BINARY SOLUTIONS OF IMPERFECT LIQUIDS[1]

R. B. PARLIN AND H. EYRING

Department of Chemistry, University of Utah, Salt Lake City, Utah

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A liquid mixture of two kinds of molecules is treated as composed of quasi-microcrystalline regions of twelve or less molecules. Interactions within these regions are explicitly represented by a Boltzmann factor with specific energies for each kind of molecular pair. Interactions between molecules in different crystalline regions are represented by a Boltzmann factor involving an averaged energy term. The partition function of the mixture is obtained by summing over all configurations, weighting each term by the appropriate Boltzmann factors. In the case of approximately equal-sized molecules, explicit expressions are obtained for the properties of the solution, notably the consolute temperature, in terms of the coördination number and the interaction energies. For mixtures of molecules of widely different sizes, the corresponding equations are derived but explicit results have not yet been obtained.

INTRODUCTION

A number of treatments have been proposed for the problem of the interactions between molecules in the liquid state (4, 5), most of which can be shown to give the essential properties of such systems in a more or less quantitative manner. Generally, the most profitable approach has been that of considering the liquid to be a distorted crystal, in which the long-range order has been replaced by smaller regions within which a lattice array of molecules is at least momentarily maintained, but between which no order is observed.

To treat this ensemble of cells, it is necessary to approximate the configurational potential energy integral in the partition function (3) in some appropriate manner. In this paper, an adaptation of the order-disorder theory originally due to Bethe (1) and later applied by Peierls (7) to the adsorption of gases on surfaces and by Cernuschi and Eyring (2; see also 6) to the theory of condensation will be used. The theory is applied directly to a simple model of approximately equal-sized molecules, and the direction of extension to more realistic systems is indicated.

THEORY

It will be assumed (*1*) that the molecules of the liquid occupy positions of a lattice (although the lattice will not be constrained to maintain any but topological identity) and each molecule will be supposed to have a number Z of nearest neighbors; (*2*) that when to a molecule of kind i a nearest neighbor of kind j is added to the lattice there is a resultant enhancement of the probability

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of i being there owing to the attraction between the molecules; (*3*) that all interactions of a molecule in the first neighboring shell with any but the central molecule will be represented by an averaged energy.

Consider then such a mixture of molecules (designated as kind 1 and kind 2), and let the ratio of the partition function for a molecule in the liquid to that in the gas be represented by f_1 and f_2. In view of the greater deviation from ideality for the liquid, the gas will for the time being be considered a perfect gas.

Suppose a given lattice site is occupied by a molecule of kind 1; several possible configurations may then arise (figure 1).

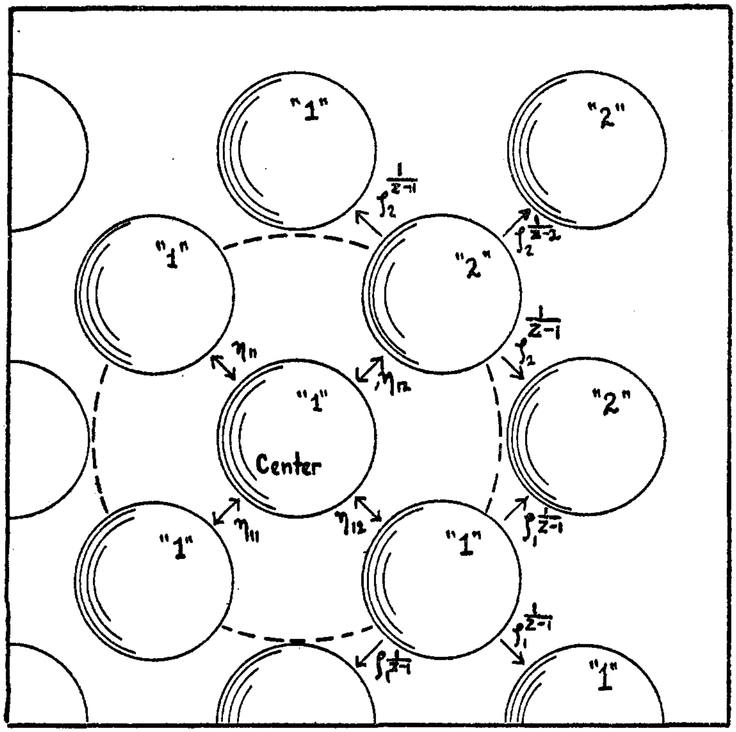

FIG. 1. Representation of a mixture of molecules of kinds 1 and 2 as a plane lattice

(*1*) If all the positions in the first shell are occupied by similar molecules, the partition function for this configuration will be given by the expression

$$f_1\cdot f_1\zeta_1\eta_{11}\cdot f_1\zeta_1\eta_{11}\cdot f_1\zeta_1\eta_{11}\ \ldots\ldots = f_1\cdot(f_1\zeta_1\eta_{11})^Z \tag{1}$$

where the factor ζ_1 corrects for all interactions of a shell molecule except the interaction with the central molecule, as assumed previously, and η_{11} provides for this omitted interaction.

(*2*) If all of the positions in the first shell except one are of kind 1 and the Z^{th} is of kind 2, the partition function will be

$$Z\cdot f_1\cdot f_1\zeta_1\eta_{11}\cdot f_1\zeta_1\eta_{11}\ \ldots\ldots\ \cdot f_2\zeta_2\eta_{12} = Z\cdot f_1\cdot(f_1\zeta_1\eta_{11})^{Z-1}\cdot(f_2\zeta_2\eta_{12}) \tag{2}$$

where the factor Z acknowledges that such a configuration may occur in Z ways. Continuing in this wise, it may readily be verified that the complete expression is the sum of the terms in the binomial expansion thus:

$$f_1[f_1\zeta_1\eta_{11} + f_2\zeta_2\eta_{12}]^Z \tag{3}$$

The partition function, one sees, is the sum of the weighted terms for each configuration. Clearly the analogous result for the case in which the central site is occupied by a molecule of kind 2 will be

$$f_2[f_1\zeta_1\eta_{12} + f_2\zeta_2\eta_{22}]^Z \tag{4}$$

The ratio of the two expressions (3 and 4) will be equal to the ratio of the probabilities of the central point being occupied by molecule 1 to that of its being occupied by molecule 2, that is, to the mole ratio $\theta/1-\theta$:

$$\frac{\theta}{1-\theta} = \frac{f_1}{f_2} \cdot \frac{[f_1\zeta_1\eta_{11} + f_2\zeta_2\eta_{12}]^Z}{[f_1\zeta_1\eta_{12} + f_2\zeta_2\eta_{22}]^Z} \tag{5}$$

On the other hand, if one counts the configurations in this manner, the mole ratio $\theta/1-\theta$ must also be given by the expression

$$\frac{\phi}{1-\theta} = \frac{f_1\zeta_1}{f_2\zeta_2} \cdot \frac{[f_1\zeta_1\eta_{11} + f_2\zeta_2\eta_{12}]}{[f_1\zeta_1\eta_{12} + f_2\zeta_2\eta_{22}]} \tag{6}$$

where attention is now focussed upon a molecule in the shell of neighbors. Here there are two configurations if the particular neighboring molecule is of kind 1, since the central molecule may be of either kind. In one case the partition function will be $f_1\zeta_1 \cdot f_1\zeta_1\eta_{11}$, while if the central molecule is of kind 2 one will have $f_1\zeta_1 \cdot f_2\zeta_2\eta_{12}$. The partition function for the case of the type 1 shell molecule will then be the sum of these expressions. A similar approach gives the result for the case of a molecule of kind 2 in a shell position, and the ratio of these two sums is then the mole ratio as indicated in equation 6. Since the distinction between a "central" position and a "neighboring" position is a purely formal one, the two partition function ratios clearly must be identical.

It is convenient, for purposes of computation, to make the substitutions

$$\begin{aligned} f &= f_1/f_2 & \eta &= \eta_{12}/\eta_{22} \\ x &= f_1\zeta_1/f_2\zeta_2 & \mu &= \eta_{11}/\eta_{22} \end{aligned} \tag{7}$$

when equations 5 and 6 become, upon rearrangement

$$f = x\left(\frac{1+\eta x}{\eta + \mu x}\right)^{z-1} \tag{8}$$

$$\frac{\theta}{1-\theta} = x\left(\frac{\eta + \mu x}{1 + \eta x}\right) \tag{9}$$

One may identify the function f with the ratio $p_1/p_1^0/p_2/p_1^0$, where p_1 is the partial pressure of component 1 and p_1^0 is the vapor pressure of the pure liquid 1. Since only for a perfect liquid mixture is the total pressure a linear function of the composition, it is necessary to obtain a third relation which will permit evaluation of the individual partial pressures, rather than their ratio alone. This desired relation is obtained from the Gibbs equation

$$\theta \left(\frac{\partial \mu_1}{\partial \theta} \right)_{T,P} = (1 - \theta) \left(\frac{\partial \mu_2}{\partial (1 - \theta)} \right)_{T,P} \tag{10}$$

(where θ represents the mole fraction of component 1, and μ_1 the partial molar free energy of the same substance in the solution). Making use of the definition of f and remembering that the gases are considered ideal, whence

$$\mu_1 = RT \ln p_1/p_1^0 \qquad \mu_2 = RT \ln p_2/p_2^0 \tag{11}$$

one obtains the result that

$$\mathrm{d} \ln \frac{p_2}{p_2^0} + \frac{\theta}{f} \mathrm{d}f = 0 \tag{12}$$

Equation 12 may be integrated in the form

$$\frac{p_2}{p_2^0} = \exp \left(- \int_0^f \frac{\theta}{f} \mathrm{d}f \right), \qquad \frac{p_1}{p_1^0} = f \cdot \frac{p_2}{p_1^0} \tag{13}$$

or, for computational purposes, expressed in terms of the variable x as

$$\ln \frac{p_2}{p_2^0} = -\eta \int_0^x \left[1 - \frac{(Z - 2)\left(\frac{\mu}{\eta} - \eta \right) x}{\mu x^2 + 2\eta x + 1} \right] \mathrm{d}x \tag{14}$$

Integrating equation 14 one finds two solutions, depending on the relative values of the constants. For $\eta^2 > \mu$

$$\ln \frac{p_2}{p_2^0} = \eta x + \frac{(Z - 2)(\eta^2 - \mu)}{2\mu} \ln [\mu x^2 + 2\eta x + 1] - \frac{(Z - 2)\eta(\eta^2 - \mu)^{1/2}}{2\mu} \ln \left\{ \frac{\eta + (\eta^2 - \mu)^{1/2}}{\eta - (\eta^2 - \mu)^{1/2}} \cdot \frac{\mu x + \eta - (\eta^2 - \mu)^{1/2}}{\mu x + \eta + (\eta^2 - \mu)^{1/2}} \right\} \tag{15}$$

while in the case $\eta^2 < \mu$,

$$\ln \frac{p_2}{p_2^0} = \eta x - \frac{(Z - 2)(\mu - \eta^2)}{2\mu} \ln [\mu x^2 + 2\eta x + 1) + \frac{(Z - 2)\eta(\mu - \eta^2)^{1/2}}{\mu} \left\{ \tan^{-1} \frac{\mu x + \eta}{(\mu - \eta^2)^{1/2}} - \tan^{-1} \frac{\eta}{(\mu - \eta^2)^{1/2}} \right\} \tag{16}$$

The two forms (equations 15 and 16) of the integral express the fact that two possibilities may arise when two liquids are mixed at a given temperature. Equation 15 gives the result for $\ln p_2/p_2^0$ when there is no maximum in the p_2–θ relation. Equation 16 permits of such a maximum, and hence expresses the result for a two-phase region (see figure 2).

To examine this point more closely, one may observe that the function θ, the mole fraction of component 1, has the derivative

$$\frac{\mathrm{d}\theta}{\mathrm{d}x} = \frac{\eta \mu x^2 + 2\mu x + 1}{[\eta \mu x^2 + 2\eta \mu x + \mu]^2} \tag{17}$$

so that θ is a monotonic function of the variable x (μ and η being intrinsically positive) while the derivative of f,

$$\frac{df}{dx} = \left(\frac{1 + \eta x}{\eta + \mu x}\right)^{Z-1}\left[1 - \frac{(Z - 1)(\mu - \eta^2)x}{(1 + \eta x)(\eta + \mu x)}\right] \tag{18}$$

shows that f has a maximum *and* a minimum if

$$\eta^2 < \left(\frac{Z - 2}{Z}\right)\mu \tag{19}$$

the corresponding values of f being determined from equation 8 and

$$x^* = \frac{(Z - 2)\mu - Z\eta^2}{2\eta\mu}\left[1 \pm \sqrt{1 - \frac{4\eta}{[(Z - 2)\mu - Z\eta^2]^2}}\right] \tag{20}$$

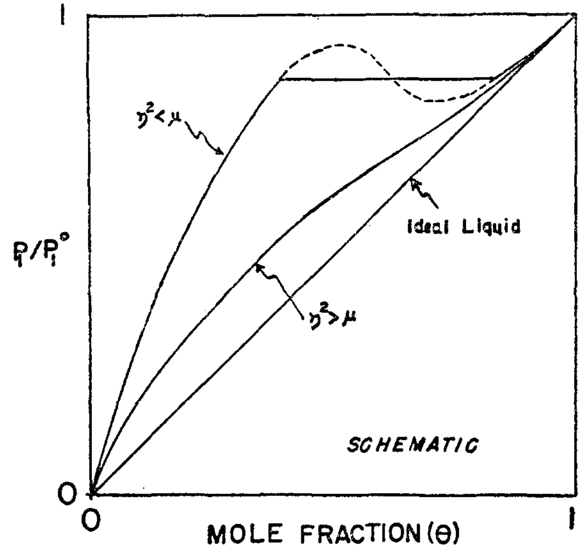

FIG. 2. Vapor pressure–composition curve for a binary solution

Now one may write, for $x = x^*$, the expression

$$\frac{\mu}{\eta^2} = \frac{\left(\theta + \frac{1}{Z - 2}\right)\left(1 - \theta + \frac{1}{Z - 2}\right)}{\theta(1 - \theta)} \tag{21}$$

Equation 21 gives the relation between the composition of the pairs of equilibrium solutions and the temperature, since the η, μ may be expressed as Boltzmann factors of the form

$$\eta = e^{(\epsilon_{12}-\epsilon_{22})/kT} \qquad \mu = e^{(\epsilon_{11}-\epsilon_{22})/kT} \tag{22}$$

Using equations 22 one obtains, setting

$$\epsilon = \frac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \tag{23}$$

the result

$$T = 2\epsilon \left[k \ln \frac{\left(\theta + \frac{1}{Z-2}\right)\left(1 - \theta + \frac{1}{Z-2}\right)}{\theta(1-\theta)} \right]^{-1} \tag{24}$$

The temperature is maximum at $\theta = 1/2$, and its maximum value is

$$T_{\text{consolute}} = \frac{\epsilon}{k \ln \frac{Z}{Z-2}} \tag{25}$$

It is interesting to note that if the coördination number Z were to change suddenly with temperature, i.e., to drop from 12 to 4 with a few degrees increase in temperature, it would be possible to be above the consolute temperature at low temperature (and low coördination) and to be below the mixing temperature at high temperatures (and high coördination). Such a situation would give rise, albeit crudely, to the phenomenon of a lower consolute point. One may also readily see that under certain circumstances, the upper consolute temperature may be impossible of attainment, at least under conditions of normal pressures. In fact, unless

$$T_{\text{melting}} < T_{\text{consolute}} < T_{\text{boiling}} \tag{26}$$

the liquid pairs will either be completely miscible or will be partially soluble over the whole range of temperatures of the liquid state. Now approximately, one may write

$$T_{\text{boiling}} \approx \frac{\Delta H_v}{21} \tag{27}$$

by Trouton's rule, and

$$\Delta H_v \approx 6(\epsilon_{11}\theta + (1-\theta)\epsilon_{22}) \tag{28}$$

since the energy of about six bonds in the liquid state must be broken to vaporize a molecule (assuming twelve neighbors). Then

$$T_{\text{boiling}} \approx 0.29(\epsilon_{11}\theta + (1-\theta)\epsilon_{22}) \tag{29}$$

Since $\theta = 1/2$ for the consolute composition we have for this composition:

$$T_{\text{boiling}} \approx 0.15(\epsilon_{11} + \epsilon_{22}) \tag{30}$$

Dividing through by equation 25 gives:

$$\frac{T_{\text{boiling}}}{T_{\text{consolute}}} \approx 0.15 \frac{\epsilon_{11} + \epsilon_{22}}{\epsilon} k \ln \frac{Z}{Z-2} \tag{31}$$

and $0.15 \frac{\epsilon_{11} + \epsilon_{22}}{\epsilon} k \ln \frac{Z}{Z-2}$ must be greater than unity for the consolute temperature to appear in the liquid region. If we write:

$$T_{\text{melting}} = \alpha T_{\text{boiling}} \tag{32}$$

whence

$$\frac{T_{\text{melting}}}{T_{\text{consolute}}} \approx 0.15k\alpha\left(\frac{\epsilon_{11}+\epsilon_{22}}{\epsilon}\right)\ln\frac{Z}{Z-2} \tag{33}$$

If we make the estimation $\alpha = 0.73$ as in the case of water we obtain:

$$\frac{T_{\text{melting}}}{T_{\text{consolute}}} = 0.11k\left(\frac{\epsilon_{11}+\epsilon_{22}}{\epsilon}\right)\ln\frac{Z}{Z-2} \tag{34}$$

Referring again to equation 25, it is apparent that since ϵ (as defined by equation 23) may be negative, there should exist systems for which no consolute temperature may be found, even in principle, above the absolute zero. That is, if the mean of the interactions between like pairs of molecules should fall below the interaction between unlike pairs, the two liquids should be miscible in all proportions at any temperature whatever, provided of course that such temperatures may be obtained without fusion or vaporization. In other cases, with sufficiently positive ϵ, a consolute or critical mixing temperature should be realizable, perhaps under high pressures.

To examine the applicability of equations 3, 9, and 14 to experimental data, it is convenient to plot the ratio of partial pressures against the ratio of mole fractions (or the mole ratio). From equations 8 and 9 one may note that

$$f = \left(\frac{1+\eta x}{\eta+\mu x}\right)^{z}\frac{\theta}{1-\theta} \tag{35}$$

and the relation is linear for f plotted against $\theta/1-\theta$ in the region of small x (hence small θ). The slope of this limiting straight line will then be η^{-z}. In addition, when $f = \dfrac{\theta}{1-\theta}$, $\dfrac{1+\eta x}{\eta+\mu x} = 1$, and

$$x = \frac{1-\eta}{\mu-\eta}$$

hence

$$f = \frac{\theta}{1-\theta} = \frac{1-\eta}{\mu-\eta} \tag{36}$$

at the point at which the curve crosses the ideal solution line, $f = \theta/1-\theta$ (figure 3).

The form of such experimental curves may be seen in the model curves of figure 4, drawn for the set of constants,

$$\begin{aligned} Z &= 12 \\ \epsilon_{12}-\epsilon_{22} &= -\ 84.0\ \text{cal./mole} \\ \epsilon_{11}-\epsilon_{22} &= 209.6\ \text{cal./mole} \end{aligned} \tag{37}$$

With this choice of constants, the consolute temperature, or critical solution temperature, will be about 400°K.

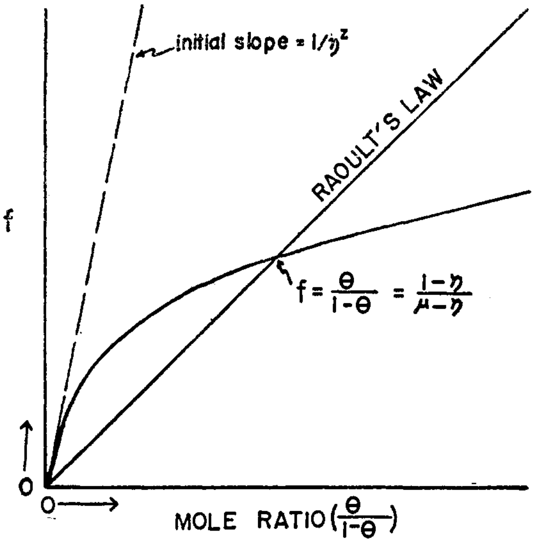

FIG. 3. Plot of partial pressure ratio *vs.* mole ratio for determining constants of equation

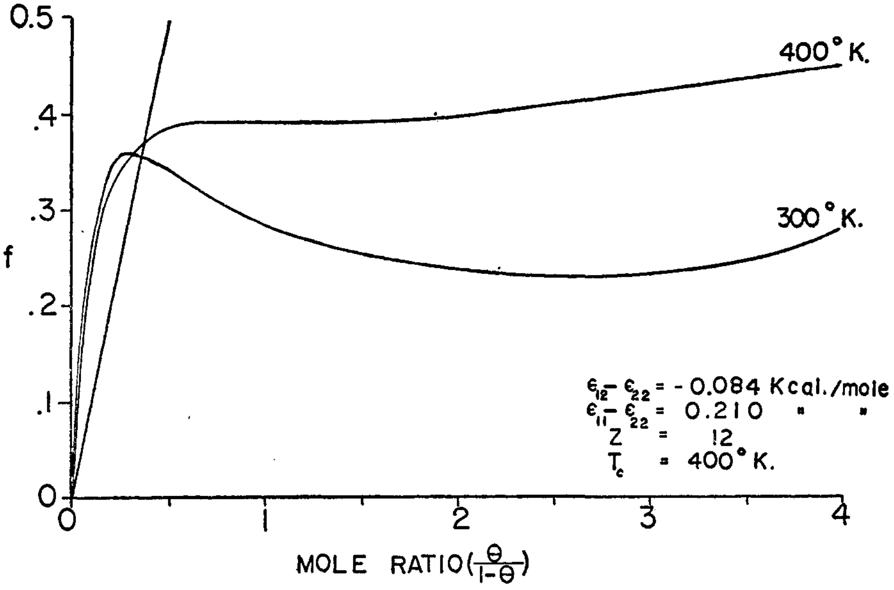

FIG. 4. Model curve

Finally, one may readily test equations 24 and 25. Equation 24 may be arranged in the form,

$$\frac{T}{T_{\text{consolute}}} = 2\,\frac{\ln Z/Z-2}{\ln \dfrac{\left(\theta + \dfrac{1}{Z-2}\right)\left(1 - \theta + \dfrac{1}{Z-2}\right)}{\theta(1-\theta)}} \tag{38}$$

which is a one-parameter family of curves for $T/T_{\text{consolute}}$ in terms of θ. Figure 5 gives this relation in graphical form for selected values of the coördination number Z. From equation 29 it should be possible to determine Z, and from the relation

$$\epsilon = kT_{\text{consolute}} \ln \frac{Z}{Z-2} \tag{39}$$

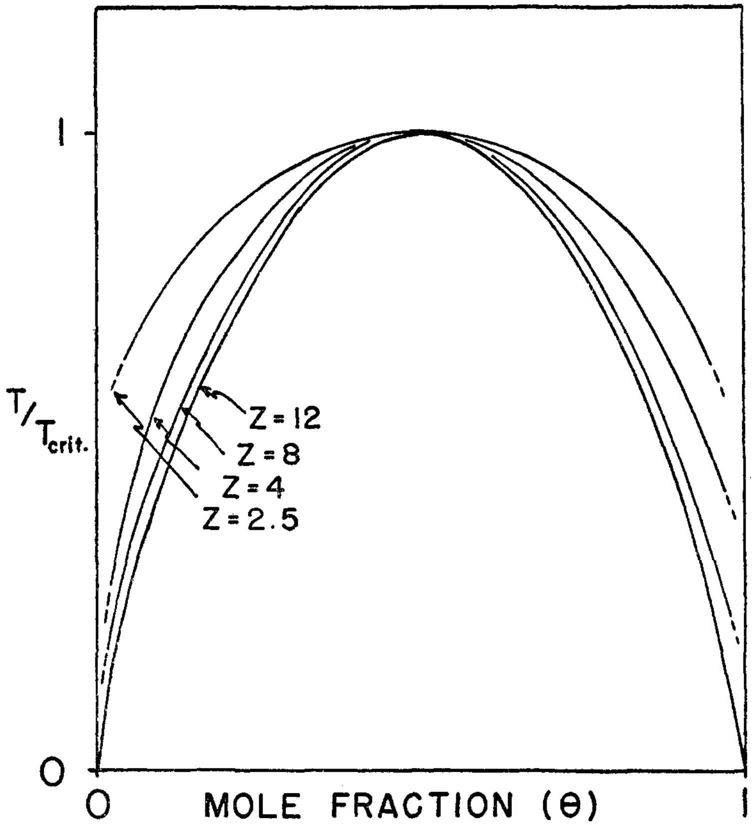

Fig. 5. Temperature (in terms of consolute temperature) as a function of solubility for various values of the coördination number Z.

one may then obtain the value of ϵ, the difference between the mean of the interaction energies between like molecules and the interaction energy for unlike molecules. It should be noted, of course, that expression 25 relates the temperature not strictly to the solubility, but to the value of θ corresponding to the maximum of the vapor pressure–composition curve. Clearly, the actual composition at the saturation point will be somewhat less than the θ of equation 29 on one branch of the curve and somewhat greater on the other. In general, however, there will be some curve of this description, and the principles involved will be the same.

Consider now the case of a mixture of two kinds of molecules, of which one sort occupies two lattice positions while the other occupies but one (figure 6). The double molecules will be designated by the subscript 2, the single particles by 1. To obtain the partition function for a molecule in the field of its nearest neighbors one writes the sum of all possible combinations; if the central molecule is of kind 2, there will be a contribution f_2 to the partition function in the absence of neighbors. If all of the $Z - 1$ nearest lattice points contain type 1 particles, the contribution is

$$(f_1\zeta_1\eta_{12})^{Z-1}\cdot f_2 \tag{40}$$

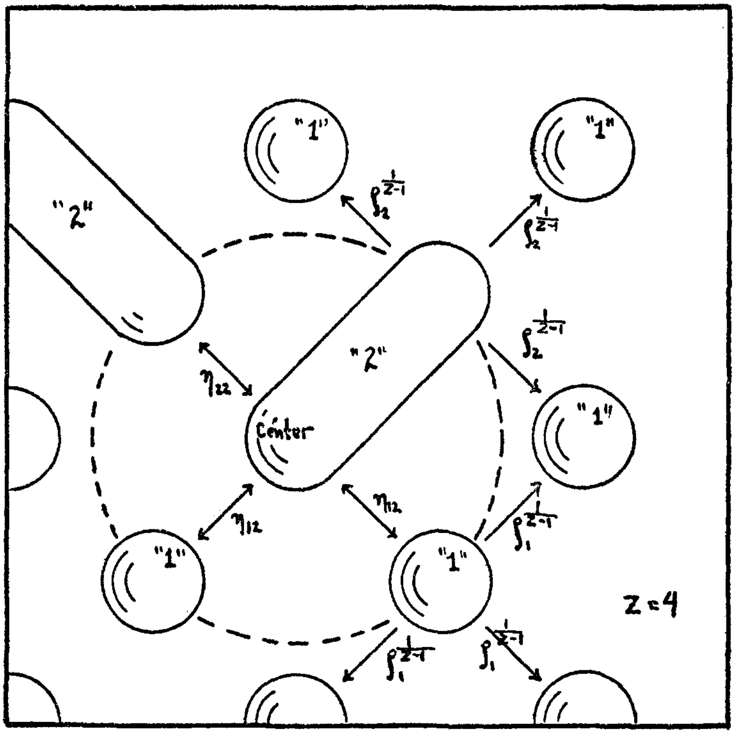

FIG. 6. Representation of a mixture of single (1) and double (2) molecules as a plane lattice

Continuing in this fashion, the total sum will be found to be

$$f_2[f_2\zeta_2\eta_{22} + f_1\zeta_1\eta_{12}]^{Z-1} \tag{41}$$

Similarly, if the central point is occupied by a molecule of kind 1, the corresponding expression will be

$$f_1[f_2\zeta_2\eta_{12} + f_1\zeta_1\eta_{11}]^{Z} \tag{42}$$

In the same way, if one considers a molecule of kind 2 in the first shell, its partition function will be

$$f_2\zeta_2\,[f_2\zeta_2\eta_{22} + f_1\zeta_1\eta_{12}]^{(Z-1)/Z} \tag{43}$$

while that for a molecule of kind 1 will be

$$f_1\zeta_1[f_2\zeta_2\eta_{12} + f_1\zeta_1\eta_{11}] \tag{44}$$

Now the ratio of expression 27 to 28, as of expression 29 to 30, must be the ratio of the probabilities of finding an arbitrary molecule to be of kind 1 or kind 2, hence the mole ratio:

$$\frac{\theta}{1-\theta} = \frac{f_2}{f_1}\,\frac{[f_2\zeta_2\eta_{22} + f_1\zeta_1\eta_{12}]^{Z-1}}{[f_2\zeta_2\eta_{12} + f_1\zeta_1\eta_{11}]^{Z}} = \frac{f_2\zeta_2}{f_1\zeta_1}\,\frac{[f_2\zeta_2\eta_{22} + f_1\zeta_1\eta_{12}]^{(Z-1)/Z}}{[f_2\zeta_2\eta_{12} + f_1\zeta_1\eta_{11}]} \tag{45}$$

Equations 31 may be written in the form

$$\frac{\theta}{1-\theta} = \frac{f_2}{f_1}\cdot\frac{(f_2\zeta_2)^{Z-1}}{(f_1\zeta_1)^Z}\cdot\frac{\left(1+\eta\dfrac{f_1\zeta_1}{f_2\zeta_2}\right)^{Z-1}}{\left(\eta+\mu\dfrac{f_1\zeta_1}{f_2\zeta_2}\right)^{Z}} \tag{46}$$

$$= \left[\frac{(f_2\zeta_2)^{Z-1}}{(f_1\zeta_1)^Z}\right]^{1/Z}\cdot\frac{\left(1+\eta\dfrac{f_1\zeta_1}{f_2\zeta_2}\right)^{(Z-1)/Z}}{\left(\eta+\mu\dfrac{f_1\zeta_1}{f_2\zeta_2}\right)} \tag{47}$$

Since in this case the expressions are not homogeneous in $f_1\zeta_1$ and $f_2\zeta_2$, the simple expressions analogous to expressions 6 and 7 are not possible, and a second implicit variable $(f_2\zeta_2)^{Z-1}/(f_1\zeta_1)^Z$ appears. However there is still a third equation, the Gibbs equation, which has again the form

$$\frac{p_2}{p_1^0} = \exp\left\{-\int_{-\infty}^{f_2/f_1}\theta\,\mathrm{d}\ln\frac{f_2}{f_1}\right\} = \frac{p_1/p_1^0}{f} \tag{48}$$

and in principle it should be possible to calculate the equilibrium curves of partial pressure *vs.* composition. In practice, the expressions have been found too unwieldy for numerical computation as yet. One may note that for large values of coördination number, Z,

$$\frac{(f_2\zeta_2)^{Z-1}}{(f_1\zeta_1)^Z} \text{ reduces approximately to } \frac{f_2\zeta_2}{f_1\zeta_1}$$

or in terms of the previous notation to x^z.

A number of difficulties arise in the manipulation of the equations for any case except the simple one of molecules of equal size. In principle, however, it should be possible to treat almost any kind of mixture of arbitrary molecules to the point of setting up the equations. In particular, it is noteworthy that special kinds of interactions such as forces between dipoles may readily be included, as it is only necessary to identify such special forces with one of the η_{ij}, the energy for which will be determined by the nature of the case.

Further, it is possible, and may in some cases be essential, to consider the various ϵ_{ij} not as energies (heats) but rather as (Helmholtz) free energies: thus if the ϵ_{ij} are considered to be linear functions of the temperature, one may write for ϵ,

$$\epsilon = \frac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} = E - TS \tag{49}$$

where the terms E and TS represent the temperature-independent (energy) and temperature-dependent (entropy) parts, respectively. The counterpart to equation 25 will then be

$$T_{\text{consolute}} = \frac{E}{S + k \ln \frac{Z}{Z-2}} \tag{50}$$

for the consolute temperature. It is apparent that if the term S in the denominator were to be larger than the coördination number term, the consolute temperature would be sensibly independent of the coördination.

Finally, one may remember the empirical fact that the use of volume fractions in place of mole fractions in many cases removes the anomalies found in some of the properties of liquids which arise from the unequal size of the molecules. It is tempting to suppose that the variation in the consequences of equations 46, 47, and 48 from those of equations 8, 9, and 13 which arise from just such a source may be reproduced by using the simpler theory with the mole fraction terms replaced by volume fractions.

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