CRITICAL PHENOMENA IN BINARY LIQUID SYSTEMS[1]

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CONTENTS

The phase relationships in a two-component liquid system are generally expressed in a temperature–composition diagram for constant (usually essentially zero) pressure, by a coexistence curve which gives the composition of the two liquid phases in equilibrium with each other at any temperature. Frequently there is a temperature above which (upper critical solution temperature) or below which (lower critical solution temperature) the two liquids are completely miscible, forming only one phase regardless of composition. It will be the object of this paper to consider the phenomena which occur in the neighborhood of such a critical point. In order to understand the problems involved, it will be well to start with a brief review of critical phenomena in the vapor–liquid equilibrium of one-component systems, which have many points of similarity.

I. CRITICAL PHENOMENA IN ONE-COMPONENT SYSTEMS

In a one-component system, the coexistence curve gives the molal volume (inverse of concentration) of the liquid and vapor phases which are in equilibrium at any temperature or any pressure. According to the van der Waals theory, the coexistence curve has a rounded, roughly parabolic shape in the neighborhood of the critical point. However, careful observations of the meniscus separating

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vapor and liquid phases in a number of cases (21, 26, 35; see the last of these for earlier references) indicate that in a diagram in which either pressure or temperature is plotted as ordinate against molal volume as abscissa, the coexistence curve has a flat top, having the appearance of a truncated parabola. There is a range of molal volumes (volume of 1 mole of the entire two-phase system) over which the meniscus disappears, within the limits of error, at exactly the same temperature, which is designated as T_m.

This observation is in accord with the results obtained from the statistical-mechanical theory of condensation of Mayer and Harrison (11, 22). They also believed, on the basis of this theory, that at temperatures just above T_m the isotherms should have a horizontal (constant-pressure) portion extending over a range of volumes.

McIntosh, Dacey, and Maass (5, 19) believed that they observed such horizontal portions in the isotherms of ethylene above the temperature at which the meniscus could be observed, but their data can be fitted just as well by curves with finite slopes in this region (31). Data on carbon dioxide (23) definitely seem to indicate that the horizontal portion is of finite length in the last isotherm which has a horizontal portion, and that only 0.15° above the critical temperature the isotherms have everywhere a finite slope. However, in this case the meniscus was not observed, so the question cannot be considered to be entirely settled experimentally.

Recently (31) I have considered the process of condensation of a vapor from the point of view of associating molecules (2, 8, 30). This involves the consideration of the equilibrium between single molecules, double molecules, triples, and higher clusters or droplets, the molecules within a cluster being held together by van der Waals or, possibly, dipole forces. As the system is compressed to smaller volumes, more and more of the larger clusters are formed. If it is compressed sufficiently clusters of macroscopic size suddenly become stable, i.e., condensation begins.

However, events will proceed in this way only if the surface tension of the droplets is positive. The surface tension of a liquid decreases with increasing temperature and will eventually approach zero. Then the sudden shift of stability to the large clusters will not occur. Instead, the number of large clusters and their average size will gradually increase until finally, when the *free* volume of the large clusters is reduced to zero, they coalesce into one. The free volume of a large cluster is determined, not by the freedom of motion of the individual molecules within it, but by the limits within which the cluster as a whole can move without becoming joined to another cluster. Thus the free volume of the large clusters may be reduced to zero when the density of the system is still rather low. The coalescence of the droplets does not result in a phase which is separated by a meniscus from the vapor, but, instead, it will produce a spongy, complexly interconnected mass of variable density. The process of condensation will now consist of the compression of the spongy mass, reducing the at first interconnected regions of low density to the status of disconnected bubbles in the liquid. In this process there will be a decrease in the surface, but there will be no resistance to the compression, since the surface tension is zero, and the pressure will remain constant until this process is finished; further compression requires actual squeezing of the liquid, rather than squeezing out of "gaseous" portions of the mass. The process which takes place at constant pressure presumably corresponds to the change of volume across the flat top of the coexistence curve.

Above the temperature T_m the surface tension will become negative. Once the spongy mass is formed, it will require a small but steady increase in pressure in order to squeeze out the interstices, for this requires a decrease in the total amount of surface, which is now resisted on account of the negative surface tension. Thus, according to this view, there will be no constant-pressure portion of an isotherm above the temperature T_m. This apparent contradiction to the statistical theory of Mayer and Harrison (11, 22) may, in my opinion, be explained in the following way (31). In the theory of Mayer and Harrison there appear certain cluster integrals, which are assumed to be volume independent. The integrals which involve numbers of molecules comparable to the total number will, however, become volume dependent when the volume actually filled by these molecules is comparable to the total volume. If these integrals are then important in Mayer and Harrison's equation, their theory will break down. It is difficult to prove at just what point this breakdown occurs, but it is reasonable to believe that it happens when the spongy mass described above is formed. If this is the case, it is shown in the previously cited work, that this will—or at least may—cause Mayer and Harrison's theory to break down before the flat portion of the isotherm, predicted in their theory, is reached.

II. FORMULATION OF THE PROBLEM FOR A TWO-COMPONENT SYSTEM

In many ways the two-phase two-component system of two partially immiscible liquids is analogous to the two-phase one-component system. With the total pressure of the two-component system held constant, the number of degrees of freedom is the same. The concentration of one of the components takes the place of the molal volume (actually it is analogous to the inverse of volume) of the one-component system, and the fugacity of this component is analogous to the pressure of the one-component system. (Often it is more convenient to work directly with the chemical potential.)

We can therefore see at once the questions which arise in the case of the two-component system. These are twofold: (*1*) Does the coexistence curve have a horizontal portion (constant temperature over a range of concentrations) at the critical temperature? (*2*) Just above or below the critical temperature, in the region where there is apparently complete miscibility, is there a range of temperatures for which an isotherm shows a constant fugacity or chemical potential for one component (and hence for the other also) over a range of concentrations? It will be the purpose of this article to consider these questions from both the theoretical and the experimental points of view.

III. GENERAL THERMODYNAMIC CONSIDERATIONS

We shall set up the following notation in dealing with a two-phase binary liquid system (see figure 1):

$'$ refers to one of the phases, "phase-prime"
$''$ refers to the other phase, "phase-double-prime"
Subscript a refers to component A
Subscript b refers to component B
x_a' , x_b' , x_a'' , x_b'' are mole fractions
By definition $x_a' \geq x_a''$ and $x_b'' \geq x_b'$, so
  Component A is solvent for phase-prime and
  Component B is solvent for phase-double-prime
μ_a' , μ_b' , μ_a'' , μ_b'' are chemical potentials
A' is $\frac{1}{RT}\left(\frac{\partial \mu_a'}{\partial \ln x_a'}\right)_{T,p} = \frac{1}{RT}\left(\frac{\partial \mu_b'}{\partial \ln x_b'}\right)_{T,p}$
A'' is $\frac{1}{RT}\left(\frac{\partial \mu_a''}{\partial \ln x_a''}\right)_{T,p} = \frac{1}{RT}\left(\frac{\partial \mu_b''}{\partial \ln x_b''}\right)_{T,p}$
  (The relations follow from the Gibbs–Duhem equation)
$\bar{s}_a'$, $\bar{s}_b'$, $\bar{s}_a''$, $\bar{s}_b''$ are partial molal entropies
$\Delta S_a = \bar{s}_a'' - \bar{s}_a'$ and $\Delta S_b = \bar{s}_b' - \bar{s}_b''$

From the general equation for constant pressure, written with either subscript and either prime

$$\mathrm{d}\mu = -\bar{s}\,\mathrm{d}T + RTA\,\mathrm{d}\ln x \qquad (1)$$

and from the general set of conditions of equilibrium

$$\mu_a' = \mu_a''; \qquad \mu_b' = \mu_b'' \qquad (2)$$
$$\mathrm{d}\mu_a' = \mathrm{d}\mu_a''; \qquad \mathrm{d}\mu_b' = \mathrm{d}\mu_b''$$

we obtain (18):

$$0 = -\Delta S_a \mathrm{d}T - A'RT\,\mathrm{d}\ln x_a' + A''RT\,\mathrm{d}\ln x_a'' \qquad (3)$$
$$0 = \Delta S_b \mathrm{d}T - A'RT\,\mathrm{d}\ln x_b' + A''RT\,\mathrm{d}\ln x_b''$$

In these equations we have used the total differentiation sign to mean differentiation along the coexistence curve. This convention will be used throughout the argument leading up to equation 10. In any differential of this sort it is understood that the displacement along one branch of the coexistence curve corresponds to (implies the same dT) as displacement along the other branch.

Since $\mathrm{d}x_a' = -\mathrm{d}x_b'$ and $\mathrm{d}x_a'' = -\mathrm{d}x_b''$, we can write

$$\mathrm{d}\ln x_a'' = -(x_b''/x_a'')\,\mathrm{d}\ln x_b'' \qquad (4)$$
$$\mathrm{d}\ln x_b' = -(x_a'/x_b')\,\mathrm{d}\ln x_a'$$

Using these in equation 3 and solving the simultaneous equations, we obtain

$$\frac{\mathrm{d}\ln x_a'}{\mathrm{d}T} = \frac{\Delta S_a - (x_b''/x_a'')\Delta S_b}{A'RT(x_a'x_b''/x_b'x_a'' - 1)} \tag{5}$$

and

$$\frac{\mathrm{d}\ln x_b''}{\mathrm{d}T} = \frac{\Delta S_b - (x_a'/x_b')\Delta S_a}{A''RT(x_a'x_b''/x_b'x_a'' - 1)} \tag{6}$$

These equations determine the coexistence curve. We shall now consider the necessary conditions that the coexistence curve should have an upper, or a lower, critical temperature. To fix the ideas, let us first consider the case of an upper critical temperature, and let us suppose that the curve does *not* have a flat top but is curved in the region of the critical temperature. Then both d ln $x_a'/\mathrm{d}T$ and d ln $x_b''/\mathrm{d}T$ will be infinite at the critical point and they will be negative in the immediate neighborhood of the critical point, as will be clear from figure 1.

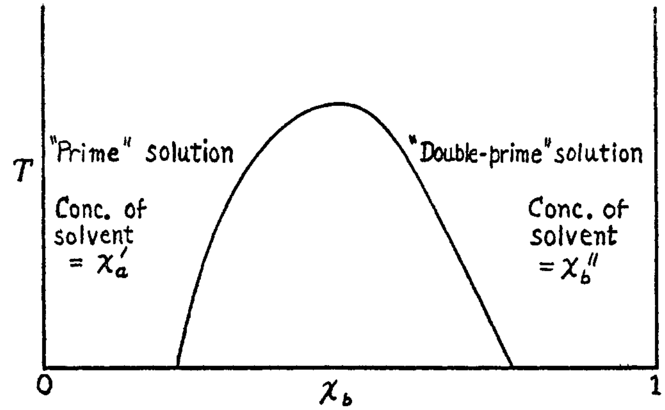

FIG. 1. Schematic diagram of a coexistence curve, illustrating the notation used

Let us now consider the behavior of the quantities in the fractions on the right-hand sides of equations 5 and 6. A' and A'' cannot be negative in any physically realizable state of the system. Since $x_a' \geq x_a''$ and $x_b'' \geq x_b'$, the factor $x_a'x_b''/x_b'x_a'' - 1$ must be greater than or equal to zero. Thus the denominators must be positive or zero; hence the numerators must be negative or zero in the neighborhood of an upper critical point. At the critical point where $x_a' = x_a''$ and $x_b' = x_b''$ they clearly must be zero. We also see that

$$\frac{\mathrm{d}}{\mathrm{d}(x_b''/x_a'')}\left(\frac{x_a'x_b''}{x_b'x_a''} - 1\right) = \frac{x_a'}{x_b'} + \frac{x_b''}{x_a''}\,\frac{\mathrm{d}(x_a'/x_b')}{\mathrm{d}(x_b''/x_a'')}$$

$\mathrm{d}(x_a'/x_b')/\mathrm{d}(x_b''/x_a'')$ must be positive; thus the above expression is positive and $x_a'x_b''/x_b'x_a'' - 1$ vanishes to the first order at the critical point.

Let us now consider the numerator of equation 5, which we shall designate as

$\mathfrak{y}$. Differentiating along the coexistence curve, remembering the definitions of ΔS_a and ΔS_b, we have

$$\frac{\mathrm{d}\mathfrak{y}}{\mathrm{d}(x_b''/x_a'')} = \left(\frac{\partial \bar{s}_a''}{\partial(x_b''/x_a'')}\right)_T - \left(\frac{\partial \bar{s}_a'}{\partial(x_b'/x_a')}\right)_T \frac{\mathrm{d}(x_b'/x_a')}{\mathrm{d}(x_b''/x_a'')} - \frac{x_b''}{x_a''}\left(\frac{\partial \bar{s}_b'}{\partial(x_b'/x_a')}\right)_T \frac{\mathrm{d}(x_b'/x_a')}{\mathrm{d}(x_b''/x_a'')} + \frac{x_b''}{x_a''}\left(\frac{\partial \bar{s}_b''}{\partial(x_b''/x_a'')}\right)_T - \Delta S_b + \frac{\partial \Delta S_a}{\partial T}\,\frac{\mathrm{d}T}{\mathrm{d}(x_b''/x_a'')} - \frac{x_b''}{x_a''}\,\frac{\partial \Delta S_b}{\partial T}\,\frac{\mathrm{d}T}{\mathrm{d}(x_b''/x_a'')} \tag{7}$$

The partial derivatives with respect to T are taken at constant mole fraction. Since, at the critical point, $x_a' = x_a''$ and $x_b' = x_b''$, both $\partial\Delta S_a/\partial T$ and $\partial\Delta S_b/\partial T$ are zero. The factor $\mathrm{d}T/\mathrm{d}(x_b''/x_a'')$ is also zero. Hence the last two terms in equation 7 will not even contribute to the second derivative at the critical point and may be completely neglected. At constant temperature we have the general relation

$$x_a''\mathrm{d}\bar{s}_a'' + x_b''\mathrm{d}\bar{s}_b'' = x_a'\mathrm{d}\bar{s}_a' + x_b'\mathrm{d}\bar{s}_b' = 0$$

Hence equation 7 reduces to

$$\frac{\mathrm{d}\mathfrak{y}}{\mathrm{d}(x_b''/x_a'')} = \left(\frac{x_b'}{x_a'} - \frac{x_b''}{x_a''}\right)\left(\frac{\partial \bar{s}_b'}{\partial(x_b'/x_a')}\right)_T \frac{\mathrm{d}(x_b'/x_a')}{\mathrm{d}(x_b''/x_a'')} - \Delta S_b \tag{8}$$

At the critical point $x_b'/x_a' - x_b''/x_a''$ and ΔS_b are both zero. Hence this expression vanishes.

Omitting terms which vanish at the critical point, the second derivative is

$$\frac{\mathrm{d}^2\mathfrak{y}}{\mathrm{d}(x_b''/x_a'')^2} = \left(\frac{\mathrm{d}(x_b'/x_a')}{\mathrm{d}(x_b''/x_a'')} - 1\right)\left(\frac{\partial \bar{s}_b'}{\partial(x_b'/x_a')}\right)_T \frac{\mathrm{d}(x_b'/x_a')}{\mathrm{d}(x_b''/x_a'')} - \left(\frac{\partial \Delta S_b}{\partial(x_b''/x_a'')}\right)_T \tag{9}$$

On account of the symmetry of the curve in the immediate neighborhood of the critical point $\mathrm{d}(x_b''/x_a'') = -\mathrm{d}(x_b'/x_a')$. Hence equation 9 becomes

$$\frac{\mathrm{d}^2\mathfrak{y}}{\mathrm{d}(x_b''/x_a'')^2} = -2\left(\frac{\partial \bar{s}_b'}{\partial(x_b''/x_a'')}\right)_T - \left(\frac{\partial \Delta S_b}{\partial(x_b''/x_a'')}\right)_T \tag{9a}$$

Actually S_b'' and S_b' are the same quantity; one of them is merely evaluated on one side of the coexistence curve, the other on the other. In the same sense, x_b''/x_a'' and x_b'/x_a' are essentially the same variable. Therefore at the critical point

$$[\partial\bar{s}_b'/\partial(x_b'/x_a')]_T \equiv [\partial\bar{s}_b''/\partial(x_b''/x_a'')]_T$$

But since along the coexistence curve $\mathrm{d}(x_b'/\mathrm{d}x_a')/\mathrm{d}(x_b''/x_a'') = -1$, we see that

$$[\partial\bar{s}_b'/\partial(x_b''/x_a'')]_T = [\partial\bar{s}_b'/\partial(x_b'/x_a')]_T\ \mathrm{d}(x_b'/x_a')/\mathrm{d}(x_b''/x_a'') = -[\partial\bar{s}_b''/\partial(x_b''/x_a'')]_T$$

With this we can reduce equation 9a to

$$\frac{\mathrm{d}^2\mathfrak{y}}{\mathrm{d}(x_b''/x_a'')^2} = -2\left(\frac{\partial \Delta S_b}{\partial(x_b''/x_a'')}\right)_T \tag{10}$$

Now we have seen that $\mathfrak{y} = 0$ at the critical point and must be negative in the neighborhood of an upper critical solution point. Since $\mathrm{d}\mathfrak{y}/\mathrm{d}(x_b''/x_a'')$ is also zero at the critical point the second derivative must be negative. Since x_b''/x_a'' increases on leaving the critical point along the coexistence curve, it is seen that this requires that ΔS_b increase also. Since ΔS_b starts at zero, it must be positive near an upper critical solution point. A similar discussion of equation 6 will show that ΔS_a must also be positive near an upper critical point, and both ΔS_a and ΔS_b will be negative near a lower critical point.

Furthermore, since the first derivatives of the numerators vanish, the numerators themselves must vanish to the second order at the critical point. Since the factor $x_a'x_b''/x_b'x_a'' - 1$ in the denominator vanishes only to the first order, this means that A' and A'' must vanish to the second order in order for the left-hand side of equations 5 and 6 to become infinite to the first order. This corresponds to the vanishing of both $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ at the critical point according to the van der Waals theory, in a one-component system.

The signs of the ΔS's can be interpreted in terms of the molecular structure of the liquids. If ΔS_a and ΔS_b are positive, this means an increase of entropy on transfer of material from a more concentrated to a less concentrated solution. This, of course, is the normal expectation, and results in an upper critical temperature. If ΔS_a and ΔS_b are negative this can result only from special interactions between the two kinds of molecules, such as hydrogen bonds, which are known to be instrumental in causing lower critical solution temperatures (13). If a molecule introduced as a solute into another liquid can cause a considerable degree of orientation of the solvent molecules, this orientation may lower the entropy of the solution to such an extent that transfer of the solute molecule from a concentrated to a dilute solution can actually result in a decrease of entropy. Since the interaction between the two kinds of molecules is mutual, it is not at all surprising that ΔS_a and ΔS_b should be negative at the same time. If they had opposite signs the coexistence curve would have neither an upper nor a lower critical temperature, and this is also a possibility which must be reckoned with.

Some pairs of liquids show both an upper and a lower critical point. It would be naturally expected that the orientation effect would be most marked at a low temperature, so it is possible for ΔS_a and ΔS_b to change sign in such a way that there is a lower critical temperature and a higher upper critical temperature, the coexistence curve then being a closed curve.

The above discussion deals only with the case where the coexistence curve is rounded at the critical temperature. If the coexistence curve is flat at the critical temperature, $\mathrm{d}\ln x_a'/\mathrm{d}T$ and $\mathrm{d}\ln x_b''/\mathrm{d}T$ are infinite for a range of concentrations, so that we do not in general have $x_a' = x_a''$ and $x_b' = x_b''$ at the critical temperature. Then the numerators of equations 5 and 6 will be finite and the factor $x_a'x_b''/x_b'x_a'' - 1$ will be finite and positive. It is thus not necessary for A' and A'' to vanish to the second order at the ends of the range of concentrations over which the coexistence curve is flat. If the two branches of the coexistence curve are to turn toward each other (as they always do) as the critical temperature is approached, then for an upper critical temperature we would have

$$\Delta S_a - (x_b''/x_a'')\Delta S_b < 0$$

and

$$\Delta S_b - (x'_a/x'_b)\Delta S_a < 0$$

Multiplying the second of these by x''_b/x''_a and adding to the first we obtain

$$(1 - x''_b x'_a/x''_a x'_b)\Delta S_a < 0$$

Since the term in parentheses is always less than zero, we find $\Delta S_a > 0$. Similarly $\Delta S_b > 0$. These then represent *necessary* conditions for coexistence curves of normal form at an upper critical temperature, regardless of whether the top of the curve is flat or rounded. Similarly $\Delta S_a < 0$ and $\Delta S_b < 0$ are in general necessary conditions for a lower critical temperature.

IV. ASSOCIATION THEORY FOR THE BINARY SYSTEM

McMillan and Mayer (20) have developed a statistical theory of multicomponent systems which can be applied to binary liquid systems. Their conclusions are very similar to those of Mayer and Harrison (11, 22) on the vapor–liquid critical point. The vanishing of A' to the second order involves two independent conditions, which McMillan and Mayer believe could be satisfied simultaneously only if the attractive forces were of a very special type. However, they apparently hesitate to exclude entirely the possibility of a critical point with a rounded coexistence curve. The normal type of coexistence curve would seem, nevertheless, to be one with a horizontal section of the critical temperature. In this case, according to McMillan and Mayer, the chemical potentials should be constant over a finite range of compositions even beyond the critical point, that is, at temperatures at which the two liquids form a single homogeneous phase. However, in this region the theory will meet with the same difficulty as does the theory of Mayer and Harrison above the critical point of a one-component system.

In this paper we shall adapt the theory of associating molecules to a binary system. This theory is not as rigorous as that of McMillan and Mayer in the region where two phases are formed; I believe, however, that it is better for the region where only one phase is formed. In any case, the mathematical formulation is much simpler. Since the theory has already been developed in detail for one component systems (31) we can make some of the discussions brief, referring the reader to the previously published work for details.

General theory

The theory will be the same for either the prime or the double-prime phase as described in Section III. Let us consider the former, in which component B is the solute and component A the solvent. Component B can occur as single molecules, as pairs, as triplets, etc., in general as clusters of s molecules each. Within these clusters of species B there may exist in turn molecules or clusters of species A. However, a cluster will be designated by the number of molecules of species B. We let the number of single molecules of B in a volume V be designated as n_{b1}, the number of pairs as n_{b2}, $\cdots$, the number of clusters of s molecules of species B as $n_{bs}, \cdots$. Then

$$\Sigma_s s n_{bs} = N_b \tag{11}$$

where N_b is the total number of B molecules. We let the concentrations (n_{b1}/V, $n_{b2}/V, \cdots n_{bs}/V, \cdots$) be designated as $c_{b1}, c_{b2} \cdots c_{bs}, \cdots$, and the respective chemical potentials (referring to single, rather than moles of, clusters) be denoted by $\mu_{b1}, \mu_{b2}, \cdots, \mu_{bs}, \cdots$. Then if the solution is sufficiently dilute so that the laws of dilute solutions may be considered valid,

$$\mu_{bs} = s\phi_{bs} + kT \ln c_{bs} \tag{12}$$

where $s\phi_{bs}$ is the value of μ_{bs} when $c_{bs} = 1$. We now define a quantity β_b by the equation

$$\beta_b = \phi_{b\infty} - \phi_{b1} \tag{13}$$

β_b, then, is the free energy of "condensation" per molecule, of single molecules at unit concentration to form a very large cluster.

If we form a cluster of s molecules of B from single molecules, this may be considered as the condensation of $s - 1$ molecules on one molecule, and the free energy of condensation at unit concentration would be $\beta_b(s - 1)$, except for some corrections. In the first place, the free energy of condensation of the molecules added to a small cluster is not typical of those added later if the cluster is made to grow. This difference in free energy will persist in the total energy even for a large cluster.[2] This correction we shall call ϵ_{bs}. For large s it should approach a limit which we shall call $\epsilon_{b\infty}$. There will also be a correction for surface, or, rather, interfacial energy of the form $\gamma s^{2/3}$, where γ is a constant related to, but not exactly equal to, the interfacial tension. This form will also break down for small s, but we may take any correction into ϵ_{bs}. Collecting all these terms we get for the free energy of condensation of s single molecules into a single cluster, both types being at unit concentration,

$$s\phi_{bs} - s\phi_{b1} = \beta_b(s - 1) + \gamma s^{2/3} + \epsilon_{bs} \tag{14}$$

For the special case $s = 1$, we see that equation 14 gives:

$$\epsilon_{b1} = -\gamma \tag{15}$$

The condition of equilibrium is that the total free energy F of the system should be a minimum. Hence

$$\delta F = \Sigma_s \mu_{bs} \delta n_{bs} = 0 \tag{16}$$

subject to the condition, which follows from equation 11, that

$$\Sigma_s s \delta n_{bs} = 0 \tag{17}$$

In equation 16 we have no term which explicitly refers to the solvent. In view of the fact that a droplet or cluster of solute molecules may have in turn solvent

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[2] In the work on condensation of a vapor (31) I assumed ϵ_∞ to be zero. It is seen that this is not correct, but actually it does not affect the conclusions of my earlier paper. This will be discussed elsewhere.

molecules dissolved in it, this may seem to be an oversight. However, the solvent within any given cluster is assumed always to be in equilibrium with its surroundings. Therefore it is only necessary to impose the condition 16 on the number of solute clusters of various sizes. The effect of solvent is taken care of implicitly in the expression for $s\phi_{bs}$ to be obtained from equation 14.

From equations 16 and 17 we obtain by the standard procedure

$$\mu_{bs} + \alpha_b' s = 0 \tag{18}$$

where α_b' is a constant to be determined (the Lagrange multiplier). With equations 12 and 14 this gives

$$c_{bs} = \exp[(\beta_b - \alpha_b s - \gamma s^{2/3} - \epsilon_{bs})/kT] \tag{19}$$

where

$$\alpha_b = \phi_{b1} + \beta_b + \alpha_b'$$

In particular, remembering equation 15,

$$c_{b1} = e^{(\beta_b - \alpha_b)/kT} \tag{20}$$

α_b is determined by equation 11, or it may be considered to be determined by equation 20, all the c_{bs} being determined in terms of c_{b1}. α_b may be interpreted as the difference between the chemical potential $\phi_{b\infty}$ of very large drops and that of the prime solution as it actually exists. We may build up the solute in the prime solution by small additions of single unassociated molecules of component B. Between the small additions we allow equilibrium between clusters to be reëstablished; this takes place with no free energy change, since we never depart appreciably from equilibrium. Hence

$$\begin{aligned} \mu_b' &= \mu_{b1} = \phi_{b1} + kT \ln c_{b1} \\ &= \phi_{b1} + \beta_b - \alpha_b = \phi_{b\infty} - \alpha_b \end{aligned}$$

Hence, as was to be shown,

$$\alpha_b = \phi_{b\infty} - \mu_b' \tag{21}$$

$\phi_{b\infty}$ may be taken as the chemical potential per molecule of B of the double-prime phase at the concentration given by the coexistence curve at temperature T. An infinitely large (macroscopic) drop of component B contains within itself droplets of component A. If the concentration of A within this large drop of B exceeds a certain value (as it would tend to if the over-all concentration of the solution were on the prime side of the coexistence curve), component A will condense out as a macroscopic droplet within the drop of B. The free energy of transfer of single B molecules at unit concentration to form a macroscopic cluster will, therefore, be the same as the free energy of transfer into the double-prime phase; in other words $\phi_{b\infty} = \mu_b''$. The concentration term in equation 12 is unimportant for $s = \infty$.

Critical point with horizontal portion of coexistence curve

One condition that the two macroscopic phases should be in equilibrium with each other is that $\phi_{b\infty} = \mu_b''$ should be equal to μ_b', hence $\alpha_b = 0$. Let us now examine equation 19 with this condition in mind. In the first place we note that a more positive value of α_b corresponds to a smaller concentration. As long as α_b is positive we see from equation 19 that large clusters are very improbable. Even when α_b is zero, the $\gamma s^{2/3}$ term makes the large clusters improbable, provided γ is positive. As soon as α_b becomes ever so slightly negative the expression 19 ceases to converge; that is to say, the large clusters suddenly become extremely probable. This corresponds to the formation of a new phase. The one-phase system is stable as long as α_b is positive.

The above deductions are based on the assumption that the ideal solution laws hold. It is clear that qualitatively the same results would be obtained if this were not the case. However, deviations from ideal solution laws become important when γ is close to zero. This has been discussed in detail in reference 31 and essentially the same method of handling the situation can be applied here. Equation 19 will still hold provided the concentrations are considered to be concentrations in free volume. This is not the same as replacing concentration by activity. Replacing concentration by concentration in free volume corrects only for the entropy effects; energy effects are implicitly taken care of by changes in the values of β_b and the ϵ_{b_s}. The free volume may, in a given solution, be different for clusters of different sizes, but we assume that it approaches a definite limit for large s. The characteristic thing about this limiting value of the free volume is that it can approach zero while the concentration is still finite. This occurs when the large clusters are compressed so closely together that they can no longer exist as separate entities but are forced to coalesce. It is to be noted that only the effect of the clusters on each other is to be considered. The volume occupied by the solvent molecules does not affect the free volume in this sense, for the concentrations at high dilution are defined in terms of the total volume of the solution.

We can now understand the situation when γ becomes zero. This case is of particular importance, since if γ becomes zero we shall no longer expect to be able to distinguish a meniscus, and we shall now show that the conditions for the occurrence of a critical temperature are fulfilled. This matter has been discussed in some detail, though from a more qualitative point of view, by Frenkel (7).

We define a total effective concentration in free volume as $C_b = N_b/V_f$, where V_f is the limiting value of the free volume for large clusters. If α is very small, so that most of the molecules of B are in large clusters, we may write

$$C_b = \Sigma_s s c_{bs} \tag{22}$$

If $\gamma = 0$, equation 19 becomes for large values of s

$$c_{bs} = e^{(\beta_b - \alpha_b s - \epsilon_{b\infty})/kT} \tag{23}$$

If we insert equation 23 into equation 22 we obtain an approximation, the sum in which is readily evaluable. With α_b/kT very small it takes the form

$$C_b = e^{(\beta_b-\epsilon_{b\infty})/kT}(kT/\alpha_b)^2 \tag{24}$$

which, solved for α_b, gives[3]

$$\alpha_b = kT[e^{(\beta_b-\epsilon_{b\infty})/kT}/C_b]^{1/2} \tag{25}$$

As we have noted, C_b is defined as N_b/V_f. Let us now investigate the properties of V_f. Let us suppose that N_b is constant and that the concentration of the solution is varied by changing the total volume, using a semipermeable piston through which solvent A can pass, but which is capable of controlling the volume V available to solute B. The free volume is the volume through which the center of a cluster is free to move, without coalescing with another cluster, and it may be considered as the cube of a free length. The latter may be set roughly equal, or at least proportional, to $V^{1/3} - V'^{1/3}$, where V' is the volume which would be occupied if the system were compressed, without change in the density of or the total amount of material in the large clusters, until the free volume just vanished. We thus write

$$\begin{aligned} V_f^{1/3} &= V^{1/3} - V'^{1/3} \\ &\cong (V - V')/3V'^{2/3} \end{aligned} \tag{26}$$

if $V - V'$ is small compared to V.

Actually, compression of the system may well cause a change in density of a cluster. And since the clusters are certainly not spherical when $\gamma = 0$ or even when γ is positive but very small, compression might change the effective volume occupied by a cluster by changing its shape. Thus V' will vary with V and, on account of the change in shape mentioned in the last sentence, we might even have $\mathrm{d}V'/\mathrm{d}V \sim 1$ in a highly concentrated solution. The actual value of V at which V_f vanishes, we shall call V_0'; at this volume $V_0' = V = V'$.

Equation 26 gives:

$$C_b = N_b/V_f = 27N_bV'^2/(V - V')^3 \tag{27}$$

Setting equation 27 into equation 25 we obtain:

$$\alpha_b = kTe^{(\beta_b-\epsilon_{b\infty})/2kT}(V - V')^{3/2}/(27N_b)^{1/2}\,V' \tag{28}$$

The terms $e^{(\beta_b-\epsilon_{b\infty})/2kT}$ and V' (in the denominator) will have a relatively small dependence on V as compared with $(V - V')^{3/2}$ when V is close to V'. We therefore can write approximately

$$(\partial\alpha_b/\partial V)_T = \tfrac{3}{2}kTe^{(\beta_b-\epsilon_{b\infty})/2kT}(27N_b)^{-1/2}(V - V')^{1/2}\,V'^{-1}\left(1 - \frac{\mathrm{d}V'}{\mathrm{d}V}\right) \tag{29}$$

We now see that $(\partial\alpha_b/\partial V)_T$ vanishes when $V = V' = V_0'$. By equation 21 this means that $(\partial\phi_{b\infty}/\partial V)_T - (\partial\mu_b'/\partial V)_T$ vanishes. In view of the discussion following equation 21, we conclude that $(\partial\phi_{b\infty}/\partial V)_T = 0$; hence at $V = V' = V_0'$ we also have $(\partial\mu_b'/\partial V)_T = 0$. Of course the argument applies just as well to the other side of the coexistence curve, where $(\partial\phi_{a\infty}/\partial V)_T$ and $(\partial\mu_a''/\partial V)_T$ will be equal to zero. This in turn means that A' and A'' of Section III will vanish. Thus it is seen that the conditions are fulfilled for a critical temperature, with the coexistence curve having a horizontal section,[3] since the left-hand sides of equations 5 and 6 will become infinite.

If the vanishing of $(\partial\alpha_b/\partial V)_T$ depends only on the term $(V - V')^{1/2}$ it vanishes to a low order. As indicated above it may vanish to a higher order on account of the term $1 - \mathrm{d}V'/\mathrm{d}V$. This has already been discussed for the liquid–vapor equilibrium of a one-phase system (in Section 5 of reference 31), and the arguments need not be repeated here. It may be added, however, that the above discussion depends on the assumption that we can always recognize the boundaries of a cluster, even when it is close to another cluster. There may actually be some haziness in this matter, which would lead to haziness in the concept and evaluation of the free volume. This might result in a further smoothing out and rounding off of the curve of chemical potential *vs.* concentration.

The manner in which the interfacial tension, or γ, which is proportional to it, vanishes is of some importance. Let us write

$$\gamma = \eta - T\sigma \tag{30}$$

where η and σ are, respectively, proportional to the interfacial energy (more exactly enthalpy) and entropy (the proportionality being the same as that which relates γ to the interfacial tension).

In general, when γ is positive η and σ have the same sign. If they are positive, then at a sufficiently high temperature γ vanishes, giving an upper critical temperature. If they are negative, then at a sufficiently *low* temperature γ vanishes, giving a lower critical temperature.

If there are no special forces involved between the molecules of components A and B, then we may in general expect σ to be positive. For the interface is then a place where the two species of molecules mix, and where there is more disorder than in the bodies of the solutions. Under the same circumstances we expect ΔS_1 and ΔS_2 to be positive, and from either σ or ΔS_1 and ΔS_2, we conclude that if we have any critical temperature it will be an *upper* critical temperature.

On the other hand, if there are special forces between the molecules there will be a tendency for the molecules of A and B to be bound to each other in a special

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[3] In reference 31 we considered the possibility that the expression for the chemical potential should have an entropy term of the form $kT\ a \ln s$, where a is a constant which would remain even when γ was zero. Such a term would be of the nature of a surface tension, but one which varied with s and became smaller for larger s. Such a term would, of course, affect the form of equations 24 and 25 and could affect the conclusions to be drawn from these equations if a became of the order of magnitude of 1. Actually, of course, our whole development is based upon the assumption that there does exist a temperature at which any term which is not proportional to s becomes negligible for large s, or is counteracted by some other effect. It seems likely that the term $1 - \mathrm{d}V'/\mathrm{d}V$ in equation 29 has more effect on the shape of the μ_b *vs.* concentration curve than the effect considered here. These details of behavior at the critical temperature obviously require further study.

way at the interface. This is likely to lead to a negative σ and a *lower* critical temperature, according to the criteria considered in Section III.

Of course, we cannot predict in any case whether or not a critical point will actually occur, but there is a general consistency between the two points of view.

One-phase region outside a horizontal coexistence curve

If the interfacial tension vanishes in the way we have just discussed, one important consequence is that it can continue in the same direction and become negative. Frenkel (7) has argued against this, but his arguments do not seem convincing to me. It is true that one cannot measure a negative interfacial tension, simply because one cannot find the interface. The interface tends to proliferate, so the clusters are no longer spherical, and in general we may expect the surface to become proportional to s rather than to $s^{2/3}$. This means that in equation 19 the surface term can be merged with the term $\alpha_b s$. Presumably, unless the relation of the surface quantities is such that sheets or filaments are stable,[4] proliferation of the surface will stop when the average curvature of the surface becomes sufficiently great. At this point the interfacial tension might be said to be zero in the sense that the free energy of the interface is a minimum with respect to changes in the surface which involve a change in average curvature. On the other hand, the free energy of the surface as a whole is negative, and the surface resists any attempt to lessen its area which leaves the average curvature unchanged. In any event, since proliferation of the interface is wasteful of free volume, it is probable that before the large clusters have coalesced into a spongy mass, the curvature of the surface will have become somewhat less than would be the case if the clusters were isolated.

The coalescence of the clusters of solute at the point where the free volume vanishes will produce a spongy mass of one phase in the other, just as in the case of liquid–vapor equilibrium there was produced a spongy mass of liquid in the vapor. We can treat the solution in much the same way as we treat the one-component system of condensing vapor, if we introduce a semipermeable piston, as above, which allows solvent A to pass through but holds back solute B. We assume osmotic equilibrium established between the molecules A outside and inside the piston. Let us now compress the piston slightly. A certain amount of A will flow out; since there is osmotic equilibrium this occurs without change of free energy. In order to maintain the concentration of phase rich in component A some material from this phase will enter into the spongy mass; as the system is in equilibrium this also occurs without free energy change. Finally the spongy mass will be compressed. This presumably lowers its surface area. If the inter-

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[4] If filaments and sheets should become stable, then since they constitute an entirely different state of the system, their appearance would manifest itself by a *sudden* drop of the interfacial tension to zero. This is, perhaps, a possibility which would be worthy of study, but we shall not consider it here. In general, however, when we go beyond the critical temperature into the range of homogeneous mixtures, we may expect the curvature of the interface to become greater and greater, so that sheets and filaments probably appear gradually and finally break up into single molecules, giving a microscopically homogeneous solution.

facial tension is zero, there is no resistance to the piston on this account. If, however, the interfacial tension is negative there will be a resistance to this process. Equilibrium will be reëstablished if a higher pressure is applied to the piston. Suppose, however, we reëstablish the equilibrium by lowering the pressure of the solvent material A outside the piston, leaving the pressure inside the same as before. We then see that μ_a, the chemical potential of A, has decreased and hence μ_b will have increased. Thus if the interfacial tension is negative in the region beyond the critical point, we cannot expect μ_a or μ_b to be constant over any range of concentrations. Hence our theory predicts no range of concentrations in an apparently homogeneous liquid phase where the chemical potential will remain constant.

Critical point with a rounded coexistence curve

Thus far Section IV has dealt only with the case in which the coexistence curve has a horizontal stretch at the critical temperature. If the curve is, instead, rounded at the critical temperature, as in the case discussed in the first part of Section III, the compositions of the two phases finally become identical at the critical temperature. The interfacial tension between two identical phases would, of course, be zero, with both terms in equation 30 vanishing. However, two phases can have the same composition without being identical in every respect, if they contain clusters of varying composition, since only the average composition of such a microscopically heterogeneous phase would be measured. If, however, the clusters were of different composition than the body of the phase, the interfacial tension at the surface of the clusters would not in general be zero. But if this were true, large clusters would not form gradually; we could have a sudden appearance of a new phase, but the conditions for a normal critical point would not be fulfilled and we would be led to a contradiction. So if we do have a rounded coexistence curve the two phases do approach identity, even when the examination is made on a molecular scale. As they approach identity, and the interfacial tension becomes very small, clusters would of course form, but they would have almost the same composition as the rest of the liquid. At the critical point they would become "ghosts."

Suppose we consider a phase in which component B is solute and A solvent (the prime phase) at a temperature such that two phases can exist in equilibrium, just before the critical point is reached. If we dilute the solution by adding A, the clusters, which are almost ghosts, could not remain in equilibrium with the body of the liquid of the new composition. Since the clusters have almost the same composition as the surrounding medium and cannot become richer in A, a rather large amount of material will be withdrawn from them, to restore the original composition. Now a rounded coexistence curve requires that A' and A'', and hence $(\partial\alpha_b/\partial V)_T$ and $(\partial\alpha_a/\partial V)_T$, vanish to the second order, which, from equation 29, means that $V - V'$ should be proportional to $(V - V_0')^2$. This would require considerable swelling of the clusters to keep the volume nearly filled as V was increased by means of the semipermeable piston starting with $V = V' = V_0'$. That this swelling should be especially great just under the circumstance in which there is considerable loss of the material rich in B does not seem probable. On this basis we would not expect to find rounded coexistence curves. However, with the situation described it would certainly become very difficult to define the boundaries of a cluster, and with the identity of the clusters becoming increasingly hazy, it may well be that we can draw no valid conclusions on the basis of the cluster or association theory as developed here. McMillan and Mayer (20), as we have seen, concluded that the vanishing of A' and A'' to the second order would occur under only rather special circumstances, but it does not seem necessary to conclude that those circumstances are at all impossible, nor do the experimental data, discussed in the next section, seem adequate to decide this question unequivocally.

V. THE EXPERIMENTAL MATERIAL

The above sections have provided at least a partial theoretical answer to the questions propounded in Section II: *(1)* The coexistence curve will in many, probably most, cases have a horizontal section at the critical temperature, though this may not be absolutely necessary. *(2)* The chemical potentials should not be constant over any part of the region of complete miscibility.

General observations

It was long ago suggested (9, 27, 28, 29), on the basis of observations of critical opalescence and anomalous viscosity, that solutions in the neighborhood of the critical point might have a colloidal structure. The theory which we have discussed in this paper seems to be in qualitative accord with the idea that the solutions in the critical region have a colloidal or emulsoidal structure, provided they are of the type which have a horizontal portion of the coexistence curve. On the other hand, in the case where the coexistence curve is rounded, if this occurs, the dispersed "ghosts" should have so nearly the properties of the dispersing medium that the solution could hardly be distinguished as a colloidal solution. In this case, however, the classical type of critical opalescence would be expected in the immediate neighborhood of the critical point.

Some solutions do not show the critical opalescence, but Mondain-Monval and Quiquerez (24) showed that this generally happens when the indices of refraction of the liquids involved are nearly alike. They interpreted this as meaning that while the solution was actually colloidal, there were simply no *visible* effects under these circumstances. These authors also investigated the anomalous viscosity of solutions in the critical region (25). They found an anomalously high viscosity in a number of cases in which critical opalescence was not seen. However, they found some ternary mixtures in which there was neither anomalous viscosity nor critical opalescence, and in these cases they supposed that there was molecular dispersion rather than a colloidal solution.

A somewhat more refined analysis can be made if the polarization of light scattered by the liquid is observed. From such measurements Krishnan (16, 17) concluded that molecular clusters of diameter of the order of the wave length were formed near the critical solution temperature. A spongy mass with surfaces having an average radius of curvature of this order of magnitude would probably give a similar effect. An average radius of curvature of the order of the wave length of light seems rather large, however, and it may be that something other than radius of curvature is the controlling factor. There is some evidence, perhaps not too certain, from ultramicroscopic examination (10) and viscosity measurements (27) that the dispersion is finer than the wave length of light.

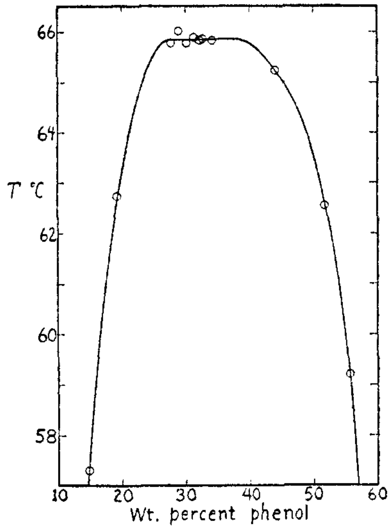

FIG. 2.

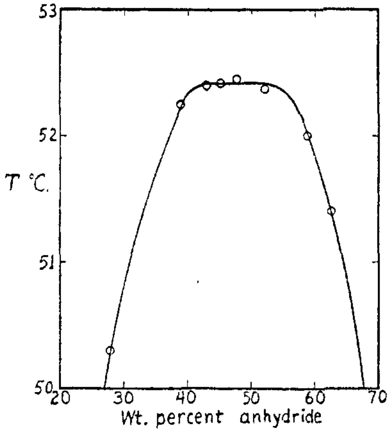

FIG. 3.

FIG. 2. Coexistence curve for phenol and water
FIG. 3. Coexistence curve for acetic anhydride and cyclohexane

The shape of the coexistence curve

If one examines the coexistence curves given in the Landolt–Börnstein tables, or elsewhere, he obtains the impression that many of them are extremely flat at the critical temperature. This has, in fact, been remarked upon by various investigators; for example, Woodburn, Smith, and Tetewsky (39), in the course of an investigation of critical solution temperatures of organic binary mixtures, found that the temperature at which the liquid became homogeneous was independent of concentration over a range of concentrations, and that this aided greatly in the determination of the critical solution temperature. Of course, it is impossible to prove experimentally from data of this sort that there is an absolutely horizontal portion to any coexistence curve; one may always be dealing merely with an extremely flat maximum. However, I think it may be reasonably safely inferred that there are curves with a horizontal portion, and I believe, in fact, that most of the curves do have such a horizontal portion. A couple of illustrative examples are given in figures 2 and 3.

On the other hand, there do seem to be curves which are rounded at the critical temperature. One such example, the best one which I have run across, is shown in figure 4. In most cases, when curves which have the rounded appearance are carefully examined, it appears that the evidence is faulty. Most often the experimental points are not close enough together to enable a decision to be reached. It is, as a matter of fact, just as impossible to exclude a short horizontal section in an apparently rounded curve, such as is shown in figure 4, as it is to exclude the possibility of a very flat maximum in a curve with an apparently completely flat top. As a matter of fact, one might well anticipate much shorter horizontal sections than frequently seem to occur. In the liquid–vapor equilibrium in the case of ethylene, the horizontal section of the coexistence curve extends over a volume range of only 10 per cent. Since the compression of the spongy mass of material at the critical point is mechanically similar in the one-component and the two-component systems, one might suppose that the horizontal section in the two-component system would correspond to a motion of the semipermeable piston considered in Section IV through a volume about 10 per cent of the total volume being compressed. Yet, in many cases, the composition range involved obviously corresponds to a greater volume range. Some rather extreme examples of this are furnished by the systems acetone–carbon disulfide (3) and methyl acetate–carbon disulfide (4), in which cases the flat section ranges from about 50 to about 75 mole per cent carbon disulfide.

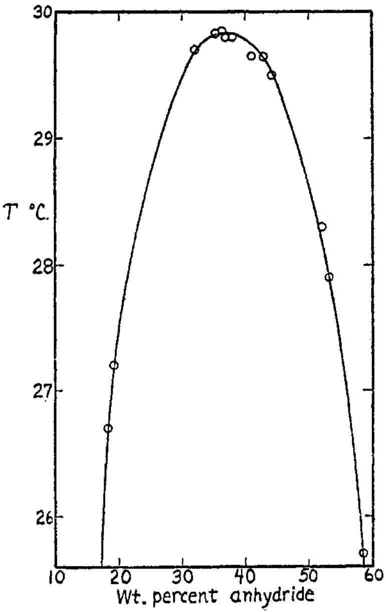

FIG. 4.

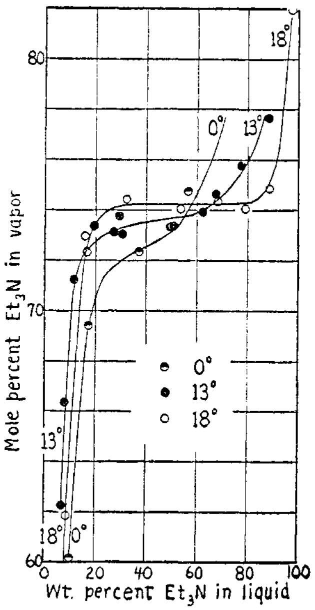

FIG. 5.

FIG. 4. Coexistence curve for acetic anhydride and carbon disulfide

FIG. 5. Vapor–liquid composition curves for triethylamine and water

Another difficulty in being sure that a coexistence curve is actually rounded at the critical point arises from the effect of impurities. It is not unusual for there to be a range of several degrees in the reported values of the critical temperature for a given pair, and the curves reported by different authors may also vary in shape. Small amounts of a surface-active impurity lower the interfacial tension, so that it would become zero before the critical temperature was reached. Emulsification would then result, with increase in the surface, but the amount of material which could be emulsified would depend on the amount of surface-active agent present. Thus the two branches of the coexistence curve might be drawn together, without actually meeting. They would be drawn closer together the lower the original value of the interfacial tension, however; thus a coexistence curve with a rounded top could be produced, even though the curve would be flat if no surface-active agent were present.

The chemical potential in the critical region

There are very few data available which would have a bearing on the question whether the chemical potential can remain constant over a range of concentrations in the region of homogeneous solutions beyond the critical temperature. Probably the best work on this subject is that of Roberts and Mayer (32) on the triethylamine–water system, which has a lower critical temperature at about 18.4°C. These authors measured the mole per cent of amine in the vapor over a range of liquid concentrations. If the chemical potential remains constant over a range of liquid concentrations, the composition of the vapor phase should also be constant over this range. These authors believed that the composition of the vapor did remain constant over a considerable range of liquid concentration at 18°, 16°, and 13°C., while the slope of the curve became definitely finite at 0°C. Of course, a curve which is experimentally of zero slope may actually have a very small slope, and such an experiment can never be absolutely conclusive. However, Roberts and Mayer argued that, since the slopes at 16°C. and 13°C. were very much smaller than would be expected from an interpolation, the slopes must suddenly become larger somewhere between 13°C. and 0°C.; therefore, it is reasonable to suppose that they rise from zero. I do not believe, however, that this argument is really valid. In figure 5 are shown the data of Roberts and Mayer for 18°, 13°, and 0°C. (the data at 16°C. are omitted to avoid confusion), and it will be seen that the curves which are passed through the data fit them reasonably well, do not show any zero slope except at 18°C., just below the critical temperature, and change gradually on going from 18° to 0°C. The slope of the curve at 13°C. is small, but not unexpectedly small if it be compared with the pressure–volume curves of the one-component system (see figure 2 of reference 31). This does not mean that Roberts and Mayer's analysis is necessarily wrong, but I do believe that it indicates that other interpretations are not excluded.

Over a region in which the chemical potentials of the constituents of a binary phase are constant, the total vapor pressure should also be constant. The vapor pressure of aqueous solutions of phenol has been measured by a number of investigators (6, 34, 36, 38). The earlier measurements are not accurate; the accurate measurements of Ferguson (6) are plotted on an exaggerated scale in figure 6. It is seen that there is an almost horizontal section of the curve from about 25 to 45 per cent phenol. We can calculate roughly from the Gibbs–Duhem equation that over this range the partial pressure of water will decrease by about 0.05 mm. and that of phenol will increase by about 0.01 mm. These quantities are zero within the limits of error; nevertheless, we shall assume that they are correct as given, and shall attempt to determine whether they are of a reasonable order of magnitude.

In Section IV we considered a hypothetical experiment involving compression by a semipermeable piston, which was the nearest analogy to compression in a one-component system. Therefore, it appears that the closest analogy to the pressure–volume isotherm for the one-component system would be an osmotic pressure–volume isotherm for the binary system. Let us, therefore, consider how the osmotic pressure Π would change over the range of concentrations from 25 to 45 per cent phenol. Π is given by the equation

$$\Pi = (RT/\bar{v}_a) \ln p_a(0)/p_a(w) \tag{31}$$

where $\bar{v}_a$ is the partial molal volume of solvent, $p_a(w)$ is its partial vapor pressure at weight per cent w, $p_a(0)$ being the vapor pressure of pure solvent. The partial vapor pressure of phenol over the range $w = 25$ to $w = 45$ per cent may be found from Schreinemakers' measurements (34) (which are not accurate enough to give differences but may be used for rough absolute values of the partial pressures) to be about 6 mm. and that of water is about 284 mm. If then we let $\Delta\Pi$ be the difference in osmotic pressure for $w = 25$ and $w = 45$ per cent, and assume that $\bar{v}_a$ is constant, application of equation 31 gives roughly:

$$\frac{\Delta\Pi}{\Pi} = \frac{\ln (284.05/284)}{\ln (290/284)} = 0.008$$

If equation 31 is applied, considering phenol instead of water as the solvent, we get, using Kahlbaum's (15) value of 10.9 mm. for the vapor pressure of phenol at 75°C.:

$$\frac{\Delta\Pi}{\Pi} = \frac{\ln (6.01/6)}{\ln (10.9/6)} = 0.003$$

As may be seen by comparing with pressure–volume curves for a one-component system just above the critical temperature (see reference 31, Fig. 2) these are not extremely small relative pressure changes, though a change in w from 25 to 45 per cent is equivalent to a rather large volume change; in any event $\Delta\Pi/\Pi$ is subject to considerable error.

To be sure 75°C. is rather far, about 10°C., above the critical temperature for phenol–water. But in this connection we may mention that Antonoff (1) has measured the interfacial tension between the phenol–water phases at 25°C. and finds it to be of the order of 0.5 dyne per centimeter. Since the critical temperature, at which the interfacial tension is presumably zero, is 65°C., it is seen that this gives a rate of change of the interfacial tension with temperature which is very much smaller than that of most surface tensions of pure liquids. Accordingly we may expect the slope of the chemical potential *vs.* concentration curve to change very slowly above the critical temperature.

Effect of addition of a third component

It has already been mentioned that impurities can have an appreciable effect on the coexistence curve of a two-phase system. A great many controlled experiments have been carried out to test the effect of a third component, and it has been found that these effects are often exceedingly large. It is not, perhaps, surprising that Timmermans (37) found that addition of 1 per cent of sodium oleate to the critical mixture of phenol and water lowered the temperature of miscibility by more than 20°C., for sodium oleate is a notoriously surface-active substance. It can lower the already low interfacial tension, so that emulsification will occur, with formation of a single highly disperse phase, at a much lower temperature than would ordinarily be the case. But at first sight it is surprising that a little over 3 per cent of sodium chloride (molal concentration 0.55 per 1000 g. of solution) raises the mixing temperature of this same solution by almost 40°C. (33, 37). This, however, can be explained in the light of the very small temperature coefficient of the interfacial tension noted just above. Because of this small temperature coefficient, a small change in the interfacial tension can cause a large change in the temperature at which it finally becomes zero.

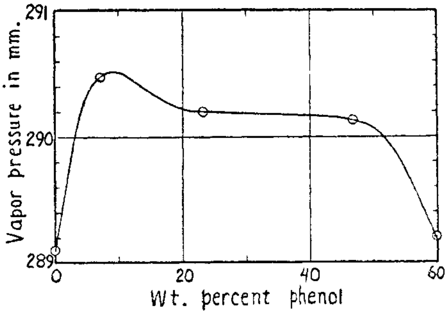

FIG. 6. Vapor pressures of phenol–water solutions at 75° C.

A rough estimate of the order of magnitude may be made by the use of the Gibbs adsorption isotherm,

$$d\gamma_\sigma = -\Gamma_a d\mu_a - \Gamma_b d\mu_b - \Gamma_c d\mu_c \qquad (32)$$

where γ_σ is the surface tension, the Γ's are the adsorptions of the various constituents per unit area, and the μ's are chemical potentials. By proper choice of the location of the surface, one of the Γ's can be made equal to zero, and we may reasonably assume that the order of magnitude of the change in γ will be given by retaining only the one term which refers to the "impurity," thus writing:

$$d\gamma_\sigma \sim -\Gamma_c d\mu_c \qquad (33)$$

If the impurity is present in small quantities generally $d\mu_c = RT \text{ d} \ln c_c$, where c_c is the concentration; in the case of sodium chloride, however, $d\mu_c = 2RT \text{ d} \ln c_c$, on account of the dissociation, so

$$d\gamma_\sigma \sim -2RT(\Gamma_c/c_c)dc_c \tag{34}$$

In the case of sodium chloride the surface tension is raised, and the adsorption is negative. Let us suppose that there is a region of thickness about 3×10^{-8} cm. near the surface from which sodium chloride is excluded. Then if the concentrations are expressed per cubic centimeter, we have $\Gamma_c/c_c \sim -3 \times 10^{-8}$ cm., $R = 8.3 \times 10^7$ ergs per degree per mole, and $T \sim 350$°K. Hence for a concentration of $c_c = 0.55$ mole per 1000 g. of solvent, $\sim 0.5 \times 10^{-3}$ mole per cubic centimeter, we will find a change in interfacial tension given by integrating equation 34:

$$\Delta\gamma_\sigma \sim 0.9 \text{ dynes cm.}^{-1}$$

In view of the low temperature coefficient of γ_σ, it is clear that this is of the right order of magnitude to raise the mixing temperature by 40°C.

Suggestions for future experiments

It is clear that what is needed now to throw further light on the questions raised in this paper is a thorough and accurate investigation of a few systems with highly purified components, rather than further experiments of a general nature with a large number of systems. Attempts to determine constancy of the chemical potentials by analysis of the composition of the vapor phase seem likely to run into experimental difficulties. Measurements of the total vapor pressure in systems in which the two components have greatly different volatilities and which do not show a vapor pressure maximum seem more promising. Such measurements, however, need to be done with a high degree of accuracy, and differential measurements in which the vapor pressure of a solution of one composition is balanced against that of another composition would be preferable. The surface tension at the liquid–vapor interface is also constant when the chemical potentials are constant. This is another property which could be profitably measured, as was also suggested by Dr. L. D. Roberts in a private communication. Measurements of either total vapor pressures or surface tension should be correlated with observations on the coexistence curve and with measurement of the interfacial tension between the liquid phase as the critical temperature is reached. Similar measurement should be made with a third substance present. It is important that *all* the relevant data should be obtained for a single liquid pair. We are starting a program along these lines in this laboratory, using the cyclohexane–aniline system.

VI. SUMMARY

The coexistence curve in the pressure–volume plane, for the equilibrium between liquid and vapor in a one-component system, is apparently not rounded at the critical point as demanded by the simple van der Waals theory. Instead it shows a horizontal (constant-pressure) portion at the critical temperature. The isotherm at the critical temperature has a horizontal portion, which coincides with the horizontal part of the coexistence curve. According to the theory of Mayer and Harrison, isotherms slightly above the critical temperature should still have a horizontal section. It is the belief of the present author, however, that these isotherms actually have a definite slope, though it is very small near the critical point.

Similar questions can arise in the case of two-component liquid systems. In terms related to the experimentally observed data, these questions are the following: (*1*) Does the coexistence curve for two liquid phases in the temperature–composition diagram show a horizontal (constant-temperature) portion? (*2*) In the temperature region near the critical temperature, but where only one liquid phase exists, can there be a range of concentrations in which the chemical potentials of the components are independent of composition?

In the attempt to answer these questions there are first considered certain thermodynamic properties of the critical solutions. It is shown that if the coexistence curve is rounded, the first and second derivatives of the chemical potentials with respect to concentration must vanish, whereas if the curve has a horizontal part only the first derivative must vanish. Necessary conditions for upper and lower critical temperatures are expressed in terms of the signs of the entropies of transfer of the components from one solution to the other.

The problem is then considered from the point of view of associating molecules. Solute molecules can associate to form clusters. At a certain concentration the very great clusters suddenly become stable, corresponding to the appearance of another phase. This depends, however, upon the interfacial tension between the solution and the large clusters being positive. When the interfacial tension vanishes, the large clusters come in gradually, and at a point where the free volume for large clusters vanishes (concentration infinite in free space) the conditions for a critical point with a horizontal section in the coexistence curve are satisfied. The condition for the vanishing of the interfacial tension is discussed. When the surface tension vanishes the large clusters coalesce to form a spongy mass, a sort of colloid structure. Beyond the critical temperature no meniscus can be seen, but the spongy mass still forms. It has a negative interfacial tension, which resists any attempt to lessen the extent of the surface. It is shown that this leads to the conclusion that there will be no region of constant chemical potential beyond the critical point.

The above paragraph describes the situation if the interfacial tension vanishes because of its temperature coefficient. It is not impossible that there are cases in which the interfacial tension vanishes merely because the two phases finally become identical. This would lead to a rounded coexistence curve.

The experimental evidence bearing on the problem may be briefly summarized as follows: The optical properties and viscosity of solution in the neighborhood of the critical point indicate, as has long been known, that there actually is a sort of colloidal structure in that region, as seems reasonable on the basis of the above discussion. Experimental coexistence curves indicate almost certainly that there are such curves with a horizontal section at the critical temperature. There is some evidence that there are also curves which are rounded in this region. The experimental evidence which bears on the question of the chemical potential consists of one or two measurements on the composition of the vapor phase in equilibrium with the liquid system and a few measurements on total vapor pressures. These data do not answer the question unequivocally, since extremely high accuracy would be required. The effect on the critical temperature of addition of a third component has been considered. It is shown that the experimental results are of a reasonable order of magnitude, by considering the effect of a third substance on the interfacial tension. Finally, a number of suggestions have been made for future experimental work.

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