The Statistical Thermodynamics of Mixtures of Lennard-Jones Molecules. I. Random Mixtures

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THE STATISTICAL THERMODYNAMICS OF MIXTURES OF LENNARD-JONES MOLECULES

I. RANDOM MIXTURES

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CONTENTS

This paper describes a development in the statistical theory of mixtures of spherical molecules. It is shown that for a mixture of molecules interacting according to the Lennard-Jones inverse-power potential, the assumption of random mixing is sufficient to relate the thermodynamic properties of the mixture *exactly* to those of a reference substance, after the manner of the law of corresponding states; and it is proved in an appendix that only the Lennard-Jones form of the potential energy function leads to this simple result. If the molar configurational Gibbs function of the reference substance is $G_0(T, P)$, then that of the random mixture is

$$G(T, P, x) = f_x G_0(T/f_x, Ph_x/f_x) - RT \ln h_x + RT \sum_\alpha x_\alpha \ln x_\alpha,$$

where x_α is the mole fraction of component α, and where f_x and h_x are dimensionless functions of the composition involving the characteristic molecular energy and size constants for the interactions of the various species.

This equation is used to discuss the phenomena peculiar to mixtures of substances, under the headings: mixing effects, phase equilibria, and critical phases. A necessary condition on the intermolecular forces for azeotropy to occur in binary mixtures is derived in a simple form which can be appreciated intuitively; the possibility of a lower critical solution point in these mixtures is examined

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and shown to be unlikely; and the difficulties in the way of deriving the critical or plait-point curve are outlined. The liquid mixing properties of the system carbon monoxide + methane are calculated from the theory, and shown to be in fair agreement with experiment.

The Gibbs function of the mixture is analyzed by a Taylor-series expansion, and it is shown that the first-order terms of the present theory are identical with those of the theory of conformal solutions, due to Longuet-Higgins, but that the second-order terms involve approximations, resulting from the assumption of random mixing. Expanded forms of the mixing functions are derived for the special class of binary mixtures whose characteristic energy and size constants obey geometric and arithmetic mean rules respectively, and the signs of these functions are discussed.

1. Introduction

During the last five or six years there have been two important advances in the statistical thermodynamics of liquid mixtures of small spherical molecules. They are the theory of conformal solutions, due to Longuet-Higgins (1951), and the cell theory of solutions, which has been developed by Prigogine and his colleagues (1950, 1953, 1956).

The importance of Longuet-Higgins's work may be described as primarily theoretical, and consisted in showing that a first-order perturbation treatment of the configuration integral for certain mixtures leads to a simple relation between the thermodynamic properties of the mixture and those of a single reference substance. The mixtures for which this is true are those whose various intermolecular energy functions obey an extended form of the relation, discovered by Pitzer (1939), leading to the law of corresponding states; these may be called *conformal mixtures*. Apart from this, no assumptions were made regarding the form of the intermolecular energy functions, or the structure of the liquid state. This first-order theory appeared to account for the existing data on non-polar solutions in a more or less quantitative manner, and had the distinction of relating the volume changes on mixing to the other mixing effects in a perfectly natural way. Since the theory is valid for all states of matter, it was also possible to apply it to liquid-vapour equilibrium phenomena, again with satisfactory results (Cook & Longuet-Higgins 1951). However, none of the mixtures to which the equations were applied could be said to consist of components which strictly satisfied two of the initial premises of the theory, namely, that the molecules are non-polar and spherically symmetrical. And, indeed, not long after the appearance of this theory, it was discovered by Prigogine and his colleagues that binary mixtures of certain strictly non-polar liquids of similar molar volume, such as *neo*-pentane and carbon tetrachloride, do not obey one of the dominant qualitative features of the first-order theory: that if the heat and volume of mixing are not zero, they must have the same sign. In fact, *neo*-pentane and carbon tetrachloride, and many other pairs of liquids discovered more recently, cool and contract when mixed (Mathot & Desmyter 1953; Thacker & Rowlinson 1953).

The cell theory of solutions has had the striking success of predicting and accounting for this unexpected behaviour of mixtures of non-polar molecules of the same size. This theory, which is an extension of the cell theory of pure liquids introduced by Lennard-Jones & Devonshire (1937), assumes that the molecules interact according to the central inverse-power potential used by Lennard-Jones, and that the distribution of the different molecules among the cells of the lattice is a random one. Although this last assumption is not actually necessary, it has been shown by Prigogine & Garikian (1950) and by Salsburg & Kirkwood

(1952) that on the cell theory the corrections introduced by deviations from random mixing are generally small, at least for molecules of the same size. In the absence of exact information it is also assumed that the characteristic molecular energy and size parameters for the interaction of two different molecules are the geometric and arithmetic means respectively of those of the pure components; this choice is associated with the dispersion forces between strictly non-polar molecules. In Longuet-Higgins's treatment, only the arithmetic mean relation for the sizes was assumed, and the intercomponent energy parameters were left as empirical constants. A first-order treatment is not sufficient when both the geometric and the arithmetic mean relations are assumed, since the leading terms in the mixing functions are then of the second order in differences between the molecular energy and size parameters. The success of Prigogine's theory therefore means that it gives correctly the sign and approximate magnitude of these second-order terms. On the other hand, the dependence of the results obtained on the cell model, the effective restriction of the equations to the liquid state, and the approximations introduced to deal with molecules of different size, are most unsatisfactory features of the theory.

The object of this paper is to show that for mixtures of Lennard-Jones molecules, the use of the cell model for the liquid state is in fact unnecessary, and that the assumption of random mixing is in itself sufficient to relate the thermodynamic properties of the mixture exactly to those of a reference substance, after the manner of the law of corresponding states. The theory developed has the theoretical advantage of Longuet-Higgins's treatment, in that it requires no assumptions regarding the state of matter concerned, and is therefore applicable to gases and liquids; and the practical advantage of the cell theory, since it can account, at least qualitatively, for the mixing effects in solutions of strictly non-polar liquids.

2. Statistical method

The treatment about to be described is based on the fundamental equation of classical statistical mechanics for the Helmholtz free-energy function of a petit ensemble of systems canonically distributed in phase (Gibbs 1902). For the system we are considering, which consists of N molecules whose mutual interactions are conservative, additive and central, the integrations over internal phases of the molecules and their translational momenta can be separated out and performed, to leave the integral

$$\exp\left(-\frac{F}{kT}\right)=\frac{1}{N_1!\,N_2!\,\ldots\,N_c!}\int\exp\left(-\frac{\mathscr{U}}{kT}\right)\mathrm{d}Q, \tag{2·1}$$

where N_α is the number of molecules of species α, and the system contains c components. This integral relates the configurational free energy F of the system to its potential energy function $\mathscr{U}$, and is over all configurations Q described by the N position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ of the molecules, within the volume V to which the system is confined. The total free-energy function is the sum of the configurational free energy and a part due to the internal degrees of freedom of the molecules and their translational motion. Since the latter can be easily evaluated, the major problem in statistical thermodynamics is to obtain information about the configurational free-energy function from equation (2·1).

No attempt will be made in this paper to evaluate the configuration integral for a mixture, and indeed this problem has not yet been solved for a pure liquid. All that we shall do is to relate the configurational free energy, $F(T, V, x)$, of certain mixtures, to that of a reference system of N identical molecules, $F_0(T, V)$, by means of the assumption of random mixing, which we now go on to consider.

3. Random-mixing approximation

The random mixing of molecules in a solution is not usually discussed until a model for the liquid state has been laid down; and this model generally involves a lattice. The idea then is simply that the probability of finding a molecule of species α on any lattice position is N_α/N, regardless of its environment; that is, to whatever species the neighbouring molecules belong. Our object here is to extend this idea to petit ensemble theory, in which the molecules of a system are not confined to any particular configuration, such as a lattice, but are distributed canonically among all possible configurations; that is, with the canonical or Boltzmann distribution function, proportional to $\exp(-\mathscr{U}/kT)$. It is clear that in this general case, the concept of random mixing is best approached directly through the potential energy function for the system, $\mathscr{U}(Q)$, and we shall therefore discuss it from this point of view.

The potential energy of a mixture of molecules, $\mathscr{U}(Q; \tau)$, depends in general on the assignment τ of the various kinds of molecules to the N position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ defining a geometrical configuration Q of the system. It is only independent of the molecular assignment for a mixture of isotopic components, and only such a mixture is strictly ideal; this is, in fact, the statistical condition for ideality.† It is therefore evident that the molecules of an ideal mixture are distributed randomly among the N positions of every geometrical configuration Q, since all such distributions or assignments have the same statistical weight. However, as we have just seen, this is never true for a non-isotopic solution, and it follows that the concept of random mixing in a non-ideal solution can only refer to an approximation, and must be defined. In view of the above remarks, we define the random-mixing approximation as that in which the properties of the system are calculated by substituting for the actual potential function $\mathscr{U}(Q; \tau)$, its *a priori* average over all assignments τ, which we shall denote simply by $\langle\mathscr{U}\rangle$. This definition evidently implies a random distribution of molecules in every geometrical configuration of the system. The approximate configurational free-energy function is defined by an equation similar to (2·1), namely,

$$\exp\left(-\frac{F}{kT}\right) = \frac{1}{N_1!\,N_2!\ldots N_c!}\int \exp\left(-\frac{\langle\mathscr{U}\rangle}{kT}\right)\mathrm{d}Q. \tag{3·1}$$

The next step is to derive an expression for the randomized potential energy function $\langle\mathscr{U}(Q)\rangle$ in terms of the intermolecular energy functions for the interaction of the various molecules. For the system we are considering, in which the molecular forces are additive, the total potential energy $\mathscr{U}$ in any configuration is the sum, over all pairs of positions, of the interaction energies u^{ik} of the molecules in position i and k, that is,

$$\mathscr{U} = \sum_{i>k}\sum u^{ik}. \tag{3·2}$$

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† This can be seen most easily from the fundamental equation for a grand canonical ensemble of multicomponent systems, when it leads directly to the well-known equations defining an ideal mixture:

$$\mu_\alpha = \mu_\alpha^0(T, P) + RT\ln x_\alpha \quad (\alpha = 1, 2, \ldots, c).$$

The randomized total potential energy is therefore

$$\langle \mathscr{U} \rangle = \sum_{i>k} \sum \langle u^{ik} \rangle, \tag{3·3}$$

where $\langle u^{ik} \rangle$ is the average interaction energy between the molecules in positions i and k. Now since the molecules are distributed randomly in every geometrical configuration Q, the probability that positions i and k are occupied by molecules of species α and β is simply $x_\alpha x_\beta$, where x_α is the mole fraction of species α, equal to N_α/N. Therefore, if $u_{\alpha\beta}(r)$ is the mutual potential energy of a molecule of species α and a molecule of species β, at a distance r apart, when i and k are occupied by molecules of species α and β they contribute $x_\alpha x_\beta u_{\alpha\beta}(r_{ik})$ to the average energy $\langle u^{ik} \rangle$, where $r_{ik} = |\mathbf{r}_i - \mathbf{r}_k|$. Hence

$$\langle u^{ik} \rangle = \sum_\alpha \sum_\beta x_\alpha x_\beta u_{\alpha\beta}(r_{ik}). \tag{3·4}$$

By substituting into equation (3·3) we get

$$\langle \mathscr{U} \rangle = \sum_{i>k} \sum \sum_\alpha \sum_\beta x_\alpha x_\beta u_{\alpha\beta}(r_{ik}). \tag{3·5}$$

The derivation of this equation may not appear rigorous, but the same result is obtained by a strictly mathematical method in part II.

These equations reveal the considerable simplification produced by the random-mixing approximation. This simplification arises from equation (3·3) for $\langle \mathscr{U} \rangle$, which has the form of the total potential energy for a system of N identical molecules whose intermolecular energy function is $\langle u(r) \rangle$. From the standpoint of statistical thermodynamics, a random mixture is equivalent to a strictly ideal mixture of the same composition, whose isotopic components have identical intermolecular energy functions, $\langle u(r) \rangle$, given by equation (3·4). The configurational free energy $F_x(T, V)$ of any one of these components, which may be called the *equivalent substance for composition* x, is given by the integral

$$\exp\left(-\frac{F_x}{kT}\right) = \frac{1}{N!}\int \exp\left(-\frac{\langle \mathscr{U} \rangle}{kT}\right) \mathrm{d}Q; \tag{3·6}$$

and therefore, by equation (3·1), the configurational free energy of the random mixture is

$$F(T, V, x) = F_x(T, V) + RT \sum_\alpha x_\alpha \ln x_\alpha. \tag{3·7}$$

However, since there is a different equivalent substance for each composition, the simplification cannot be exploited unless the various free-energy functions F_x can be related in some way. The possibility of such relations evidently depends on the form of the intermolecular energy functions, and in the next section we shall choose a basic form which makes the desired interrelations possible.†

4. Lennard-Jones molecules

For a system of molecules interacting according to the Lennard-Jones inverse-power potential, the random-mixing approximation leads to particularly simple results. This potential can be written in the form (see Fowler & Guggenheim 1939)

$$u(r) = -\mu/r^m + \nu/r^n \quad (n>m), \tag{4·1}$$

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† The problem of finding a suitable form for the intermolecular energy functions is attacked *a priori* in an appendix.

where μ and ν are two positive constants, or alternatively as

$$u(r) = u^*\left[\frac{n}{n-m}\left(\frac{r^*}{r}\right)^m - \frac{m}{n-m}\left(\frac{r^*}{r}\right)^n\right], \tag{4·2}$$

where u^* (<0) is the minimum energy, and r^* the corresponding distance. These quantities are related to the attractive and repulsive energy constants μ and ν by the equations

$$u^* = -(n-m)\left(\frac{\mu}{n}\right)^{n/(n-m)}\left(\frac{m}{\nu}\right)^{m/(n-m)} \quad \text{and} \quad r^* = \left(\frac{n\nu}{m\mu}\right)^{1/(n-m)}. \tag{4·3}$$

We suppose that the different pairs of molecular species interact with potentials of the form (4·1) having the same indices n and m, but different attractive and repulsive energy constants, $\mu_{\alpha\beta}$ and $\nu_{\alpha\beta}$, and therefore different characteristic energies and sizes, $u^*_{\alpha\beta}$ and $r^*_{\alpha\beta}$. It follows immediately from the above formulae that such a system is a particular example of a conformal mixture (Longuet-Higgins 1951), defined as one in which

$$u_{\alpha\beta}(r) = f_{\alpha\beta}u_{00}(r/g_{\alpha\beta}) \quad (\alpha, \beta = 1, 2, \ldots, c), \tag{4·4}$$

where $f_{\alpha\beta}$ and $g_{\alpha\beta}$ are positive dimensionless constants, and $u_{00}(r)$ is the potential for some reference species;† the energy parameter $f_{\alpha\beta}$ is the ratio of the potential minimum of the α-β interaction to that of two reference molecules, and the size parameter $g_{\alpha\beta}$ is the ratio of the corresponding distances. For the special case in which the intermolecular potential functions are of the form (4·1), we find by means of (4·3) that the interaction parameters $f_{\alpha\beta}$ and $g_{\alpha\beta}$ are related to the constants introduced above by the equations

$$\left.\begin{aligned} f_{\alpha\beta} &= \frac{u^*_{\alpha\beta}}{u^*_{00}} = \left(\frac{\mu_{\alpha\beta}}{\mu_{00}}\right)^{n/(n-m)}\left(\frac{\nu_{00}}{\nu_{\alpha\beta}}\right)^{m/(n-m)}, \\ \text{and} \qquad g_{\alpha\beta} &= \frac{r^*_{\alpha\beta}}{r^*_{00}} = \left(\frac{\mu_{00}\nu_{\alpha\beta}}{\mu_{\alpha\beta}\nu_{00}}\right)^{1/(n-m)}, \end{aligned}\right\} \tag{4·5}$$

where μ_{00}, ν_{00} and u^*_{00}, r^*_{00} are the corresponding (arbitrary) constants for the reference substance.

The significance of the random-mixing approximation for mixtures of Lennard-Jones molecules can be seen immediately by combining equation (3·4) for the average potential $\langle u\rangle$ with an equation like (4·1) for the $u_{\alpha\beta}$, when we get

$$\langle u(r)\rangle = -\langle\mu\rangle/r^m + \langle\nu\rangle/r^n, \tag{4·6}$$

where

$$\langle\mu\rangle = \sum_\alpha\sum_\beta x_\alpha x_\beta \mu_{\alpha\beta} \quad \text{and} \quad \langle\nu\rangle = \sum_\alpha\sum_\beta x_\alpha x_\beta \nu_{\alpha\beta}. \tag{4·7}$$

The average potential is therefore also conformal to the reference potential $u_{00}(r)$, and we may write

$$\langle u(r)\rangle = f_x u_{00}(r/g_x), \tag{4·8}$$

where f_x and g_x are now functions of the composition x, defined in terms of the quadratic functions $\langle\mu\rangle$ and $\langle\nu\rangle$ by equations similar to (4·5). By substituting for $\mu_{\alpha\beta}$ and $\nu_{\alpha\beta}$ in terms of $f_{\alpha\beta}$ and $g_{\alpha\beta}$ in these equations, we obtain the relations

$$f_x = \left(\sum_\alpha\sum_\beta x_\alpha x_\beta f_{\alpha\beta}g^m_{\alpha\beta}\right)^{n/(n-m)}\left(\sum_\alpha\sum_\beta x_\alpha x_\beta f_{\alpha\beta}g^n_{\alpha\beta}\right)^{-m/(n-m)} \tag{4·9}$$

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† This differs slightly from the original definition of a conformal solution in that we do not demand that the $f_{\alpha\beta}$ and $g_{\alpha\beta}$ are all close to unity, or that $g_{\alpha\beta}$ is equal to $\frac{1}{2}(g_{\alpha\alpha}+g_{\beta\beta})$. Also the g parameter introduced here is the reciprocal of that used by Longuet-Higgins.

and
$$g_x = \Big(\sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta} g_{\alpha\beta}^n \Big/ \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta} g_{\alpha\beta}^m\Big)^{1/(n-m)}. \tag{4·10}$$

For mixtures of molecules of equal size, or more exactly when the $g_{\alpha\beta}$ are equal for all α, β, these relations reduce to the simple form

$$f_x = \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta} \quad \text{and} \quad g_x = \text{constant}. \tag{4·11}$$

On the other hand, when the $f_{\alpha\beta}$ parameters are all equal, but some or all of the $g_{\alpha\beta}$ differ, neither f_x nor g_x is independent of composition, and the formulae cannot be simplified.†

Equation (4·8) can be described by saying that the equivalent substance for composition x conforms to the reference substance with parameters f_x and g_x; and therefore the potentials of all the equivalent substances are simply related to that of the reference substance. In particular, the minimum energy u_x^* and corresponding distance r_x^* of the hypothetical molecules of an equivalent substance are related to those of the reference substance by the formulae

$$u_x^* = f_x u_{00}^* \quad \text{and} \quad r_x^* = g_x r_{00}^*. \tag{4·12}$$

The conformal relation of the average potential energy in a random mixture of Lennard-Jones molecules to that of the reference substance is the key to the treatment given in this paper. Since pure substances whose intermolecular energies are conformal obey the law of corresponding states, we can now relate the thermodynamic properties of the random mixture exactly to those of the reference substance.

5. LAW OF CORRESPONDING STATES

It has been shown by Pitzer (1939) that substances whose intermolecular energies are conformal, in the sense that they can be written in the form

$$u(r) = f u_{00}(r/g), \tag{5·1}$$

where f and g are constants and $u_{00}(r)$ is a common reference potential, form a family whose molar configurational free-energy functions are related by the equation

$$F(T, V) = fF_0(T/f, V/h) - RT \ln h, \tag{5·2}$$

where $h = g^3$. This follows from the configuration integral by dimensional considerations, and implies that the substances obey the same reduced equation of state. The Gibbs function is more useful for our purposes than the Helmholtz free energy, and it follows from equation (5·2) that the molar configurational Gibbs functions of conformal substances are related by

$$G(T, P) = fG_0(T/f, Ph/f) - RT \ln h. \tag{5·3}$$

Thus the configurational Gibbs functions for the components of the mixture we are considering are related to that of the reference substance by equations like (5·3); for component α we have

$$G_\alpha(T, P) = f_{\alpha\alpha} G_0(T/f_{\alpha\alpha}, Ph_{\alpha\alpha}/f_{\alpha\alpha}) - RT \ln h_{\alpha\alpha}. \tag{5·4}$$

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† This difference between the parameters is apparent in their mathematical nature: f_x is homogeneous and of degree 2 in the composition variables, homogeneous and of degree 1 in the energy parameters $f_{\alpha\beta}$, and homogeneous and of degree 0 in the size parameters; on the other hand, g_x is homogeneous and of degree 0 in the composition variables and the energy parameters, and homogeneous and of degree 1 in the size parameters $g_{\alpha\beta}$.

The same arguments can be applied to the equivalent substance for composition x, whose intermolecular energy function is given by equation (4·8), and show that the configurational free-energy functions F_x are related by an equation like (5·2), and that the configurational Gibbs function is

$$G_x(T, P) = f_x G_0(T/f_x, Ph_x/f_x) - RT\ln h_x, \tag{5·5}$$

where $h_x = g_x^3$. The molar configurational Gibbs function of the random mixture is therefore given by the equation, which can be derived from (3·7),

$$G(T, P, x) = f_x G_0(T/f_x, Ph_x/f_x) - RT\ln h_x + RT\sum_\alpha x_\alpha \ln x_\alpha. \tag{5·6}$$

This completes the demonstration that the thermodynamic properties of a random mixture of Lennard-Jones molecules can be related exactly to those of a reference substance. In particular, it should be noticed that single phases of the mixture must obey the same reduced equation of state as the reference substance, in the sense that if

$$\phi_0(P, V, T) = 0 \tag{5·7}$$

is the equation of state of the reference substance, then that of the mixture is

$$\phi(P, V, T) \equiv \phi_0(Ph_x/f_x, V/h_x, T/f_x) = 0, \tag{5·8}$$

where f_x and h_x are given by (4·9) and (4·10). We shall postpone discussion of the rather difficult question of the liquid-vapour critical phases until § 10.

It is evident that equation (5·6) suffices to discuss all the phenomena peculiar to mixtures of substances, such as mixing effects, phase equilibria, critical phases and so on, and in the succeeding sections we shall use the equation for this purpose. It should be noticed that (5·6) is valid for all values of the interaction parameters $f_{\alpha\beta}$ and $g_{\alpha\beta}$, subject only to the condition that the mixing is random, in the sense of § 3; deviations from random mixing will be discussed in part II. No special assumptions have been made which limit the application of the equation to any particular phase, but reflexion suggests that the random-mixing approximation is more appropriate to condensed phases than to gases, since in the former a molecule has many neighbours, but in the latter only one or two. The interest in this paper is therefore principally in liquid mixtures, and in the next section expressions will be derived for the excess mixing functions.

6. Thermodynamic functions of mixing

The thermodynamic functions of mixing for constant temperature and pressure can all be derived by differentiation from the molar Gibbs function of mixing, G^M, which is defined by

$$G^M(T, P, x) = G(T, P, x) - \sum_\alpha x_\alpha G_\alpha(T, P), \tag{6·1}$$

where $G, G_1, G_2, \ldots, G_c$ are the total Gibbs functions of the mixture and the pure components respectively. Since the contributions of the components to the non-configurational part of the total Gibbs function for a mixture are additive, this definition holds if the functions on the right-hand side are only the configurational parts we have been dealing with.

We can therefore use equations (5·6) and (5·4) to obtain an expression for G^M, and this yields the following equation for the excess molar Gibbs function of mixing, G^E:

$$G^E(T,P,x) = f_x G_0(T/f_x, Ph_x/f_x) - \sum_\alpha x_\alpha f_{\alpha\alpha} G_0(T/f_{\alpha\alpha}, Ph_{\alpha\alpha}/f_{\alpha\alpha}) - RT\sum_\alpha x_\alpha \ln(h_x/h_{\alpha\alpha}). \tag{6·2}$$

In general this function will vanish for all compositions x only if the conformal energy and size parameters, $f_{\alpha\beta}$ and $h_{\alpha\beta}$, are all equal. Since the thermodynamic condition for an ideal mixture is that G^E is zero for all compositions, this means that only isotopic mixtures are strictly ideal. This conclusion is in keeping with the remarks on ideal mixtures in § 3. The condition frequently quoted on the basis of the theory of strictly regular solutions (Guggenheim 1952), namely, that for molecules of equal size,

$$f_{\alpha\beta} = \tfrac{1}{2}(f_{\alpha\alpha}+f_{\beta\beta}) \quad \text{for all } \alpha,\ \beta,$$

is inadequate. In § 11 it will be shown that this merely ensures that the first-order terms are zero in a Taylor-series expansion of G^E, and that in general the higher-order terms will not be negligible unless the parameters $f_{\alpha\alpha}$ are almost equal for all components.

By differentiating equation (6·2) with respect to temperature, we find that the excess molar entropy of mixing is given by

$$S^E(T,P,x) = S_0(T/f_x, Ph_x/f_x) - \sum_\alpha x_\alpha S_0(T/f_{\alpha\alpha}, Ph_{\alpha\alpha}/f_{\alpha\alpha}) + R\sum_\alpha x_\alpha \ln(h_x/h_{\alpha\alpha}), \tag{6·3}$$

where $S_0(T,P)$ is the molar configurational entropy of the reference substance at temperature T and pressure P. It should be emphasized that this expression has nothing to do with deviations from random mixing, since the latter has, of course, been assumed in the derivation. Indeed, it is quite correct to call it the excess entropy of *random* mixing. The heat or enthalpy of mixing can be obtained from (6·2) and (6·3), and may be written in the form

$$H^E(T,P,x) = f_x H_0(T/f_x, Ph_x/f_x) - \sum_\alpha x_\alpha f_{\alpha\alpha} H_0(T/f_{\alpha\alpha}, Ph_{\alpha\alpha}/f_{\alpha\alpha}), \tag{6·4}$$

where $H_0(T,P)$ is the molar configurational enthalpy of the reference substance. The volume of mixing is readily found by differentiating equation (6·2) with respect to pressure, and is

$$V^E(T,P,x) = h_x V_0(T/f_x, Ph_x/f_x) - \sum_\alpha x_\alpha h_{\alpha\alpha} V_0(T/f_{\alpha\alpha}, Ph_{\alpha\alpha}/f_{\alpha\alpha}), \tag{6·5}$$

where $V_0(T,P)$ is the molar volume of the reference substance.

Expressions for the change in second-order derivatives on mixing, such as the heat capacity, thermal expansivity and compressibility, can be found by differentiating equation (6·2) once more. The thermodynamic functions of mixing for constant temperature and volume can also be derived in a similar way from the configurational Helmholtz free-energy functions, but are not of comparable interest.

(*a*) *Approximate equations*

The formulae above give the mixing functions as actual differences between expressions for the functions of the mixture, and those of the components at the same temperature and pressure. It is evidently more convenient to express the mixing functions in terms of various parameter differences, having thermodynamic coefficients. Approximate expressions of this type can be obtained by assuming that in the vicinity of any state (T,P) of the reference substance, the volume is a linear function of the temperature and pressure, and the isobaric configurational heat capacity is constant. These assumptions may be expressed in the form

$$\left.\begin{aligned} C_{P0} &= -T\left(\frac{\partial^2 G_0}{\partial T^2}\right)_P = \text{constant}, \\ V_0\alpha_0 &= \left(\frac{\partial^2 G_0}{\partial T\partial P}\right)_P = \text{constant}, \\ V_0\kappa_0 &= -\left(\frac{\partial^2 G_0}{\partial P^2}\right)_T = \text{constant}, \end{aligned}\right\} \tag{6·6}$$

where C_{P0}, V_0, α_0 and κ_0 are the molar isobaric configurational heat capacity, the molar volume, the expansivity and the compressibility of the reference substance. By integrating equations (6·6) over the range (T, P) to (T', P') we obtain

$$G_0(T', P') = U_0 - T'S_0 + P'V_0 + (T'-T)\,C_{P0} - T'C_{P0}\ln(T'/T) \\ + (T'-T)\,(P'-P)\,V_0\alpha_0 - \tfrac{1}{2}(P'-P)^2\,V_0\kappa_0, \tag{6·7}$$

where U_0 and S_0 are the molar configurational energy and entropy of the reference substance, and all functions on the right-hand side with suffix zero are for temperature T and pressure P. By using this expression in equation (6·2) for the excess molar Gibbs function we get

$$G^E(T, P, x) = (U_0 - TC_{P0} + PTV_0\alpha_0 - \tfrac{1}{2}P^2V_0\kappa_0)\,f^E + TC_{P0}\ln^E f - RT\ln^E h \\ + PV_0(1 - T\alpha_0 + P\kappa_0)\,h^E + PTV_0\alpha_0(h/f)^E - \tfrac{1}{2}P^2V_0\kappa_0(h^2/f)^E, \tag{6·8}$$

where the superscript E denotes the excess of any parameter over its average for the components; that is,

$$\left.\begin{aligned} f^E &= f_x - \sum_\alpha x_\alpha f_{\alpha\alpha}, \\ \ln^E f &= \ln f_x - \sum_\alpha x_\alpha \ln f_{\alpha\alpha}, \\ &\text{etc.} \end{aligned}\right\} \tag{6·9}$$

Expressions for the other mixing functions can be obtained from (6·8) by differentiating with respect to temperature and pressure. For liquids under ordinary pressures it is justifiable to put the pressure equal to zero, which leads to the equations

$$\left.\begin{aligned} G^E &= (U_0 - TC_{P0})\,f^E + TC_{P0}\ln^E f - RT\ln^E h, \\ H^E &= (U_0 - TC_{P0})\,f^E, \\ S^E &= -C_{P0}\ln^E f + R\ln^E h, \\ V^E &= V_0[(1 - T\alpha_0)\,h^E + T\alpha_0(h/f)^E]. \end{aligned}\right\} \tag{6·10}$$

Expressions of this kind are used in § 12 to calculate the liquid mixing properties of carbon monoxide and methane at 90° K.

We shall now consider, on the basis of equations (6·10), the qualitative features of the mixing effects in two special kinds of mixture: those in which the size parameters are all equal, and those in which the energy parameters are all equal.

(*b*) *Isochoric mixtures*

For mixtures of molecules of equal size (the same as that of the reference substance), which we shall call *isochoric mixtures*, we have

$$h^E = 0, \quad \ln^E h = 0 \quad \text{and} \quad (h/f)^E = (1/f)^E,$$

so that equations (6·10) become

$$\left.\begin{aligned} G^E &= U_0 f^E + TC_{P0}(\ln^E f - f^E), \\ H^E &= (U_0 - TC_{P0}) f^E, \\ S^E &= -C_{P0} \ln^E f, \\ V^E &= V_0 T\alpha_0 (1/f)^E. \end{aligned}\right\} \tag{6·11}$$

In this case the parameter f_x is given by equation (4·11), so that

$$f^E = \sum_\alpha \sum_\beta x_\alpha x_\beta (2f_{\alpha\beta} - f_{\alpha\alpha} - f_{\beta\beta}). \tag{6·12}$$

It is interesting to compare the above formulae with those derived from the first-order theory of conformal solutions (Longuet-Higgins 1951). For zero pressure the latter may be written in the form

$$\left.\begin{aligned} G^E &= U_0 f^E, \\ H^E &= (U_0 - TC_{P0}) f^E, \\ S^E &= -C_{P0} f^E, \\ V^E &= -V_0 T\alpha_0 f^E. \end{aligned}\right\} \tag{6·13}$$

We see that the two equations for the heat of mixing are identical, while those for the Gibbs free energy, entropy and volume differ in the excess parameters. Although this difference is evidently a 'second-order' one, it is nevertheless important. It means that the excess mixing functions of equations (6·11) are no longer proportional to one another as in the first-order theory, and in certain cases this can lead to a difference in the sign of the predicted mixing effect.

The excess parameters in question may be written in the form

$$\left.\begin{aligned} f^E &= f_x - f_A, \\ \ln^E f &= \ln (f_x/f_G), \\ (1/f)^E &= 1/f_x - 1/f_H, \end{aligned}\right\} \tag{6·14}$$

where

$$\left.\begin{aligned} f_A &= \sum_\alpha x_\alpha f_{\alpha\alpha}, \\ f_G &= \prod_\alpha (f_{\alpha\alpha})^{x_\alpha}, \\ 1/f_H &= \sum_\alpha x_\alpha / f_{\alpha\alpha}. \end{aligned}\right\} \tag{6·15}$$

Since, in general, the arithmetic mean is greater than the geometric, which is greater than the harmonic, we have

$$f_A > f_G > f_H. \tag{6·16}$$

Now, according to the first-order equations (6·13), the excess mixing functions G^E, H^E, S^E and V^E all vanish for f_x equal to f_A, and are all positive or all negative depending on whether

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

f_x is less than or greater than f_A. On the other hand, we see from equations (6·11) and (6·14) that on the more general theory based on the random-mixing approximation,

$$\left.\begin{array}{lll} V^E \geqslant 0 & \text{if} & f_x \leqslant f_H, \\ S^E \geqslant 0 & \text{if} & f_x \leqslant f_G, \\ H^E \geqslant 0 & \text{if} & f_x \leqslant f_A, \\ G^E \geqslant 0 & \text{if} & f_x \leqslant f', \end{array}\right\} \qquad (6{\cdot}17)$$

where f' is the value of f_x for which G^E vanishes, and is necessarily greater than f_A. This means that for small values of the equivalent energy parameter f_x, the excess mixing functions are all positive, and that as f_x is increased, the functions decrease to zero and become negative in the order V^E, S^E, H^E, G^E. This behaviour is illustrated graphically in figure 1 for a hypothetical case. We imagine that the components of the mixture and its composition are fixed, and that the interaction between molecules of different species is varied; f_x will therefore vary owing to the change in the intercomponent energy parameters $f_{\alpha\beta}$ $(\alpha \neq \beta)$.

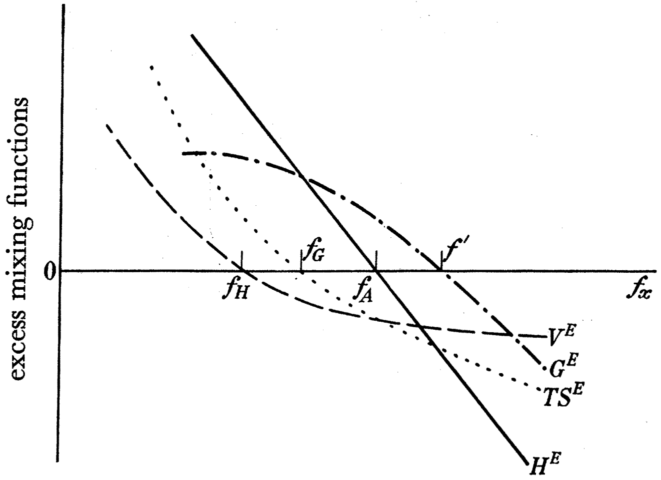

FIGURE 1. Variation of the excess mixing functions with the equivalent conformal parameter f_x, for a hypothetical isochoric mixture of fixed composition and fixed components.

We note that for an equimolar binary mixture in which $f_{12}^2 = f_{11} f_{22}$, we have

$$f_x = \tfrac{1}{2}(f_A + f_G),$$

so that in this case $\qquad G^E,\ H^E > 0 \quad \text{and} \quad S^E,\ V^E < 0.$

This type of mixture is discussed in greater detail in § 11.

(c) *Mixtures with energy parameters equal*

It has already been mentioned in § 4 that when the conformal energy parameters $f_{\alpha\beta}$ are all equal, but the size parameters differ, neither of the equivalent parameters, f_x and h_x, has a simple form. However, it can be shown quite generally that f_x is less than unity, so that

$$f^E < 0, \quad \ln^E f < 0 \quad \text{and} \quad (h/f)^E > h^E.$$

Furthermore, if the intercomponent size parameters $g_{\alpha\beta}$ are given by

$$g_{\alpha\beta} = \tfrac{1}{2}(g_{\alpha\alpha}+g_{\beta\beta}) \quad (\alpha, \beta = 1, 2, \ldots, c),$$

it can be shown that $$h^E > 0 \quad \text{and} \quad \ln^E h > 0.$$

This means that such mixtures always cool and expand when formed, and that the excess entropy of mixing is positive. It is not possible to predict the sign of G^E from these inequalities, but it will be shown in § 11 that it is positive.

(*d*) *General case*

In the general case in which both the energy and the size parameters are different, it is only possible to make one general statement about the mixing effects. This statement rests on an important inequality, which is proved in § 8: if f_χ is the value of the equivalent conformal energy parameter for an isochoric mixture, and f is the value for a mixture of the same composition and with the same energy parameters, but any size parameters whatever, then

$$f \leqslant f_\chi, \tag{6·18}$$

where the equality holds only for isochoric mixtures. It follows that $f^E \leqslant f^E_\chi$, and therefore that

$$H^E \geqslant H^E_\chi, \tag{6·19}$$

where H^E_χ is the heat of mixing for the isochoric mixture; size differences therefore always increase the heat of mixing.

Unfortunately, it is not possible to tell by mere inspection of the equations what the sign of the mixing effects will be in the general case. These depend too intimately on the relative values of the conformal parameters, and also to a lesser extent on the thermodynamic behaviour of the reference substance. In any case the equations (6·10) are only approximate. It is therefore more enlightening to analyze the exact equations, given at the beginning of the section, by a Taylor-series expansion, and this will be undertaken in § 11.

7. CHEMICAL POTENTIALS

The complete chemical potentials of the components of a mixture, or their configurational parts, are defined in terms of the corresponding molar Gibbs function $G(T, P, x)$ by the equations

$$\mu_\alpha(T, P, x) = \left(\frac{\partial MG}{\partial M_\alpha}\right)_{T,P} \quad (\alpha = 1, 2, \ldots, c), \tag{7·1}$$

where M_α is the mass in moles of component α, and M is the total mass of the mixture. Since G does not depend on the total masses of the components, but only on the mole fractions x, it is convenient to have a formula for obtaining the potentials which only involves G and its derivatives with respect to the mole fractions. Furthermore, although only $c-1$ of the mole fractions $x_1, x_2, \ldots, x_c$ are independent, it is much simpler to work with equations in which all the mole fractions can be regarded as independent when differentiating. The required formula may be derived from equation (7·1), and can be written in the form

$$\mu_\alpha = G + \frac{\mathrm{D}G}{\mathrm{D}x_\alpha} \quad (\alpha = 1, 2, \ldots, c), \tag{7·2}$$

where G may depend on all the mole fractions, and

$$\frac{\mathrm{D}}{\mathrm{D}x_\alpha} \equiv \frac{\partial}{\partial x_\alpha} - \sum_{\beta=1}^{c} x_\beta \frac{\partial}{\partial x_\beta} \quad (\alpha = 1, 2, \ldots, c), \tag{7·3}$$

where the c mole fractions may be treated as independent when differentiating; we observe that

$$\frac{\mathrm{D}x_\beta}{\mathrm{D}x_\alpha} = \delta_{\alpha\beta} - x_\beta \quad (\alpha, \beta = 1, 2, \ldots, c), \tag{7·4}$$

where $\delta_{\alpha\beta}$ is the Krönecker delta, equal to unity if α is the same as β, and equal to zero otherwise.

The molar configurational Gibbs function of the random mixture is given by equation (5·6), and, apart from the ideal mixing term, depends on the composition x only through the conformal parameters f_x and h_x. The configurational chemical potentials are therefore given by

$$\mu_\alpha(T, P, x) = G_x(T, P) + RT \ln x_\alpha + \frac{\mathrm{D}f}{\mathrm{D}x_\alpha}\frac{\partial G_x}{\partial f} + \frac{\mathrm{D}h}{\mathrm{D}x_\alpha}\frac{\partial G_x}{\partial h} \quad (\alpha = 1, 2, \ldots, c), \tag{7·5}$$

where $G_x(T, P)$ is the molar configurational Gibbs function of the equivalent substance, given by equation (5·5), and where the suffix x on the conformal parameters has been dropped. The derivatives of G_x with respect to f and h can be obtained by differentiating the latter equation, and may be written in the following forms:

$$\begin{aligned}\left(\frac{\partial G_x}{\partial f}\right)_{T,P,h} &= U(T, P)/f \\ &= U_0(T/f, Ph/f);\end{aligned} \tag{7·6}$$

$$\begin{aligned}\left(\frac{\partial G_x}{\partial h}\right)_{T,P,f} &= \mathscr{V}(T, P)/h \\ &= f\mathscr{V}_0(T/f, Ph/f)/h.\end{aligned} \tag{7·7}$$

In these expressions $U(T, P)$ is the molar configurational energy of the mixture or the equivalent substance, and $U_0(T, P)$ is that of the reference substance, while

$$\mathscr{V}(T, P) = PV(T, P) - RT \tag{7·8}$$

is a molar function closely related to the virial of Clausius, and $\mathscr{V}_0(T, P)$ is the corresponding function for the reference substance.

To obtain an expression for the derivative $\mathrm{D}f/\mathrm{D}x_\alpha$ which occurs in equation (7·5), we note that according to equations (4·12) and (3·4) the equivalent energy parameter $f = f_x$ may be written

$$f = \sum_\alpha \sum_\beta x_\alpha x_\beta u_{\alpha\beta}(r_x^*)/u_{00}^*. \tag{7·9}$$

By differentiating this expression with the help of (7·4), and remembering that r_x^* is a function of composition, we get

$$\frac{\mathrm{D}f}{\mathrm{D}x_\alpha} = 2\sum_\beta x_\beta \frac{[u_{\alpha\beta}(r_x^*) - u_x^*]}{u_{00}^*} + \frac{\mathrm{D}\ln r_x^*}{\mathrm{D}x_\alpha} \sum_\beta \sum_\gamma x_\beta x_\gamma \frac{v_{\beta\gamma}(r_x^*)}{u_{00}^*}, \tag{7·10}$$

where the functions $v(r)$ are the intermolecular 'virial' functions, defined by

$$v(r) = r\frac{\mathrm{d}u(r)}{\mathrm{d}r}. \tag{7·11}$$

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Now the virial function for the equivalent substance can be derived by differentiating equation (3·4) with respect to $\ln r$, and is therefore

$$\langle v(r)\rangle = \sum_\alpha \sum_\beta x_\alpha x_\beta v_{\alpha\beta}(r); \tag{7·12}$$

and it follows from (7·11) that at the distance of minimum energy, the virial corresponding to any potential function must vanish. Hence the average virial

$$v^*_x = \langle v(r^*_x)\rangle = 0, \tag{7·13}$$

and consequently the last term in equation (7·10) vanishes. The derivative of f can therefore be written in the form

$$\frac{\mathrm{D}f}{\mathrm{D}x_\alpha} = 2\sum_\beta x_\beta(f^*_{\alpha\beta}-f) \quad (\alpha = 1, 2, \ldots, c), \tag{7·14}$$

where the $f^*_{\alpha\beta}(x)$ are a new set of parameters, also depending on the composition, defined by

$$f^*_{\alpha\beta} = u_{\alpha\beta}(r^*_x)/u^*_{00}. \tag{7·15}$$

For isochoric mixtures (molecules the same size) $f^*_{\alpha\beta}$ is equal to $f_{\alpha\beta}$, while for the pure component α, that is when x_α is unity, we have $f^*_{\alpha\alpha}$ and f both equal to $f_{\alpha\alpha}$. We observe that according to (7·9)

$$f = \sum_\alpha \sum_\beta x_\alpha x_\beta f^*_{\alpha\beta}(x). \tag{7·16}$$

The derivative of the conformal size parameter $h = h_x$ for the random mixture or equivalent substance is most easily obtained indirectly by differentiating v^*_x, given by equations (7·12) and (7·13), with respect to x_α. This leads to the relation

$$\frac{\mathrm{D}\langle v(r^*_x)\rangle}{\mathrm{D}x_\alpha} = 2\sum_\beta x_\beta v_{\alpha\beta}(r^*_x) + \frac{\mathrm{D}\ln r^*_x}{\mathrm{D}x_\alpha} w^*_x = 0, \tag{7·17}$$

where w^*_x denotes $\langle w(r^*_x)\rangle$, and $w(r)$ is an intermolecular function defined by

$$w(r) = r\frac{\mathrm{d}v(r)}{\mathrm{d}r}, \tag{7·18}$$

which occurs naturally in the statistical expression for the elasticity of a substance. Since

$$r^*_x = g r^*_{00}, \quad h = g^3 \quad \text{and} \quad w^*_x = f w^*_{00},$$

equation (7·17) yields the following expression for $\mathrm{D}h/\mathrm{D}x_\alpha$:

$$\frac{\mathrm{D}h}{\mathrm{D}x_\alpha} = -\frac{6h}{f}\sum_\beta x_\beta v_{\alpha\beta}(r^*_x)/w^*_{00}. \tag{7·19}$$

It is convenient here to introduce another set of composition-dependent parameters $k^*_{\alpha\beta}(x)$, defined by

$$k^*_{\alpha\beta} = -3v_{\alpha\beta}(r^*_x)/w^*_{00}. \tag{7·20}$$

These parameters vanish for isochoric mixtures and for the pure components. The sign of the $k^*_{\alpha\beta}$ has been chosen so that they are positive for molecules larger than the average, and in general for $h_{\alpha\beta}$ greater than h, and negative for $h_{\alpha\beta}$ less than h. We observe that, according to (7·12) and (7·13),

$$\sum_\alpha \sum_\beta x_\alpha x_\beta k^*_{\alpha\beta} = 0. \tag{7·21}$$

In terms of this parameter, equation (7·19) becomes

$$\frac{\mathrm{D}h}{\mathrm{D}x_\alpha} = \frac{2h}{f}\sum_\beta x_\beta k^*_{\alpha\beta} \quad (\alpha = 1, 2, \ldots, c). \tag{7·22}$$

The expressions derived in equations (6), (7), (14) and (22) of this section for the quantities occurring in equation (7·5) may now be substituted to give the following equations for the configurational chemical potentials:

$$\mu_\alpha(T,P,x) = G_x(T,P) + RT\ln x_\alpha + 2U(T,P)\sum_\beta x_\beta(f^*_{\alpha\beta}-f)/f$$
$$+2\mathscr{V}(T,P)\sum_\beta x_\beta k^*_{\alpha\beta}/f \quad (\alpha = 1, 2, \ldots, c). \tag{7·23}$$

It is evident from (7·16) and (7·21) that these expressions satisfy the thermodynamic relation

$$G(T,P,x) = \sum_\alpha x_\alpha \mu_\alpha(T,P,x), \tag{7·24}$$

where $G(T,P,x)$ is the molar configurational Gibbs function of the mixture, given by equation (5·6), and it can also be seen that the equations reduce to the correct form for the pure components; for example, when x_α is unity we have

$$\mu^0_\alpha(T,P) = G_\alpha(T,P), \tag{7·25}$$

the molar configurational Gibbs function for component α, given by equation (5·4). The Gibbs–Duhem equation is, of course, automatically satisfied by the method of derivation. The excess chemical potentials $\mu^E_\alpha(T,P,x)$ and the activity coefficients $\gamma_\alpha(T,P,x)$ are given in terms of the chemical potentials of equation (7·23) by

$$\mu^E_\alpha = RT\ln\gamma_\alpha = \mu_\alpha - \mu^0_\alpha - RT\ln x_\alpha. \tag{7·26}$$

Hence
$$\mu^E_\alpha = G_x - G_\alpha + 2U\sum_\beta x_\beta(f^*_{\alpha\beta}-f)/f + 2\mathscr{V}\sum_\beta x_\beta k^*_{\alpha\beta}/f \quad (\alpha = 1, 2, \ldots, c). \tag{7·27}$$

It is interesting to note that the particular form chosen for the intermolecular potential, namely, that of Lennard-Jones, is not explicitly evident in equations (7·23) or (7·27), nor in the expressions for the parameters $f^*_{\alpha\beta}$ and $k^*_{\alpha\beta}$. However, the possibility of relating the properties of mixtures of any composition to the same reference substance, which is implicit in these equations, does rest exclusively with the Lennard-Jones form of the potential, as shown in the appendix.

The calculation of the chemical potentials in a random mixture of Lennard-Jones molecules requires, therefore, the values of the parameters f_x, h_x, $f^*_{\alpha\beta}$ and $k^*_{\alpha\beta}$ over the whole composition range, and a knowledge of the Gibbs function of the reference substance over ranges of temperature and pressure determined by the extreme values of f_x and h_x. Such calculations will not be undertaken in this paper, but in § 9 equations (7·23) will be used to discuss phase equilibria in mixtures.

8. Starred conformal parameters

The parameters $f^*_{\alpha\beta}$ and $k^*_{\alpha\beta}$, which may be called the *starred conformal parameters*, were introduced in the last section in connexion with the chemical potentials, but also occur naturally in the theory of deviations from random mixing, which is presented in part II. In view of their importance, we shall pause here to consider their physical significance, and to derive alternative expressions for them.

The starred conformal parameters are defined by equations (7·15) and (7·20); if in the latter we replace w^*_{00} by its value $-nmu^*_{00}$, these equations become

$$f^*_{\alpha\beta} = u_{\alpha\beta}(r^*_x)/u^*_{00} \quad (\alpha, \beta = 1, 2, \ldots, c), \tag{8·1}$$

and

$$k^*_{\alpha\beta} = \frac{3}{nm} v_{\alpha\beta}(r^*_x)/u^*_{00} \quad (\alpha, \beta = 1, 2, \ldots, c). \tag{8·2}$$

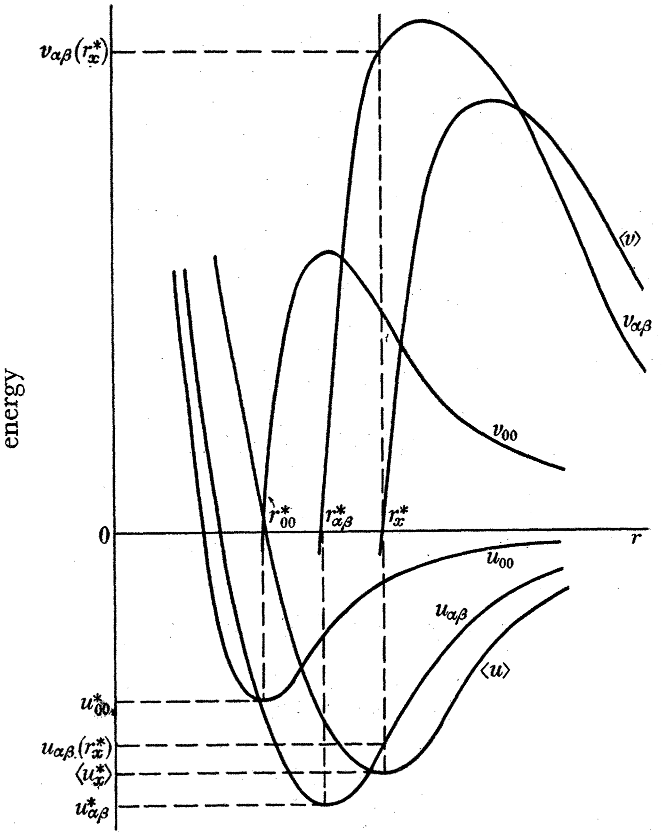

FIGURE 2. Variation of hypothetical intermolecular energy (u) and virial (v) functions with distance r for the following interactions: two reference molecules (subscript 00); two molecules of the equivalent substance (brackets $\langle\ \rangle$); a molecule of species α and one of species β (subscript $\alpha\beta$).

We note that the composition dependence of the parameters is due to r^*_x, the characteristic size of the molecules of the equivalent substance for composition x. It can easily be shown that to the first order in $(g_{\alpha\beta} - g_x)$ and $(h_{\alpha\beta} - h_x)$ we have

$$f^*_{\alpha\beta} = f_{\alpha\beta}, \tag{8·3}$$

$$\begin{aligned} k^*_{\alpha\beta} &= 3f_{\alpha\beta}(g_{\alpha\beta} - g_x)/g_x \\ &= f_{\alpha\beta}(h_{\alpha\beta} - h_x)/h_x. \end{aligned} \tag{8·4}$$

It follows from these equations that, as we have already mentioned, for isochoric mixtures (molecules of equal size),

$$f^*_{\alpha\beta} = f_{\alpha\beta} \quad \text{and} \quad k^*_{\alpha\beta} = 0 \quad (\alpha, \beta = 1, 2, \ldots, c). \tag{8·5}$$

The physical significance of these parameters should be clear from figure 2, in which the hypothetical energy and virial functions† for the interactions between the following pairs

---

† In this connexion it is useful to note that for Lennard-Jones molecules, the intermolecular virial and energy functions are related by equation (9·12).

of molecules have been plotted against the intermolecular distance: (*a*) two reference molecules, (*b*) two molecules of the equivalent substance, and (*c*) a molecule of species α and one of species β. The energy curve for the last, $u_{\alpha\beta}(r)$, crosses the vertical line $r = r_x^*$ at energy $f_{\alpha\beta}^* u_{00}^*$, and the virial curve $v_{\alpha\beta}(r)$ crosses this line at energy $\frac{1}{3}nm\,k_{\alpha\beta}^* u_{00}^*$.

The starred energy parameters $f_{\alpha\beta}^*$ obey important inequalities, which arise from the fact that the intermolecular energy function $u_{\alpha\beta}(r)$ has a minimum value of $u_{\alpha\beta}^*$, so that

$$u_{\alpha\beta}(r) \geqslant u_{\alpha\beta}^* = f_{\alpha\beta} u_{00}^*.$$

Therefore, by (8·1),

$$f_{\alpha\beta}^* \leqslant f_{\alpha\beta} \quad (\alpha, \beta = 1, 2, \ldots, c); \tag{8·6}$$

the inequalities all hold only for an isochoric mixture. The origin of these inequalities is readily apparent from figure 2. Since, by equation (7·16),

$$f_x = \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta}^*, \tag{8·7}$$

it follows from (8·6) that†

$$f_x \leqslant \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta}. \tag{8·8}$$

This inequality was used in discussing mixing effects in § 5 (*d*). The starred size parameters $k_{\alpha\beta}^*$ similarly obey the inequalities

$$k_{\alpha\beta}^* \geqslant -\frac{3\lambda}{nm} f_{\alpha\beta} \quad (\alpha, \beta = 1, 2, \ldots, c), \tag{8·9}$$

where $-\lambda$ is the ratio of the maximum of a virial function to the minimum of the corresponding energy function, given by

$$\lambda = (m^n/n^m)^{1/(n-m)}. \tag{8·10}$$

However, these relations are not of comparable importance with those satisfied by the $f_{\alpha\beta}^*$, since the equalities represent a very extreme case, and cannot all occur together.

To conclude this section alternative expressions will be derived for the starred conformal parameters. A dimensionless form ψ of the reference potential may be defined by

$$\psi(t) = \frac{n}{n-m} t^m - \frac{m}{n-m} t^n, \tag{8·11}$$

and the corresponding form χ of the reference virial defined by

$$\begin{aligned} \chi(t) &= -t \frac{\mathrm{d}\psi}{\mathrm{d}t} \\ &= \frac{nm}{n-m}(t^n - t^m). \end{aligned} \tag{8·12}$$

According to equations (4·2) and (7·11) the reference energy and virial functions can then be written as

$$u_{00}(r) = u_{00}^* \psi(r_{00}^*/r), \tag{8·13}$$

and

$$v_{00}(r) = u_{00}^* \chi(r_{00}^*/r). \tag{8·14}$$

---

† Relation (8·8) can be deduced directly from equation (4·9) defining f by the use of Hölder's inequality (see Ferrar 1943).

It follows from equations (8·1) and (8·2), and the conformal relations (4·4), that the expressions for $f^*_{\alpha\beta}$ and $k^*_{\alpha\beta}$ in terms of these functions are

$$f^*_{\alpha\beta} = f_{\alpha\beta}\psi(g_{\alpha\beta}/g_x), \tag{8·15}$$

and

$$k^*_{\alpha\beta} = \frac{3}{nm} f_{\alpha\beta}\chi(g_{\alpha\beta}/g_x). \tag{8·16}$$

In these formulae the composition dependence of the starred conformal parameters is relegated to the molecular size parameter of the equivalent substance, g_x, which is given by equation (4·10). The inequalities (8·6) follow from (8·15) by observing that ψ has the maximum value $\psi(1)$, equal to unity.

After this short interlude, we shall now proceed to develop some of the thermodynamic consequences of the equations for the chemical potentials derived in the previous section.

9. Phase equilibria

In this section we shall discuss briefly some aspects of two different kinds of phase equilibria of special interest in mixtures: the equilibrium between two or more liquid phases containing partially miscible components, and the equilibrium between a liquid mixture and its vapour. While the latter is, of course, a universal phenomenon, the occurrence of limited miscibility depends on the nature of the various molecular interactions in a mixture. Some of the conditions on the parameters $f_{\alpha\beta}$ and $h_{\alpha\beta}$ for this to happen will be discussed in connexion with the conditions for material stability in the next section. For the moment we shall merely formulate the conditions for such an equilibrium on the assumption that it can occur.

(a) *Liquid-liquid phase equilibrium*

The condition for material equilibrium between two phases at the same temperature and pressure is that the chemical potentials for each component shall be equal in the two phases. Since in this theory the non-configurational parts of the chemical potentials will be identical in both phases, in formulating the condition it is only necessary to equate the configurational chemical potentials, given by equations (7·23). Therefore, distinguishing the phases by single (′) and double (″) primes, the condition is that

$$\mu'_\alpha(T, P, x') = \mu''_\alpha(T, P, x'') \quad (\alpha = 1, 2, \ldots, c), \tag{9·1}$$

where x' and x'' are the compositions of the two phases. However, since the phases are both associated with the liquid state of the reference substance, the potential for any component is the same function of temperature, pressure and composition in either phase, and the condition may be written simply as

$$\mu_\alpha(T, P, x') = \mu_\alpha(T, P, x'') \quad (\alpha = 1, 2, \ldots, c), \tag{9·2}$$

where the $\mu_\alpha(T, P, x)$ are given by equations (7·23), with the reference functions as properties of the liquid state. We shall not write down the explicit form of these equations, which may be easily obtained by substitution, but merely note that the equivalent conformal parameters f_x and h_x, and also the starred parameters $f^*_{\alpha\beta}$ and $k^*_{\alpha\beta}$, will have different values in each phase, since they are, in general, functions of composition. The generalization of the condition (9·2) to more than two phases is obvious.

(*b*) *Liquid-vapour phase equilibrium: azeotropy*

In the case of the equilibrium between a liquid mixture and its vapour, the potentials are different functions of temperature, pressure and composition in the two phases, since in one they are associated with the liquid state of the reference substance, and in the other with the gaseous state. The condition for equilibrium is therefore that

$$\mu_\alpha^{\mathrm{G}}(T,P,x^{\mathrm{G}}) = \mu_\alpha^{\mathrm{L}}(T,P,x^{\mathrm{L}}) \quad (\alpha = 1,2,\ldots,c), \tag{9·3}$$

where the superscripts denote the gas (G) and liquid (L) phases. By substituting for the configurational chemical potentials from (7·23), we can express this in the form

$$-\Delta G_x = RT\ln(x_\alpha^{\mathrm{G}}/x_\alpha^{\mathrm{L}}) + 2\Delta[U\sum_\beta x_\beta(f_{\alpha\beta}^*-f)/f] + 2\Delta[\mathscr{V}\sum_\beta x_\beta k_{\alpha\beta}^*/f] \quad (\alpha = 1,2,\ldots,c), \tag{9·4}$$

where Δ subtracts the value of a function in the liquid phase from that in the gas phase; for example, putting $f^{\mathrm{G}} = f(x^{\mathrm{G}})$, etc.,

$$\begin{aligned}\Delta G_x(T,P) &= G_x^{\mathrm{G}}(T,P) - G_x^{\mathrm{L}}(T,P)\\ &= f^{\mathrm{G}}G_0(T/f^{\mathrm{G}}, Ph^{\mathrm{G}}/f^{\mathrm{G}}) - f^{\mathrm{L}}G_0(T/f^{\mathrm{L}}, Ph^{\mathrm{L}}/f^{\mathrm{L}}) - RT\ln(h^{\mathrm{G}}/h^{\mathrm{L}}).\end{aligned} \tag{9·5}$$

It is evident from equation (9·4) that in this theory the liquid-vapour equilibrium depends on the functions $G_0^{\mathrm{G}}(T,P)$ and $G_0^{\mathrm{L}}(T,P)$, and their first derivatives with respect to temperature and pressure. Now the liquid-vapour coexistence curve for the reference substance, which is the boundary between those temperatures and pressures for which the liquid is the stable state and those for which the gas is stable, is given by

$$\Delta G_0(T,P) = G_0^{\mathrm{G}}(T,P) - G_0^{\mathrm{L}}(T,P) = 0. \tag{9·6}$$

It can be seen, therefore, that in order to calculate the compositions of the coexistent liquid and vapour phases of the mixture from the properties of the reference substance, it will in general be necessary to know not only the values of G_0^{G} and G_0^{L} for the stable phases, but also for certain metastable phases; that is, for certain temperature and pressure ranges of the supersaturated vapour and superheated liquid forms of the reference substance, which will be determined by extreme values of the parameters f_x and h_x for the coexistent phases. This is, of course, a disadvantage of the theory from a practical point of view.

The case in which the mixture exhibits azeotropy is particularly simple and interesting, and we shall examine it in some detail. For azeotropic states of the system, or in other words states of uniform composition ($x_\alpha^{\mathrm{G}} = x_\alpha^{\mathrm{L}} = x_\alpha$ for all α), the equations (9·4) become

$$-\Delta_a G_x = 2\Delta_a U\sum_\beta x_\beta(f_{\alpha\beta}^*-f)/f + 2\Delta_a\mathscr{V}\sum_\beta x_\beta k_{\alpha\beta}^*/f \quad (\alpha = 1,2,\ldots,c), \tag{9·7}$$

where the suffix *a* has been attached to Δ to indicate that the compositions of the two phases are the same, and therefore that the parameters f and h are identical in the liquid and gas functions; for example

$$\Delta_a G_x(T,P) = f\Delta G_0(T/f, Ph/f), \tag{9·8}$$

where $\Delta G_0(T,P)$ is given by (9·6). From these equations we can deduce a very simple feature of the azeotropic line (that is, the relations between the temperature, pressure and composition of the azeotropic states). For by multiplying each equation by the appropriate mole fraction and adding the resulting expressions together, we find, with the help of (7·16) and (7·21), that

$$\Delta_a G_x(T,P) = 0. \tag{9·9}$$

According to equation (9·8) this is the liquid-vapour coexistence curve of the equivalent substance for the azeotropic composition x^a; and therefore the azeotropic line 'corresponds' to the coexistence curve of the reference substance, (9·6), in the sense that it can be derived from it by means of the scale factors $f(x^a)$ and $h(x^a)$ after the manner of the law of corresponding states.

The other $c-1$ independent equations in addition to (9·9) may be regarded as determining the azeotropic composition; they can be chosen to be any $c-1$ of the equations

$$\Delta_a U \sum_\beta x_\beta (f^*_{\alpha\beta} - f) + P\Delta_a V \sum_\beta x_\beta k^*_{\alpha\beta} = 0 \quad (\alpha = 1, 2, \ldots, c), \tag{9·10}$$

where we have replaced $\Delta_a \mathscr{V}$ by $P\Delta_a V$, in accordance with equation (7·8). These equations are suitable for determining the conditions on the parameters for azeotropy to occur, and we shall now proceed to consider this aspect of the theory.

In general the condition for azeotrope formation is that the equations (9·10) have a physically significant solution; that is, one for which all the mole fractions x_α lie between 0 and 1. For binary mixtures, which are the only type we shall consider here, only one of the equations (9·10) is independent. By subtracting the two dependent equations from one another and rearranging the relation obtained, we get

$$1 - 2x_2 = \frac{(f^*_{11} - f^*_{22}) + (k^*_{11} - k^*_{22})\,(P\Delta V/\Delta U)_a}{(2f^*_{12} - f^*_{11} - f^*_{22}) + (2k^*_{12} - k^*_{11} - k^*_{22})\,(P\Delta V/\Delta U)_a}. \tag{9·11}$$

This somewhat formidable equation can be thrown into a simpler form by means of the linear combination relations satisfied by the Lennard-Jones potential functions. To derive this form, we note first of all that the Lennard-Jones intermolecular 'virial' function, $v(r)$, defined by equation (7·11), is functionally related to the energy function, $u(r)$, by the equation

$$v(r) = -\lambda u(r/\rho), \tag{9·12}$$

where λ and ρ are positive constants given by

$$\lambda\rho^n = n \quad \text{and} \quad \lambda\rho^m = m. \tag{9·13}$$

By using equation (9·12) in equation (8·2) we find that $k^*_{\alpha\beta}$ can be expressed in the form

$$k^*_{\alpha\beta} = -\frac{3\lambda}{nm} u_{\alpha\beta}(r^*_x/\rho) u^*_{00} \quad (\alpha, \beta = 1, 2, \ldots, c). \tag{9·14}$$

Now it follows directly from equation (4·1) that if a and b are any two constants, then

$$u(r) + au(r/b) = Au(r/B), \tag{9·15}$$

where and

$$\left.\begin{aligned} A &= (1+ab^m)^{n/(n-m)}\,(1+ab^n)^{-m/(n-m)}, \\ B &= [(1+ab^n)/(1+ab^m)]^{1/(n-m)}. \end{aligned}\right\} \tag{9·16}$$

Therefore, by equations (8·1) and (9·14), if C is any number,

$$\begin{aligned} f^*_{\alpha\beta} + Ck^*_{\alpha\beta} &= \left[u_{\alpha\beta}(r^*_x) - \frac{3\lambda C}{nm} u_{\alpha\beta}(r^*_x/\rho)\right] \Big/ u^*_{00} \\ &= Au_{\alpha\beta}(r^*_x/B)/u^*_{00}, \end{aligned} \tag{9·17}$$

where

$$B = \left(\frac{1-3C/m}{1-3C/n}\right)^{1/(n-m)}. \tag{9·18}$$

(B is real as long as C is greater than $\frac{1}{3}n$, or less than $\frac{1}{3}m$.) Hence, replacing C by $(P\Delta V/\Delta U)_a$, we can write (9·11) in the form

$$1-2x_2=\frac{u_{11}(r_x^*/B)-u_{22}(r_x^*/B)}{2u_{12}(r_x^*/B)-u_{11}(r_x^*/B)-u_{22}(r_x^*/B)}; \tag{9·19}$$

we observe that since $\quad 0<(P\Delta V/\Delta U)_a<1 \quad$ and $\quad n>m>3$,

B must be less than 1, and therefore r_x^*/B is greater than r_x^*.

If the average molecular size r_x^* was independent of composition, the necessary and sufficient condition for azeotrope formation would be that the modulus of the right-hand side of equation (9·19) was less than unity, or

$$(u_{12}-u_{11})\,(u_{12}-u_{22})>0 \quad \text{for} \quad r=r_x^*/B. \tag{9·20}$$

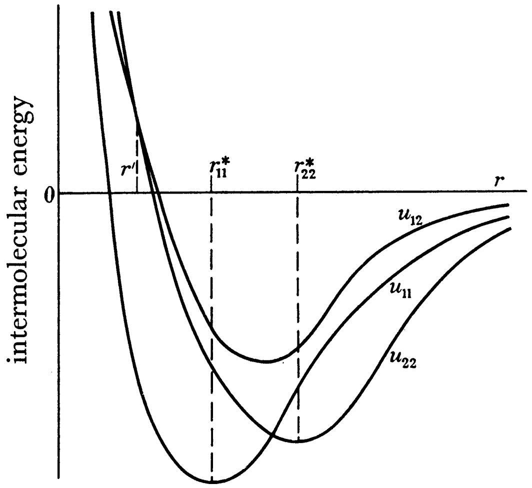

FIGURE 3. Variation of the intermolecular energy functions of a binary mixture, u_{11}, u_{12} and u_{22}, with intermolecular distance r.

This condition has a simple interpretation on the intermolecular energy diagram, figure 3. It means that at distance r_x^*/B the 'mixed' potential function u_{12} must lie outside the energy interval u_{11} to u_{22}. The molecular size r_x^* is only independent of composition for isochoric mixtures, when (9·20) reduces accurately to

$$(f_{12}-f_{11})\,(f_{12}-f_{22})>0. \tag{9·21}$$

Since the $f_{\alpha\beta}$ are true constants, such a mixture will either form an azeotrope of fixed composition at all temperatures (absolute azeotropy), or not at all. In particular, isochoric mixtures satisfying the geometric mean hypothesis, $f_{12}^2=f_{11}f_{22}$, can never form an azeotrope. In general r_x^* depends on composition, and usually varies between r_{11}^* and r_{22}^*. A sufficient, but not necessary condition for azeotropy in most cases is therefore that (9·20) holds for r equal to r_{11}^*/B_1 and r_{22}^*/B_2, where B_1 and B_2 are the values of B for the components. This is true in the case illustrated in figure 3, where (9·20) only breaks down for r less than r', where $u_{12}(r)$ and $u_{11}(r)$ have crossed over.

A more thorough analysis of equation (9·19) will not be attempted here, as it requires a careful classification of mixtures on the basis of the relative values of the conformal and Lennard-Jones constants of the components. However, it may be mentioned that if the usually slight composition dependence of B is ignored, (9·19) can be reduced to a cubic equation in x_2. The condition that one of the roots lies between 0 and 1 then provides a necessary and sufficient condition on the parameters for azeotrope formation.

The ratio C, equal to $(P\Delta V/\Delta U)_a$, occurring in equations (9·11) and (9·19), is related to the slope of the vapour-pressure curve of the equivalent substance for composition x^a, which is the same as that of the projection of the azeotropic line onto the T, P plane (see Prigogine & Defay 1954). This relation can be deduced from equations (9·9) and (9·10) and is

$$\left(\frac{\Delta U}{P\Delta V}\right)_a = \left(\frac{\mathrm{d}\ln P}{\mathrm{d}\ln T}\right)_a - 1. \tag{9·22}$$

For a pure substance the derivative $\mathrm{d}\ln P/\mathrm{d}\ln T$ is of the order of 10 at the critical point, where it is a minimum, so that $P\Delta V/\Delta U$ will be about $\frac{1}{10}$ or less. This ratio will be approximately proportional to the absolute temperature, since

$$P\Delta V \simeq RT \quad \text{and} \quad \Delta U \simeq \text{constant}.$$

This means that although the azeotropic composition is fixed for isochoric mixtures, it will in general vary with temperature for mixtures of molecules of different size.

When the conformal parameters $f_{\alpha\beta}$ and $h_{\alpha\beta}$ are all close to unity, equation (9·11) can be reduced to the form derived by Cook & Longuet-Higgins (1951) from the first-order theory of conformal solutions.

This concludes our discussion of azeotropy,† and phase equilibria in general. We shall now go on to consider the reasons for the breakdown in stability leading to phase separation in mixtures, and the two types of critical phase associated with the equilibria discussed in parts (*a*) and (*b*) of this section.

10. Stability and critical phases

It is interesting to show, from first principles, the possibility of three distinct kinds of phase separation in the liquid mixtures under discussion: the liquid-liquid, the liquid-vapour, and the liquid-solid. This has not been shown previously for any theory of mixtures, and is only possible with the present theory because no assumptions have been made which limit consideration to a particular phase. The following analysis is confined to binary mixtures, but could be extended to a greater number of components without difficulty.

In order to examine the possible types of phase separation in binary mixtures we require an expression for the coefficient $(\partial^2 G/\partial x^2)_{T,P}$, which determines the material stability (stability with respect to diffusion) of a single phase. This coefficient is positive for stable phases, vanishes in cases of limiting stability, such as a critical phase, and is negative for unstable phases. To obtain an expression for it we start from equation (5·6) for the molar configurational Gibbs function, which may be written

$$G(T, P, x) = G_x(T, P) + RT\sum_{\alpha} x_\alpha \ln x_\alpha, \tag{10·1}$$

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† Expressions for the derivative $(\partial^2 \Delta G/\partial x^2)$ determining the 'sign' of the azeotropy of a mixture may be readily obtained from the equations of the next section.

where $G_x(T, P)$ is the molar configurational Gibbs function for the equivalent substance for composition x, given by (5·5). The coefficient determining the material stability of a binary mixture is then

$$\frac{\partial^2 G}{\partial x^2} = \frac{RT}{x(1-x)} + \frac{\partial^2 G_x}{\partial x^2}; \tag{10·2}$$

we observe that for instability the derivative $\partial^2 G_x/\partial x^2$ must be negative, and less than the ideal term $RT/x(1-x)$. Since G_x depends on x only through the conformal parameters f_x and h_x, its second derivative has the form

$$\frac{\partial^2 G_x}{\partial x^2} = f_x'' G_f + h_x'' G_h + [(f_x')^2 G_{ff} + 2(f_x' h_x') G_{fh} + (h_x')^2 G_{hh}], \tag{10·3}$$

where the primes denote differentiation with respect to x, and the quantities G_f, G_h, etc., are defined as follows:

$$\left.\begin{aligned} G_f &= \left(\frac{\partial G}{\partial f}\right)_x = U/f_x, \\ G_h &= \left(\frac{\partial G}{\partial h}\right)_x = (PV - RT)/h_x; \end{aligned}\right\} \tag{10·4}$$

$$\left.\begin{aligned} G_{ff} &= \left(\frac{\partial^2 G}{\partial f^2}\right)_x = \left(T^2 \frac{\partial^2 G}{\partial T^2} + 2TP \frac{\partial^2 G}{\partial T \partial P} + P^2 \frac{\partial^2 G}{\partial P^2}\right) \Big/ f_x^2 \\ &= -(TC_P - 2PTV\alpha + P^2 V\kappa)/f_x^2, \\ G_{fh} &= \left(\frac{\partial^2 G}{\partial f \partial h}\right)_x = -\left(TP \frac{\partial^2 G}{\partial T \partial P} + P^2 \frac{\partial^2 G}{\partial P^2}\right) \Big/ f_x h_x \\ &= -(PTV\alpha - P^2 V\kappa)/f_x h_x, \\ G_{hh} &= \left(\frac{\partial^2 G}{\partial h^2}\right)_x = \left(RT + P^2 \frac{\partial^2 G}{\partial P^2}\right) \Big/ h_x^2 \\ &= (RT - P^2 V\kappa)/h_x^2. \end{aligned}\right\} \tag{10·5}$$

In these expressions U, V and C_P are the molar configurational energy, the molar volume and the molar configurational isobaric heat capacity, α and κ are the thermal expansivity and isothermal compressibility, and all functions are properties of the equivalent substance for composition x at temperature T and pressure P. The derivatives f_x', h_x', etc., may be obtained from the defining relations of § 4. Choosing x to be the mole fraction of the second component we find that

$$\left.\begin{aligned} f_x' &= \frac{\partial f_x}{\partial x} = -[\theta_{12}^* + (2x-1)\, e_{12}^*], \\ h_x' &= \frac{\partial h_x}{\partial x} = -[\phi_{12}^* + (2x-1)\, s_{12}^*]\, h_x/f_x; \end{aligned}\right\} \tag{10·6}$$

$$\left.\begin{aligned} f_x'' &= \frac{\partial^2 f_x}{\partial x^2} = -2e_{12}^* + \frac{nm}{9} f_x (h_x'/h_x)^2, \\ h_x'' &= \frac{\partial^2 h_x}{\partial x^2} = -2s_{12}^* h_x/f_x - \left(\frac{n+m}{3} - 1\right) (h_x')^2/h_x - 2f_x' h_x'/f_x; \end{aligned}\right\} \tag{10·7}$$

where

$$\left.\begin{aligned} e^*_{12} &= 2f^*_{12}-f^*_{11}-f^*_{22}, \\ s^*_{12} &= 2k^*_{12}-k^*_{11}-k^*_{22}, \\ \theta^*_{12} &= f^*_{11}-f^*_{22}, \\ \phi^*_{12} &= k^*_{11}-k^*_{22}. \end{aligned}\right\} \tag{10·8}$$

In deriving these formulae we have made use of the following relations, which may be obtained from (8·1) and (8·2):

$$\left.\begin{aligned} \frac{\partial f^*_{\alpha\beta}}{\partial x} &= \frac{nm}{9}(h'_x/h_x)\,k^*_{\alpha\beta}, \\ \frac{\partial k^*_{\alpha\beta}}{\partial x} &= -\left(\frac{n+m}{3}-1\right)(h'_x/h_x)\,k^*_{\alpha\beta}-(h'_x/h_x)\,f^*_{\alpha\beta}. \end{aligned}\right\} \tag{10·9}$$

For the present it is sufficient to appreciate that f'_x, f''_x, etc., depend only on the composition, and involve parameter differences in such a way that they vanish for a mixture of isotopic components.

We are now ready to consider the different ways in which material instability or phase separation can arise. In the first place, we see from the equations (10·5) defining G_{ff}, G_{fh} and G_{hh}, that these functions are indefinitely large along the liquid-vapour and liquid-solid coexistence curves of the equivalent substance. Examination of the quadratic form in brackets on the right-hand side of equation (10·3) reveals that it is always indefinitely large and negative under these conditions,† and consequently $\partial^2G_x/\partial x^2$ will be large and negative along these coexistence curves. This potential instability extends over the whole composition range of the mixture, since it is always possible to make $-(\partial^2G_x/\partial x^2)$ greater than the ideal term of equation (10·2), no matter what the value of x. In the limits when x goes to 0 or 1, the instability is evidently associated with the phase changes from liquid to vapour and from liquid to solid in the pure components. Every mixture will therefore exhibit these phase changes in the vicinity of the corresponding transitions for the pure components.

Apart from these universal types of phase separation, it is evidently possible for $\partial^2G_x/\partial x^2$ to be negative at temperatures between the melting and boiling points of the equivalent substance. For example, even if the components have similar molecules so that the $(f'_x)^2$, $(f'_x\,h'_x)$ and $(h'_x)^2$ terms are small, when f''_x is positive and of sufficient magnitude, then since G_f is negative at ordinary pressures, it is possible for $-(\partial^2G_x/\partial x^2)$ to be greater than the ideal term of equation (10·2). We note, however, that this type of instability does not extend over the whole composition range; in particular, it can never exist for the pure components, since $\partial^2G_x/\partial x^2$ will always be finite, while the positive ideal term $RT/x(1-x)$ can be made indefinitely large by letting x approach 0 or 1. This instability therefore corresponds to a separation of the mixture into two coexistent liquid phases; it is evidently dependent on the sign and magnitude of the parameter differences, and will therefore be confined to a certain class of mixtures.

Having thus shown qualitatively how the different kinds of phase separation in liquids can arise, we will now consider some further aspects of the phenomena.

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† The sign of the quadratic form follows from the stability conditions for a pure substance, which demand that

$$(\partial^2G/\partial T^2)<0 \quad\text{and}\quad (\partial^2G/\partial T^2)\,(\partial^2G/\partial P^2)>(\partial^2G/\partial T\partial P)^2.$$

(*a*) *Partial and critical miscibility*

We shall first examine in more detail the conditions for liquid-liquid immiscibility at ordinary pressures, and the nature of the corresponding critical solution points. For this purpose we can neglect all the terms involving the pressure in equation (10·4), and use the approximate equation

$$\frac{\partial^2 G}{\partial x^2} = RT[1/x(1-x) + (h'_x/h_x)^2 - (h''_x/h_x) - (f'_x/f_x)^2 C_P/R] + (f''_x/f_x)\,U, \qquad (10\cdot 10)$$

where the configurational functions U and C_P refer to the mixture or corresponding equivalent substance. In order to discuss the nature of a critical solution point, we need an expression for the coefficient $\partial^2 H/\partial x^2$, which is negative at an upper critical solution point and positive at a lower one (see Prigogine & Defay 1954). From equation (10·10) we find by differentiation that

$$\frac{\partial^2 H}{\partial x^2} = -(f''_x/f_x)\,(TC_P - U) + (f'_x/f_x)^2\, T^2 \left(\frac{\partial C_P}{\partial T}\right)_P. \qquad (10\cdot 11)$$

An examination of equation (10·10), bearing in mind that U is negative and C_P is positive, reveals two possible reasons for material instability leading to liquid-liquid phase separation:

(i) If we suppose that the components are roughly similar, then (h''_x/h_x) and (f'_x/f_x) will be small compared with $1/x(1-x)$ (which has a minimum value of 4), and the factor in brackets in equation (10·10) will be positive. Instability is then possible if f''_x is positive, and since it follows from equation (10·11) that $\partial^2 H/\partial x^2$ is negative in this case, phase separation will terminate at an upper critical solution point. This is the reason for the kind of instability usually encountered in practice with non-polar mixtures. It can be seen from equations (10·7) and (10·6) that f''_x will be positive if e^*_{12} is negative or if $|\phi^*_{12}|$ is large. Immiscibility caused by the former can be interpreted as primarily an energy effect, while that caused by the latter is primarily due to differences in molecular size.

(ii) If the components differ widely in their critical constants† and if the configurational heat capacity of the equivalent substance increases strongly as the temperature is lowered, then the coefficient of RT in equation (10·10) may be negative at low temperatures. If f''_x is positive, the situation is not qualitatively different from that discussed in (i) above. On the other hand if f''_x is negative there is the possibility of a closed solubility curve with upper and lower critical solution points; this can be verified by considering the sign of $\partial^2 H/\partial x^2$ at high and at low temperatures. However, such behaviour is unlikely to be found with mixtures of spherical molecules for two reasons. First, for isochoric mixtures, f''_x is equal to $2(f_{11}+f_{22}-2f_{12})$, which is probably always positive for mixtures of actual non-polar substances, and it can be seen from equation (10·7) that the effect of differences in molecular size is to increase the value of f''_x. Secondly, it seems unlikely that the configurational heat capacity of a substance composed of spherical molecules could increase strongly as the temperature is lowered; for example, the isobaric configurational heat capacity of liquid argon decreases as the temperature is lowered. We conclude that although it appears theoretically possible for mixtures of spherical molecules to exhibit a lower

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† Since deviations from random mixing will be important if the components differ widely, the present treatment is not strictly adequate to deal with this second possibility.

consolute temperature, such behaviour is unlikely to be found in practice. Actual mixtures which possess closed solubility curves at atmospheric pressure always appear to contain polar components. It is of interest, however, to note the existence of a class of liquid mixtures exhibiting lower consolute points at elevated pressures, to which Klinkenberg (1953) has drawn attention, in which the components have widely differing critical temperatures. The simplest example is ethane + ethanol, but others are known involving only slightly polar components, and even, apparently, two non-polar components.

Before leaving the subject of partial miscibility, it should be emphasized that the treatment given here assumes random mixing of the molecules, and that this assumption will, in general, be a poor one at temperatures as low as the critical mixing temperature of a mixture. Deviations from random mixing will be examined in part II.

(*b*) *Liquid-vapour critical phases*

We now turn to consider briefly the liquid-vapour critical phases or plait points of mixtures, in order to draw attention to the limited sense in which the mixtures being discussed obey the law of corresponding states. This is necessary in case an uncritical attitude leads one to the erroneous conclusion that the critical constants T^c, V^c and P^c of a mixture having conformal parameters f_x and h_x are related to those of the reference substance, T_0^c, V_0^c and P_0^c, by the simple equations

$$T^c = f_x T_0^c, \quad V^c = h_x V_0^c \quad \text{and} \quad P^c = (f_x/h_x)\, P_0^c. \tag{10·12}$$

In § 5 it was shown that a random mixture of Lennard-Jones molecules must obey the same reduced equation of state as the reference substance, in the sense that if (5·7) is the equation of state of the reference substance, then that of the mixture is (5·8). But not all the states of the mixture corresponding to actual states of the reference substance are necessarily stable. This is because phase separation in pure substances is determined by their limiting mechanical stability, while that in mixtures is determined by the breakdown of *material* stability, which always limits the extent of the single phase region more than the breakdown of the mechanical stability of the mixture (see Prigogine & Defay 1954).

The plait-point curve of the mixture is given by the solution of the equations for critical material stability,

$$\left.\begin{aligned}\frac{\partial^2 G}{\partial x^2} &= \frac{RT}{x(1-x)} + \frac{\partial^2 G_x}{\partial x^2} = 0,\\ \frac{\partial^3 G}{\partial x^3} &= \frac{RT(2x-1)}{x^2(1-x)^2} + \frac{\partial^3 G_x}{\partial x^3} = 0.\end{aligned}\right\} \tag{10·13}$$

On the other hand, the critical point of the equivalent substance is given by the conditions for critical mechanical stability, which leads to the equations

$$\left.\begin{aligned}&\frac{\partial^2 G_x}{\partial x^2} = -\infty\\ \text{and}\qquad &\frac{\partial^3 G_x}{\partial x^3} = \pm\infty;\end{aligned}\right\} \tag{10·14}$$

these equations have the simple solution (10·12) for the critical constants T_x^c, V_x^c and P_x^c of the equivalent substance. It is clear from equations (10·13) and (10·14) that the plait-point curve of the mixture can never coincide with the critical-point curve for the various equivalent substances, except in the limiting cases of the pure components. In some recent papers (Cook & Longuet-Higgins 1951; Rowlinson & Sutton 1955*a*) it is assumed that in a first-order perturbation treatment it is legitimate to identify these two curves. This assumption requires further justification, as the authors of these papers were aware. However, for closely similar components, equations (10·12) are no doubt approximations to the plait points of the mixtures, and we may note in passing that the temperature factor f_x is not solely an energy parameter, as for a pure substance, since it involves both the energy parameters $f_{\alpha\beta}$ and the size parameters $g_{\alpha\beta}$; similarly, both sorts of parameter are involved in h_x.

The solution of equations (10·13) is not a simple matter in the general case, as it depends on the behaviour of the reference substance in the vicinity of its critical phase. It is hoped to discuss this problem in detail in a later paper.

11. TAYLOR-SERIES EXPANSIONS OF THERMODYNAMIC FUNCTIONS

In this section we shall derive the Taylor-series expansion of the Gibbs function for a random mixture of any number of kinds of Lennard-Jones molecules, in powers and products of various conformal parameter differences up to the second order. This expansion will then be used to discuss the mixing properties of a special class of binary mixtures in detail.

The expansion of the molar configurational Gibbs function G, given by equation (5·6), in powers and products of $\delta f_x = (f_x - 1)$ and $\delta h_x = (h_x - 1)$ about that of an isotopic reference mixture of the same composition, G^0, is

$$G(T,P,x) = G^0(T,P,x) + (\delta f_x)\, G_{f0} + (\delta h_x)\, G_{h0} + \tfrac{1}{2}(\delta f_x)^2\, G_{ff0} + (\delta f_x\, \delta h_x)\, G_{fh0} + \tfrac{1}{2}(\delta h_x)^2\, G_{hh0} + O(\delta^3), \qquad (11·1)$$

where the functions G_{f0}, etc., are related to those of equations (10·5) and (10·6), but refer to the reference substance and not to an equivalent substance. They are independent of composition, and are given by the following formulae:

$$\left.\begin{aligned} G_{f0} &= \left(\frac{\partial G}{\partial f}\right)_0 = U_0, \\ G_{h0} &= \left(\frac{\partial G}{\partial h}\right)_0 = PV_0 - RT, \\ G_{ff0} &= \left(\frac{\partial^2 G}{\partial f^2}\right)_0 = -TC_{P0} + 2PTV_0\alpha_0 - P^2V_0\kappa_0, \\ G_{fh0} &= \left(\frac{\partial^2 G}{\partial f\,\partial h}\right)_0 = P^2V_0\kappa_0 - PTV_0\alpha_0, \\ G_{hh0} &= \left(\frac{\partial^2 G}{\partial h^2}\right)_0 = RT - P^2V_0\kappa_0. \end{aligned}\right\} \qquad (11·2)$$

The configurational Gibbs function of the isotopic reference mixture is given by the equation, similar to (10·2),

$$G^0(T,P,x) = G_0(T,P) + RT \sum_\alpha x_\alpha \ln x_\alpha. \qquad (11·3)$$

In these expressions, G_0, U_0, V_0 and C_{P0} are the molar configurational Gibbs function, the molar configurational energy, the molar volume and the molar isobaric configurational heat capacity, α_0 and κ_0 are the thermal expansivity and isothermal compressibility, and all functions are properties of the reference substance at temperature T and pressure P. For convenience the suffix zero, indicating a property of the reference substance, will henceforth be omitted from the functions G_{f0}, etc., of equations (11·2); care must therefore be taken to avoid confusing them with the functions G_f, etc., of the last section, which differ in belonging to an equivalent substance.

The parameters f_x and h_x, defined by equations (4·9) and (4·10), may be expanded in powers and products of the differences $\delta f_{\alpha\beta} = (f_{\alpha\beta}-1)$ and $\delta h_{\alpha\beta} = (h_{\alpha\beta}-1)$ as follows:

$$\delta f_x = \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} - \frac{nm}{18} \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h^2_{\alpha\beta} + \frac{nm}{18} (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta})^2 + O(\delta^3), \tag{11·4}$$

$$\begin{aligned}\delta h_x = {} & \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta} + \sum_\alpha \sum_\beta x_\alpha x_\beta \left[\delta h_{\alpha\beta} \delta f_{\alpha\beta} + \left(\frac{n+m-3}{6}\right) \delta h^2_{\alpha\beta}\right] \\ & - (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta}) (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta}) - \left(\frac{n+m-3}{6}\right) (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta})^2 + O(\delta^3).\end{aligned} \tag{11·5}$$

When these expressions are substituted into the series (11·1), we find that to the second order in $\delta f_{\alpha\beta}$ and $\delta h_{\alpha\beta}$,

$$\begin{aligned}G = G^0 & + G_f \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} + G_h \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta} + \tfrac{1}{2} G_{ff} (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta})^2 \\ & + G_h \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} \delta h_{\alpha\beta} + (G_{fh} - G_h) (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta}) (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta}) \\ & + \frac{1}{2}\left[G_{hh} - \left(\frac{n+m}{3} - 1\right) G_h + \frac{nm}{9} G_f\right] (\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta})^2 \\ & + \frac{1}{2}\left[\left(\frac{n+m}{3} - 1\right) G_h - \frac{nm}{9} G_f\right] \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h^2_{\alpha\beta}.\end{aligned} \tag{11·6}$$

The following points should be noticed about this expansion:

(i) To the first order in $\delta f_{\alpha\beta}$ and $\delta h_{\alpha\beta}$ the expansion is

$$G = G^0 + U_0 \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} + (PV_0 - RT) \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta}. \tag{11·7}$$

This is identical with the equation derived and used by Longuet-Higgins in his first-order theory of conformal solutions (1951), and does not depend in any way on the Lennard-Jones form of the potential energy. We note in passing that the first-order change in the Gibbs free energy due to changes of molecular size is small compared with that due to changes in the parameters $f_{\alpha\beta}$.

(ii) The coefficient of the second-order terms in $\delta f_{\alpha\beta}$ likewise does not depend on the form of the intermolecular potential. In fact it is evident from § 4 that for isochoric mixtures the general equation for the Gibbs function does not depend on the form of the intermolecular potential.

(iii) The last two terms of the second order in $\delta h_{\alpha\beta}$ have coefficients depending on the Lennard-Jones indices n and m. Furthermore, it can be seen that the summation factors in these terms are positive, and that the second, which is the larger, has a coefficient which is effectively given by $-\frac{1}{9}nmU_0$. This quantity will be large and positive for the usual values of n and m (i.e. $n = 8$ to 14, $m = 6$). The second-order change in the Gibbs free energy due to differences in molecular size is therefore always large and positive.

This last point introduces one of the most important results of this treatment, since it means that small differences in molecular size are sufficient to account for considerable deviations from ideality in mixtures. This is in agreement with intuition, although such deviations have too often been attributed entirely to first-order energy terms. A similar conclusion has been reached by Prigogine & Bellemans (1953), but these authors unnecessarily employ the cell model for the liquid state. The present treatment makes no such assumption, and therefore places this result on a more satisfactory basis.

(*a*) *Comparison with rigorous expansion*

It is relevant to recall here that it is possible to expand the Gibbs function of a conformal mixture directly in powers and products of the differences $\delta f_{\alpha\beta}$ and $\delta h_{\alpha\beta}$, without assuming random mixing, or postulating the Lennard-Jones potential (Brown & Longuet-Higgins 1951). To the second order this expansion has the form (Brown 1953)

$$\begin{aligned} G = G^0 &+ G_f \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} + G_h \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta} \\ &+ \tfrac{1}{2} G^{(2)}_{ff} \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f^2_{\alpha\beta} + \tfrac{1}{2} G^{(3)}_{ff} \sum_\alpha \sum_\beta \sum_\gamma x_\alpha x_\beta x_\gamma \delta f_{\alpha\beta} \delta f_{\alpha\gamma} + \tfrac{1}{2} G^{(4)}_{ff} \Big(\sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta}\Big)^2 \\ &+ G^{(2)}_{fh} \sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta} \delta h_{\alpha\beta} + G^{(3)}_{fh} \sum_\alpha \sum_\beta \sum_\gamma x_\alpha x_\beta x_\gamma \delta f_{\alpha\beta} \delta h_{\alpha\gamma} \\ &+ G^{(4)}_{fh} \Big(\sum_\alpha \sum_\beta x_\alpha x_\beta \delta f_{\alpha\beta}\Big)\Big(\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta}\Big) + \tfrac{1}{2} G^{(2)}_{hh} \sum_\alpha \sum_\beta x_\alpha x_\beta \delta h^2_{\alpha\beta} \\ &+ \tfrac{1}{2} G^{(3)}_{hh} \sum_\alpha \sum_\beta \sum_\gamma x_\alpha x_\beta x_\gamma \delta h_{\alpha\beta} \delta h_{\alpha\gamma} + \tfrac{1}{2} G^{(4)}_{hh} \Big(\sum_\alpha \sum_\beta x_\alpha x_\beta \delta h_{\alpha\beta}\Big)^2. \end{aligned} \tag{11·8}$$

In this equation the functions $G^{(2)}_{ff}$, etc., are non-thermodynamic properties of the reference substance, such that

$$\left.\begin{aligned} G^{(2)}_{ff} + G^{(3)}_{ff} + G^{(4)}_{ff} &= G_{ff}, \\ G^{(2)}_{fh} + G^{(3)}_{fh} + G^{(4)}_{fh} &= G_{fh}, \\ G^{(2)}_{hh} + G^{(3)}_{hh} + G^{(4)}_{hh} &= G_{hh}. \end{aligned}\right\} \tag{11·9}$$

The non-thermodynamic parts of these functions are given by statistical formulae which can be reduced to integrals over pair, triplet and quadruplet configurational distribution functions; in fact the set $G^{(2)}_{ff}$, $G^{(3)}_{ff}$ and $G^{(4)}_{ff}$ are the contributions to G_{ff} from groups of two, three and four molecules, and the same is true of the other two sets of functions (see § 7 of part II). The composition dependence of the various terms involving these functions is evidently in keeping with this interpretation; for example, the term with the coefficient $G^{(3)}_{ff}$ is cubic in the mole fractions.

This general and direct expansion makes it clear that the assumption of random mixing is only correct to the first-order terms in $\delta f_{\alpha\beta}$ and $\delta h_{\alpha\beta}$. The approximate thermodynamic forms implied by the random-mixing approximation for the non-thermodynamic functions $G^{(2)}_{ff}$, etc., can be readily obtained by comparing the two expansions (11·6) and (11·8); we note that these forms are such that the relations (11·9) are satisfied. The general expansion also enables an estimate to be made of the magnitude of the second-order terms due to molecular ordering, but as a more powerful method of examining this problem will be given in part II, such an estimate will not be undertaken here. These non-random or ordering terms are, of course, all negative, since the molecules will distribute themselves in such a way as to minimize the free energy. This means, for instance, that equation (11·6) over-emphasizes the effect of differences in molecular size.

(*b*) *Excess Gibbs free energy of mixing*

We shall now use equation (11·6) to obtain the Taylor-series expansion of the excess molar Gibbs function of mixing, given by equation (6·2). For this purpose we require the expanded forms of the molar Gibbs functions for the pure components. For component α we have

$$G_\alpha = G_0 + G_f(\delta f_{\alpha\alpha}) + G_h(\delta h_{\alpha\alpha}) + \tfrac{1}{2}G_{ff}(\delta f_{\alpha\alpha})^2 + G_{fh}(\delta f_{\alpha\alpha}\,\delta h_{\alpha\alpha}) + \tfrac{1}{2}G_{hh}(\delta h_{\alpha\alpha})^2 + O(\delta^3). \quad (11{\cdot}10)$$

The expansion of G^E is now obtained by substituting from equations (11·6) and (11·10) into (6·2). This enormous expression can be simplified by introducing the (constant) parameter differences

$$\left.\begin{aligned} e_{\alpha\beta} &= 2f_{\alpha\beta} - f_{\alpha\alpha} - f_{\beta\beta},\\ s_{\alpha\beta} &= 2h_{\alpha\beta} - h_{\alpha\alpha} - h_{\beta\beta},\\ \theta_{\alpha\beta} &= f_{\alpha\alpha} - f_{\beta\beta},\\ \phi_{\alpha\beta} &= h_{\alpha\alpha} - h_{\beta\beta},\end{aligned}\right\} \quad (\alpha, \beta = 1, 2, \ldots, c), \quad (11{\cdot}11)$$

and by breaking the equation up into terms of different order; that is, we put

$$G^E = {}^{(1)}G^E + {}^{(2)}G^E + \ldots. \quad (11{\cdot}12)$$

The terms of the first order in $\delta f_{\alpha\beta}$ and $\delta h_{\alpha\beta}$ then take the simple form, quadratic in the mole fractions,

$${}^{(1)}G^E = U_0 \sum_{\alpha>\beta}\sum x_\alpha x_\beta e_{\alpha\beta} + (PV_0 - RT)\sum_{\alpha>\beta}\sum x_\alpha x_\beta s_{\alpha\beta}, \quad (11{\cdot}13)$$

which is the equation derived by Longuet-Higgins (who uses the symbol $d_{\alpha\beta}$ for our $e_{\alpha\beta}$). We see that this first-order expression does not depend on the absolute values of the conformal parameters $f_{\alpha\beta}$ and $h_{\alpha\beta}$, but only on the combinations $e_{\alpha\beta}$ and $s_{\alpha\beta}$ given by (11·11). However, as might be expected, the second-order contribution, ${}^{(2)}G^E$, does involve the absolute values of the parameters. We shall not quote the general expression obtained for ${}^{(2)}G^E$ for a mixture of c components since, unlike that for the Gibbs function itself, it cannot be easily interpreted. For a binary mixture we find, omitting the suffixes 1 and 2 from the parameters e_{12}, etc.,

$$\begin{aligned} {}^{(2)}G^E = \tfrac{1}{2}x(1-x)\{&-[\theta^2 G_{ff} + 2\theta\phi(G_{fh} - \tfrac{1}{2}G_h) + \phi^2(G_{hh} - \tfrac{1}{2}Z_{hh})]\\ &+ \tfrac{1}{4}[e^2 G_{ff} + 2es(G_{fh} + G_h) + s^2(G_{hh} + Z_{hh})] + (1-2x)\,[e\theta G_{ff} + (e\phi + s\theta)\,(G_{fh} - G_h)\\ &+ s\phi(G_{hh} - Z_{hh})] - \tfrac{1}{4}(1-2x)^2\,[e^2 G_{ff} + 2es(G_{fh} - G_h) + s^2(G_{hh} - Z_{hh})]\}, \end{aligned} \quad (11{\cdot}14)$$

where x is the mole fraction of the second component, and the reference substance has been chosen so that

$$\tfrac{1}{2}(f_{11} + f_{22}) = 1 \quad \text{and} \quad \tfrac{1}{2}(h_{11} + h_{22}) = 1;$$

if the reference substance is arbitrary, then the following terms must be added to (11·14):

$$\tfrac{1}{2}(eG_{ff} + sG_{fh})\,\delta(f_{11} + f_{22}) + \tfrac{1}{2}(eG_{fh} + sG_{hh})\,\delta(h_{11} + h_{22}). \quad (11{\cdot}15)$$

The function denoted by Z_{hh}, which is the large positive quantity connected with the second-order size terms, is given by

$$\begin{aligned} Z_{hh} &= \left(\frac{n+m}{3}-1\right)G_h-\frac{nm}{9}G_f \\ &= \left(\frac{n+m}{3}-1\right)(PV_0-RT)-\frac{nm}{9}U_0; \end{aligned} \tag{11·16}$$

it is the only function in equation (11·14) which depends on the Lennard-Jones form of the potential.

The second-order excess Gibbs function inevitably contains a large number of terms; we note that the composition dependence is no longer quadratic or symmetrical, and that the five thermodynamic functions of the reference substance defined in (11·2) are involved. The general expressions for the latter can be simplified for liquids under low pressure by neglecting PV_0 terms compared with RT, U_0 and TC_{P0}, as in equation (10·9). The approximate formulae are

$$\left.\begin{aligned} G_f &= U_0, & G_{ff} &= -TC_{P0}, \\ G_h &= -RT, & G_{fh} &= 0, \\ Z_{hh} &= -\left(\frac{n+m}{3}-1\right)RT-\frac{nm}{9}U_0, & G_{hh} &= RT. \end{aligned}\right\} \tag{11·17}$$

From the signs and approximate magnitudes of these functions it is possible to appreciate the effect of the various parameter differences e_{12}, s_{12}, θ_{12} and ϕ_{12} on the excess Gibbs free energy of mixing. For this purpose we shall put n and m equal to 12 and 6, and consider the expression obtained for an equimolar mixture, which is

$$\begin{aligned} G^E(x=\tfrac{1}{2}) = \tfrac{1}{4}\{eU_0-sRT+\tfrac{1}{2}[\theta^2TC_{P0}+\theta\phi RT-\phi^2(4U_0+\tfrac{3}{2}RT)] \\ -\tfrac{1}{8}[e^2TC_{P0}+2esRT+4s^2(2U_0+RT)]\}. \end{aligned} \tag{11·18}$$

The following points about this equation are of interest:

(i) Mixtures in which e_{12} and s_{12} vanish are not ideal, but show a positive deviation from Raoult's law. The condition for the ideality of isochoric mixtures derived from the theory of strictly regular solutions, namely that e_{12} is zero, is therefore inadequate. The only truly ideal solution is an isotopic one.

(ii) Differences between the critical constants of the two components always increase the excess Gibbs free energy, which is particularly sensitive to differences in size, owing to the large positive coefficient of ϕ^2. These effects are in full agreement with physical intuition.

(iii) The second-order terms due to deviations, e_{12}, of the intercomponent energy parameter from the arithmetic mean of those of the components causes a decrease in G^E, while the corresponding size difference, s_{12}, causes an increase. The latter difference is not likely to be important, as it is difficult to imagine that g_{12} deviates very much from $\frac{1}{2}(g_{11}+g_{22})$.

The expanded forms of the derived excess functions of mixing, S^E, H^E and V^E, are most easily obtained by differentiating that for G^E with respect to temperature and pressure. We shall not quote the equations obtained, but merely point out that it is necessary to differentiate the general expressions (11·13) and (11·14) with respect to pressure *before* approximating after the manner of (11·17); this is because the pressure derivatives of otherwise negligible terms, like PV_0, are large.

(*c*) *Lorentz–Berthelot mixtures*

For the remainder of this section we shall confine our attention to mixing effects in a particular class of mixtures which cannot be treated by the first-order theory of conformal solutions. This class is defined by the following relations between the intercomponent conformal parameters $f_{\alpha\beta}$ and $g_{\alpha\beta}$ and those of the pure components α and β:

$$f_{\alpha\beta}^2 = f_{\alpha\alpha} f_{\beta\beta} \quad \text{and} \quad g_{\alpha\beta} = \tfrac{1}{2}(g_{\alpha\alpha} + g_{\beta\beta}) \quad (\alpha, \beta = 1, 2, \ldots, c). \tag{11·19}$$

These relations are usually associated with the London dispersion forces between spherically symmetrical molecules, and are similar to those proposed many years ago between the constants in van der Waals's equation of state for mixtures. As the arithmetic and geometric mean type of relations were first suggested by Lorentz (1881) and by Berthelot (1898), we shall call conformal mixtures whose parameters satisfy the above relations *Lorentz–Berthelot mixtures*.

There is some evidence that actual mixtures of non-polar substances approximate to Lorentz–Berthelot mixtures:

(i) The experimental values for the second virial coefficient in binary mixtures of non-polar gases, such as carbon monoxide + hydrogen and methane + ethane, are in agreement with those calculated from the critical constants using relations (11·19) (Guggenheim & McGlashan 1951).

(ii) Prigogine and his colleagues (1953, 1956) have found that certain binary liquid mixtures of strictly non-polar molecules of about the same size, for example, carbon tetrachloride and *neo*-pentane, show mixing effects whose signs contradict the first-order theory of Longuet-Higgins, but which can be accounted for on a cell theory of solutions which includes second-order terms and assumes the relations (11·19). This is, however, a very indirect test of the latter.

It follows from the relations (11·19) that the otherwise arbitrary differences $e_{\alpha\beta}$ and $s_{\alpha\beta}$ are given by

$$\left.\begin{aligned} e_{\alpha\beta} &= -\tfrac{1}{4}\theta_{\alpha\beta}^2 + O(\theta^4), \\ \text{and} \qquad s_{\alpha\beta} &= -\tfrac{1}{6}\phi_{\alpha\beta}^2 + O(\phi^4). \end{aligned}\right\} \tag{11·20}$$

By substituting these formulae into equations (11·13) and (11·14), and retaining only terms of the second order, we find that for a binary mixture

$$G^E = \tfrac{1}{2}x(1-x)\,[\theta^2 G_{\theta\theta} + 2\theta\phi G_{\theta\phi} + \phi^2 G_{\phi\phi}], \tag{11·21}$$

where

$$\left.\begin{aligned} G_{\theta\theta} &= -G_{ff} - \tfrac{1}{2}G_f &&\simeq TC_{P0} - \tfrac{1}{2}U_0, \\ G_{\theta\phi} &= -G_{fh} + \tfrac{1}{2}G_h &&\simeq -\tfrac{1}{2}RT, \\ G_{\phi\phi} &= -G_{hh} + \tfrac{1}{2}X_{hh} - \tfrac{1}{3}G_h &&\simeq -\frac{nm}{18}U_0 - \left(\frac{n+m+1}{6}\right)RT; \end{aligned}\right\} \tag{11·22}$$

the formulae on the extreme right-hand side involve the usual approximations for a liquid. The excess Gibbs free energy of a Lorentz-Berthelot mixture is therefore quadratic in the composition to the second order in θ and ϕ.

The other excess functions can be obtained from (11·21) by differentiation. The excess entropy is given by

$$S^E = \tfrac{1}{2}x(1-x)\,[\theta^2 S_{\theta\theta}+2\theta\phi S_{\theta\phi}+\phi^2 S_{\phi\phi}], \tag{11·23}$$

where

$$\left.\begin{aligned} S_{\theta\theta} &= -\left(\frac{\partial G_{\theta\theta}}{\partial T}\right)_P \simeq -\tfrac{1}{2}C_{P0}-T\left(\frac{\partial C_{P0}}{\partial T}\right)_P,\\ S_{\theta\phi} &= -\left(\frac{\partial G_{\theta\phi}}{\partial T}\right)_P \simeq \tfrac{1}{2}R,\\ S_{\phi\phi} &= -\left(\frac{\partial G_{\phi\phi}}{\partial T}\right)_P \simeq \frac{nm}{18}C_{P0}+\left(\frac{n+m+1}{6}\right)R. \end{aligned}\right\} \tag{11·24}$$

The heat of mixing is therefore given by

$$H^E = \tfrac{1}{2}x(1-x)\,[\theta^2 H_{\theta\theta}+2\theta\phi H_{\theta\phi}+\phi^2 H_{\phi\phi}], \tag{11·25}$$

where

$$\left.\begin{aligned} H_{\theta\theta} &= G_{\theta\theta}+TS_{\theta\theta} \simeq \tfrac{1}{2}TC_{P0}-\tfrac{1}{2}U_0-T^2\left(\frac{\partial C_{P0}}{\partial T}\right)_P,\\ H_{\theta\phi} &= G_{\theta\phi}+TS_{\theta\phi} \simeq 0,\\ H_{\phi\phi} &= G_{\phi\phi}+TS_{\phi\phi} \simeq \frac{nm}{18}(TC_{P0}-U_0). \end{aligned}\right\} \tag{11·26}$$

And the volume of mixing is

$$V^E = \tfrac{1}{2}x(1-x)\,[\theta^2 V_{\theta\theta}+2\theta\phi V_{\theta\phi}+\phi^2 V_{\phi\phi}], \tag{11·27}$$

where

$$\left.\begin{aligned} V_{\theta\theta} &= \left(\frac{\partial G_{\theta\theta}}{\partial P}\right)_T \simeq -V_0\left[\tfrac{3}{2}T\alpha_0+(T\alpha_0)^2+T^2\left(\frac{\partial \alpha_0}{\partial T}\right)_P\right],\\ V_{\theta\phi} &= \left(\frac{\partial G_{\theta\phi}}{\partial P}\right)_T \simeq V_0[\tfrac{1}{2}+T\alpha_0],\\ V_{\phi\phi} &= \left(\frac{\partial G_{\phi\phi}}{\partial P}\right)_T \simeq V_0\left[\left(\frac{n+m-5}{6}\right)+\frac{nm}{18}T\alpha_0\right]. \end{aligned}\right\} \tag{11·28}$$

These formulae are strictly correct only at zero pressure. The values of the functions $G_{\theta\theta}$, etc., for orthobaric liquid argon at 90·67° K (vapour pressure 1·41 atm), have been calculated from data quoted by Din (1956), and are given in table 1.

Table 1. Thermodynamic random-mixing coefficients for orthobaric liquid argon at 90·67° K

		suffixes $\xi\eta$		
coefficient	units	$\theta\theta$	$\theta\phi$	$\phi\phi$
$G_{\xi\eta}$	J/mole	+5628	−377	+20630
$H_{\xi\eta}$	J/mole	+3259	0	+34020
$TS_{\xi\eta}$	J/mole	−2369	+377	+13390
$V_{\xi\eta}$	ml./mole	− 30·17	+ 26·73	+ 111·8

The first question of interest concerning these equations is whether they show the same behaviour as those obtained for Lorentz–Berthelot mixtures from the cell theory of solutions. The unexpected feature of the latter is that when the molecules are the same size, so that ϕ is zero, they predict that

$$G^E > 0, \quad H^E > 0 \quad \text{and} \quad V^E < 0.$$

This was shown to be possible according to the approximate equations of § 6 (*a*), and it can be seen from the above equations that the more accurate analysis of this section confirms this result as far as the second-order terms. We also observe that in this case the excess entropy is negative.

It is now natural to inquire whether the excess functions for Lorentz–Berthelot mixtures always have the same sign according to these equations, or for which mixtures they vanish, if any. Since the excess functions are all simply binary quadratic forms in θ and ϕ, we have merely to formulate the conditions for such forms to have real roots. For G^E this condition is evidently

$$G^2_{\theta\phi} \geqslant G_{\theta\theta}\,G_{\phi\phi}. \tag{11·29}$$

If this is true, then the values of θ and ϕ for which G^E vanishes are related by

$$\theta G_{\theta\theta} = \phi\{-G_{\theta\phi} \pm \surd(G^2_{\theta\phi} - G_{\theta\theta}\,G_{\phi\phi})\}. \tag{11·30}$$

On examining the coefficients $G_{\theta\theta}$, etc., in the light of condition (11·29), we find that for the mixtures under consideration, the excess Gibbs free energy and heat of mixing are always positive, while the excess entropy and volume of mixing can have either sign. This means that it is theoretically possible to have Lorentz–Berthelot mixtures which possess large excess free energies and heats of mixing, but ideal entropies or zero volumes of mixing, and possibly both. These possibilities are interesting with regard to actual mixtures of non-polar substances, some of which exhibit this type of behaviour. It should be noticed that in systems in which the quadratic composition coefficient for V^E or S^E vanishes, the cubic terms (which are of the third order in θ and ϕ) could become dominant.

If the components differ greatly in their critical constants, they will not be completely miscible at all temperatures, but will exhibit an upper critical solution point; this follows generally for Lorentz–Berthelot mixtures from the treatment of partial miscibility in § 10 (*a*). From the second-order equation (11·21) for the excess Gibbs function we can deduce that the critical mixing phase is equimolar in the components, and that its temperature is given by

$$\theta^2 G_{\theta\theta} + 2\theta\phi G_{\theta\phi} + \phi^2 G_{\phi\phi} = 4RT. \tag{11·31}$$

Alternatively, at a given temperature, we can regard equation (11·31) as the boundary relation between the critical temperatures and volumes of components which are completely miscible, and those which are only partially miscible. If, as is usually the case,

$$G_{\theta\theta} > 0, \quad G_{\phi\phi} > 0 \quad \text{and} \quad G^2_{\theta\phi} < G_{\theta\theta}\,G_{\phi\phi},$$

then equation (11·31) represents an ellipse, first introduced by Scott (1956), which may be called the miscibility ellipse.

To show clearly the qualitative behaviour of all possible Lorentz–Berthelot mixtures, it is convenient to represent the components by points in a diagram having the conformal energy parameters $f_{\alpha\alpha}$ as abscissae and the conformal size parameters $h_{\alpha\alpha}$ as ordinates; this is equivalent to plotting the critical volumes of the components against their critical temperatures. If the position of one of the components in a binary mixture is fixed in this conformal parameter diagram, say (f_{22}, h_{22}), then the parameters of other components (f_{11}, h_{11}) which are completely miscible with the first lie within the ellipse, given by equation (11·31), whose centre is (f_{22}, h_{22}). The parameters of the other component for mixtures for which S^E and V^E are zero will lie on straight lines through (f_{22}, h_{22}) given by equations similar to (11·30). This type of diagram has been drawn in figure 4 from the data for liquid argon in table 1. If the point representing the first component (f_{11}, h_{11}) lies within the ellipse, then the mixture will be homogeneous. If it lies in the shaded region between the pair of lines $V^E = 0$, then the components will contract on mixing; if it lies outside this region, expansion will occur. Similarly, if the first component lies in the shaded region between the lines $S^E = 0$, then the excess entropy of the mixture will be negative; otherwise it will be positive. As mentioned above, all Lorentz–Berthelot mixtures have positive excess Gibbs free energies and heats of mixing. The four possible types of behaviour are therefore:

$$G^E > 0, \quad H^E > 0 \quad \begin{cases} S^E > 0, & V^E > 0, \\ S^E < 0, & V^E > 0, \\ S^E > 0, & V^E < 0, \\ S^E < 0, & V^E < 0. \end{cases}$$

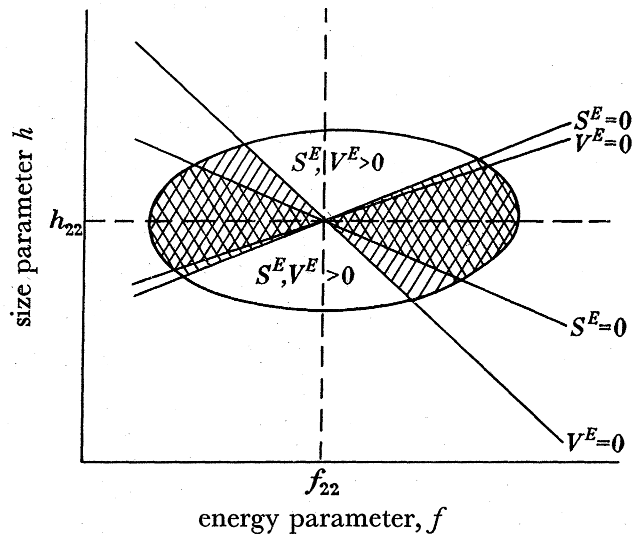

FIGURE 4. Conformal parameter diagram for binary Lorentz–Berthelot mixtures with the parameters of component 2 fixed (f_{22}, h_{22}), showing the miscibility ellipse, and the dependence of the sign of S^E and V^E on the parameters (f_{11}, h_{11}) of the other component.

Of these possible types of behaviour, only the first and last have so far been found experimentally with mixtures of roughly spherical and non-polar molecules. The first type, in which all the excess properties are positive, is well known, and is shown, for example, by mixtures of *cyclo*hexane and carbon tetrachloride. Englert-Chwoles (1955) has reported that the excess entropy of an equimolar mixture of *neo*-pentane and carbon tetrachloride is negative, and at present this system provides the only known example of the last type. Both the present theory and the cell theory predict that mixtures of carbon monoxide and methane should have negative volumes and excess entropies of mixing (see § 12), but the latter has not yet been confirmed experimentally.

12. COMPARISON OF THEORY WITH EXPERIMENT

There are comparatively few liquid mixtures to which the theory presented in this paper could be applied with complete confidence. The only mixtures which can be assumed to satisfy the premises of the theory with sufficient accuracy are those formed from substances accurately obeying the same reduced equation of state. Of the substances listed by Guggenheim (1945) as satisfying this condition, only the liquid mixtures formed from carbon monoxide and methane have been studied with a view to obtaining the functions of mixing; the comparison of theory with experiment will therefore be confined to this system.

However, before proceeding to describe the results of this comparison, it should be mentioned that Prigogine and his colleagues (1953, 1956) have applied the equations of the cell theory of solutions to a wider variety of binary liquid systems. The equations of the present theory are similar to those of the cell theory, and agree with the latter in suggesting that the major part of the mixing effects in most of the strictly non-polar solutions studied (with the exception of those involving fluorocarbons†) can be accounted for by a theory whose leading terms are of the second order in differences between molecular energy and size parameters; for example, a theory assuming the Lorentz–Berthelot relations (11·19). It does not seem worth while to apply the present theory in detail to the liquid mixtures which have been carefully investigated at ordinary temperatures, such as benzene + *cyclo*hexane, since none of the molecules can be assumed to be spherical with any confidence, and Rowlinson & Sutton (1955*b*) have already shown that the mixing effects in such solutions could be accounted for by attributing them mainly to deviations from central interactions. It is sufficient to know that the bulk of the departures from ideality can be accounted for simply by differences between the properties of the pure components. To examine these departures in greater detail for mixtures containing substances such as carbon tetrachloride, benzene, *cyclo*hexane and the fluorocarbons, one requires a theory capable of distinguishing between mixing effects due to differences between central forces, non-central forces and forces which are not conformal.

The liquid system carbon monoxide + methane has recently been carefully studied by Mathot, Staveley, Young & Parsonage (1956) at the triple-point temperature of methane, 90·67° K. They have measured the vapour pressures and densities of the liquid mixtures, and derived the excess Gibbs free energy and the volume of mixing as functions of the composition. Their smoothed results are shown by the continuous lines in figures 7 and 8. In principle, the calculation of the mixing properties of this system from the equations of the present theory is straightforward. We assume tentatively that the Lorentz–Berthelot relations are obeyed, and calculate the equivalent parameters f_x and h_x as functions of the composition. From the properties of the chosen reference substance as functions of temperature and pressure, we can then calculate the corresponding properties for the mixture and the components by using the law of corresponding states. By subtracting these according to the equations of § 6, we obtain the excess mixing properties as functions of composition at a given temperature and pressure.

In practice, however, there are a number of difficulties, the most important of which is the failure of carbon monoxide and methane to obey the law of corresponding states exactly. For example, at a reduced temperature of 0·5, the reduced orthobaric volumes are 0·353 and 0·363 respectively, and the configurational isobaric heat capacities, which should also be identical, are 39·5 and 28·7 J/mole respectively. Since methane obeys the same reduced equation of state as argon, the failure is almost certainly due to non-central forces in carbon

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† It seems likely that the fluorocarbons, and other perfluorocompounds, belong to a family of quasi-conformal substances which is distinct from that of the hydrocarbons.

monoxide. These deviations mean that the results of the calculations will depend on the choice of the reference substance. Calculations have therefore been made using both carbon monoxide and methane as the reference substance.

There is also a difficulty in calculating the excess mixing functions from the exact equations (6·2) to (6·5), since these involve the difference between two large quantities, and this difference is usually only about 1% of the value of the quantities subtracted. Errors due to interpolation, whether graphical or numerical, are thus magnified. The calculations have therefore been made by representing the thermodynamic properties of the reference substance by simple formulae over the required temperature range, and using these to derive equations of the same type as those introduced in § 6 (*a*). These equations involve differences between conformal parameters, which can be calculated accurately, instead of differences between thermodynamic functions.

Throughout the calculations it is assumed that the functions involved are for the orthobaric reference liquid, since this corresponds more closely to the experiments from which the excess mixing properties were obtained than the assumption of constant pressure. In any case, the pressure dependence of the thermodynamic properties is small, because of the low pressures and small pressure range involved, namely, 0 to 2·5 atm.

TABLE 2. CRITICAL CONSTANTS AND CONFORMAL PARAMETERS FOR CARBON MONOXIDE AND METHANE

substance	crit. temp. (°K)	crit. vol. (ml./mole)	conformal parameters energy, f	 size, h
carbon monoxide $(1-1)$	133·0	93·1	1·00000	1·00000
methane $(2-2)$	191·1	99·0	1·43684	1·06337
$(1-2)$	(159·4)	(96·0)	1·19868	1·03136

The first step is to calculate the equivalent conformal parameters as functions of composition. The critical temperatures and volumes of carbon monoxide (1) and methane (2), and the values of the conformal parameters f_{11}, h_{11}, etc., for carbon monoxide as the reference substance, are given in table 2. The values of f_{12} and h_{12} have been calculated from the Lorentz–Berthelot relations (11·19), namely,

$$f_{12} = \surd(f_{11}f_{22}) \quad \text{and} \quad h_{12} = [\tfrac{1}{2}(\sqrt[3]{h_{11}}+\sqrt[3]{h_{22}})]^3. \tag{12·1}$$

Graphs of the equivalent parameters f and h (equal to g^3), calculated from equations (4·9) and (4·10) for n and m equal to 12 and 6, have been drawn against composition in figure 5. It can be seen that they are very nearly linear in the mole fraction of methane. The deviations from linearity, f^E and h^E, and the various other excess conformal parameters required, are drawn in figure 6; these excess parameters are defined by (6·9) and similar equations.

(*a*) *Calculation of the heat and excess entropy of mixing*

To within the experimental error of the existing thermodynamic measurements for liquid carbon monoxide and liquid methane, the orthobaric molar configurational enthalpy of either reference substance can be represented by the formula

$$H(T) = \overline{H} + (T-\overline{T})\,\overline{H}' + \tfrac{1}{2}(T-\overline{T})^2\,\overline{H}'', \tag{12·2}$$

where $\bar{T}$ is 90·67° K and $\bar{H}$, $\bar{H}'$ and $\bar{H}''$ are constants. If we neglect the pressure dependence of the enthalpy, then according to equation (6·4) the heat of mixing at temperature $\bar{T}$ is given by

$$H^E = Af^E + C(1/f)^E, \tag{12·3}$$

and similarly, according to (6·3), the excess entropy of mixing is given by

$$\bar{T}S^E = -B\ln^E f + 2C(1/f)^E + R\bar{T}\ln^E h, \tag{12·4}$$

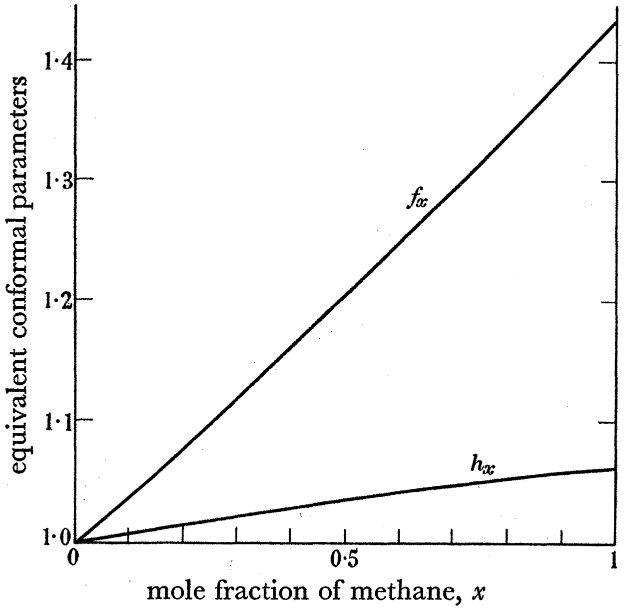

FIGURE 5. Variation of the conformal parameters of the equivalent substance, f_x and h_x, with composition for the system carbon monoxide + methane.

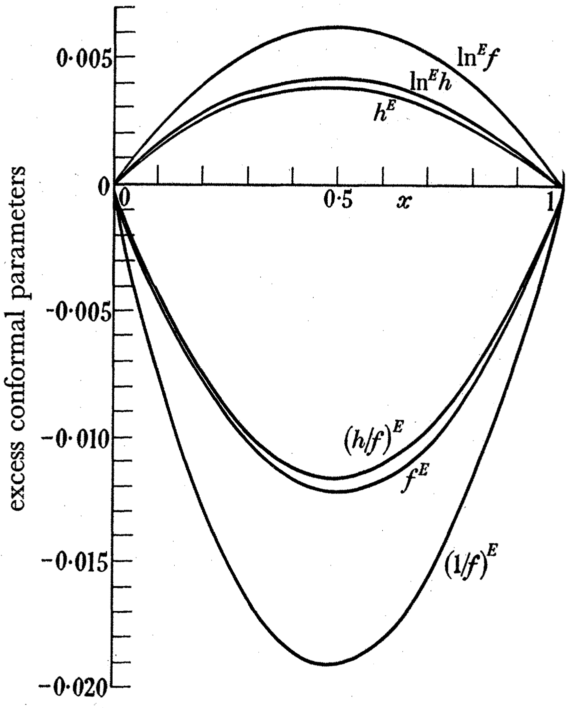

FIGURE 6. Variation of the excess conformal parameters with composition for the system carbon monoxide + methane.

where

$$\left.\begin{aligned} A &= \overline{H} - T\overline{H}' + \tfrac{1}{2}T^2\overline{H}'', \\ B &= T\overline{H}' - T^2\overline{H}'', \\ C &= \tfrac{1}{2}T^2\overline{H}''. \end{aligned}\right\} \qquad (12\cdot5)$$

The excess Gibbs function of mixing can be found from the relation

$$G^E = H^E - TS^E. \qquad (12\cdot6)$$

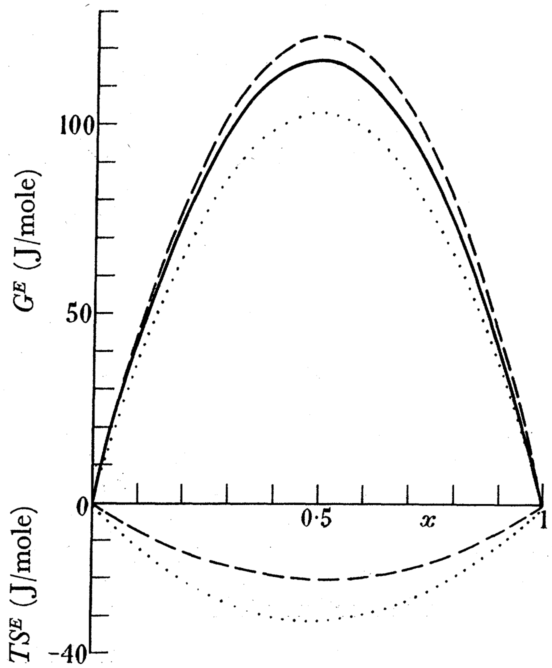

FIGURE 7. Variation of the excess Gibbs function and entropy of mixing with mole fraction of methane for the system carbon monoxide + methane at 90·67° K. ——, experimental results; – – – –, calculated using carbon monoxide as reference substance; · · · ·, calculated using methane as reference substance.

The values of the configurational enthalpy of liquid carbon monoxide and its derivatives with respect to temperature can be calculated from measurements of its heat of vaporization and heat capacity (Clayton & Giauque 1932). This procedure requires the configurational enthalpy of the saturated vapour, which can be estimated from calculated values of the second virial coefficient and its temperature derivative. The values obtained for the coefficients A, B and C are as follows (units J/mole):

$$A = -8680, \quad B = 3616, \quad C = 0.$$

The configurational enthalpy of liquid methane, and its derivatives with respect to temperature, can be calculated in a similar fashion from measurements of its heat of vaporization (Frank & Clusius 1939) and heat capacity (Clusius & Perlick 1934). The values obtained for the coefficients A, B and C, when reduced by the law of corresponding states to apply to carbon monoxide, are as follows (units J/mole):

$$A = -7038, \quad B = 1716, \quad C = 603.$$

The excess Gibbs free energies and entropies of mixing calculated from these sets of figures are plotted against composition in figure 7 (broken curves), and compared with the smoothed experimental results for the excess Gibbs free energy (continuous curve); the error in the latter is estimated to be within 1 %. The calculated values for the free energy of random mixing should lie slightly above the true values for the slightly ordered mixture. However, the two calculated curves for G^E lie above and below the experimental curve, and differ appreciably from one another, the difference being a measure of the deviation of the two components from the law of corresponding states. In view of this deviation, the agreement between theory and experiment must be regarded as satisfactory. We note that the sense of the asymmetry of G^E is correctly reproduced by the theory, although the displacements of the calculated maxima towards carbon monoxide-rich mixtures are rather less than that of the experimental curve; however, this feature would probably be improved if more extensive measurements for the heat capacities of the components were available.

The effects of molecular ordering on the excess free energy and entropy of mixing are estimated in part II.

(*b*) *Calculation of the volume of mixing*

The orthobaric molar volumes of liquid carbon monoxide and liquid methane can be represented by the equation

$$V(T) = \bar{V} + (T-\bar{T})\,\bar{V}' + \tfrac{1}{2}(T-\bar{T})^2\,\bar{V}'' + \tfrac{1}{6}(T-\bar{T})^3\,\bar{V}''', \qquad (12{\cdot}7)$$

within the temperature ranges required, namely, 63·10 to 90·67° K and 90·67 to 130·28° K respectively. If we neglect the effect of the difference between the vapour pressure of the mixture and that of the equivalent substance, then according to equation (6·5) and the law of corresponding states, the volume of mixing obtained from orthobaric measurements at temperature $\bar{T}$ is given by

$$V^E = ah^E + b(h/f)^E + c(h/f^2)^E + d(h/f^3)^E, \qquad (12{\cdot}8)$$

where

$$\left.\begin{aligned} a &= \bar{V} - \bar{T}\bar{V}' + \tfrac{1}{2}\bar{T}^2\bar{V}'' - \tfrac{1}{6}\bar{T}^3\bar{V}''', \\ b &= \bar{T}\bar{V}' - \bar{T}^2\bar{V}'' + \tfrac{1}{2}\bar{T}^3\bar{V}''', \\ c &= \tfrac{1}{2}\bar{T}^2\bar{V}'' - \tfrac{1}{2}\bar{T}^3\bar{V}''', \\ d &= \tfrac{1}{6}\bar{T}^3\bar{V}'''. \end{aligned}\right\} \qquad (12{\cdot}9)$$

The values of the derivatives in equation (12·7) for liquid carbon monoxide can be obtained from the density measurements of Mathias & Crommelin (1936), and those for liquid methane from the density measurements quoted by Keyes (1928) and by the American Petroleum Institute (1953). The coefficients defined by equations (12·9) have the following values for carbon monoxide (units ml./mole):

$$a = 14{\cdot}57, \quad b = 52{\cdot}31, \quad c = -58{\cdot}48, \quad d = 28{\cdot}83.$$

Those for methane, when reduced by the law of corresponding states to apply to carbon monoxide, are (units ml./mole):

$$a = 21{\cdot}89, \quad b = 27{\cdot}56, \quad c = -26{\cdot}51, \quad d = 15{\cdot}13.$$

The volumes of mixing calculated from equation (12·8) using these sets of coefficients are plotted against composition in figure 8 (lower broken curves), and compared with the smoothed experimental results (continuous curve). The calculated volumes of the random mixtures should be larger than those of the actual slightly ordered mixtures, but in fact the volume of mixing curves calculated using carbon monoxide and methane as reference substances are both lower than the experimental curve. This is simply due to the difference between the reduced orthobaric volumes of the two components at the same reduced temperatures. This difference is such that whichever component is used as the reference substance, the change of volume with temperature is greater than the molar volumes of the pure components at 90·67° K imply. This suggests that we construct a hypothetical reference substance whose orthobaric volume is the same as that of carbon monoxide at 90·67° K, and reproduces the volume of methane at the corresponding temperature (63·10° K). The second and third derivatives of the orthobaric volume with respect to temperature are

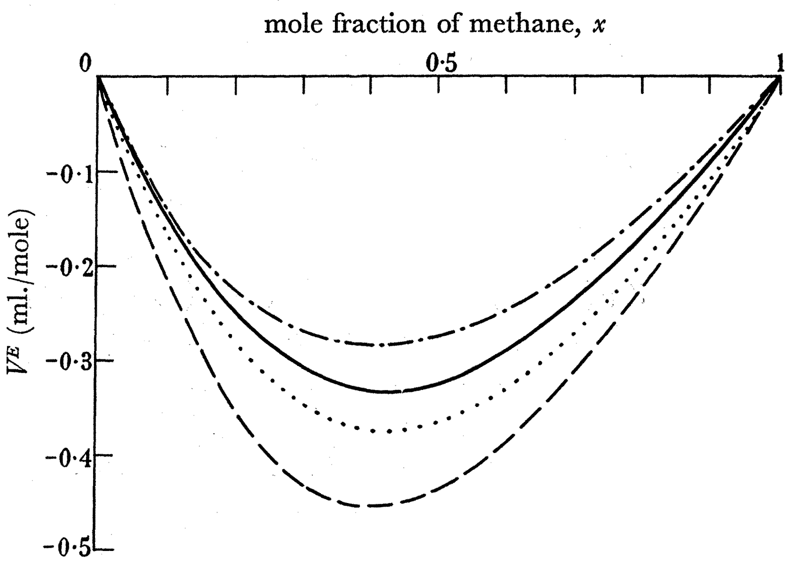

FIGURE 8. Variation of the volume of mixing with composition for the system carbon monoxide + methane at 90·67° K. ——, experimental results; – – – –, calculated using carbon monoxide as reference substance; ····, calculated using methane as reference substance; –·–·–, calculated using constructed reference substance.

important, and can be calculated from data for argon (Din 1956) by using the law of corresponding states. The values of the coefficients *a*, *b*, *c* and *d* obtained in this way are as follows (units ml./mole):

$$a = 22{\cdot}07, \quad b = 29{\cdot}59, \quad c = -30{\cdot}03, \quad d = 15{\cdot}65.$$

The volume of mixing calculated from equation (12·8) using these figures is shown by the upper broken curve in figure 8. We see that it is closer to the experimental curve than the other calculated curves, and even lies slightly above it, in agreement with the qualitative effects of randomizing the molecular distribution. However, too much weight cannot be placed on the agreement of this calculation with experiment, since a numerical examination reveals that an error in the value of the curvature of the volume-temperature curve for the reference substance gives rise to an equal percentage error in the volume of mixing; the calculations are therefore sensitive to slight errors in the experimental results for the reference substance. It is interesting to note that the calculated curves are all asymmetric in the same sense as the experimental curve (and actually to a greater degree). This asymmetry is mainly due to the increasing curvature of the orthobaric volume curve of any reference substance with temperature, and would be less for mixtures whose components differed less in their critical temperatures. It is not, therefore, an effect primarily due to deviations from the law of corresponding states.

The method of constructing a reference substance which reproduces correctly certain properties of the pure components can, of course, also be used in calculating the heat and excess entropy of mixing. However, the calculations have not been presented, as the values obtained for the excess free energy are much lower than the experimental figures. This only serves to show that, even in this apparently simple case, a theory assuming spherical molecules is inadequate. Nevertheless, the rough agreement of theory and experiment can be regarded as further evidence in favour of the Lorentz–Berthelot type of relations between the intercomponent energy and size parameters. A more thorough comparison of theory and experiment must await the measurement of the heat of mixing of this system, and the extension of the present theory to slightly non-spherical molecules.

13. Discussion

The approach to the theory of simple mixtures presented in this paper has also been recently proposed by Scott (1956), and only differs from that of Prigogine and his colleagues (1956) in the recognition that the fundamental definition of random mixing renders the use of the cell model for a liquid unnecessary. It should also be mentioned that the random-mixing approximation introduced in § 3 has already been used by Salsburg & Kirkwood (1953), although these authors confined its use to a theory based on the cell model. The present approach therefore appears as the one towards which research in this field has been leading during the last decade. Indeed, we may go further back and regard it as the proper realization of the ideas with which Hildebrand created his semi-empirical theory of regular solutions (see Hildebrand & Scott 1950). In this connexion it is interesting to note that in his Spiers Memorial Lecture to the Faraday Society in 1953, Hildebrand re-defined a regular solution as 'one in which thermal agitation is sufficient to give practically complete randomness'.

In spite of Hildebrand's new molecular definition of a regular solution, it is not suggested that the existing terminology be confused by referring to the mixtures treated here by this name. It seems preferable to refer to them by the descriptive title 'random mixtures of Lennard-Jones molecules', and to abbreviate this, when convenient, to 'R.L.-J. mixtures'. This terminology is supported by the conclusion which can be drawn from the appendix, namely, that the rigorous application of the law of corresponding states to random mixtures is confined to the Lennard-Jones form of the intermolecular energy function.

The restriction of a corresponding states type of treatment to mixtures of Lennard-Jones molecules, while unfortunate, is probably not serious. It may well be true that, as Guggenheim (1953), for example, has suggested, the derivatives of the intermolecular energy are not well reproduced by the Lennard-Jones function in the vicinity of the energy minimum. However, we know from the theory of conformal solutions that the form of the potential-energy function does not affect the first-order terms in the excess functions of mixing, and it has been shown in § 10 that the form only appears in the higher-order size terms; the exact shape of the potential is therefore probably only important for mixtures of molecules of very different size. How important it is evidently requires further investigation, but it seems likely that in actual mixtures the deviations from random mixing, and from central and conformal interaction, will be of much greater importance. This opinion is supported by the results of § 12, where it appears that the relatively small deviations from the law of corresponding states of such a simple molecule as carbon monoxide interfere seriously with the calculation of the mixing effects with methane.

In the treatment presented above, the random-mixing approximation has been employed on the grounds of its physical plausibility and mathematical simplicity. The validity of this approximation will be examined in the second part of this paper.

The author would like to thank Dr J. S. Rowlinson for many useful discussions during the course of this work and in the preparation of the manuscript, and to thank Mr J. B. McLeod of Oxford University for his solution of the mathematical problem in the appendix. The author is also grateful to Mr L. A. K. Staveley of Oxford University for communicating the experimental results for the system carbon monoxide + methane, and to Dr F. Din of the British Oxygen Company for permission to use his tables for argon before their publication.

APPENDIX. ON THE FORM OF THE INTERMOLECULAR ENERGY FUNCTION IMPLIED BY THE CONDITION THAT A RANDOM CONFORMAL MIXTURE OBEYS THE LAW OF CORRESPONDING STATES

It is shown in § 3 that a random mixture is essentially equivalent to a single substance whose intermolecular energy function is given by equation (3·4), or

$$\langle u(r)\rangle = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta u_{\alpha\beta}(r). \tag{A 1}$$

If the various intermolecular energy functions $u_{\alpha\beta}(r)$ are conformal, then according to (4·4) we have

$$\langle u(r)\rangle = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta f_{\alpha\beta} u(r/g_{\alpha\beta}), \tag{A 2}$$

where $u(r)$ is the intermolecular energy function of a reference substance. The condition that a random conformal mixture obeys the law of corresponding states for all compositions is simply that $\langle u(r)\rangle$ is also conformal to $u(r)$, in the sense of equation (4·8); this condition may therefore be expressed in the form

$$\sum_{\alpha}\sum_{\beta} x_\alpha x_\beta f_{\alpha\beta} u(r/g_{\alpha\beta}) = fu(r/g) \quad (0<r<\infty), \tag{A 3}$$

where f and g depend only on the positive numbers $f_{\alpha\beta}$, $g_{\alpha\beta}$ and x_α. This equation is evidently a condition on the function $u(r)$, and it is shown in § 4 that it is satisfied by the Lennard-Jones form (4·1). The question therefore arises: Are there any other functions $u(r)$ which satisfy condition (A 3), or is the Lennard-Jones form the only one? The most direct route to an answer, and that which we shall adopt, is to regard condition (A 3) as a functional equation for $u(r)$, and to attempt to obtain the general solution.

We begin by reducing equation (A 3) to its simplest form, which is

$$u(r) + au(rb) = Au(rB) \quad (0<r<\infty), \tag{A 4}$$

where A and B depend only on the real arbitrary parameters a and b $(0<a<\infty,\ 0<b<\infty)$; this equation follows from (A 4) by combining the terms of the latter two at a time. Next we transform the equation by introducing the variable $x = \ln r$ and putting $\phi(x) = u(r)$, so that it becomes

$$\phi(x)+a\phi(x+p)-A\phi(x+P) = 0, \tag{A 5}$$

where $p = \ln b$ and $P = \ln B$. The equation now has the form of a homogeneous linear difference equation with constant coefficients. If p and P are commensurable, that is if $p = hi$ and $P = hj$ where i and j are integers, then the general solution is (Fort 1948)

$$\phi(x) = \sum_r \omega_r(x)\, t_r^x, \tag{A 6}$$

where the $\omega_r(x)$ are arbitrary functions of period h, and the t_r are the roots of the auxiliary equation

$$1+at^p-At^P = 0. \tag{A 7}$$

However, we are interested in the solution of equation (A 5) which is valid for all positive values of a and b, and therefore for the case in which p and P are incommensurable. It is plausible to argue that in this case the period h must be zero, so that equation (A 6) becomes

$$\phi(x) = \sum_r c_r t_r^x, \tag{A 8}$$

where the c_r and t_r are absolute constants. It can be proved rigorously that this is in fact the general solution of equation (A 5) under these conditions (McLeod 1956), but as the analysis is rather long we shall not reproduce it here. Accepting this solution, it now follows that, since the constants t_r must be independent of a and b, the auxiliary equation (A 7) can be true for only two values of t, say t_1 and t_2. Hence in equation (A 8) only c_1 and c_2 can be non-zero, and the general solution is simply

$$\phi(x) = c_1 t_1^x + c_2 t_2^x. \tag{A 9}$$

By transforming back to the original variable and introducing the conditions for a physically acceptable intermolecular energy function, namely,

$$u(\infty) = 0, \quad u(0) = \infty \quad \text{and} \quad u(\sigma) = 0 \quad \text{where} \quad 0<\sigma<\infty,$$

we find that $u(r)$ must have the Lennard-Jones form

$$u(r) = -\mu/r^m + \nu/r^n \quad (\mu, \nu > 0;\ n > m > 0). \tag{A 10}$$

The answer to the question posed at the beginning of the appendix is therefore that the only solution of equation (A 3) is the Lennard-Jones form (A 10). And consequently the Lennard-Jones form of the intermolecular energy function is implied by the condition that a random conformal mixture obeys the law of corresponding states.

Note added in proof, 17 *July* 1957. Chaundy & McLeod (1957) have derived the solution (A 10) directly from the functional equation (A 4) by means of elementary, and very elegant, mathematics.

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