -mer will usually be only a small fraction of the total

vapour pressure, if not entirely negligible. It is then easy by applying, if necessary, a small correction to convert the measured values of the total vapour pressure to values of the partial vapour pressure p_1 of the solvent monomer. The experimental value of the activity coefficient f_1 of the solvent is then obtained from the relation

$$f_1 = \frac{p_1}{p_1^0(1-x)}, \quad (10.17.1)$$

TABLE 10.7

Values of $-\log_{10} f_1$ in athermal solutions calculated for $r = 2, 3$, and 4 with $z = 6$ and with $z = \infty$ (Flory's approximation)

x	Dimers		Trimers		Tetramers	
	$z = 6$	$z = \infty$	$z = 6$	$z = \infty$	$z = 6$	$z = \infty$
0.01	0.00002	0.00002	0.00006	0.00008	0.00013	0.00019
0.02	0.00008	0.00008	0.00023	0.00033	0.00049	0.00072
0.05	0.00035	0.00051	0.00130	0.00191	0.00278	0.00405
0.10	0.00130	0.00191	0.00472	0.00680	0.00966	0.01372
0.15	0.00278	0.00405	0.00966	0.01372	0.01909	0.02659
0.20	0.00472	0.00880	0.01574	0.02204	0.03014	0.04128
0.25	0.00702	0.01005	0.02264	0.03133	0.04220	0.05691
0.30	0.00966	0.01372	0.03015	0.04126	0.05485	0.07304
0.35	0.01258	0.01774	0.03810	0.05162	0.06784	0.08931
0.40	0.01573	0.02204	0.04637	0.06225	0.08097	0.10554
0.45	0.01910	0.02659	0.05486	0.07304	0.09413	0.12158
0.50	0.02264	0.03133	0.06349	0.08388	0.10721	0.13736
0.55	0.02638	0.03623	0.07221	0.09473	0.12017	0.15284
0.60	0.03015	0.04123	0.08098	0.10554	0.13295	0.16797
0.65	0.03407	0.04640	0.08975	0.11626	0.14554	0.18275
0.70	0.03810	0.05162	0.09850	0.12387	0.15791	0.19716
0.75	0.04220	0.05691	0.10721	0.13733	0.17005	0.21122
0.80	0.04636	0.06225	0.11587	0.14772	0.18196	0.22492
0.85	0.05059	0.06763	0.12445	0.15792	0.19384	0.23827
0.90	0.05485	0.07304	0.13296	0.16797	0.20507	0.25123
0.95	0.05916	0.07846	0.14137	0.17786	0.21627	0.26397
0.98	0.06176	0.08171	0.14637	0.18372	0.22288	0.27143
0.99	0.06262	0.08280	0.14804	0.18566	0.22507	0.27389

where, as usual, p_1^0 denotes the vapour pressure of the pure solvent and x denotes the mole fraction of the solute. This experimental value of f_1 can then be compared with theoretical values given by the formulae obtained earlier in this chapter. For the purpose of such comparisons we give in Table 10.7 the theoretical values† of $\log_{10} f_1$ for solutions of linear dimers, linear trimers, and linear tetramers calculated from

† Calculated by McGlashan; not previously published.

formula (10.09.4) for $z = 6$, and also values calculated according to Flory's approximation, namely

$$\ln f_1 = -\ln\{1+(r-1)x\} + \frac{(r-1)x}{1+(r-1)x}. \quad (10.17.2)$$

The value $z = 6$ has been chosen as the smallest value likely to have physical significance. For larger values of z the deviations from the values given by Flory's approximation will be smaller.

10.18. Higher approximation for dimers

We have in § 10.06 obtained a formula for α the ratio of the frequency that a pair of neighbouring sites be occupied by a dimer to the frequency that both sites be vacant, that is to say ultimately filled by monomers. In § 10.12 we similarly obtained the corresponding formula for a triangular trimer on three sites forming an equilateral triangle. In § 10.13 we obtained the corresponding formula for a tetrahedral tetramer on four sites forming a regular tetrahedron. For dimers on a close packed lattice we can of course take formula (10.06.3) putting $z = 12$

$$\alpha = \frac{1}{12} \frac{\phi}{(1-\phi)^2} \left(1 - \frac{\phi}{12}\right). \quad (10.18.1)$$

Alternatively we can obtain a formula for α for dimers on a close packed lattice by considering a group of three sites forming an equilateral triangle as in § 10.12. The formula so obtained is

$$\alpha = \frac{1}{z} \frac{\phi}{(1-\phi)^2} \frac{(1-2\phi/z)^2}{(1-3\phi/z)} \quad (z = 12). \quad (10.18.2)$$

Yet another alternative procedure for dimers on a close packed lattice is to consider a group of four sites forming a regular tetrahedron as in § 10.13. This leads to the formula

$$\alpha = \frac{1}{z} \frac{\phi}{(1-\phi)^2} \frac{(1-3\phi/z)(1-2\phi/z)}{(1-4\phi/z)} \quad (z = 12). \quad (10.18.3)$$

Formulae (1), (2), (3) are different approximations† to the same quantity and it is not certain which is the best approximation.

We recall formula (10.04.12) for the molar free energy of mixing, which becomes for dimers when we put $r = 2$

$$\frac{\Delta_m F}{RT} = -\frac{\Delta_m S}{R} = \frac{1}{2-\phi} \left\{ \int_0^\phi \ln \alpha d\phi - \phi \int_0^1 \ln \alpha d\phi \right\}. \quad (10.18.4)$$

† McGlashan (1951), *Trans. Faraday Soc.* **47**, 1042.

By substituting from (1), (2), (3) in turn into (4) and performing the integrations we obtain, after putting $z = 12$, the alternative approximations

$$\frac{\Delta_m S}{R} = \frac{1}{2-\phi} \left\{ -\phi \ln \phi - 2(1-\phi) \ln(1-\phi) + (12-\phi) \ln(12-\phi) - \right. \\ \left. -(1-\phi) 12 \ln 12 - \phi 11 \ln 11 \right\}. \quad (10.18.5)$$

$$\frac{\Delta_m S}{R} = \frac{1}{2-\phi} \left\{ -\phi \ln \phi - 2(1-\phi) \ln(1-\phi) + 2(6-\phi) \ln(6-\phi) - \right. \\ \left. -(4-\phi) \ln(4-\phi) - (1-\phi)(12 \ln 6 - 4 \ln 4) - \phi(10 \ln 5 - 3 \ln 3) \right\}. \quad (10.18.6)$$

$$\frac{\Delta_m S}{R} = \frac{1}{2-\phi} \left\{ -\phi \ln \phi - 2(1-\phi) \ln(1-\phi) + (4-\phi) \ln(4-\phi) + \right. \\ \left. +(6-\phi) \ln(6-\phi) - (3-\phi) \ln(3-\phi) - \right. \\ \left. -(1-\phi)(4 \ln 4 + 6 \ln 6 - 3 \ln 3) - \phi(3 \ln 3 + 5 \ln 5 - 2 \ln 2) \right\}. \quad (10.18.7)$$

Formulae (5), (6), and (7) have been used to compute entropies of mixing and the values obtained are given in the fifth, sixth, and seventh columns of Table 10.8. In the fourth column are given for comparison the values obtained from Flory's formula

$$\frac{\Delta_m S}{R} = -(1-x) \ln(1-\phi) - x \ln \phi, \quad (10.18.8)$$

which can be obtained formally from (4) by assuming

$$\alpha = \frac{1}{12} \frac{\phi}{(1-\phi)^2}. \quad (10.18.9)$$

The third column contains the values given by the formula of an ideal solution, namely

$$\frac{\Delta_m S}{R} = -(1-x) \ln(1-x) - x \ln x. \quad (10.18.10)$$

The last column of the table will be considered later. We see that the values obtained by considering a pair of sites, a triangle of sites, and a tetrahedron of sites are exceedingly close to one another. This strengthens our confidence that the approximations are good. Moreover, the values differ from Flory's formula by less than one per cent., again indicating that this is a good approximation.

TABLE 10.8

*Values of $\Delta_m S/R$ calculated according to Various Approximations
for Dimers on a Face-centred Cubic Lattice*

ϕ	x	Ideal solution	Flory's formula	Pair of sites	Triangle of sites	Tetrahedron of sites	Higher approximation
0.05	0.0256	0.1193	0.1268	0.1258	0.1258	0.1259	0.1261
0.1	0.0526	0.2062	0.2210	0.2190	0.2191	0.2193	0.2196
0.2	0.1111	0.3488	0.3772	0.3734	0.3737	0.3741	0.3746
0.3	0.1765	0.4680	0.5062	0.5009	0.5014	0.5019	0.5028
0.4	0.2500	0.5623	0.6122	0.6057	0.6064	0.6071	0.6083
0.5	0.3333	0.6365	0.6932	0.6859	0.6867	0.6876	0.6890
0.6	0.4286	0.6829	0.7425	0.7350	0.7359	0.7370	0.7385
0.7	0.5385	0.6902	0.7477	0.7407	0.7416	0.7427	0.7441
0.8	0.6667	0.6365	0.6852	0.6794	0.6802	0.6812	0.6824
0.9	0.8182	0.4741	0.5049	0.5013	0.5018	0.5025	0.5033
0.95	0.9048	0.3145	0.3317	0.3297	0.3300	0.3304	0.3309
0.98	0.9608	0.1655	0.1728	0.1720	0.1721	0.1723	0.1725
0.99	0.9802	0.0973	0.1011	0.1006	0.1007	0.1008	0.1009

In obtaining formulae for α , whether considering two, three, or four sites, we have always assumed that when two neighbouring sites are not occupied by the same molecule their probabilities of being occupied in any particular manner are independent. It is clear that this assumption is at least sometimes false. Consider for example a pair of neighbouring sites a, a' . Let b denote a third site which is a nearest neighbour of both a and a' . When we state that a dimer molecule occupies the site a but not the site a' , it may also occupy the site b . When we state that two different dimers occupy the sites a and a' , then either of them, but not both, may also occupy the site b . Hence the manners of occupation of the two sites a and a' are not independent even when they are occupied by the same dimer molecule. We shall now give a treatment† of dimers on a close packed lattice which avoids this false assumption.

We consider a pair of sites a and a' on a face-centred cubic lattice. There are four sites b which are closest neighbours of both a and a' . The site a has seven other closest neighbour sites c and the site a' has seven other closest neighbour sites c' . We now construct Table 10.9 for the various manners of occupation of the pair of sites a, a' . The first column merely gives a number by which to refer to each type of configuration. The second column shows the several types of configuration. In number 1 the same dimer occupies the pair of sites a, a' .

† McGlashan (1951), *Trans. Faraday Soc.* 47, 1042.

TABLE 10.9

*Higher Approximation for Dimers on a Pair of Sites of
a Face-centred Cubic Lattice*

Reference number	Configuration		Relative probability
	<i>a</i>	<i>a'</i>	
1			α
2	<i>Db</i>	<i>Db</i>	$12\delta^2$
3a	<i>Db</i>	0	4δ
3b	0	<i>Db</i>	4δ
4a	<i>Db</i>	<i>Dc'</i>	$4\delta \times 7\gamma$
4b	<i>Dc</i>	<i>Db</i>	$7\gamma \times 4\delta$
5	<i>Dc</i>	<i>Dc'</i>	$7\gamma \times 7\gamma$
3a	<i>Dc</i>	0	7γ
6b	0	<i>Dc'</i>	7γ
7	0	0	1

In the other configurations the notation *Db* denotes that a dimer occupies one of the sites *a* or *a'* and one of the sites *b*. Similarly *Dc* denotes that a dimer occupies the site *a* and a site *c*, while *Dc'* denotes that a dimer occupies the site *a'* and a site *c'*. The symbol 0 denotes that the site is not occupied by a dimer, that is to say it is occupied by a monomer. The third column gives the relative probabilities of the several types of configuration. The factors 4 take account of the four sites *b* and the factors 7 of the seven sites *c* and seven sites *c'*. The factor 12 in the second row is the number of ways of choosing one of the four sites *b* to be paired with *a* and then one of the remaining three to be paired with *a'*.

We have the two equivalence relations

$$\alpha = 3\delta^2 + \delta + 7\delta\gamma, \quad (10.18.11)$$

$$\alpha = 4\gamma\delta + 7\gamma^2 + \gamma. \quad (10.18.12)$$

If we equate $\phi/(1-\phi)$ to the ratio of the sum of all the relative probabilities when the site *a* is occupied by a dimer to the sum of all those when *a* is vacant, that is to say ultimately to be occupied by a monomer, we obtain, using Table 10.9,

$$\frac{\phi}{1-\phi} = \frac{\alpha + 12\delta^2 + 4\delta + 56\delta\gamma + 49\gamma^2 + 7\gamma}{4\delta + 7\gamma + 1}, \quad (10.18.13)$$

which by use of (11) and (12) can be reduced to

$$\frac{\phi}{1-\phi} = 12\gamma, \quad (10.18.14)$$

as might be expected from the physical meaning of γ . By eliminating δ from (11) and (12) we obtain

$$3\alpha^2 - 2\gamma(15\gamma+1)\alpha - \gamma^2(7\gamma+1)^2 = 0, \quad (10.18.15)$$

having the solution

$$\alpha = \frac{1}{3}\gamma[(15\gamma+1) + \{(15\gamma+1)^2 + 3(7\gamma+1)^2\}^{\frac{1}{2}}]. \quad (10.18.16)$$

When we substitute from (14) into (16) we obtain

$$\alpha = \frac{1}{12} \frac{\phi}{(1-\phi)^2} \left\{ \frac{1}{3} + \frac{1}{12}\phi + \frac{2}{3}(1 - \frac{1}{2}\phi + \frac{7}{48}\phi^2)^{\frac{1}{2}} \right\}. \quad (10.18.17)$$

If we expand the last factor $\{\}$ in powers of ϕ we obtain

$$\alpha = \frac{1}{12} \frac{\phi}{(1-\phi)^2} \left\{ 1 - \frac{1}{12}\phi + \frac{1}{36}\phi^2 + \frac{1}{144}\phi^3 + \frac{1}{864}\phi^4 + \dots \right\}, \quad (10.18.18)$$

and we observe the similarity between (18) and the earlier approximations (1), (2), (3).

To obtain the molar entropy of mixing we have to substitute from (17) or (18) into (4) and perform the integrations. For this purpose we use the expansion

$$\ln \alpha = \ln \left\{ \frac{1}{12} \frac{\phi}{(1-\phi)^2} \right\} - \frac{1}{12}\phi + \frac{1}{36}\phi^2 + \frac{1}{144}\phi^3 + \dots \quad (10.18.19)$$

and this can be integrated term by term, the convergence being quite sufficiently rapid.

Values of $\Delta_m S/R$ thus calculated are given in the last column of Table 10.8. We see that the values so obtained are very close to those obtained by any of formulae (5), (6), or (7) and lie between those values and those given by Flory's simple formula (8). We cannot say with complete certainty which of these four approximations is the best, but since they lie so close to one another we can be confident that they are all near to the exact values.

10.19. Relation to experimental material

No comparison will be made here between our formulae and experimental material for the simple reason that, apart from a few ideal mixtures, no strictly athermal mixtures have been proved to exist. The reader may well wonder why then so much space and effort has been devoted to the theory of athermal mixtures. The answer is that

the theory of athermal mixtures provides a firm basis for developing in the next chapter the more general theory of mixtures which are not athermal. Moreover, mixtures are known having an energy of mixing which is small though not zero. For such mixtures it will be shown that to a useful degree of approximation the entropy of mixing, though not the free energy of mixing, is given by the same formula as for athermal mixtures. The experimental material for such mixtures will be discussed in the following chapter.

XI

MOLECULES OF DIFFERENT SIZES: MIXTURES NOT ATHERMAL

11.01. Introduction

IN this chapter we shall consider molecules of different sizes whose mixtures are not athermal. We shall continue to use the quasi-crystalline model, this being the only model which leads to closed formulae without the introduction of additional arbitrary assumptions. We shall continue, as in the last chapter, to imagine each molecule as being divided into *elements*, each such element occupying one site on the quasi-crystalline lattice. We shall assume that the configurational potential energy may be expressed as a sum of contributions from pairs of neighbouring elements, the contribution from each pair depending on the nature of both elements forming the pair. We shall find it convenient to use the word *contact* to denote the geometrical relation of an element to the element of some other molecule on a neighbouring site. We shall thus say that an open-chain r -mer containing r elements has zq contacts where q is related to r by

$$\frac{1}{2}z(r-q) = r-1. \quad (11.01.1)$$

The mixtures of this chapter are related to the athermal mixtures of the previous chapter in much the same manner as regular mixtures are related to ideal mixtures. Just as for regular mixtures, we may use several different approximations. In particular we shall consider the zeroth approximation according to which there is a completely random arrangement of the molecules, and the first approximation according to which the numbers of the several kinds of contacts are determined by equations of quasi-chemical equilibrium.

There is at least one important respect in which the mixtures of this chapter are more diverse and consequently more complicated than regular mixtures, namely in the possibility that the several elements of the same molecule may be energetically different from one another. We shall accordingly distinguish between *homogeneous* molecules whose elements are energetically all alike and *heterogeneous* molecules whose elements are not energetically all alike. For the sake of simplicity and brevity we shall, however, confine our treatment to binary mixtures containing only two kinds of elements. The treatment can, if required, be extended to more complicated systems. Moreover, the treatment is

entirely restricted to molecules having the form of chains either branched or unbranched, but containing no closed rings.

11.02. Crude treatment. (Zeroth approximation)

Just as for regular mixtures, we use the name zeroth approximation for the crude treatment which assumes a completely random arrangement of the molecules. It is an immediate consequence of this approximation that the entropy of mixing is independent of the energy of interchange w and that the energy of mixing is directly proportional to w and is otherwise independent of the temperature. Thus for a binary mixture of N_A molecules each having r_A elements and N_B molecules each having r_B elements we have according to formula (10.10.8) for the molar entropy of mixing

$$\frac{N_A + N_B}{R} \Delta_m S = -N_A \ln \frac{r_A N_A}{r_A N_A + r_B N_B} - \frac{1}{2} z q_A N_A \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} - N_B \ln \frac{r_B N_B}{r_A N_A + r_B N_B} - \frac{1}{2} z q_B N_B \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)}. \quad (11.02.1)$$

11.03. Classification of contacts. Total energy

We shall denote the two kinds of elements by a and b respectively. Each kind of molecule may or may not contain both kinds of elements. Of the zq_A contacts of each A molecule we suppose that $zq_A u_A$ come from a elements and $zq_A v_A$ from b elements. Similarly of the zq_B contacts of each B molecule we suppose that $zq_B u_B$ come from a elements and $zq_B v_B$ from b elements. We have by definition the identities

$$u_A + v_A = 1, \quad u_B + v_B = 1. \quad (11.03.1)$$

We denote by $2w_{aa}/z$ the contribution of an aa contact and by $2w_{bb}/z$ the contribution of a bb contact to the configurational potential energy. We further define w such that the contribution of each ab contact to the configurational potential energy is

$$\frac{1}{z} (w_{aa} + w_{bb} + w). \quad (11.03.2)$$

We introduce the following abbreviations:

$$Q = \frac{1}{2} z (N_A q_A + N_B q_B), \quad (11.03.3)$$

$$u = \frac{N_A q_A u_A + N_B q_B u_B}{N_A q_A + N_B q_B}, \quad (11.03.4)$$

$$v = \frac{N_A q_A v_A + N_B q_B v_B}{N_A q_A + N_B q_B}. \quad (11.03.5)$$

From (1), (4), (5) it follows immediately that

$$u+v=1. \quad (11.03.6)$$

We now construct Table 11.1 for a completely random distribution.

TABLE 11.1
Completely Random Distribution of Contacts

<i>Kind of contact</i>	<i>Number of contacts</i>	<i>Energy of all such contacts</i>
<i>aa</i>	Qu^2	$\frac{2Q}{z} u^2 w_{aa}$
<i>ab</i>	Quv	$\frac{Q}{z} uv(w_{aa}+w_{bb}+w)$
<i>ba</i>	Qvu	$\frac{Q}{z} vu(w_{aa}+w_{bb}+w)$
<i>bb</i>	Qv^2	$\frac{2Q}{z} v^2 w_{bb}$
All	Q	$\frac{2Q}{z} (uw_{aa}+vw_{bb}+uvw)$

In this table we have artificially introduced a distinction between *ab* and *ba* contacts as if they were distinguishable by orientation. This artifice, already used in § 4.14 and § 7.11, is convenient because it enables us to dispense with symmetry numbers in some of our later formulae of the first approximation. From the table we see that the configurational energy for a random distribution is

$$\begin{aligned} U_c &= \frac{2Q}{z} (uw_{aa}+vw_{bb}+uvw) \\ &= (N_A q_A + N_B q_B)(uw_{aa}+vw_{bb}+uvw) \\ &= (N_A q_A u_A + N_B q_B u_B)w_{aa} + (N_A q_A v_A + N_B q_B v_B)w_{bb} + \\ &\quad + \frac{(N_A q_A u_A + N_B q_B u_B)(N_A q_A v_A + N_B q_B v_B)}{N_A q_A + N_B q_B} w. \quad (11.03.7) \end{aligned}$$

At this stage it is convenient to distinguish between homogeneous and heterogeneous molecules. We obtain the case where both kinds of molecules are homogeneous but different from each other by setting

$$u_A = 1, \quad v_A = 0, \quad (11.03.8)$$

$$u_B = 0, \quad v_B = 1. \quad (11.03.9)$$

Formula (7) now reduces to

$$U_e = N_A q_A w_{aa} + N_B q_B w_{bb} + \frac{N_A q_A N_B q_B}{N_A q_A + N_B q_B} w, \quad (11.03.10)$$

and consequently the molar total energy of mixing is given by

$$\frac{\Delta_m U}{N} = \frac{N_A q_A N_B q_B}{(N_A + N_B)(N_A q_A + N_B q_B)} w. \quad (11.03.11)$$

In particular if we put $q_A = 1, q_B = 1$ we recover the formula for a regular mixture

$$\frac{\Delta_m U}{N} = \frac{N_A N_B}{(N_A + N_B)^2} w. \quad (11.03.12)$$

When the molecules are not homogeneous there is no simplification of formula (7). If, however, we introduce the abbreviations

$$\phi'_A = \frac{N_A q_A}{N_A q_A + N_B q_B}, \quad \phi'_B = \frac{N_B q_B}{N_A q_A + N_B q_B}, \quad (11.03.13)$$

then (7) can be rewritten as

$$\begin{aligned} \frac{U_e}{N_A q_A + N_B q_B} &= (\phi'_A u_A + \phi'_B u_B) w_{aa} + (\phi'_A v_A + \phi'_B v_B) w_{bb} + \\ &\quad + (\phi'_A u_A + \phi'_B u_B)(\phi'_A v_A + \phi'_B v_B) w. \end{aligned} \quad (11.03.14)$$

We observe that ϕ' is related to the volume fraction ϕ by the substitution of q_A, q_B for r_A, r_B respectively. It follows from (14) that the molar total energy of mixing is given by

$$\begin{aligned} \frac{\Delta_m U}{N} &= \frac{N_A q_A + N_B q_B}{N_A + N_B} \{(\phi'_A u_A + \phi'_B u_B)(\phi'_A v_A + \phi'_B v_B) - \phi'_A u_A v_A - \phi'_B u_B v_B\} w, \\ &= \frac{N_A q_A + N_B q_B}{N_A + N_B} \phi'_A \phi'_B (u_A v_B + u_B v_A - u_A v_A - u_B v_B) w. \end{aligned} \quad (11.03.15)$$

In particular for homogeneous molecules we set $v_A = 0, u_B = 0$ and formula (15) reduces to

$$\frac{\Delta_m U}{N} = \frac{N_A q_A + N_B q_B}{N_A + N_B} \phi'_A \phi'_B w, \quad (11.03.16)$$

which is the same as (11).

11.04. Free energy

By combining formula (11.02.1) for the molar entropy of mixing with formula (11.03.15) for the molar total energy of mixing we obtain for the molar free energy of mixing

$$\begin{aligned} \frac{N_A + N_B}{N} \Delta_m F &= N_A kT \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A N_A kT \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} + \\ &+ N_B kT \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B N_B kT \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)} + \\ &+ (N_A q_A + N_B q_B) \phi'_A \phi'_B (u_A v_B + u_B v_A - u_A v_A - u_B v_B) w. \quad (11.04.1) \end{aligned}$$

In particular for a mixture of homogeneous molecules

$$\begin{aligned} \frac{N_A + N_B}{N} \Delta_m F &= N_A kT \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A N_A kT \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} + \\ &+ N_B kT \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B N_B kT \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)} + \\ &+ \frac{q_A N_A q_B N_B}{q_A N_A + q_B N_B} w. \quad (11.04.2) \end{aligned}$$

11.05. Absolute activities and fugacities

Differentiating (11.04.2) with respect to N_A we obtain for the chemical potential μ_A , the absolute activity λ_A , and the fugacity p_A for homogeneous molecules

$$\begin{aligned} \mu_A - \mu_A^0 &= kT \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A kT \ln \frac{N_A + r_B N_B / r_A}{N_A + q_B N_B / q_A} + \\ &+ \left(\frac{q_B N_B}{q_A N_A + q_B N_B} \right)^2 q_A w, \quad (11.05.1) \end{aligned}$$

$$\frac{\lambda_A}{\lambda_A^0} = \frac{p_A}{p_A^0} = \frac{r_A N_A}{r_A N_A + r_B N_B} \left(\frac{N_A + r_B N_B / r_A}{N_A + q_B N_B / q_A} \right)^{\frac{1}{2} z q_A} \exp \left\{ \left(\frac{q_B N_B}{q_A N_A + q_B N_B} \right)^2 \frac{q_A w}{kT} \right\}, \quad (11.05.2)$$

where as usual we use the superscript 0 to denote the value for the pure substance. The formulae for the component B are precisely analogous. In particular we have

$$\frac{\lambda_B}{\lambda_B^0} = \frac{p_B}{p_B^0} = \frac{r_B N_B}{r_A N_A + r_B N_B} \left(\frac{N_B + r_A N_A / r_B}{N_B + q_A N_A / q_B} \right)^{\frac{1}{2} z q_B} \exp \left\{ \left(\frac{q_A N_A}{q_A N_A + q_B N_B} \right)^2 \frac{q_B w}{kT} \right\}. \quad (11.05.3)$$

More complicated formulae can be similarly obtained from (11.04.1) for heterogeneous molecules.

It would be possible to use these formulae for investigating separation into two phases and the conditions of critical mixing. This will, however, not be done here as it is at least as easy to investigate these phenomena by using the better first approximation. We shall moreover see that the formulae of the zeroth approximation can be derived immediately from those of the first approximation.

11.06. First approximation. Combinatory formula

We turn now to the treatment which we call the first approximation† because it is entirely analogous to the first approximation for regular mixtures and also for superlattices. We shall continue to consider mixtures containing two kinds of molecules A and B composed of two kinds of elements a and b . Initially we shall assume that the molecules are not necessarily homogeneous. Using the same notation as in § 11.03 we assume that of the zq_A contacts of each A molecule a fraction u_A come from a elements and a fraction $v_A = 1 - u_A$ come from b elements. Likewise we assume that of the zq_B contacts from each B molecule a fraction u_B come from a elements and a fraction $v_B = 1 - u_B$ come from b elements.

We now abandon the assumption of randomness. We denote the number of ab or ba contacts in a given configuration by $z(q_A N_A + q_B N_B)y$; this is a definition of y . We shall for brevity use the symbols Q , u , v to denote the quantities defined by (11.03.3), (11.03.4), and (11.03.5) respectively. By direct counting of contacts of a elements and of b elements we are able to construct Table 11.2. We have further introduced a quantity κ defined by

$$y = \kappa uv. \quad (11.06.1)$$

By comparison of Tables 11.1 and 11.2 we see that in a completely random distribution κ becomes unity.

We shall now construct an approximate formula for $g(N_A, N_B, y)$, the number of distinct configurations for given values of N_A , N_B , and y . The reasoning is precisely analogous to that used in § 4.14 and in § 7.11. If there were no mutual interference between the various types of pairs

† The treatment given here embraces as special cases that for homogeneous molecules given by Guggenheim (1944), *Proc. Roy. Soc. A* **183**, 213, and that for a particular class of heterogeneous molecules given by Tompa (1949), *Trans. Faraday Soc.* **45**, 101. Formulae for the former case had been obtained earlier by Orr (1944), *Trans. Faraday Soc.* **11**, 320, using Bethe's method.

of nearest neighbours the number of configurations of specified N_A , N_B , y would according to Table 11.2 be

$$\frac{Q!}{(Qu-Qy)!(Qy)!(Qy)!(Qv-Qy)!}. \quad (11.06.2)$$

TABLE 11.2
Enumeration of Contacts

<i>Kind of contact</i>	<i>Number of contacts</i>
<i>aa</i>	$Q(u-y) = Qu(1-\kappa v)$
<i>ab</i>	$Qy = Q\kappa uv$
<i>ba</i>	$Qy = Q\kappa vu$
<i>bb</i>	$Q(v-y) = Qv(1-\kappa u)$
All	Q

In the denominator of (2) we have placed two factors $(Qy)!$ where at first sight a single factor $(2Qy)!$ might seem more appropriate. This means that we are regarding the pairs of sites as orientated. If we took the opposite view of ignoring orientations of the pairs of sites we should have to introduce symmetry numbers. Such procedure would be slightly more complicated and the final result would be the same.

Formula (2) is of course inexact, firstly because the different pairs necessarily interfere with one another and secondly because (2) when summed over all possible values of y would not give the correct total number of configurations (10.10.5). We can remove the second defect by inserting the appropriate normalizing factor independent of y . We are thus led to the approximate combinatory formula

$$g(N_A, N_B, Qy) = \left(\frac{\rho_A}{\sigma_A}\right)^{N_A} \left(\frac{\rho_B}{\sigma_B}\right)^{N_B} \frac{(r_A N_A + r_B N_B)!}{N_A! N_B!} \left\{ \frac{(q_A N_A + q_B N_B)!}{(r_A N_A + r_B N_B)!} \right\}^{1/2} \times \\ \times \frac{(Qu-Qy^*)!(Qy^*)!(Qy^*)!(Qv-Qy^*)!}{(Qu-Qy)!(Qy)!(Qy)!(Qv-Qy)!}, \quad (11.06.3)$$

where y^* denotes the random value of y which maximizes the expression (2), namely

$$y^* = uv. \quad (11.06.4)$$

11.07. Maximization. Quasi-chemical equations

From Table 11.2 we see that for a given value of y the configurational energy is

$$E_c = 2 \frac{Q}{z} \{ (u-y)w_{aa} + y(w_{aa} + w_{bb} + w) + (v-y)w_{bb} \} \\ = 2 \frac{Q}{z} (uw_{aa} + vw_{bb} + yw). \quad (11.07.1)$$

Consequently the configurational partition function Ω is given by

$$\Omega = \sum_y g(N_A, N_B, Qy) \exp\{-2Q(uw_{aa} + vw_{bb} + yw)/zkT\}, \quad (11.07.2)$$

where we use the approximate formula (11.06.3) for $g(N_A, N_B, Qy)$.

As usual we may replace the sum by its maximum term. We accordingly replace (2) by

$$\Omega = g(N_A, N_B, Qy) \exp\{-2Q(uw_{aa} + vw_{bb} + yw)/zkT\}, \quad (11.07.3)$$

where y now has the value determined by

$$\frac{\partial \ln \Omega}{\partial y} = 0. \quad (11.07.4)$$

When we use formula (11.06.3) for $g(N_A, N_B, y)$ equation (4) becomes

$$(u-y)(v-y) = y^2\eta^2, \quad (11.07.5)$$

where η is defined by $\eta = e^{w/zkT}$. (11.07.6)

We may usefully compare equation (5) with the equation satisfied by y^*

$$(u-y^*)(v-y^*) = y^{*2}, \quad (11.07.7)$$

which has the solution $y^* = uv$. (11.07.8)

Substituting $y = \kappa uv$ (11.07.9)

into (5) we obtain

$$(1-\kappa v)(1-\kappa u) = \kappa^2 uv \eta^2. \quad (11.07.10)$$

Equation (10) is a quadratic in κ whose solution can be written in the form

$$\kappa = \frac{2}{\beta - 1}, \quad (11.07.11)$$

where $\beta = \{1 + 4uv(\eta^2 - 1)\}^{\frac{1}{2}}$. (11.07.12)

11.08. Absolute activities. Free energy

The configurational free energy is given by

$$F_c = -kT \ln \Omega$$

$$= -kT \ln g(N_A, N_B, Qy) + (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb} + yw), \quad (11.08.1)$$

where y is determined by (11.07.9), (11.07.11), and (11.07.12). Instead of evaluating F_c directly it is more convenient first to obtain formulae for the chemical potentials μ_A , μ_B by differentiation of F_c with respect to N_A , N_B respectively. In performing this differentiation we must remember that Qy in (11.06.3) and (11.07.2) is a function of N_A , N_B , but since Qy has the value that minimizes F_c , it follows that all terms

coming from differentiation with respect to Qy cancel. We may therefore omit all such terms and this greatly reduces the work. At the same time it follows from the definition of Qy^* that the differential coefficient of $g(N_A, N_B, y)$ with respect to Qy^* vanishes. Consequently all terms in $\partial(Qy^*)/\partial N_A$ or $\partial(Qy^*)/\partial N_B$ cancel. Taking note of these simplifications and using an asterisk to denote the value which a quantity would have if the mixture were athermal, i.e. if w were zero, we find

$$\begin{aligned}\mu_A &= \mu_A^* + \frac{1}{2}zq_A u_A kT \ln \frac{u-y}{u-y^*} + \frac{1}{2}zq_A v_A kT \ln \frac{v-y}{v-y^*} \\ &= \mu_A^* + \frac{1}{2}zq_A u_A kT \ln \frac{1-\kappa v}{u} + \frac{1}{2}zq_A v_A kT \ln \frac{1-\kappa u}{v},\end{aligned}\quad (11.08.2)$$

and a similar formula for μ_B . The absolute activity λ_A is related to the value λ_A^* for an athermal mixture of the same composition by

$$\lambda_A = \lambda_A^* \left\{ \frac{1-\kappa v}{u} \right\}^{\frac{1}{2}zq_A u_A} \left\{ \frac{1-\kappa u}{v} \right\}^{\frac{1}{2}zq_A v_A} \quad (11.08.3)$$

and there is a similar formula for λ_B . The free energy F is related to the free energy F^* of an athermal mixture of the same composition by

$$\begin{aligned}F &= N_A \mu_A + N_B \mu_B \\ &= F^* + \frac{1}{2}z(q_A u_A N_A + q_B u_B N_B) kT \ln \frac{1-\kappa v}{u} + \\ &\quad + \frac{1}{2}z(q_A v_A N_A + q_B v_B N_B) kT \ln \frac{1-\kappa u}{v} \\ &= F^* + \frac{1}{2}z(q_A N_A + q_B N_B) kT \left\{ u \ln \frac{1-\kappa v}{u} + v \ln \frac{1-\kappa u}{v} \right\}.\end{aligned}\quad (11.08.4)$$

If we substitute for λ_A^* in (3) its value given by (10.10.6) and compare the formula so obtained with that for the pure substance we find

$$\begin{aligned}\frac{\lambda_A}{\lambda_A^0} &= \frac{r_A N_A}{r_A N_A + r_B N_B} \left(\frac{N_A + r_B N_B / r_A}{N_A + q_B N_B / q_A} \right)^{\frac{1}{2}zq_A} \times \\ &\quad \times \left\{ \frac{u_A (1-\kappa v)}{u (1-\kappa_A^0 v_A)} \right\}^{\frac{1}{2}zq_A u_A} \left\{ \frac{v_A (1-\kappa u)}{v (1-\kappa_A^0 u_A)} \right\}^{\frac{1}{2}zq_A v_A},\end{aligned}\quad (11.08.5)$$

where κ_A^0 denotes the value of κ in the pure substance A . There is, of course, a similar formula for λ_B/λ_B^0 .

We recall that in the above formulae κ , and likewise κ_A^0 , is determined by (11.07.11) and (11.07.12).

If both kinds of molecules are homogeneous the formulae simplify as follows:

$$u_A = 1, \quad v_A = 0; \quad (11.08.6)$$

$$u_B = 0, \quad v_B = 1; \quad (11.08.7)$$

$$u = \frac{q_A N_A}{q_A N_A + q_B N_B} = 1 - \phi', \quad v = \frac{q_B N_B}{q_A N_A + q_B N_B} = \phi'. \quad (11.08.8)$$

Consequently (5) reduces to

$$\frac{\lambda_A}{\lambda_A^0} = \frac{r_A N_A}{r_A N_A + r_B N_B} \left\{ \frac{N_A + r_B N_B / r_A}{N_A + q_B N_B / q_A} \right\}^{\frac{1}{zq_A}} \left\{ \frac{1 - \kappa \phi'}{1 - \phi'} \right\}^{\frac{1}{zq_A}}, \quad (11.08.9)$$

while the analogous formula for λ_B reduces to

$$\frac{\lambda_B}{\lambda_B^0} = \frac{r_B N_B}{r_A N_A + r_B N_B} \left\{ \frac{N_B + r_A N_A / r_B}{N_B + q_A N_A / q_B} \right\}^{\frac{1}{zq_B}} \left\{ \frac{1 - \kappa + \kappa \phi'}{\phi'} \right\}^{\frac{1}{zq_B}}. \quad (11.08.10)$$

11.09. Total energy

The total energy U is related to the free energy F by

$$U = \frac{d(F/T)}{d(1/T)}. \quad (11.09.1)$$

The athermal configurational terms U^* corresponding to F^* are

$$U^* = (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb}). \quad (11.09.2)$$

We then obtain from (11.08.4)

$$U_0 = U^* + \frac{1}{2}z(q_A N_A + q_B N_B)k \frac{d}{d(1/T)} \{u \ln(1 - \kappa v) + v \ln(1 - \kappa u)\}. \quad (11.09.3)$$

From (11.07.11) we have

$$1 - \kappa v = \frac{\beta + 1 - 2v}{\beta + 1}, \quad (11.09.4)$$

and so

$$\frac{d \ln(1 - \kappa v)}{d(1/T)} = \left\{ \frac{1}{\beta + 1 - 2v} - \frac{1}{\beta + 1} \right\} \frac{d\beta}{d\eta} \frac{d\eta}{d(1/T)} = \frac{2v}{(\beta + 1 - 2v)(\beta + 1)} \frac{w\eta}{zk} \frac{d\beta}{d\eta}. \quad (11.09.5)$$

From (11.07.12) we have, remembering that $u + v = 1$,

$$\beta \frac{d\beta}{d\eta} = 4uv\eta = \frac{(\beta + 1 - 2u)(\beta + 1 - 2v)}{\eta}. \quad (11.09.6)$$

Substituting from (6) into (5) we obtain

$$\frac{1}{2}zku \frac{d \ln(1 - \kappa v)}{d(1/T)} = \frac{uv(\beta + 1 - 2u)}{\beta(\beta + 1)} w. \quad (11.09.7)$$

$$\text{Similarly } \frac{1}{2}zkv \frac{d \ln(1 - \kappa u)}{d(1/T)} = \frac{uv(\beta + 1 - 2v)}{\beta(\beta + 1)} w. \quad (11.09.8)$$

Adding (7) and (8), remembering that $u+v=1$, and substituting into (3) we obtain

$$\begin{aligned} U_c &= (q_A N_A + q_B N_B) \left(uw_{aa} + vw_{bb} + \frac{2uv}{\beta+1} w \right) \\ &= (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb} + \kappa uvw), \quad (11.09.9) \end{aligned}$$

which in view of the definition of κ is physically obvious.

In the case where both kinds of molecules are homogeneous (9) becomes

$$U_c = q_A N_A w_{aa} + q_B N_B w_{bb} + \frac{q_A N_A q_B N_B}{q_A N_A + q_B N_B} \frac{2}{\beta+1} w, \quad (11.09.10)$$

and so the molar total energy of mixing $\Delta_m U$ is given by

$$\frac{N_A + N_B}{N} \Delta_m U = \frac{q_A N_A q_B N_B}{q_A N_A + q_B N_B} \frac{2}{\beta+1} w, \quad (11.09.11)$$

with β determined by

$$\beta = \left\{ 1 + \frac{4q_A N_A q_B N_B}{(q_A N_A + q_B N_B)^2} (\eta^2 - 1) \right\}^{\frac{1}{2}}. \quad (11.09.12)$$

11.10. Critical mixing

Just as for regular mixtures, there is a critical temperature below which mixtures of some compositions are metastable and split into two phases. In the case of regular mixtures we obtained a simple closed formula relating the composition of each coexisting phase to the temperature. We were able to do this by making use of the fact that $\Delta_m F$ was symmetrical with respect to x and $1-x$. For the mixtures with which we are now concerned $\Delta_m F$ is not symmetrical with respect to x and $1-x$; nor with respect to ϕ and $1-\phi$; nor yet with respect to ϕ' and $1-\phi'$. We cannot then obtain closed formulae relating the composition of the coexisting phases to the temperature. We can, however, obtain simple closed formulae for the conditions of critical mixing.

It is convenient to consider $\ln(\lambda_A/\lambda'_A)$ plotted against ϕ' . This is shown schematically in Fig. 11.1. At temperatures above the critical the curve is monotonic, but at temperatures below the critical the curve has a minimum and a maximum, shown as P and Q respectively. The two coexisting phases are shown as L , M . Whereas we cannot obtain a closed formula relating to L , M we shall obtain a closed formula relating the compositions at P and Q to the temperature. We then obtain the critical conditions by making P and Q coincident. We confine ourselves to mixtures in which both kinds of molecules are homogeneous.

We begin by rewriting (11.08.9) in the form

$$\begin{aligned} \frac{\lambda_A}{\lambda_A^0} &= \left\{ (1-\phi')^{-1} \left(1 - \phi' + \frac{r_B q_A}{r_A q_B} \phi' \right) \right\}^{1/2q_A-1} \left\{ \frac{\beta+1-2\phi'}{\beta+1} \right\}^{1/2q_A} \\ &= \left\{ (1-\phi')^{-1} \left(1 - \phi' + \frac{r_B q_A}{r_A q_B} \phi' \right) \right\}^{(1z-1)r_A} \left\{ \frac{\beta+1-2\phi'}{\beta+1} \right\}^{1/2q_A}, \quad (11.10.1) \end{aligned}$$

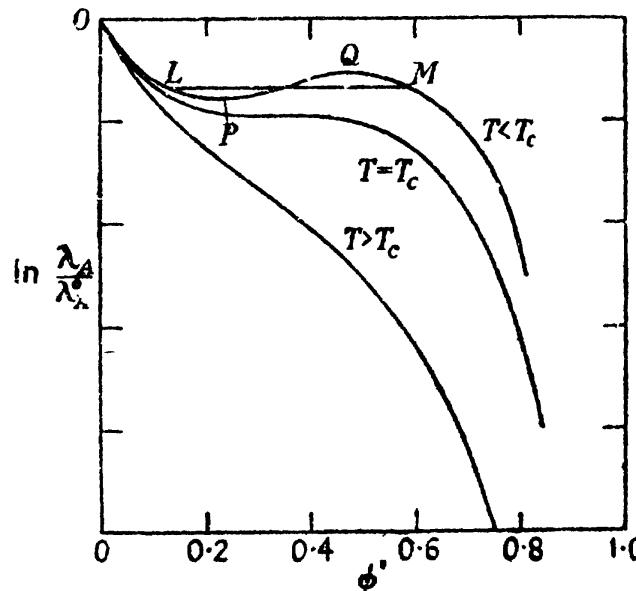


FIG. 11.1. Schematic plot of $\ln(\lambda_A/\lambda_A^0)$ against ϕ' for three temperatures.

where we recall that ϕ' is defined by

$$\phi' = \frac{q_B N_B}{q_A N_A + q_B N_B}, \quad 1 - \phi' = \frac{q_A N_A}{q_A N_A + q_B N_B}. \quad (11.10.2)$$

In obtaining (1) we have used the relations (11.07.11), namely

$$\kappa = \frac{2}{\beta+1}, \quad 1 - \kappa\phi' = \frac{\beta+1-2\phi'}{\beta+1}, \quad (11.10.3)$$

and relation (10.08.1), namely

$$\frac{1}{2}zq-1 = (\frac{1}{2}z-1)r. \quad (11.10.4)$$

We also recall that β satisfies (11.07.12) which we now rewrite as

$$\beta^2 - 1 = 4\phi'(1-\phi')(\eta^2 - 1). \quad (11.10.5)$$

Differentiating (5) we obtain

$$\frac{d\beta}{d\phi'} = \frac{(1-2\phi')(\beta^2-1)}{2\beta\phi'(1-\phi')}. \quad (11.10.6)$$

Taking the logarithm of (1) and differentiating with respect to ϕ' , we obtain, using (6),

$$\begin{aligned} \frac{d \ln \lambda_A}{d \phi'} &= (\frac{1}{2}z - 1)r_A \left\{ \frac{(r_B q_A / r_A q_B) - 1}{1 - \phi' + (r_B q_A / r_A q_B) \phi'} + \frac{1}{1 - \phi'} \right\} + \\ &\quad + \frac{1}{2} z q_A \left\{ \frac{1}{\beta + 1 - 2\phi'} - \frac{1}{\beta + 1} \right\} \frac{d\beta}{d\phi'} - \frac{1}{2} z q_A \frac{2}{\beta + 1 - 2\phi'} \\ &= \frac{(\frac{1}{2}z - 1)r_A}{(1 - \phi') \{ (r_A q_B / r_B q_A) (1 - \phi') + \phi' \}} + \\ &\quad + \frac{1}{2} z q_A \frac{(1 - 2\phi')(\beta - 1)}{(\beta + 1 - 2\phi') \beta (1 - \phi')} - \frac{1}{2} z q_A \frac{2}{\beta + 1 - 2\phi'} \\ &= \frac{\frac{1}{2}(z-2)r_A}{(1-\phi')\{(r_A q_B / r_B q_A)(1-\phi')+\phi'\}} - \frac{1}{2} z q_A \frac{1}{\beta(1-\phi')}. \quad (11.10.7) \end{aligned}$$

The points P , Q in Fig. 11.1 are characterized by

$$\frac{d \ln \lambda_A}{d \phi'} = 0. \quad (11.10.8)$$

From (7) we see that (8) is equivalent to

$$\frac{zq_A}{\beta} = \frac{(z-2)r_A}{(r_A q_B / r_B q_A)(1-\phi')+\phi'}. \quad (11.10.9)$$

For the sake of brevity we introduce two new constants a and b defined by

$$a = \frac{zq_A}{(z-2)r_A} = \frac{zq_A}{zq_A - 2}, \quad (11.10.10)$$

$$b = \frac{zq_B}{(z-2)r_B} = \frac{zq_B}{zq_B - 2}. \quad (11.10.11)$$

We can now rewrite (9) as

$$\beta = a\phi' + b(1 - \phi'). \quad (11.10.12)$$

Substituting (12) into (5) we obtain

$$(a^2 - 1)\phi'^2 - 2(2\eta^2 - 1 - ab)\phi'(1 - \phi') + (b^2 - 1)(1 - \phi')^2 = 0. \quad (11.10.13)$$

Equation (13) is a quadratic in $\phi'/(1 - \phi')$. When the roots are real one root corresponds to the point P and the other to Q in Fig. 11.1. The condition of critical mixing is that the two roots should coincide. Thus the critical value η_c of η is determined by

$$(2\eta_c^2 - 1 - ab)^2 = (a^2 - 1)(b^2 - 1), \quad (11.10.14)$$

$$\text{or } e^{2w/zkT_e} = \eta_c^2 = \frac{1}{2}\{1 + ab + (a^2 - 1)^{\frac{1}{2}}(b^2 - 1)^{\frac{1}{2}}\}. \quad (11.10.15)$$

The critical composition ϕ'_c is given by

$$\frac{\phi'_c}{1-\phi'_c} = \left(\frac{b^2-1}{a^2-1} \right)^{\frac{1}{2}}, \quad (11.10.16)$$

or when we use (10), (11), and (2)

$$\frac{N_B}{N_A} = \frac{r_A q_A}{r_B q_B} \left(\frac{q_B z - 1}{q_A z - 1} \right)^{\frac{1}{2}}. \quad (11.10.17)$$

11.11. Relation of first approximation to zeroth approximation

We shall now show that the zeroth approximation described in §§ 11.02 to 11.05 can be obtained from the first approximation by expanding in powers of w/kT and retaining only the leading terms.†

By comparing the quasi-chemical equation (11.07.5) with (11.07.7) it is clear that $y - y^*$ vanishes with w . A formula can therefore be obtained for the configurational free energy F_c of the required degree of accuracy by expressing F_c as a power series in $(y - y^*)$ and neglecting terms of order higher than the first. Taylor's series for $F_c(N_A, N_B, Qy)$ is

$$F_c(N_A, N_B, Qy) = F_c(N_A, N_B, Qy^*) + \frac{\partial F_c(N_A, N_B, Qy^*)}{\partial (Qy^*)} Q(y - y^*) + \\ + \text{terms in } (y - y^*)^2. \quad (11.11.1)$$

Since $F_c(N_A, N_B, Qy)$ is minimized with respect to Qy it is known that $\partial F_c(N_A, N_B, Qy^*)/\partial (Qy^*)$ is small of the first order in $(y - y^*)$ and so the second term on the right of (1) is small of the second order in $(y - y^*)$. Hence to the required degree of accuracy

$$F_c(N_A, N_B, Qy) = F_c(N_A, N_B, Qy^*). \quad (11.11.2)$$

Formula (2) must be interpreted with care. The meaning of the right-hand side is according to (11.08.1)

$$F_c(N_A, N_B, Qy^*) = -kT \ln g(N_A, N_B, Qy^*) + \\ + (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb} + y^*w) \\ = -kT \ln g(N_A, N_B) + \\ + (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb} + y^*w). \quad (11.11.3)$$

It is not the same as the configurational term of F^* in (11.08.4) which would be

$$F_c^* = -kT \ln g(N_A, N_B) + (q_A N_A + q_B N_B)(uw_{aa} + vw_{bb}). \quad (11.11.4)$$

† Guggenheim (1944), Proc. Roy. Soc. A 183, 225, § 15.

By substituting (11.07.8)

$$y^* = uv = \frac{(q_A N_A u_A + q_B N_B u_B)(q_A N_A v_A + q_B N_B v_B)}{(q_A N_A + q_B N_B)^2}, \quad (11.11.5)$$

into (3) we recover immediately the zeroth approximation formulae of § 11.04. If alternatively we wish to obtain the zeroth approximation from formula (11.08.4) we must not simply put $\kappa = 1$ but use the next better approximation retaining terms in w/kT . To this approximation we have from (11.07.12)

$$\beta = 1 + \frac{4uvw}{zkT}, \quad (11.11.6)$$

and so from (11.07.11) to the same approximation

$$\kappa = 1 - \frac{2uvw}{zkT}. \quad (11.11.7)$$

Hence to the same degree of accuracy

$$u \ln \frac{1-\kappa v}{u} + v \ln \frac{1-\kappa u}{v} = u \ln \left(1 + \frac{2v^2 w}{zkT} \right) + v \ln \left(1 + \frac{2u^2 w}{zkT} \right) = \frac{2uvw}{zkT}. \quad (11.11.8)$$

Substituting (8) into (11.08.4) we obtain .

$$F = F^* + (q_A N_A + q_B N_B)uvw, \quad (11.11.9)$$

which is the correct zeroth approximation. In particular for homogeneous molecules (9) becomes

$$F = F^* + (q_A N_A + q_B N_B) \phi'_A \phi'_B w. \quad (11.11.10)$$

11.12. Flory's approximation

The approximation, which we have called the zeroth approximation, is obtained from the first approximation by making $z \rightarrow \infty$ in the thermal terms depending on w . On the other hand, the approximation which we have called Flory's† approximation is obtained by making $z \rightarrow \infty$ in the athermal terms, which implies making $(r-q)/r \rightarrow 0$. When we use both approximations making $z \rightarrow \infty$ throughout we obtain for a mixture of homogeneous molecules

$$\Delta_m F = RT\{(1-x)\ln \phi_A + x \ln \phi_B\} + \{r_A(1-x) + r_B x\} \phi_A \phi_B Nw. \quad (11.12.1)$$

† Flory (1942), *J. Chem. Phys.* **10**, 51.

All other thermodynamic properties can be derived from (1), in particular

$$\frac{\Delta_m S}{R} = -(1-x)\ln \phi_A - x\ln \phi_B, \quad (11.12.2)$$

$$\Delta_m U = \{r_A(1-x) + r_B x\}\phi_A \phi_B Nw. \quad (11.12.3)$$

In this approximation the formula[†] for the temperature of critical mixing takes a strikingly simple form for homogeneous molecules. We can conveniently obtain this by making $z \rightarrow \infty$ in formula (11.10.15). From the definitions (11.10.10), (11.10.11), of a , b we have

$$a \simeq 1 + \frac{2}{zq_A} \simeq 1 + \frac{2}{zr_A}, \quad (11.12.4)$$

$$b \simeq 1 + \frac{2}{zq_B} \simeq 1 + \frac{2}{zr_B}, \quad (11.12.5)$$

$$(a^2 - 1)^{\frac{1}{2}}(b^2 - 1)^{\frac{1}{2}} \simeq \frac{4}{z(r_A r_B)^{\frac{1}{2}}}, \quad (11.12.6)$$

$$e^{2w/zkT_c} \simeq 1 + \frac{2w}{zkT_c}. \quad (11.12.7)$$

Substituting (4), (5), (6), (7) into (11.10.15) we obtain

$$1 + \frac{2w}{zkT_c} = 1 + \frac{1}{zr_A} + \frac{1}{zr_B} + \frac{2}{z(r_A r_B)^{\frac{1}{2}}}, \quad (11.12.8)$$

or $\frac{w}{kT_c} = \frac{1}{2} \left(\frac{1}{\sqrt{r_A}} + \frac{1}{\sqrt{r_B}} \right)^2. \quad (11.12.9)$

In particular (9) becomes for a regular solution with $r_A = r_B = 1$

$$\frac{w}{kT_c} = 2 \quad (r_A = r_B = 1). \quad (11.12.10)$$

On the other hand, for a mixture of monomers $r_A = 1$ and macromolecules $r_B \gg 1$, the relation becomes

$$\frac{w}{kT_c} = \frac{1}{2} \quad (r_A = 1, r_B \gg 1). \quad (11.12.11)$$

11.13. Dependence of w on temperature

Whereas we have throughout this chapter tacitly assumed that w has a value independent of the temperature, this assumption is not an essential feature of the method of treatment or of the quasi-crystalline model. We have already in § 4.27 pointed out that in the treatment of regular mixtures w may depend on the temperature. Most of what

[†] Guggenheim (1944), *Proc. Roy. Soc. A* 183, 226, § 16.

is said there is also applicable to the more general kind of mixture treated in the present chapter. We shall not repeat the argument[†] but shall merely summarize the effect on our formulae of admitting that w may depend on the temperature.

All our formulae for the configurational free energy F_c , the molar free energy of mixing $\Delta_m F$, the chemical potentials μ_A and μ_B , the absolute activities λ_A and λ_B contain w in the form of the ratio w/kT or $\eta = e^{w/zkT}$. We may regard either of these quantities as a single parameter whose value determines all the above thermodynamic properties at a given temperature. None of the formulae for any of these quantities is affected by removing the restriction that w should be independent of the temperature. Nor are the formulae for the conditions of critical mixing affected.

The formulae for the configurational total energy or heat function and for the molar heat of mixing are obtained from the formulae for the free energy by operations including differentiation with respect to T . The formulae for these quantities are therefore affected by the dependence of w on the temperature in the following way. In all these formulae we must replace

$$\frac{d(w/T)}{d(1/T)} = w \frac{d(1/T)}{d(1/T)} = w \quad (11.13.1)$$

throughout by

$$\frac{d(w/T)}{d(1/T)} = w \frac{d(1/T)}{d(1/T)} + \frac{1}{T} \frac{dw}{d(1/T)} = w - T \frac{dw}{dT}. \quad (11.13.2)$$

This rule applies equally to the zeroth and to the first approximations.

One consequence of this change is that even in the zeroth approximation the entropy will contain terms in $-dw/dT$ corresponding to the terms in w in the free energy. We may point out, as we have already done for regular mixtures, that the assumption that w depends on the temperature does not necessarily imply that the heat of mixing varies with the temperature. In fact differentiating the expression on the right of (2) with respect to T we obtain

$$\frac{d}{dT} \left(w - T \frac{dw}{dT} \right) = - T \frac{d^2 w}{dT^2}, \quad (11.13.3)$$

which can be zero even though dw/dT differs significantly from zero.

[†] Guggenheim (1948), *Trans. Faraday Soc.* **44**, 1007; (1949) *Supp. Nuovo Cimento*, **6**, 181.

11.14. Numerical values for activity coefficients

We shall now transcribe some of our relations into a form convenient for comparison with experiment. For the sake of brevity we shall confine ourselves to mixtures of monomers denoted by the subscript 1 and homogeneous r -mers denoted by the subscript r .

One of the most readily measurable properties of a solution is the vapour pressure. At the temperatures at which such measurements can conveniently be made, the partial vapour pressure of the solute r -mer will usually be only a small fraction of the total vapour pressure, if not entirely negligible. It is then easy by applying, if necessary, a small correction to convert the measured values of the total vapour pressure to values of the partial vapour pressure of the solvent monomer. When the required information concerning the second virial coefficient of the vapour is available, a correction can be applied to the partial vapour pressure so as to obtain the fugacity. The experimental value of the activity coefficient f_1 of the solvent is then obtained from the relation

$$f_1 = \frac{p_1}{p_1^0(1-x)}, \quad (11.14.1)$$

where p_1 denotes the fugacity of the solvent in the mixture and p_1^0 the fugacity of the pure solvent, while x denotes the mole fraction of the solute. This experimental value of f_1 can then be compared with the theoretical formulae.

We shall denote by f_1^* the calculated value of f_1 in an athermal mixture having the same composition as the mixture being considered. Values of f_1^* for solutions of dimers, trimers, or tetramers have already been given in Table 10.7. The relation between f_1 and f_1^* can then be transcribed to the form

$$f_1 = f_1^* t^{1/2}, \quad (11.14.2)$$

where t denotes the ratio of the equilibrium number of monomer-monomer contacts to the number in a completely random configuration. The value of t is determined by the quasi-chemical quadratic equation

$$(1-\phi')^2 \alpha t^2 - (1+\alpha-2\phi'\alpha)t + 1 = 0, \quad (11.14.3)$$

where ϕ' is defined by $\phi' = \frac{qx}{1-x+qx}$, (11.14.4)

and for the sake of brevity α is defined by

$$\alpha = 1 - \eta^{-2} = 1 - e^{-2w/skT}. \quad (11.14.5)$$

In the zeroth approximation, obtained by making $z \rightarrow \infty$ in the factor $t^{1/z}$ in (2) after substituting for t from (3), we have

$$f_1 = f_1^* \exp\left(\phi'^2 \frac{w}{kT}\right) \quad (\text{zeroth approximation}). \quad (11.14.6)$$

TABLE 11.3

Values of $\log_{10} t$ calculated at Round Values of ϕ' and of α

ϕ'	$\alpha = 0.04$	$\alpha = 0.06$	$\alpha = 0.08$	$\alpha = 0.10$	$\alpha = 0.12$	$\alpha = 0.14$	$\alpha = 0.16$	$\alpha = 0.18$	$\alpha = 0.20$	$\alpha = 0.22$
0.01	0.00000	0.00000	0.00000	0.00000	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
0.02	0.00001	0.00001	0.00002	0.00002	0.00002	0.00003	0.00003	0.00004	0.00004	0.00006
0.05	0.00004	0.00007	0.00009	0.00012	0.00015	0.00017	0.00020	0.00023	0.00026	0.00030
0.1	0.00016	0.00027	0.00037	0.00047	0.00058	0.00069	0.00080	0.00092	0.00104	0.00116
0.2	0.00071	0.00108	0.00147	0.00186	0.00226	0.00268	0.00311	0.00355	0.00401	0.00448
0.3	0.00160	0.00242	0.00327	0.00418	0.00502	0.00592	0.00685	0.00780	0.00877	0.00977
0.4	0.00283	0.00428	0.00576	0.00727	0.00881	0.01038	0.01198	0.01362	0.01528	0.01699
0.5	0.00441	0.00667	0.00896	0.01129	0.01366	0.01607	0.01852	0.02101	0.02355	0.02614
0.6	0.00634	0.00958	0.01286	0.01620	0.01958	0.02302	0.02651	0.03006	0.03366	0.03738
0.7	0.00863	0.01303	0.01750	0.02208	0.02663	0.03130	0.03604	0.04086	0.04576	0.05078
0.8	0.01128	0.01705	0.02290	0.02885	0.03489	0.04103	0.04727	0.05362	0.06008	0.06664
0.9	0.01481	0.02165	0.02912	0.03678	0.04447	0.05236	0.06040	0.06860	0.07696	0.08549
0.95	0.01597	0.02418	0.03255	0.04109	0.04980	0.05869	0.06776	0.07708	0.08651	0.09620
0.98	0.01701	0.02578	0.03472	0.04385	0.05318	0.06272	0.07246	0.08244	0.09264	0.10210
0.99	0.01737	0.02632	0.03546	0.04480	0.05434	0.06410	0.07408	0.08450	0.09476	0.10488

ϕ'	$\alpha = 0.24$	$\alpha = 0.26$	$\alpha = 0.28$	$\alpha = 0.30$	$\alpha = 0.32$	$\alpha = 0.34$	$\alpha = 0.36$	$\alpha = 0.38$	$\alpha = 0.40$	$\alpha = 0.42$
0.01	0.00001	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002	0.00003	0.00008	0.00003
0.02	0.00005	0.00006	0.00007	0.00007	0.00008	0.00009	0.00010	0.00010	0.00011	0.00012
0.05	0.00088	0.00087	0.00041	0.00045	0.00049	0.00053	0.00058	0.00063	0.00068	0.00074
0.1	0.00130	0.00148	0.00152	0.00173	0.00188	0.00205	0.00222	0.00240	0.00258	0.00278
0.2	0.00496	0.00547	0.00598	0.00652	0.00708	0.00765	0.00825	0.00887	0.00952	0.01018
0.3	0.01080	0.01185	0.01294	0.01405	0.01520	0.01637	0.01759	0.01884	0.02013	0.02147
0.4	0.01878	0.02051	0.02238	0.02420	0.02610	0.02806	0.03007	0.03213	0.03424	0.03641
0.5	0.02878	0.03146	0.03420	0.03700	0.03986	0.04278	0.04576	0.04881	0.05198	0.05513
0.6	0.04106	0.04485	0.04872	0.05268	0.05667	0.06076	0.06494	0.06920	0.07356	0.07801
0.7	0.05580	0.06094	0.06618	0.07152	0.07695	0.08250	0.08814	0.09391	0.09980	0.10581
0.8	0.07338	0.08014	0.08708	0.09415	0.10136	0.10872	0.11624	0.12391	0.13175	0.13977
0.9	0.09419	0.10309	0.11217	0.12146	0.13096	0.14068	0.15064	0.16084	0.17130	0.18203
0.95	0.10611	0.11625	0.12664	0.13729	0.14821	0.15941	0.17091	0.18273	0.19488	0.20790
0.98	0.11380	0.12479	0.13606	0.14762	0.15951	0.17178	0.18430	0.19725	0.21060	0.22438
0.99	0.11647	0.12775	0.13938	0.15122	0.16345	0.17604	0.18900	0.20236	0.21614	0.23038

Equation (3) has been solved for round values of ϕ' and for values of α between 0.04 and 0.42. Values of $\log_{10} t$ so obtained† are shown in Table 11.3. It is to be noted that this table is valid for any values of r and z .

For purposes of accurate interpolation it is convenient to compare the value of f_1 according to the quasi-chemical treatment with its value according to the zeroth approximation. By comparison of (2) with (6) we have

$$\ln f_1 - \ln f_1(\text{zeroth}) = \frac{1}{2}z \left(\ln t - \phi'^2 \frac{2w}{zkT} \right). \quad (11.14.7)$$

A quantity proportional to the expression (7) is tabulated for $z = 6$

† Values calculated by McGlashan; not previously published.

and values of α between 0.04 and 0.42 in Table 11.4. The value $z = 6$ has been chosen as the smallest value of z likely to occur. A good estimate of values of the difference function (7) for other values of z can be obtained by linear interpolation with respect to $1/z$ between the values $\frac{1}{6}$ and 0.

TABLE 11.4

Values of the Difference $10^5 \times \left\{ \frac{1}{\ln 10} \frac{w}{kT} \phi'^2 - \frac{1}{2} z \log_{10} t \right\}$ calculated at Round Values of ϕ' and of α for $z = 6$

ϕ'	$\alpha = 0.04$	$\alpha = 0.06$	$\alpha = 0.08$	$\alpha = 0.10$	$\alpha = 0.12$	$\alpha = 0.14$	$\alpha = 0.16$	$\alpha = 0.18$	$\alpha = 0.20$	$\alpha = 0.22$
0.01	0	0	0	0	0	0	0	0	0	0
0.02	0	0	0	0	0	-1	-1	-1	-1	-2
0.05	0	0	-1	-2	-2	-3	-4	-6	-7	-8
0.1	0	-2	-3	-5	-7	-9	-13	-16	-21	-26
0.2	-2	-3	-6	-9	-13	-19	-24	-31	-40	-48
0.3	-1	-2	-2	-4	-6	-8	-10	-13	-16	-19
0.4	2	5	9	14	21	30	40	52	67	83
0.5	7	16	28	45	67	92	124	160	203	251
0.6	12	28	52	83	122	169	226	292	368	456
0.7	18	40	73	116	171	238	318	411	519	642
0.8	19	45	81	130	191	266	356	462	584	725
0.9	15	35	63	101	150	209	280	364	462	575
0.95	9	21	38	62	92	128	172	225	286	356
0.98	4	9	17	28	41	58	78	101	129	161
0.99	2	5	9	14	21	30	40	53	67	84

ϕ'	$\alpha = 0.24$	$\alpha = 0.26$	$\alpha = 0.28$	$\alpha = 0.30$	$\alpha = 0.32$	$\alpha = 0.34$	$\alpha = 0.36$	$\alpha = 0.38$	$\alpha = 0.40$	$\alpha = 0.42$
0.01	0	-1	-1	-1	-1	-1	-1	-2	-2	-2
0.02	-2	-2	-3	-3	-4	-5	-6	-6	-7	-8
0.05	-10	-13	-15	-18	-21	-25	-29	-33	-38	-43
0.1	-31	-38	-45	-53	-62	-72	-84	-96	-110	-125
0.2	-59	-71	-84	-98	-114	-131	-150	-170	-192	-216
0.3	-22	-26	-29	-33	-36	-40	-44	-47	-50	-53
0.4	102	124	149	177	208	244	283	327	377	432
0.5	306	369	439	517	605	702	809	928	1 059	1 204
0.6	555	667	792	932	1 087	1 260	1 450	1 660	1 891	2 148
0.7	782	940	1 117	1 315	1 535	1 778	2 048	2 345	2 673	3 038
0.8	884	1 065	1 268	1 495	1 749	2 030	2 343	2 688	3 070	3 491
0.9	704	851	1 017	1 203	1 413	1 646	1 907	2 197	2 520	2 878
0.95	437	530	634	753	886	1 036	1 204	1 391	1 600	1 834
0.98	198	241	289	344	405	475	552	640	738	848
0.99	103	126	151	180	212	248	289	335	387	445

11.15. Experiments on benzene/diphenyl

We shall now illustrate the use of the formulae of the previous section by applying them to the experimental measurements of Baxendale, Enüstün, and Stern† on the system benzene/diphenyl. They measured

† Baxendale, Enüstün, and Stern (1951), *Phil. Trans. Roy. Soc. A* 243, 169.

the vapour pressure of the benzene, that of diphenyl being negligible, at six temperatures over a range of concentrations extending up to saturation with the solid phase of diphenyl. We shall apply the model with $r = 1$ for benzene and $r = 2$ for diphenyl, although the actual ratio of volumes is not 2 but 1·7.

The first step is to correct the partial vapour pressures to fugacities. For this purpose we assume for the second virial coefficient of benzene the empirical formula†

$$\frac{B}{\text{cm.}^3/\text{mole}} = 68 - \frac{13.2 \times 10^7}{T^2}, \quad (11.15.1)$$

which is a fair representation of all available experimental data.

Baxendale, Enüstün, and Stern in their analysis used their own measured values of B . Since these measured values showed a trend with the pressure about a thousand times greater than can be accounted for, there is probably some systematic error in their measured values of B , which we therefore do not use. Consequently our tabulated values of the experimental activity coefficients are slightly different from those evaluated by the original authors.

In Table 11.5 is shown a comparison‡ between the experimental values of $\log_{10} f_1$ and those predicted by the theory using the value $w/k = 76.0^\circ$. The first column gives the temperature, the second the mole fraction x of diphenyl, and the third the value of ϕ' determined by

$$\phi' = \frac{x}{x + (1-x)/q}, \quad (11.15.2)$$

with $q = \frac{1}{2}$. The third column gives the values of $\log_{10} f_1$ calculated by the zeroth approximation and the fourth column the values of the first approximation, these values being obtained from those in the previous column by use of Table 11.4. The difference between these two columns is almost negligible owing to the small value of $2w/zkT$, being between 0·08 and 0·07. The last column gives the differences between the theoretical and experimental values of $\log_{10} f_1$. It will be seen that except for compositions in which the mole fraction of diphenyl exceeds 0·8, such solutions being nearly saturated with respect to the solid phase, the agreement between theoretical and experimental values of $\log_{10} f_1$ is nearly always better than 0·0015. This corresponds to an agreement of about $\frac{1}{2}$ per cent. in f_1 .

† Everett, private communication.

‡ Everett and McGlashan, not yet published.

TABLE 11.5

Comparison of Theoretical Values of the Activity Coefficients of Benzene in mixtures of Benzene and Diphenyl with Experimental Values of Baxendale et al.

<i>t° C.</i>	<i>x</i>	ϕ'	$\log_{10} f_1$ zeroth	$\log_{10} f_1$ quasi-chemical	$\log_{10} f_1$ experiment	$\log_{10} \frac{f_1 \text{ (theor.)}}{f_1 \text{ (exp.)}}$
30	0.1005	0.1570	0.0014	0.0015	0.0006	0.001
	0.2010	0.2954	0.0048	0.0049	0.0027	0.002
	0.3000	0.4167	0.0093	0.0091	0.0075	0.002
	0.4000	0.5263	0.0144	0.0141	0.0123	0.002
40	0.1002	0.1576	0.0013	0.0014	0.0013	0.000
	0.2024	0.2972	0.0045	0.0048	0.0033	0.001
	0.3002	0.4169	0.0087	0.0085	0.0076	0.001
	0.4004	0.5267	0.0135	0.0132	0.0120	0.001
	0.4988	0.6239	0.0185	0.0180	0.0172	0.001
50	0.1014	0.1583	0.0013	0.0013	0.0010	0.000
	0.2043	0.2997	0.0043	0.0043	0.0031	0.001
	0.3006	0.4174	0.0082	0.0081	0.0073	0.001
	0.4010	0.5274	0.0126	0.0123	0.0115	0.001
	0.4996	0.6246	0.0173	0.0167	0.0162	0.001
	0.6037	0.7174	0.0221	0.0215	0.0209	0.001
60	0.1021	0.1593	0.0011	0.0012	0.0013	0.000
	0.2068	0.3029	0.0041	0.0042	0.0031	0.001
	0.3011	0.4179	0.0075	0.0075	0.0067	0.001
	0.4017	0.5281	0.0122	0.0115	0.0108	0.001
	0.5006	0.6256	0.0162	0.0157	0.0154	0.000
	0.6049	0.7184	0.0205	0.0199	0.0199	0.000
	0.7034	0.7931	0.0246	0.0240	0.0251	-0.001
	0.7981	0.8682	0.0285	0.0279	0.0318	-0.004
70	0.1030	0.1606	0.0011	0.0011	0.0009	0.000
	0.2101	0.3071	0.0039	0.0039	0.0025	0.001
	0.3016	0.4185	0.0071	0.0070	0.0063	0.001
	0.4026	0.5290	0.0110	0.0107	0.0103	0.000
	0.5018	0.6267	0.0150	0.0145	0.0144	0.000
	0.6063	0.7196	0.0192	0.0186	0.0181	0.001
	0.7048	0.7992	0.0229	0.0223	0.0231	-0.001
	0.7994	0.8691	0.0262	0.0257	0.0295	-0.004
	0.9034	0.9397	0.0298	0.0295	0.0383	-0.009
80	0.1041	0.1622	0.0011	0.0011	0.0011	0.000
	0.2148	0.3125	0.0038	0.0038	0.0030	0.001
	0.3023	0.4193	0.0067	0.0066	0.0062	0.000
	0.4038	0.5303	0.0102	0.0100	0.0101	0.000
	0.5033	0.6281	0.0141	0.0136	0.0137	0.000
	0.6081	0.7211	0.0178	0.0173	0.0180	-0.001
	0.7067	0.8006	0.0212	0.0206	0.0218	-0.001
	0.8010	0.8703	0.0243	0.0237	0.0278	-0.004
	0.9044	0.9404	0.0273	0.0270	0.0357	-0.009

TABLE 11.6

Comparison of Theoretical Values of the Activity Coefficients of Benzene in mixtures of Benzene and Diphenyl with Experimental Values of Everett and Penney

<i>t° C.</i>	<i>x</i>	<i>φ'</i>	$\log_{10} f_1$ zeroth	$\log_{10} f_1$ quasi-chemical	$\log_{10} f_1$ experiment	$\log_{10} \frac{f_1 \text{ (theor.)}}{f_1 \text{ (exp.)}}$
15	0.0781	0.1237	0.0009	0.0009	0.0005	0.000
	0.1198	0.1850	0.0022	0.0023	0.0033	-0.001
	0.1449	0.2202	0.0030	0.0031	0.0042	-0.001
	0.1515	0.2293	0.0033	0.0034	0.0048	-0.001
25	0.0782	0.1239	0.0008	0.0008	0.0005	0.000
	0.1200	0.1852	0.0020	0.0021	0.0033	-0.001
	0.1453	0.2208	0.0029	0.0030	0.0033	-0.001
	0.1520	0.2300	0.0030	0.0031	0.0047	-0.002
	0.3040	0.4213	0.0100	0.0099	0.0104	-0.001
35	0.0784	0.1242	0.0003	0.0008	0.0006	0.000
	0.1204	0.1858	0.0019	0.0020	0.0028	-0.001
	0.1459	0.2216	0.0027	0.0027	0.0030	0.000
	0.1526	0.2303	0.0029	0.0029	0.0038	-0.001
	0.3044	0.4217	0.0094	0.0093	0.0081	0.001
	0.3382	0.4800	0.0111	0.0109	0.0096	0.001
	0.4051	0.5316	0.0147	0.0143	0.0184	0.001
	0.4339	0.5609	0.0161	0.0157	0.0168	-0.001
	0.4827	0.6153	0.0192	0.0186	0.0192	-0.001
45	0.0786	0.1245	0.0007	0.0007	0.0005	0.000
	0.1209	0.1865	0.0019	0.0020	0.0024	0.000
	0.1466	0.2226	0.0026	0.0026	0.0034	-0.001
	0.1534	0.2319	0.0028	0.0028	0.0041	-0.001
	0.3050	0.4224	0.0088	0.0087	0.0075	0.001
	0.3402	0.4622	0.0105	0.0103	0.0095	0.001
	0.4072	0.5338	0.0137	0.0134	0.0132	0.000
	0.4362	0.5632	0.0152	0.0148	0.0149	0.000
	0.4924	0.6178	0.0180	0.0175	0.0184	-0.001
	0.5971	0.7118	0.0234	0.0227	0.0229	0.000
55	0.0790	0.1251	0.0007	0.0007	0.0003	0.000
	0.1217	0.1876	0.0017	0.0018	0.0024	-0.001
	0.1477	0.2241	0.0024	0.0024	0.0033	-0.001
	0.1546	0.2336	0.0027	0.0027	0.0035	-0.001
	0.3057	0.4232	0.0083	0.0082	0.0070	0.001
	0.3424	0.4646	0.0096	0.0094	0.0087	0.001
	0.4099	0.5365	0.0129	0.0126	0.0120	0.001
	0.4392	0.5662	0.0144	0.0140	0.0135	0.001
	0.4958	0.6210	0.0169	0.0164	0.0164	0.000
	0.6012	0.7153	0.0218	0.0211	0.0212	0.000
	0.6656	0.7684	0.0249	0.0242	0.0264	-0.002
	0.7146	0.8067	0.0270	0.0263	0.0289	-0.003

TABLE 11.6 (Cont.)

<i>T° C.</i>	<i>x</i>	<i>φ'</i>	$\log_{10} f_1$ zeroth	$\log_{10} f_1$ quasi-chemical	$\log_{10} f_1$ experiment	$\log_{10} \frac{f_1(\text{theor.})}{f_1(\text{exp.})}$
65	0.0794	0.1257	0.0007	0.0007	0.0018	-0.001
	0.1226	0.1889	0.0016	0.0017	0.0010	0.001
	0.1267	0.1947	0.0017	0.0018	0.0010	0.001
	0.1490	0.2259	0.0023	0.0023	0.0017	0.001
	0.1560	0.2355	0.0025	0.0025	0.0028	0.000
	0.1744	0.2604	0.0030	0.0030	0.0031	0.000
	0.1918	0.2834	0.0035	0.0035	0.0032	0.000
	0.2693	0.3805	0.0063	0.0062	0.0057	0.001
	0.2883	0.4030	0.0071	0.0070	0.0054	0.002
	0.3041	0.4214	0.0077	0.0076	0.0076	0.000
	0.3068	0.4245	0.0078	0.0077	0.0075	0.000
	0.3161	0.4351	0.0081	0.0080	0.0064	0.002
	0.3451	0.4676	0.0093	0.0091	0.0079	0.001
	0.3601	0.4840	0.0100	0.0098	0.0089	0.001
	0.4076	0.5342	0.0120	0.0117	0.0107	0.001
	0.4135	0.5402	0.0123	0.0120	0.0112	0.001
	0.4431	0.5701	0.0135	0.0131	0.0123	0.001
	0.4602	0.5869	0.0143	0.0139	0.0136	0.000
	0.5002	0.6252	0.0161	0.0156	0.0150	0.001
	0.5036	0.6284	0.0161	0.0156	0.0166	-0.001
	0.5459	0.6671	0.0180	0.0175	0.0205	-0.003
	0.6063	0.7196	0.0206	0.0200	0.0199	0.000
	0.6683	0.7705	0.0231	0.0225	0.0249	-0.002
	0.7197	0.8106	0.0253	0.0247	0.0262	-0.002
	0.8417	0.8986	0.0300	0.0295	0.0412	-0.012
75	0.0800	0.1266	0.0006	0.0006	0.0020	-0.001
	0.1245	0.1916	0.0016	0.0016	0.0018	0.000
	0.1507	0.2282	0.0022	0.0022	0.0025	0.000
	0.1579	0.2381	0.0024	0.0024	0.0039	-0.002
	0.1760	0.2625	0.0029	0.0029	0.0036	-0.001
	0.1930	0.2850	0.0034	0.0034	0.0032	0.000
	0.2714	0.3830	0.0060	0.0059	0.0046	0.001
	0.2903	0.4054	0.0067	0.0066	0.0053	0.001
	0.3080	0.4259	0.0073	0.0072	0.0066	0.001
	0.3178	0.4371	0.0077	0.0076	0.0066	0.001
	0.3486	0.4714	0.0088	0.0086	0.0088	0.000
	0.3622	0.4862	0.0094	0.0092	0.0085	0.001
	0.4101	0.5368	0.0113	0.0110	0.0100	0.001
	0.4180	0.5448	0.0115	0.0112	0.0112	0.000
	0.4480	0.5749	0.0127	0.0123	0.0120	0.000
	0.4626	0.5893	0.0134	0.0130	0.0128	0.000
	0.5059	0.6305	0.0151	0.0147	0.0150	0.000
	0.5063	0.6309	0.0151	0.0147	0.0157	-0.001
	0.5487	0.6696	0.0169	0.0164	0.0187	-0.002
	0.6714	0.7730	0.0216	0.0210	0.0228	-0.002
	0.7260	0.8154	0.0237	0.0231	0.0254	-0.002
	0.8436	0.8999	0.0278	0.0273	0.0355	-0.008

Still more recent measurements of a similar nature on the same system have been made by Everett and Penney.[†] These measurements cover the same range of temperature as those of Baxendale, but the actual temperatures used by the two groups of authors alternate. These results have been analysed in precisely the same manner as that applied above to those of Baxendale, again assuming formula (1) for the second virial coefficient. A comparison between the experimental results and the theory, using the value $w/k = 77.0^\circ$ is shown in Table 11.6. Again it is found that the agreement between observed and calculated values is nearly always better than 0.001 in $\log_{10} f_1$. This corresponds to an agreement of about $\frac{1}{2}$ per cent. in f_1 .

The small difference between the values 76.0° and 77.0° of w/k which best fit the two independent sets of experiments shows that the internal consistency of each set is, as is not unusual, slightly better than their mutual consistency.

Finally we may compare these values of $w/k = 76^\circ$ or 77° chosen to fit these data with the value 89° obtained by Tompa[‡] from a measurement at 25° C. of the heat of dilution from $x = 0.335$ to $x = 0.150$.

11.16. Experiments on alkanes

We turn now to a comparison with experiment on heterogeneous molecules. Brönsted and Koefoed[§] have measured vapour pressures at 20° C. of three mixtures of normal alkanes, namely hexane/hexadecane, heptane/hexadecane, and hexane/dodecane. The partial vapour pressures of the hexadecane and the dodecane are negligible. They corrected their results for gas imperfections, thus obtaining fugacities and activity coefficients of the hexane or heptane.

It has been shown^{||} that the extent of agreement between theory and experiment is insensitive to the value chosen for z , the agreement being comparable for $z = 8$ and $z = 4$. We shall accordingly confine our comparison to a single value of z and we arbitrarily choose the value $z = 8$ of a body-centred cubic lattice.

We shall use the subscript A to refer to the volatile component, hexane or heptane, and the subscript B to refer to the non-volatile component, hexadecane or dodecane. We shall regard all the molecules concerned as comprised of two kinds of elements, namely —CH₂—

[†] Everett and Penney (1952), *Proc. Roy. Soc. A* **212**.

[‡] Tompa (1948), *J. Chem. Phys.* **4**, 296.

[§] Brönsted and Koefoed (1946), *Kgl. Danske Vid. Selsk. Mat-Fys. Medd.* **22**, No. 17.

^{||} Tompa (1949), *Trans. Faraday Soc.* **45**, 105, § 3.

groups and $-\text{CH}_3$ end-groups. We accordingly assume the following values for u_A , v_A , u_B , v_B :

Hexane	$u_A = 24/38$,	$v_A = 14/38$
Heptane	$u_A = 30/44$,	$v_A = 14/44$
Hexadecane	$u_B = 84/98$,	$v_B = 14/98$
Dodecane	$u_B = 60/74$,	$v_B = 14/74$

Tompa† has given geometrical reasons for assuming the elements to be $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_3$. van der Waals‡ has given still

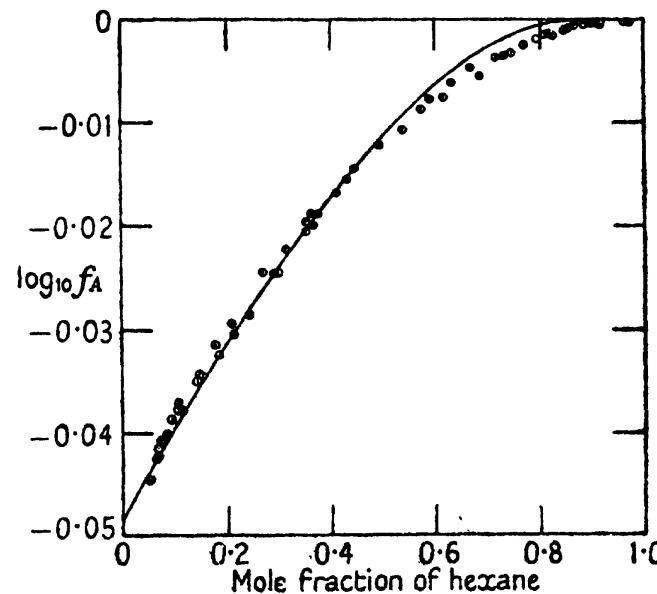


FIG. 11.2. Dependence on the composition of the activity coefficient of hexane in mixtures of hexane and hexadecane. \odot experimental data of Brönsted and Koefoed; — calculated by Tompa.

stronger reasons for choosing as elements $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_3$ groups. Since, however, both these proposals lead to molecules consisting of half-integral numbers of elements, which can have no geometrical interpretation, and since moreover the final effect on the extent of agreement between theory and experiment is unimportant we prefer to make the simple choice specified above.

In Figs. 11.2, 11.3, and 11.4 the experimental values of $\log_{10} f_A$ are compared with theoretical values obtained by Tompa using the values of u_A , v_A , u_B , v_B specified above. The curves shown are calculated using the following values of w/kT

Hexane/hexadecane	$w/kT = 0.975$
Heptane/hexadecane	$w/kT = 0.991$
Hexane/dodecane	$w/kT = 0.941$

† Tompa (1949), *Trans. Faraday Soc.* 45, 107.

‡ van der Waals and Hermans (1949), *Rec. Trav. Chim. Pays-Bas*, 68, 181.

These values were chosen independently in each case to give a good fit with experiment. According to the assumed model they should all be equal since all the molecules are assumed constructed of the same

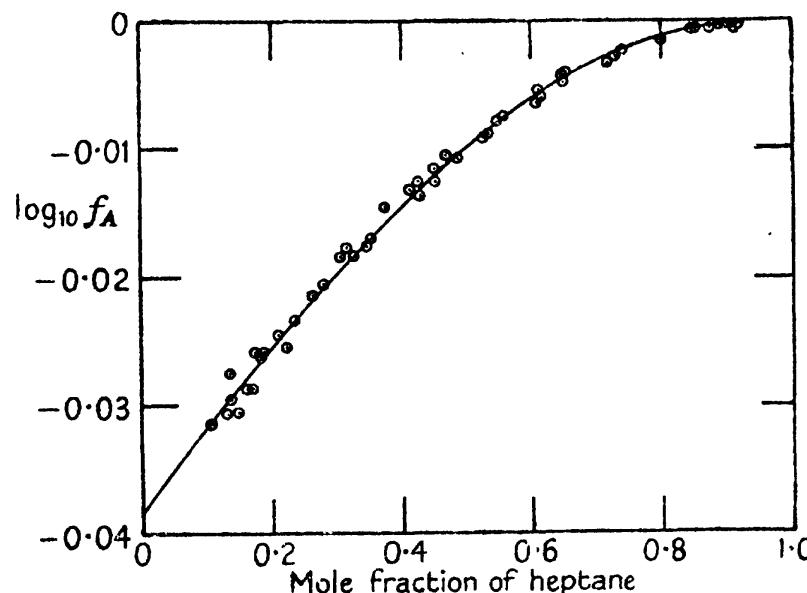


FIG. 11.3. Dependence on the composition of the activity coefficient of heptane in mixtures of heptane and hexadecane. \odot experimental data of Brönsted and Koefoed; —— calculated by Tompa.

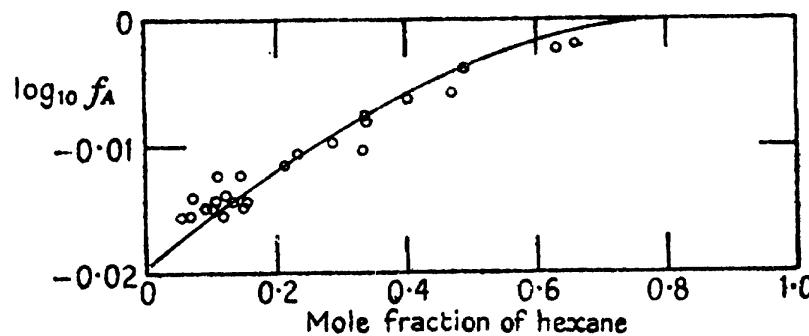


FIG. 11.4. Dependence on the composition of the activity coefficient of hexane in mixtures of hexane and dodecane. \odot experimental data of Brönsted and Koefoed; —— calculated by Tompa.

two kinds of elements. The fact that these independently fitted values of w/kT do in fact agree within ± 3 per cent. is striking.

Using these values of w/kT and assuming w independent of temperature Tompa has calculated the molar heat of mixing of an equimolar mixture, and these values can be compared with the values directly measured for two of the mixtures by van der Waals.[†] The comparison is given in Table 11.7. The agreement is far from good. It must be mentioned that van der Waals found that his measured values

[†] van der Waals (1950), Thesis, University of Groningen.

of the heats of mixing depended significantly on the temperature. This result is surprising and, up to the present, not understood. Until it has been explained a more detailed analysis of the experimental results does not seem justified.

TABLE 11.7

Comparison of $\Delta_m H$ for an Equimolar Mixture: (a) calculated from Values of w deduced from Vapour Pressures and (b) directly measured at 20° C.

	$\Delta_m H/\text{cal.}$	
	<i>Calculated</i>	<i>Measured</i>
Hexane/hexadecane	48.2	28.5
Heptane/hexadecane	33.2	26

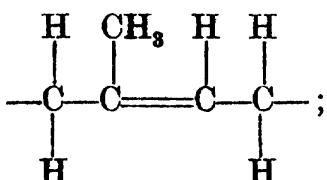
XII

SOLUTIONS OF MACROMOLECULES

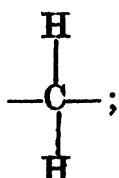
12.01. Introduction

The subject matter of this chapter is the study of solutions in ordinary non-polar solvents, such as benzene or carbon tetrachloride, of *macromolecules*, that is to say molecules having a molecular weight many hundred, sometimes many thousand, times that of the solvent. The most important macromolecules are polymers of simple unsaturated molecules. Examples are:

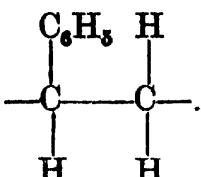
rubber, the polymer of isoprene, having the repeating unit



polythene, the polymer of ethylene, having the repeating unit



polystyrene, the polymer of styrene, having the repeating unit



Such substances have considerable practical importance as well as theoretical interest, and a vast amount of research, both experimental and theoretical, has been devoted to polymers during the past fifteen years. Accounts of this work are available in monographs† devoted entirely to polymers to which the reader specially interested in polymers must turn. No attempt will be made here to review, still less to discuss, most of this work. We shall on the contrary confine ourselves strictly to a study of the following question: to what extent can the equilibrium properties of solutions of polymers, or other macromolecules, in typical non-polar solvents be accounted for by the theory already

† For example Bawn (1948), *Chemistry of High Polymers*, Butterworth.

developed for ordinary chain-shaped r -mers without any new *ad hoc* assumptions? We shall find that this general theory already developed in the two preceding chapters gives a remarkably good semi-quantitative description of the actual behaviour of polymer solutions. The agreement between the theory in its simplest possible form and the experimental data is, however, far from accurate. The discrepancies can be reduced, but not eliminated, by making the theory more complicated and introducing new adjustable parameters.

12.02. Athermal mixtures

We shall initially neglect any heat of mixing and suppose the mixtures to be athermal. The equilibrium property most amenable to direct experimental measurement is the dependence of the vapour pressure of the solvent on the volume fraction of the polymer. We accordingly choose as our starting point formula (10.10.6). Replacing the subscript A by 1 for the solvent and the subscript B by p for the polymer, we can write this formula as

$$\frac{p_1}{p_1^0} = (1 - \phi) \left(1 - \phi + \frac{q_p r_1}{q_1 r_p} \phi \right)^{-\frac{1}{1-q_1}}, \quad (12.02.1)$$

where ϕ is the volume fraction of polymer defined by

$$\phi = \frac{r_p N_p}{r_1 N_1 + r_p N_p}. \quad (12.02.2)$$

At first sight it would seem that the simplest possible model would be that in which the solvent molecule is a monomer so that $r_1 = 1$, $q_1 = 1$. We shall, however, find that equally simple formulae are obtained† having a greater range of validity without imposing this restriction. We accordingly for the present leave the value of r_1 unspecified. If we vary the model by varying the value assigned to r_1 , then the value assigned to r_p must be simultaneously modified so as to keep the ratio r_p/r_1 equal to the ratio of the molecular volumes of polymer and solvent. It is convenient to denote this ratio by ρ so that

$$\frac{r_p}{r_1} = \rho. \quad (12.02.3)$$

According to the definition (10.08.1) of q_1 , q_p we have

$$q_1 = \left(1 - \frac{2}{z} \right) r_1 + \frac{2}{z}, \quad (12.02.4)$$

$$q_p = \left(1 - \frac{2}{z} \right) r_p + \frac{2}{z}, \quad (12.02.5)$$

† Gee (1947), *J. Chim. Phys.* **44**, 66.

from which it follows that

$$q_1 r_p - r_1 q_p = \frac{2}{z} (r_p - r_1) = \frac{2}{z} r_p \left(1 - \frac{1}{\rho}\right). \quad (12.02.6)$$

Substituting from (6) into (1) we obtain

$$\frac{p_1}{p_1^0} = (1-\phi) \left\{ 1 - \frac{2}{z q_1} \phi \left(1 - \frac{1}{\rho}\right) \right\}^{-\frac{1}{z q_1}}. \quad (12.02.7)$$

If now we introduce the abbreviation Z defined by

$$Z = z q_1, \quad (12.02.8)$$

formula (7) becomes

$$\frac{p_1}{p_1^0} = (1-\phi) \left\{ 1 - \frac{2}{Z} \phi \left(1 - \frac{1}{\rho}\right) \right\}^{-\frac{1}{Z}}. \quad (12.02.9)$$

We have thus obtained a relation between p_1/p_1^0 and the volume fraction ϕ in which the only parameters are Z and ρ . We see then that if we had unnecessarily imposed the restriction $r_1 = 1, q_1 = 1$ the final result (9) would have been unaffected; only the distinction between Z and z would have disappeared.

If we now assume that $\frac{1}{2}Z \gg 1$ we may replace (9) by

$$\frac{p_1}{p_1^0} = (1-\phi) \exp \left\{ \phi \left(1 - \frac{1}{\rho}\right) \right\}, \quad (12.02.10)$$

which we recognize as Flory's† approximation, already described in § 10.15. We shall to a great extent use Flory's approximation (10) instead of (9) for the following reasons:

1. Formula (10) is simpler and quicker to use than (9).
2. Formula (10) contains one less adjustable parameter through the disappearance of Z .
3. If $Z > 6$ the numerical difference between (9) and (10) is no greater than the discrepancy between experiment and formula (9). Anticipating comparison between experiment and theory, we may say that the rough agreement with the simpler formula is more impressive than any slight improvement in agreement when the more complicated formula is used.

We have already mentioned that the difference between (9) and (10) is not very important provided $Z > 6$. The difference is of course the less the greater Z . If further $q_1 > 1$, then the condition $\frac{1}{2}Z \gg 1$ is less restrictive than $\frac{1}{2}z \gg 1$. It is for this reason that we prefer not to impose the unnecessary restriction $r_1 = 1, q_1 = 1$. If, for example, z

† Flory (1942), *J. Chem. Phys.* 10, 51.

has the smallest likely value 6 corresponding to a simple cubic lattice, while $r_1 = 4$, then $q_1 = 3$ so that $\frac{1}{2}Z = 9$ which is sufficiently large for Flory's approximation to be good.

Formula (10) can in practice be still further simplified. For macromolecules ρ is at least several hundred and sometimes several thousand. Hence over almost the whole range of composition ρ^{-1} will be negligible compared with ϕ and we may then replace (10) by

$$\frac{p_1}{p_1^0} = (1-\phi)e^\phi \quad (\phi \gg \rho^{-1}). \quad (12.02.11)$$

We emphasize that this approximation is valid over the whole range of composition except for extremely small values of ϕ , namely ϕ comparable to or smaller than ρ^{-1} .

Whenever ϕ is small compared to unity, and in particular when ϕ is comparable to or smaller than ρ^{-1} , we may expand the exponential in (10) and retain only the leading terms. We thus find

$$\frac{p_1}{p_1^0} = 1 - \frac{\phi}{\rho} \quad (\phi \ll 1), \quad (12.02.12)$$

or
$$\frac{p_1^0 - p_1}{p_1^0} = \frac{\phi}{\rho} = \frac{N_p}{N_1 + \rho N_p} \quad (\phi \ll 1). \quad (12.02.13)$$

Since $\phi \ll 1$ implies $\rho N_p \ll N_1$ it follows that (13) does not differ significantly from

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{N_p}{N_1 + N_p} \quad (\phi \ll 1), \quad (12.02.14)$$

which means that at high dilutions, where $\phi \ll 1$, Raoult's law is obeyed even by macromolecules.

Since the accuracy of measurement of p_1 is roughly independent of the value of p_1 , the fractional accuracy of $p_1^0 - p_1$ decreases as the dilution increases. Consequently at high dilutions a more useful experimental quantity is the osmotic pressure Π . According to (1.06.5) this is related to p_1 by the thermodynamic formula

$$\Pi = \frac{RT}{V_1} \ln \frac{p_1^0}{p_1}, \quad (12.02.15)$$

where V_1 is the molar volume of the solvent. Substituting (10) into (15) we have

$$\frac{\Pi V_1}{RT} = -\ln(1-\phi) - \phi \left(1 - \frac{1}{\rho}\right) = \frac{\phi}{\rho} + \frac{1}{2}\phi^2 + \frac{1}{3}\phi^3 + \dots \quad (12.02.16)$$

The determination of molecular weight by measurement of osmotic pressure requires the evaluation of the first term in the series on the

right of (16). This term is negligible compared with later terms unless ϕ is comparable to ρ^{-1} or smaller still; hence the great difficulty of determining molecular weights of macromolecules by measurement of osmotic pressure.

12.03. Comparison with experiment

Extensive and accurate vapour pressure measurements have been made on the system rubber/benzene by Gee† and his collaborators. Their results are shown in Fig. 12.1, where p_1/p_1^0 is plotted against ϕ . On the same

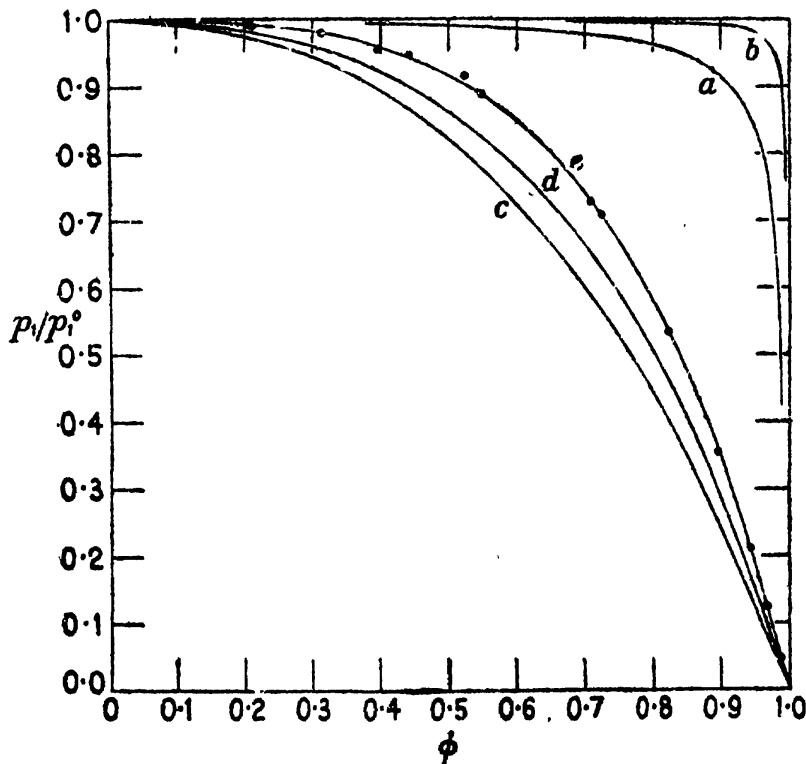


FIG. 12.1. Dependence of the vapour pressure of the solvent in polymer solutions on the volume fraction of polymer.
 a, Raoult's law for $\rho = 100$. b, Raoult's law for $\rho = 1000$.
 c, Flory's formula (12.02.11). d, Formula (12.02.9) with
 $Z = 6$ and ρ^{-1} negligible. e, Formula (12.04.17) with
 $w/kT = 0.43$. ○ Experimental data of Gee and his collabora-
 tors for rubber/benzene.

diagram are shown five curves. Curves *a* and *b* are calculated from Raoult's law for $\rho = 100$ and $\rho = 1000$ respectively. Curve *c* is calculated from Flory's formula (12.02.11) and curve *d* from formula (12.02.9) with $Z = 6$, the smallest physically acceptable value, and ρ^{-1} negligible. The remaining curve *e* which allows for an energy of interchange will be discussed later.

We see at once that there is not the remotest resemblance between the experimental curve and that of Raoult's law. Incidentally if we

† Gee and Treloar (1942), *Trans. Faraday Soc.* **38**, 147; Gee and Orr (1946), *Trans. Faraday Soc.* **42**, 507. Numerical values obtained privately from Gee.

use a larger more realistic value for ρ , then the Raoult's law curve will hug the axes still more closely. In contrast the general shape of the experimental curve has a striking resemblance to the theoretical curves for either $Z = \infty$ or $Z = 6$. There remains, however, a real and by no means negligible discrepancy between the theory and experiment. In view of this discrepancy the difference between the theory for

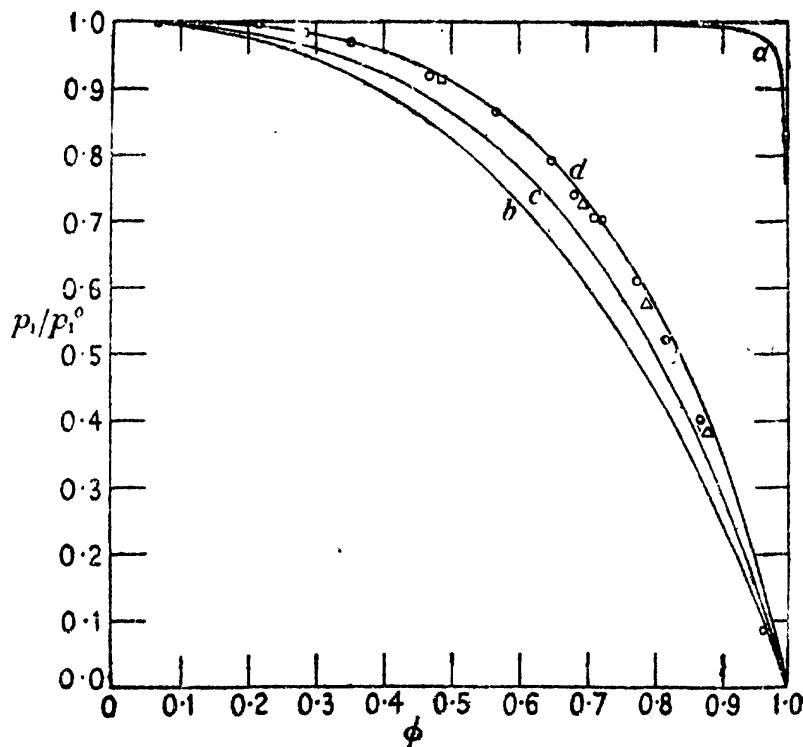


FIG. 12.2. Dependence of the vapour pressure of the solvent in polymer solutions on the volume fraction of polymer. *a*, Raoult's law for $\rho = 1000$. *b*, Flory's formula (12.02.11). *c*, Formula (12.02.9) with $Z = 6$ and ρ^{-1} negligible. *d*, Formula (12.04.17) with $\omega/kT = 0.38$. The experimental data are those of Bawn and his collaborators for polystyrene/toluene at three temperatures. \circ , 25°C.; Δ , 60°C.; \square , 80°C.

$Z = \infty$ and $Z = 6$ is unimportant. We shall henceforth for the sake of brevity and simplicity mostly use Flory's simpler version of the theory corresponding formally to $Z \rightarrow \infty$.

In Fig. 12.2 are shown similar data obtained by Bawn, Freeman, and Kamaliddin† on the system polystyrene/toluene. Once again we see a striking resemblance between the experimental results and the theoretical curves for either $Z = \infty$ or $Z = 6$ and no resemblance whatever with the curve corresponding to Raoult's law. The estimated molecular weight of the polystyrene was about 3×10^5 so that $\rho \approx 3000$ and the curve corresponding to Raoult's law hugs the axes even more than that

† Bawn, Freeman, and Kamaliddin (1950), *Trans. Faraday Soc.* **46**, 677.

shown for $\rho = 1000$. It should be noted that the experimental data for the three temperatures lie within the experimental error on a single curve. It follows that the heat of mixing of these solutions must be very small. We also observe that the best curve through the points for polystyrene/toluene is not very different from the best curve for rubber/benzene.

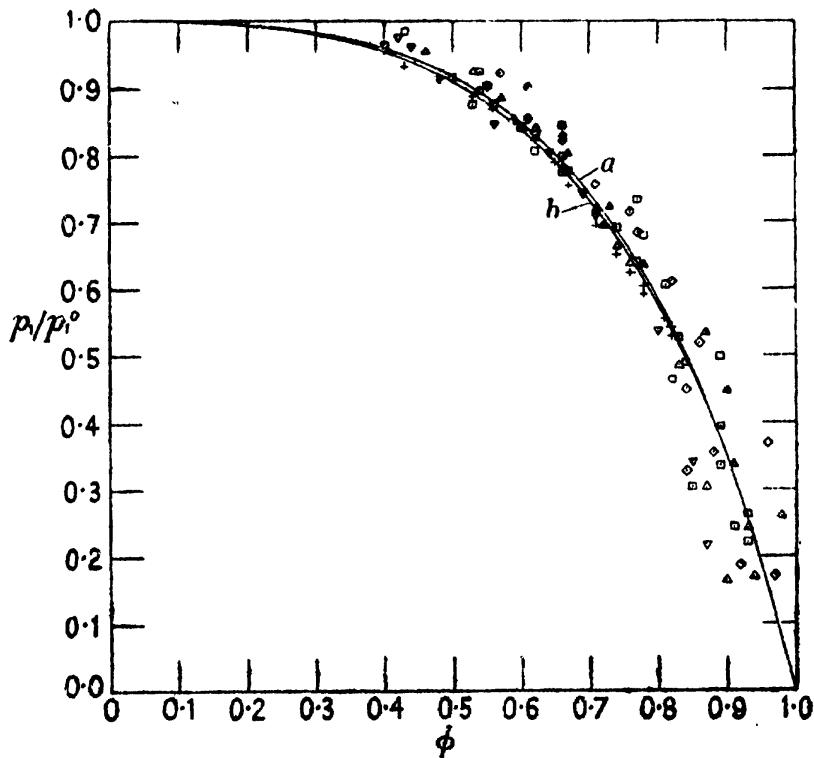


FIG. 12.3. Dependence of the vapour pressure of the solvent in polymer solutions on the volume fraction of polymer. Curve *a*, identical with curve *e* in Fig. 12.1, represents the data of Gee and his collaborators for rubber/benzene at 25° C. Curve *b*, identical with curve *d* in Fig. 12.2, represents the data of Bawn and his collaborators for polystyrene/toluene at several temperatures. Individual points represent data of Baughan for polystyrene in several solvents as follows: \square benzene; Δ toluene; ∇ *m*-xylene; $+$ carbon tetrachloride; \diamond dioxane.

We turn now to the more extensive but less accurate measurements of Baughan† on polystyrene with the five non-polar solvents benzene, toluene, *m*-xylene, carbon tetrachloride, and dioxane. These numerous measurements are shown plotted in Fig. 12.3. On the same diagram are included two smoothed curves, one through the experimental points of Bawn for polystyrene/toluene and the other through those of Gee and his collaborators for rubber/benzene. In spite of the scatter of the experimental points it is strikingly clear that they could all be represented roughly by a single curve which departs widely from Raoult's

† Baughan (1948), *Trans. Faraday Soc.* **44**, 495.

law. This means not only that the curve is roughly the same for five different non-polar solvents, but it is also the same for at least four quite different kinds of polymer molecules because Baughan's results include measurements on three different samples of polystyrene having molecular weights estimated roughly as twenty thousand, two hundred thousand, and five hundred thousand.

This rough superposition of the data for several polymers and five solvents suggests that the discrepancy between experiment and Flory's theoretical curve is due to some general fundamental cause rather than to the neglect of the heat of mixing. We shall see in later sections that the discrepancy can be reduced by introducing corrections for a non-zero heat of mixing, but as these corrections are partly empirical and contain an adjustable parameter they should not be taken too seriously. The striking success of the theory is the similarity between the experimental curve and Flory's curve, which contains no adjustable parameter whatever, as opposed to the complete contrast between the experimental curve and Raoult's law. Further successes obtained by elaboration of the theory are comparatively slight.

12.04. Mixtures not athermal

We shall now consider what modifications to the formulae are to be expected when the heat of mixing is not zero. We begin by obtaining an estimate of the maximum heat of mixing likely to be met in the systems under consideration. For the purpose of this estimate we assume that the solvent molecule is a monomer and that the polymer molecule is homogeneous in the sense defined in § 11.01. We recall that for such a mixture the temperature T_c of critical mixing is determined by equation (11.10.15),

$$e^{2w/zkT_c} = \frac{1}{2}\{1 + ab + (a^2 - 1)^{\frac{1}{2}}(b^2 - 1)^{\frac{1}{2}}\}. \quad (12.04.1)$$

According to the definitions (11.10.10), (11.10.11) of a , b we have

$$a = \frac{zq_1}{zq_1 - 2} = \frac{z}{z - 2}, \quad (12.04.2)$$

since we are assuming the solvent molecule to be a monomer, while for b we have

$$b = \frac{zq_p}{zq_p - 2} \simeq 1, \quad (12.04.3)$$

since for the polymer $2/zq_p$ is negligible compared with 1. Putting these values of a and b into (1) we obtain

$$e^{2w/zkT_c} = \frac{z - 1}{z - 2}, \quad (12.04.4)$$

or $\frac{w}{kT_c} = \frac{z}{2} \ln \frac{z-1}{z-2}$ (solution of polymer). (12.04.5)

We may contrast (5) with formula (4.12.13) for a regular mixture

$$\frac{w}{kT_c} = z \ln \frac{z}{z-2} \quad (\text{regular solution}). \quad (12.04.6)$$

In the limit $z \rightarrow \infty$ the value of w/kT_c is thus only $\frac{1}{2}$ for a solution of a polymer whereas it is 2 for a regular solution. If z has the value 6, the smallest physically likely value corresponding to a simple cubic lattice, we have

$$\frac{w}{kT_c} = 3 \ln \frac{5}{4} = 0.669 \quad (z = 6). \quad (12.04.7)$$

Since all the systems considered in the previous section are completely miscible, we may safely conclude that for such systems $w/zkT_c \leq 0.11$. Consequently with amply sufficient accuracy for our present purpose we may neglect terms in the free energy of the second and higher orders in w/zkT . In other words, we may with sufficient accuracy use the zeroth approximation as defined in § 11.02. We recall that according to this approximation the entropy is the same as in an athermal system of the same composition while the total energy of the mixture exceeds that of the unmixed components by

$$\Delta U = \frac{q_1 N_1 q_p N_p}{q_1 N_1 + q_p N_p} w. \quad (12.04.8)$$

The partial molar energy U_1 of the solvent in the mixture is then related to the molar energy U_1^0 of the pure solvent by

$$U_1 - U_1^0 = \frac{\partial}{\partial N_1} \Delta U = \left(\frac{q_p N_p}{q_1 N_1 + q_p N_p} \right)^2 q_1 w. \quad (12.04.9)$$

If we assume that the solvent is a monomer, then $r_1 = 1$, $q_1 = 1$ and $q_p/r_p \simeq (z-2)/z$ so that (9) reduces to

$$U_1 - U_1^0 = \left(\frac{q_p N_p}{N_1 + q_p N_p} \right)^2 w = \left(\frac{r_p N_p}{z N_1 / (z-2) + r_p N_p} \right)^2 w. \quad (12.04.10)$$

We can rewrite (10) in terms of the volume fraction ϕ of polymer as

$$U_1 - U_1^0 = \left\{ \frac{\phi}{z(1-\phi)/(z-2) + \phi} \right\}^2 w = \left\{ \frac{(z-2)\phi}{z-2\phi} \right\}^2 w. \quad (12.04.11)$$

Formula (11) gives the simplest expression for U_1 which is consistent with the quasi-crystalline model used. It is the formula which should be used for comparison with experimental values of the heat of dilution,

but reliable and accurate experimental values of this quantity are not available for the systems under consideration. For rough comparisons we may replace (11) by its limiting form for $z \rightarrow \infty$, namely

$$U_1 - U_1^0 = \phi^2 w. \quad (12.04.12)$$

Formula (12) is the only one yet used in the analysis of experimental data.

Flory's formula (12.02.10) is equivalent to

$$S_1 - S_1^0 = -\ln(1-\phi) - \phi \left(1 - \frac{1}{\rho}\right), \quad (12.04.13)$$

and in this form it is, in the zeroth approximation, still applicable to mixtures which are not athermal. Combining (12) with (13) we deduce

$$\frac{F_1 - F_1^0}{RT} = \ln(1-\phi) + \phi \left(1 - \frac{1}{\rho}\right) + \frac{w}{kT} \phi^2, \quad (12.04.14)$$

or in terms of vapour pressures

$$\ln \frac{p_1}{p_1^0} = \ln(1-\phi) + \phi \left(1 - \frac{1}{\rho}\right) + \frac{w}{kT} \phi^2. \quad (12.04.15)$$

The corresponding formula for the osmotic pressure is

$$\frac{\Pi V_1}{RT} = -\ln(1-\phi) - \phi \left(1 - \frac{1}{\rho}\right) - \frac{w}{kT} \phi^2. \quad (12.04.16)$$

Except in the region of extreme dilution, say $\phi \leq 0.001$, we may neglect ρ^{-1} compared with ϕ and replace (15) by

$$\ln \frac{p_1}{p_1^0} = \ln(1-\phi) + \phi + \frac{w}{kT} \phi^2, \quad (12.04.17)$$

and the corresponding formula for the osmotic pressure Π is

$$\frac{\Pi V_1}{RT} = -\ln(1-\phi) - \phi - \frac{w}{kT} \phi^2 = \left(\frac{1}{2} - \frac{w}{kT}\right) \phi^2 + \frac{1}{3} \phi^3 + \frac{1}{4} \phi^4 + \dots \quad (12.04.18)$$

12.05. Comparison with experiment

We now compare formula (12.04.17) with the experimental data for rubber/benzene, one of the systems for which the experimental measurements are most accurate and complete. The comparison between the values of p_1/p_1^0 measured at 25° C. by Gee† and his collaborators and the values calculated by means of formula (12.04.17) when the parameter w/kT is assigned the value 0.43 is shown by curve *e* in Fig. 12.1 and also in Table 12.1. The agreement between the experimental and calculated values is rather striking.

† Gee and Treloar (1942), *Trans. Faraday Soc.* **38**, 147; Gee and Orr (1946), *Trans. Faraday Soc.* **42**, 507.

TABLE 12.1

Comparison of Observed and Calculated Partial Vapour Pressures of Benzene over the System Rubber/Benzene

ϕ Volume fraction of rubber	p_1/p_1^0 experiment	p_1/p_1^0 calculated	Reference
0.119	0.998	0.998	G. and O.
0.205	0.993	0.994	G. and O.
0.211	0.990	0.993	G. and T.
0.312	0.979	0.980	G. and O.
0.395	0.956	0.960	G. and T.
0.441	0.948	0.945	G. and O.
0.524	0.916	0.905	G. and O.
0.549	0.890	0.889	G. and T.
0.710	0.729	0.733	G. and T.
0.727	0.719	0.709	G. and T.
0.823	0.534	0.539	G. and T.
0.894	0.352	0.365	G. and T.
0.945	0.212	0.208	G. and T.
0.969	0.124	0.122	G. and T.
0.988	0.048	0.050	G. and T.

G. and O. denotes Gee and Orr.

G. and T. denotes Gee and Treloar.

At volume fractions of rubber less than 0.1 the value of p_1/p_1^0 is so near to unity that it is difficult to obtain useful information from measurements of vapour pressure. At high dilutions measurements of osmotic pressure are more useful. Measurements of the osmotic pressure of solutions of rubber in benzene at high dilutions have been made recently by Freeman.[†] In Fig. 12.4 the experimental values of $\Pi V_1/RT$ are shown plotted against ϕ^2 . According to formula (12.04.18) we should expect the curve to be not greatly different from a straight line through the origin with an initial slope $(\frac{1}{2} - w/kT)$. The curve shown has been calculated from formula (12.04.18) using the value $w/kT = 0.41$, as compared with the value 0.43 which fitted the vapour pressure measurements.

The question now arises whether the term $\phi^2 w/kT$ really represents a heat of dilution or is just an empirical correction to the formula for athermal mixtures. A satisfying answer to this question requires accurate measurements of the heat of mixing and unfortunately these measurements do not exist. Such measurements are difficult owing to the considerable time required for the attainment of equilibrium. The best we can do is to use experimental data at 16° C. for the heat of mixing.

[†] Private communication from Dr. Gee.

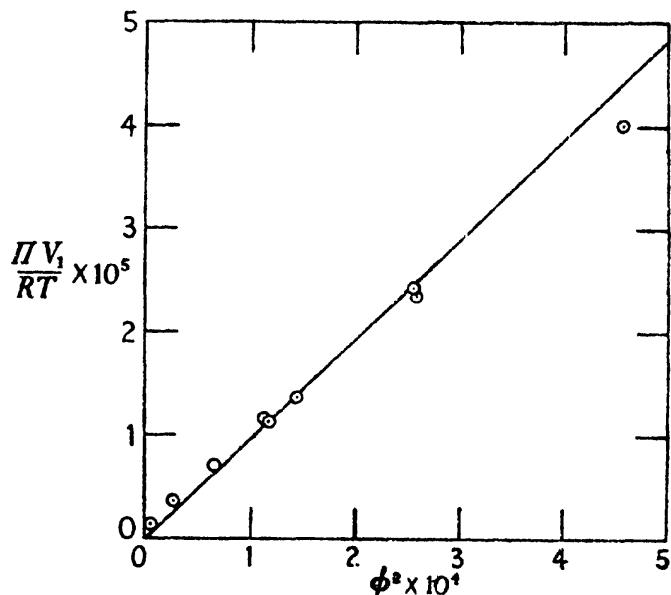


FIG. 12.4. Dependence on the volume fraction of rubber of the osmotic pressure of solutions of rubber in benzene. \circ experimental data of Gee and his collaborators; —— calculated from formula (12.04.18) with $w/kT = 0.41$.

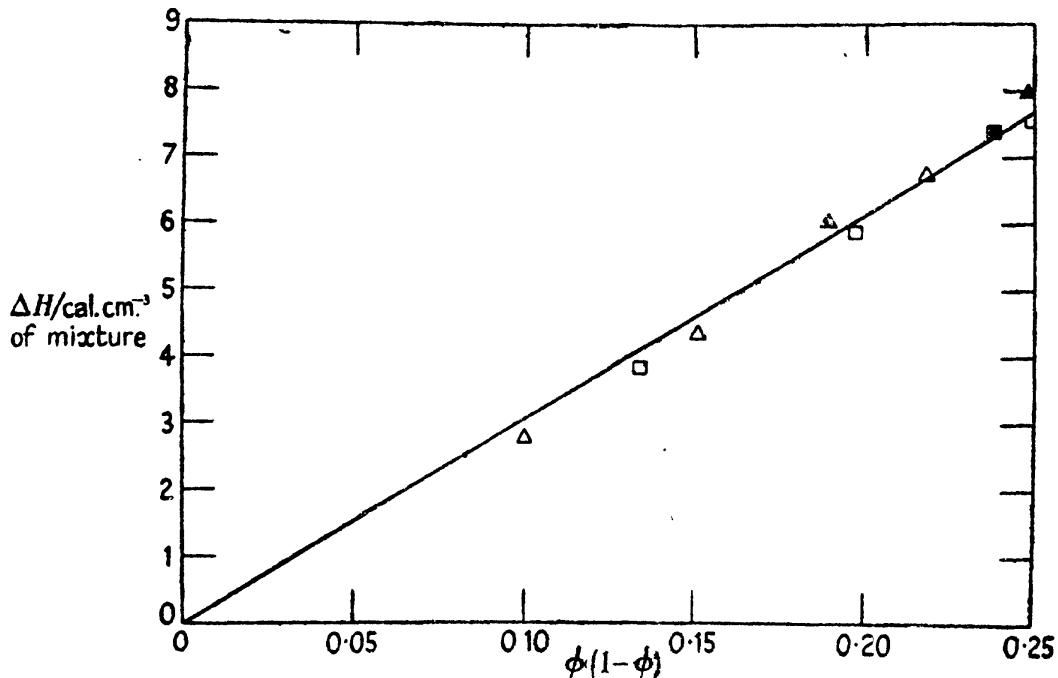


FIG. 12.5. Heat of mixing per unit volume of polyisoprene and benzene plotted against $\phi(1-\phi)$ where ϕ is the volume fraction of polyisoprene. The open symbols represent measurements with $\phi < \frac{1}{2}$ and the filled symbols those with $\phi > \frac{1}{2}$. Triangles and squares correspond to two series of measurements. The straight line has a slope of 3.1 cal. cm.⁻³

with benzene of polyisoprene, a lower homologue of rubber. The measurements by Miss Ferry† are shown in Fig. 12.5, where the heat of mixing per unit volume of mixture is plotted against the product $\phi(1-\phi)$, where

† Gee and Orr (1946), *Trans. Faraday Soc.* 42, 508.

ϕ denotes the volume fraction of the polyisoprene. According to formula (12.04.8), ignoring the distinction between q and r and that between H and U , we have for the mixing process

$$\Delta H = \phi(1-\phi)Nw \quad (12.05.1)$$

for a volume of mixture equal to the molar volume of benzene. With the method of plotting used in Fig. 12.5 every value of the abscissa represents two values of ϕ , one greater, the other less than $\frac{1}{2}$. If formula (1) is a good representation of the experiments we should expect both sets of points, namely those for $\phi < \frac{1}{2}$ and those for $\phi > \frac{1}{2}$, to be on the same straight line through the origin. It is evident that this requirement is fulfilled at least approximately. The straight line shown has a slope 3.1 cal./cm.³ Since for benzene $V_1 = 90$ cm.³, we have $Nw = 279$ cal. and so $w/kT = Nw/RT = 279/574 = 0.49$. This value is to be compared with the value 0.43 obtained from vapour pressure measurements and 0.41 obtained from osmotic pressure measurements.

It is noticeable in Fig. 12.5 that there is a small but systematic deviation from the straight line of the points representing low values of ϕ . Possible explanations of this have been discussed by Gee† and his collaborators. For these refinements of the theory we must refer the reader to the original papers.

For several systems other than rubber/benzene the situation is similar but rather less satisfactory. In particular we may usefully consider the measurements made by Bawn, Freeman, and Kamaliddin‡ of osmotic pressures in solutions of various polystyrenes in toluene. The volume fractions ϕ in these solutions were so small that ρ^{-1} may not be neglected compared to ϕ . Consequently we must use formula (12.04.16) rather than (12.04.18). There are thus two adjustable parameters ρ and w/kT . Of these we may expect ρ to vary from one polystyrene sample to another while w/kT should have the same value for all the samples. It has been shown§ that by assuming $w/kT = 0.443$ and various values for ρ all the measurements on twelve different polystyrene samples can be represented by formula (12.04.16). The comparison between calculated and observed values of $\Pi V_1/RT$ is shown in Table 12.2. For the sake of brevity only six samples of polystyrene are included, the two with the smallest molecules having $\rho^{-1} = 16.7 \times 10^{-4}$ and $\rho^{-1} = 12.6 \times 10^{-4}$, the two with largest molecules

† Gee (1947), *J. Chem. Soc.* 280.

‡ Bawn, Freeman, and Kamaliddin (1950), *Trans. Faraday Soc.* **46**, 862, supplemented by private communication from Bawn.

§ Guggenheim and McGlashan (1952), *Trans. Faraday Soc.* **48**.

TABLE 12.2

Comparison of Observed and Calculated Osmotic Pressures in Solutions of Various Polystyrenes in Toluene at 25° C.

Sample	<i>C</i> g./ml.	ϕ	$\frac{\Pi}{g./cm.^2}$ (exp.)	$10^6 \times \Pi V_1/RT$	
				exp.	calc.
$\frac{10^4}{\rho} = 16.7$	0.00165	0.00153	0.61	2.58	2.69
	0.00297	0.00275	1.16	4.91	5.03
	0.00480	0.00444	2.00	8.46	8.57
	0.00766	0.00709	3.52	14.90	14.82
$\frac{10^4}{\rho} = 12.6$	0.00161	0.00149	0.46	1.05	2.00
	0.00242	0.00224	0.70	2.96	3.11
	0.00310	0.00287	0.94	3.98	4.09
	0.00491	0.00455	1.62	6.86	6.94
	0.00785	0.00727	2.93	12.40	12.30
	0.01016	0.00941	4.16	17.61	17.18
$\frac{10^4}{\rho} = 3.57$	0.00155	0.00144	0.16	0.68	0.63
	0.00256	0.00237	0.28	1.18	1.17
	0.00293	0.00271	0.32	1.35	1.39
	0.00380	0.00352	0.47	1.99	1.98
	0.00538	0.00498	0.77	3.26	3.23
	0.00780	0.00722	1.36	5.78	5.68
	0.00868	0.00804	1.60	6.77	6.73
	0.00229	0.00212	0.23	0.97	0.97
$\frac{10^4}{\rho} = 3.35$	0.00349	0.00323	0.40	1.69	1.69
	0.00413	0.00382	0.50	2.12	2.13
	0.00464	0.00430	0.59	2.50	2.52
	0.00624	0.00578	0.92	3.89	3.90
	0.00785	0.00727	1.34	5.67	5.58
	0.00888	0.00822	1.65	6.98	6.79
	0.00260	0.00241	0.10	0.42	0.37
	0.00507	0.00469	0.32	1.35	1.36
$\frac{10^4}{\rho} = 0.15$	0.00516	0.00478	0.33	1.40	1.41
	0.00654	0.00606	0.52	2.20	2.26
	0.00919	0.00851	1.09	4.61	4.46
	0.00950	0.00880	1.17	4.95	4.78
	0.00427	0.00395	0.22	0.93	0.91
	0.00697	0.00645	0.58	2.45	2.46
$\frac{10^4}{\rho} = 0.0$	0.00900	0.00833	1.00	4.23	4.15
	0.01096	0.01015	1.53	6.47	6.22

having $\rho^{-1} = 0.0 \times 10^{-4}$ and $\rho^{-1} = 0.15 \times 10^{-4}$, and two of intermediate size having $\rho^{-1} = 3.57 \times 10^{-4}$ and $\rho^{-1} = 3.35 \times 10^{-4}$. The first column of the table specifies the sample of polystyrene and the value assumed for ρ^{-1} . The second column gives the concentration *C* in g./ml. and the third column the volume fraction ϕ . The fourth column gives the experimental value of the osmotic pressure Π . The fifth column gives the experimental value of $\Pi V_1/RT$ and the sixth column

the value calculated by formula (12.04.16) assuming the values of ρ^{-1} in the first column and $w/kT = 0.443$. The agreement is excellent.

We have already mentioned the vapour pressure measurements of the same authors† on solutions of polystyrene in toluene and these were plotted in Fig. 12.2. Curve *d* in this diagram has been calculated from formula (12.04.17) assuming $w/kT = 0.38$. The agreement between measured and calculated values is good, but we must point out that this value of w/kT is not the same as that used to fit the osmotic pressures at high dilutions. Moreover, the same value of w/kT is used to fit the vapour pressures over the whole temperature range from $T = 298^\circ$ to $T = 353^\circ$. If then w is truly an interchange energy its value must be almost exactly proportional to the temperature. Such a coincidence, though not impossible, is difficult to believe.

In conclusion we can hardly do better than quote the opinions of several authorities in this field.

Gee‡ says: 'It will be evident that a full comparison of theory and experiment is as yet hardly possible, and in particular much more accurate data are needed for the heats of dilution of rubber-liquid systems'; and again: 'Des mesures grossières de pression de vapeur pour un certain nombre de systèmes polymère-liquide donnent des valeurs relativement précises de l'énergie libre de dilution mais dans fort peu de cas on arrive à connaître même avec certitude le signe de la chaleur de dilution.'

Huggins§ has said: 'The empirical constant w/kT which must be used in most cases to obtain close agreement when ϕ is not small, approximately takes care of the heat of mixing effect, the difference between the entropy of mixing for infinite coordination number and that for small effective average coordination number, and any deviation from the complete randomness assumed in the theoretical treatment.' We particularly draw attention to the second word of this sentence.

We conclude with some more recent quotations from two monographs. Miller|| writes: 'This analysis provides a justification of the original assumption that in a first approximation it was reasonable to consider a system with zero energy of mixing. It also indicates that

† Bawn, Freeman, and Kamaliddin (1950), *Trans. Faraday Soc.* **46**, 677.

‡ Gee (1948), *Advances in Colloid Science*, vol. ii, p. 168, Interscience; (1947), *J. Chim. Phys.* **44**, 70.

§ Huggins (1942), *Ann. New York Acad. Sci.* **43**, 9.

|| Miller (1948), *Theory of Solutions of High Polymers*, p. 102, Oxford University Press.

the greater part of the divergence between the experimental results and the elementary theory which assumes random mixing must be due to some factor other than the non-zero energy or heat of mixing.' Bawn[†] writes: 'In spite of the success of the theoretical interpretation of $\frac{w}{kT}$ and its dependence on various factors, agreement with experiment is attained by assigning to w/kT an arbitrary value which does not agree with theory.'

The present author entirely concurs in these expressions of opinion. There seems little doubt that there is need for an improved theoretical model, but there is a far more urgent need for accurate and reliable measurements of heats of dilution. The experimental difficulties are great, but we can only hope that they are not insuperable.

[†] Bawn (1948), *Chemistry of High Polymers*, p. 126, Butterworth.

[‡] w/kT is our notation; Bawn's is different.

APPENDIX TO CHAPTER VII

7.28. AuCu superlattice

We have discussed in considerable detail the systems CuZn and AuCu₃. We have also mentioned Au₃Cu which behaves similarly† to AuCu₃. There is another alloy AuCu which exhibits a phase transition from a disordered to an ordered structure. Until recently the theory of this alloy has been rather neglected, possibly because the zeroth approximation wrongly predicts a lambda point instead of a phase transition. To obtain correct results one needs to apply the first approximation, that is to say the combinatorial or quasi-chemical method, to a tetrahedral group of four sites. We shall describe this treatment‡ which is analogous to that already applied to AuCu₃. This treatment is essentially equivalent to that described by Li.§ There are differences in details of algebra, but the conclusions are identical.

The lattice of AuCu may be described at least approximately as the same as that of AuCu₃. The face-centred cubic lattice may be regarded as composed of four interpenetrating simple cubic lattices, which we now rename as sub-lattices a_1 , a_2 , c_1 , c_2 . Every lattice site has $z = 12$ nearest neighbours of which $\frac{1}{2}z = 4$ are on each of the other three sub-lattices. A lattice site has no nearest neighbours on its own sub-lattice. We shall now describe the structure of AuCu using as previously the abbreviations A for Au and C for Cu. We consider a crystal containing $2N$ atoms A and $2N$ atoms C , that is $4N$ atoms in all. At high temperatures these atoms are distributed at random so that the four sub-lattices are indistinguishable. At low temperatures on the contrary all the A atoms are on the sub-lattices a_1 , a_2 and all the C atoms on the sub-lattices c_1 , c_2 . Our problem is to study the change from the completely disordered structure at high temperatures to the completely ordered structure at low temperatures. We shall find that, as for AuCu₃, there is an ordinary phase change with a discontinuity in the energy.

The ordered structure can be described as follows. The two sub-lattices a_1 , a_2 together constitute a lattice of planes; in each plane the sites form a square lattice and the distance between the planes is $\sqrt{2}$ times the side of a square. The two sub-lattices c_1 , c_2 together constitute a similar lattice. The planes of the a_1 , a_2 lattice and those of the c_1 , c_2 lattice alternate. Consequently the ordered structure of AuCu should be tetragonal, the sides of the unit cell being in the ratios $1:1:\sqrt{2}$.

† Hirabayashi (1951), *J. Phys. Soc. Japan*, 6, 129.

‡ McGlashan, unpublished work.

§ Li (1949), *J. Chem. Phys.* 17, 447.

Actually the formation of the ordered structure is accompanied by a distortion† so that the sides of the unit cell are in the ratios $1 \cdot 08 : 1 \cdot 08 : \sqrt{2}$. This deviation between $1 \cdot 08$ and 1 is inevitably ignored in the present theory.

7.29. First approximation

We consider a system of $\frac{1}{2}zN = 4N$ tetrahedral quadruplets of sites in order that the total number of pairs of neighbouring sites shall have the correct value $\frac{1}{2}z4N = 24N$ for a crystal of $4N$ sites, N on each of the four sub-lattices a_1, a_2, c_1, c_2 . For most purposes we do not need to distinguish between the two sub-lattices a_1, a_2 nor between the two sub-lattices c_1, c_2 and we then drop the subscripts 1, 2. We begin by constructing Table 7.9 which is analogous to Table 7.8. Since, however, the reader will by now be familiar with the technique of the combinatorial method we have taken some short cuts. Instead of first

TABLE 7.9

Distribution of Quadruplets and their Contributions to the Configurational Energy

Manner of occupation of group $a \ a \ c \ c$	Number of groups so occupied	Energy of all groups so occupied
$A \ A \ C \ C$	$\frac{1}{2}zN\nu\eta^{-4}$	$-\frac{1}{2}N\nu\eta^{-4}(6\chi_A + 6\chi_C + 4w_s)$
$A \ A \ A \ C$	$\frac{1}{2}zN\nu2\epsilon\eta^{-3}$	$-\frac{1}{2}N\nu2\epsilon\eta^{-3}(9\chi_A + 3\chi_C + 3w_s)$
$A \ C \ C \ C$	$\frac{1}{2}zN\nu2\epsilon\eta^{-3}$	$-\frac{1}{2}N\nu2\epsilon\eta^{-3}(3\chi_A + 9\chi_C + 3w_s)$
$A \ A \ A \ A$	$\frac{1}{2}zN\nu\epsilon^2$	$-\frac{1}{2}N\nu\epsilon^212\chi_A$
$C \ C \ C \ C$	$\frac{1}{2}zN\nu\epsilon^2$	$-\frac{1}{2}N\nu\epsilon^212\chi_C$
$A \ O \ A \ C$	$\frac{1}{2}zN\nu4\epsilon^2\eta^{-4}$	$-\frac{1}{2}N\nu4\epsilon^2\eta^{-4}(6\chi_A + 6\chi_C + 4w_s)$
$A \ C \ A \ A$	$\frac{1}{2}zN\nu2\epsilon^3\eta^{-3}$	$-\frac{1}{2}N\nu2\epsilon^3\eta^{-3}(9\chi_A + 3\chi_C + 3w_s)$
$C \ C \ A \ C$	$\frac{1}{2}zN\nu2\epsilon^3\eta^{-3}$	$-\frac{1}{2}N\nu2\epsilon^3\eta^{-3}(3\chi_A + 9\chi_C + 3w_s)$
$C \ C \ A \ A$	$\frac{1}{2}zN\nu\epsilon^4\eta^{-4}$	$-\frac{1}{2}N\nu\epsilon^4\eta^{-4}(6\chi_A + 6\chi_C + 4w_s)$

introducing parameters a, \dots, h of unspecified values and then minimizing the free energy by quasi-chemical equations between these parameters, we introduce a much smaller number of parameters such that the quasi-chemical equations between them are automatically satisfied. In other words we revert to Bethe's method for specifying the relative numbers of the several kinds of groups while retaining the combinatorial formula to give directly an explicit expression for the configurational free energy.

† Gorsky (1928), *Z. Physik*, 50, 64.

The second column in Table 7.9 is constructed as follows. The common factor $\frac{1}{2}zN$ represents the total number of tetrahedral groups considered. As usual there is a Boltzmann factor $\eta^{-1} = \exp(w_s/zkT)$ for each AC pair of neighbours in the tetrahedral group. There is also a factor ϵ for each atom on a wrong lattice, that is to say an A atom on a c lattice or a C atom on an a lattice. There are also numerical factors 2 or 4 to take account of the two equivalent a sites and the two equivalent c sites. Finally ν is a normalizing factor introduced to ensure that the total number of groups adds up correctly to $\frac{1}{2}zN$. The condition for this is

$$\nu^{-1} = \eta^{-4} + 4\epsilon\eta^{-3} + 2\epsilon^2 + 4\epsilon^2\eta^{-4} + 4\epsilon^3\eta^{-3} + \epsilon^4\eta^{-4}. \quad (7.29.1)$$

With ν thus defined the distribution given in Table 7.9 ensures that the total number of atoms of each kind is $2N$, that the total number of pairs of neighbouring sites is $\frac{1}{2}z4N$ and that the quasi-chemical equations for minimizing the free energy are satisfied. This is equivalent to saying that the configurational free energy is automatically minimized with respect to the parameter ϵ , when ν is defined by (1).

If as usual we denote the fraction of A atoms on a sites by r then by direct counting we have

$$\frac{r}{1-r} = \frac{\eta^{-4} + 3\epsilon\eta^{-3} + \epsilon^2 + 2\epsilon^2\eta^{-4} + \epsilon^3\eta^{-3}}{\epsilon\eta^{-3} + \epsilon^2 + 2\epsilon^2\eta^{-4} + 3\epsilon^3\eta^{-3} + \epsilon^4\eta^{-4}}. \quad (7.29.2)$$

Formula (2) determines ϵ for given r and η , that is to say for given r and w_s/zkT .

The combinatorial factor $g(N, r, \eta)$ takes the form

$$\begin{aligned} g(N, r, \eta) &= \frac{(2N)!}{\{2Nr\}! \{2N(1-r)\}!} \frac{(2N)!}{\{2Nr\}! \{2N(1-r)\}!} \times \\ &\times \frac{\{\frac{1}{2}zNr^4\}! [\{\frac{1}{2}zNr^3(1-r)\}!]^4 [\{\frac{1}{2}zNr^2(1-r)^2\}!]^2 [\{\frac{1}{2}zNr^2(1-r)^2\}!]^4}{\{\frac{1}{2}zN\nu\eta^{-4}\}! [\{\frac{1}{2}zN\nu\epsilon\eta^{-3}\}!]^4 [\{\frac{1}{2}zN\nu\epsilon^2\}!]^2 [\{\frac{1}{2}zN\nu\epsilon^2\eta^{-4}\}!]^4} \times \\ &\times \frac{[\{\frac{1}{2}zNr(1-r)^3\}!]^4 [\{\frac{1}{2}zN(1-r)^4\}!]}{[\{\frac{1}{2}zN\nu\epsilon^3\eta^{-3}\}!]^4 [\{\frac{1}{2}zN\nu\epsilon^4\eta^{-4}\}!]}, \end{aligned} \quad (7.29.3)$$

with ϵ determined by (2) and ν defined by (1). Factors in the numerator of (3) are obtained from the corresponding factors in the denominator by randomizing, which means replacing η by 1 and ϵ by $(1-r)/r$ and ν by r^4 . By using Stirling's theorem we can rewrite (3) more concisely as

$$\begin{aligned} \ln g(N, r, \eta) &= -4Nr \ln r - 4N(1-r) \ln(1-r) + \\ &+ \frac{1}{2}zN \{4r \ln r + 4(1-r) \ln(1-r) - \ln \nu - 4(1-r) \ln \epsilon\} - \\ &- \frac{4}{3}N\nu \frac{w_s}{kT} (\eta^{-4} + 3\epsilon\eta^{-3} + 4\epsilon^2\eta^{-4} + 3\epsilon^3\eta^{-3} + \epsilon^4\eta^{-4}). \end{aligned} \quad (7.29.4)$$

The contributions of the several groups to the configurational energy are given in the third column of Table 7.9. They are obtained by merely counting the numbers of atoms of each kind and the numbers of pairs of each kind in the tetrahedral group. By addition we obtain for the total configurational energy E_c ,

$$E_c = -2N\chi_A - 2N\chi_O - \frac{1}{2}N\nu w_s(\eta^{-4} + 3\epsilon\eta^{-3} + 4\epsilon^2\eta^{-2} + 3\epsilon^3\eta^{-1} + \epsilon^4\eta^0). \quad (7.29.5)$$

Combining (4) with (5) we obtain for the configurational free energy F_c ,

$$\begin{aligned} \frac{F_c(N, r, \eta)}{4NkT} = & r \ln r + (1-r) \ln(1-r) - \\ & - \frac{1}{2}z \{r \ln r + (1-r) \ln(1-r) - \frac{1}{2} \ln \nu - (1-r) \ln \epsilon\} - \frac{1}{2} \left(\frac{\chi_A}{kT} + \frac{\chi_O}{kT} \right), \end{aligned} \quad (7.29.6)$$

in which we recall that ϵ is determined by (2) and ν is defined by (1).

The equilibrium value of r is determined by minimizing the free energy. In doing this we make use of our knowledge that F_c is already minimized with respect to ϵ . We thus obtain immediately

$$\frac{1}{4NkT} \frac{\partial F_c(N, r, \eta)}{\partial r} = \ln \frac{r}{1-r} - \frac{1}{2}z \ln \frac{r}{1-r} - \frac{1}{2}z \ln \epsilon. \quad (7.29.7)$$

Hence for all stationary values of F_c we have the simple relation between ϵ and r

$$\epsilon = \left(\frac{1-r}{r} \right)^{1-3/z} \quad (F_c \text{ stationary}), \quad (7.29.8)$$

or when we put $z = 12$

$$\epsilon = \left(\frac{1-r}{r} \right)^{\frac{1}{12}} \quad (F_c \text{ stationary}). \quad (7.29.9)$$

We now consider the configurational total energy U_c which is equal to the equilibrium value of E_c given by (5). In the disordered state $r = \frac{1}{2}$ and this leads to $\epsilon = 1$. In an ordered state on the other hand the equilibrium values of ϵ and r are related by (9). Substituting this into (2) we obtain the equilibrium relation between ϵ and η . The equilibrium values of ν and of r for given η are then determined by (1) and (9) respectively. These values have then to be substituted into (5) to give U_c as a function of η , that is of w_s/zkT .

7.30. Numerical results

The formulae of the previous section are sufficient to determine all the equilibrium properties of the system. The rest is lengthy but straightforward calculation. For any given η or w_s/zkT and for each

value of r one calculates ϵ from formula (7.29.2) and then v from formula (7.29.1). These values substituted into (7.29.6) determine the configurational free energy.

By such calculations we obtain the dependence of the configurational free energy on r and this is shown for several temperatures in Fig. 7.10. It is found that there is a phase transition at a temperature T_t determined by

$$\eta_t^{-1} = 3.9251, \quad w_s/kT_t = 16.409.$$

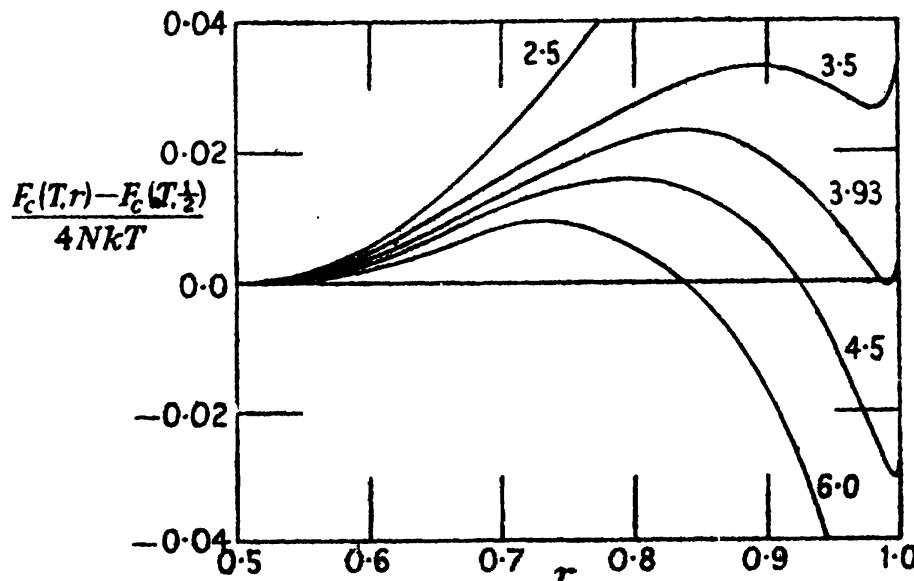


FIG. 7.10. Dependence of the configurational free energy $F_c(T, r)$ on r for the alloy $AuCu$, according to the first approximation for several temperatures. The numbers attached to the curves are values of $\eta_t^{-1} = \exp(w_s/12kT)$.

In this transition the equilibrium value of r jumps from its random value $\frac{1}{2}$ to the value $r^* = 0.9914$.

At temperatures above T_t the equilibrium value of r is $\frac{1}{2}$ while at temperatures below T_t the equilibrium values of r and ϵ are determined by equations (7.29.9) and (7.29.11). In both cases the configurational total energy can be calculated as a function of η or of w_s/zkT as described in the previous section. The relation thus obtained between U_c and the temperature is shown in Fig. 7.11.

Experimental data on AuCu are less extensive and less accurate than for AuCu₃. It is definitely established† that there is a phase change, not a lambda point, at 681° K. There are no direct calorimetric measurements under equilibrium conditions, but the energy of transition has recently been determined by Borelius, Larsson, and Selberg† as follows. The alloy was maintained at equilibrium about 20° above the transition

† Borelius, Larsson, and Selberg (1950), *Arkiv för Fysik*, 2, 161.

temperature and then rapidly chilled to a temperature below the transition temperature. The heat evolved as the alloy gradually attained its equilibrium ordered state was then measured. It was found that not one, but two rearrangements took place with well distinguished characteristic times. Until the nature of these two changes has been disentangled there is some uncertainty in the interpretation of the results.

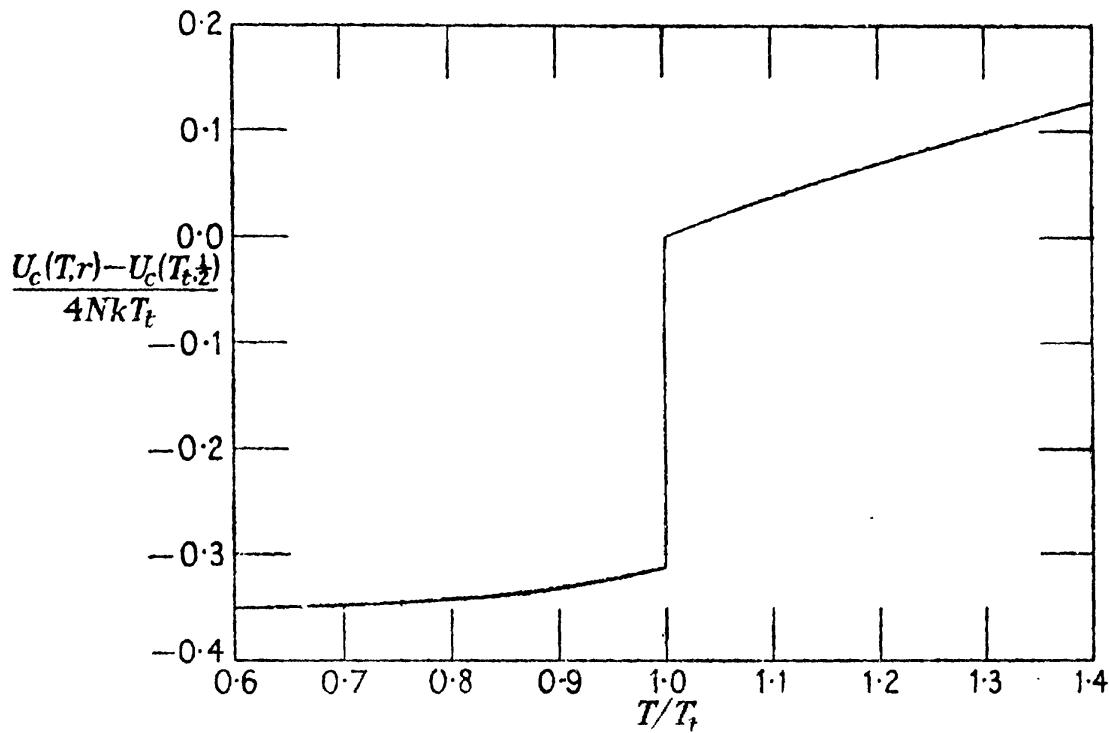


FIG. 7.11. Equilibrium configurational energy as function of temperature for the alloy A_2C_1 according to the first approximation.

Borelius considers that it is the heat in the combined changes which is relevant to the disorder-order rearrangement. If we accept this interpretation the experimental value of $\Delta U_c/4NkT_t$ is 0.43 as compared with the theoretical value 0.314.

A more definite test of the theory is afforded by the ratio of the transition temperatures for the three gold+copper alloys. The comparison between the theoretical and observed ratios is as follows:

		AuCu ₃	AuCu	Au ₃ Cu
T_t , experimental	664° K.	681° K.	516° K.
Ratios, experimental	:	1	1.03	0.78
Ratios, theoretical	:	1	0.889	1

The extent of agreement is not impressive. As we have already mentioned an adequate theory would need to take detailed account of the electronic structures of these alloys. It would also have to explain the change in spacing which accompanies the disorder-order transition in AuCu.

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