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by

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Abstract

THEORY OF UPPER AND LOWER CRITICAL SOLUTION TEMPERATURES

by

Donald J. Mintz

Advisor: Professor David C. Locke

The phenomenon of the lower critical solution temperature is proposed to be due to the formation of a clathrate hydrate. The statistical thermodynamic properties of a simplified model of a clathrate hydrate is shown to have the required dependency of the excess entropy at the lower consolute point. In addition, a fundamental variation in the approach to the quantification of Pauling's model of water is presented as a logical consequence of the above.

The compositions of the conjugate phases in vapor-liquid and liquid-liquid equilibria are shown to be dependent upon two functions. The ratio of these two functions is shown to be a system characteristic of fundamental importance. The variation in this ratio is in agreement with the theory of lower critical solution temperatures, and, in addition, adds insight into the detailed processes of the control of molecular movement between conjugate phases. The concept of active and passive components is used throughout. Pure component vapor-liquid equilibria are shown to be amenable to treatment as pseudobinary systems.

Expressions for the temperature dependence of the aforementioned functions are introduced and shown to be in agreement with experimental results throughout the entire two-phase temperature range.

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I must not overlook two other individuals whose encouragement and guidance must be counted as important contributions to this work. In this regard, Professor Harvey Cohn of the City University of New York Department of Mathematics is thanked for his wise counsel that I apply combinatorial mathematics to the problems of chemistry. Lastly, I would like to thank Professor John Riordan for his help with the combinatorial aspects of this work.

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HISTORICAL SURVEY

When two liquids are mixed and two phases form, the compositions of both phases represent different ratios of the two components. In most cases an increase in temperature will effect a greater mixing and the compositions of the two phases will approach each other. At the upper critical solution temperature (UCST) the compositions of both phases become identical and the phase boundary disappears.

The type of behavior described above is relatively common. Francis(1) lists over six thousand mixtures which exhibit this type of behavior. In a few cases mixtures are formed in which an increase in mixing will result from a decrease in temperature. This apparently strange behavior has never been quantitatively explained. In fact, both types of phenomena have withstood a logical quantitative explanation.

Work in the field of partially miscible binary liquid mixtures dates back approximately one hundred years(2). The reason for this is the extreme simplicity of the experiment that is performed. The purpose of the experiment is to determine the compositions of the co-existent phases as a function of temperature. Early workers distinguished between two versions of the experiment. One version they called the "Analytical Method" in which the compositions of the coexisting phases at a given temperature were determined in the same experiment. The data from this type of experiment consists of pairs of composition points, each pair representing a different temperature. According to the phase rule of Gibbs, in a binary system, the compositions of the coexisting phases at a given temperature and pressure are invariant. Thus, a second method, called the "Synthetic Method" was developed for performing the experiment. This version of the experiment consists of heating a partially miscible liquid mixture until opalescence is observed. The data from this experiment consist of single points at which opalescence is observed. When these points are plotted on temperature-composition coordinates the result is the same as the curve obtained by the more tedious Analytical Method.

The success of van der Waals' equation of state in predicting the existence of a critical point in pure component vapor-liquid equilibria gave early workers some discomfort when it was realized that the difference in the densities of coexisting liquid and vapor phases ($\rho_l - \rho_v$) was not proportional to the square root of T_c-T as predicted by van der Waals, but instead followed a cubic relationship(3). Many workers consider this realization to be the delineation between the classical and modern era of critical phenomena(4). The difference $\rho_l - \rho_v$ is called an <u>order parameter</u> because it is non-zero only in the ordered phase. In partially miscible binary liquid mixtures the density difference and also the mole fraction difference of a given component in the two phases are used as suitable order parameters. Thus, Zimm(5) has found that $(x'' - x')^3$ is proportional to $T_c - T$ in the perfluoromethylcyclohexane- carbon tetrachloride system. Atack and Rice(6) have found that $(\rho'' - \rho')^3$ is proportional to $T_c - T$ in the cyclohexane-aniline system. It should be emphasized that these relationships are for $T_c - T$ of the order of one degree or less. At temperatures further removed from the critical temperature Cox and Herington(7) found that that the cubic relationship between the order parameter and the difference in temperature from the critical temperature does not represent a generally valid relationship for all partially miscible binary liquid mixtures. Instead, they proposed that the ratio of the mole fractions of the two components within a given phase (x_1'/x_2' and x_1''/x_2'') can be represented by the equations

$$(T_c-T)=\left[A'\log_{10}(x_1'/x_2')+B'\right]^3 \text{ and } (T_c-T)=\left[A''\log_{10}(x_1''/x_2'')+B''\right]^3$$

Thus, each equation represents one branch of the coexistence curve. Since $x_1+x_2=1$ in each phase, the composition of a phase as a function of temperature can be determined. This is an improvement over the order parameter type of relationship which only gives the difference of the compositions of the phases and not the individual value for each phase.

If the two lines represented by these equations intersect at the critical point, then, since $T_c - T = 0$ at the critical point, $B'/A' = B''/A''$.

It should be pointed out that the A term in the equations represents an exponent of the log term and hence a modifier of the cubic relationship. It should also be pointed out that this is a purely empirical relationship for which the authors offer no hint of a possible theoretical explanation. Nonetheless, the work of Cox and Herington represents a significant contribution in that it advanced the state of the art away from the order parameter approach to the individual phase compositions.

We have now completed our historical survey of the equations that have been developed to deal with partially miscible binary liquid mixtures. The next part of our history will be concerned with the explanation of the phenomenon of the lower critical solution temperature (LCST).

The first published system to exhibit both an UCST and a LCST was the Nicotine-Water system(8). In 1937 Hirschfelder, Stevenson and Eyring(9) proposed that the phenomenon of the LCST was due to intermolecular forces such as hydrogen bonding. These intermolecular forces were assumed to be of sufficient strength to interfere with the free rotation of the molecules. Rushbrooke(10) showed that the restriction of the free rotation of the molecules could give rise to a LCST . Barker and Fock(11) published a paper in 1953 which used the following approach:

"...The variation of solubility with temperature is determined by the sign of the heat of mixing-if the heat of mixing is positive the solubility increases with temperature, and vice versa. Thus if we are to find closed temperature against composition curves, with upper and lower CST, the heat of mixing must be positive at higher temperatures and negative at lower temperatures...This may be so if the interaction between unlike molecules is repulsive for a majority of relative orientations, and attractive for a few. For at higher temperatures the orientations will be nearly random, and the repulsive interaction will give positive heat of mixing, while at lower temperatures the attractive orientation will be favored, and may give rise to a negative heat of mixing..."

The main argument we have with this explanation of the variation of the heat of mixing with temperature is that when there is sufficient thermal energy to effect a random orientation of molecules, we should expect, by definition of "random orientation," complete mixing of the phases. In addition, the correspondence between this theory and any real system was never shown.

In 1962, Kirginttsev(12) proposed the existence of two liquid lattices in the statistical-mechanical sense of mathematical cells being occupied by the two different molecular species.

Recent work in this field has centered around direct experimental observation of systems that exhibit a LCST in order to obtain a better understanding of the detailed molecular mechanism. This approach has centered around ultrasonic studies. In 1969 a paper appeared which came very close to uncovering the mystery of the mechanism responsible for the LCST(13). The important contribution of this paper is the linkage in the same paper of clathrate hydrates and the phenomenon of the LCST. The authors did not realize how close they were to the answer. Instead, they present a collection of unattached pieces. Nonetheless, their work represents a significant contribution.

Ten years prior to the above paper, Pauling(14) proposed a clathrate hydrate structure for pure water. This model of pure water was given a thermodynamic foundation by Frank and Quist(15). The shift in equilibrium with temperature that Frank and Quist propose for the species that are assumed to exist in pure water would not explain the phenomenon of the LCST. However, with a fundamental modification in the equilibrium,that we propose, Pauling's model of water and the phenomenon of the LCST are shown to be subject to the same equilibrium.

REFERENCES

(1) Francis, A.W., "Critical Solution Temperatures," American Chemical Society, Washington,D.C.,(1961).

(2) Alekseev, V., Ann. physik Chem., (2) 28,305(1886).

(3) Guggenheim, E.A., J. Chem. Phys., 13,253(1945).

(4) Stanley, H.E., "Introduction to Phase Transitions and Critical Phenomena," Oxford Univ. Press, New York(1971)p 9.

(5) Zimm, B.H., J. Phys. & Colloid Chem., 54, 1306(1950).

(6) Atack, D. and Rice, O.K., Discussions Faraday Soc., 15, 210(1953).

(7) Cox, J.D. and Herington, E.F.G., Trans. Faraday Soc., 52, 926(1956).

(8) Hudson, C.S., Z. physik. Chem., 47, 113(1904).

(9) Hirschfelder, J.O., Stevenson and Eyring,H., J. Chem. Phys., 5, 896(1937).

(10) Rushbrooke, G.S., Proc. Camb. Phil. Soc., 34, 424(1938).

(11) Barker, J.A. and Fock, W., Discussions Faraday Soc., 15, 188(1953).

(12) Kirginttsev,A.N., Bulletin of the Siberian Section of the Academy of Sciences of the U.S.S.R., 2, 43(1962).

(13) Blandamer, M.J., Hidden, N.J., Symons, M.C.R. and Treloar, Trans. Faraday Soc., 65, 2663(1969).

(14) "Hydrogen Bonding," ed D. Hadzi, Pergamon Press, London (1959), p 1.

(15) Frank, H.S. and Quist, A.S., J. Chem. Phys., 34, 604(1960).

CHAPTER I

DERIVATION OF THE FUNDAMENTAL EQUATION OF BINARY LIQUID PHASE EQUILIBRIA

The compositions of the conjugate phases in partially miscible binary liquid mixtures are invariant at constant temperature and pressure. Different initial ratios of the two components within the range of limited miscibility will only result in different ratios of the amounts of the conjugate phases that are formed. If we mix the two partially miscible components A and B at a constant temperature and pressure at which the mole fraction of A in the B-rich phase is XAB and the mole fraction of B in the A-rich phase is XBA, we would expect to find the formation of two conjugate phases at all ratios of the pure components A/B such that

(1) $$\frac{1-XBA}{XBA} > A/B > \frac{XAB}{1-XAB}$$

If we view the formation of the two conjugate phases from the point of view of the transport of A and B, we can develop expressions for XAB and XBA in terms of the number of moles of B that are transported into the A-rich phase (NBA), the number of moles of A that are transported into the B-rich phase (NAB), the initial number of moles of A (NA), and the initial number of moles of B (NB).

(2) $$XBA = \frac{NBA}{NA-NAB+NBA}$$

(3) $$XAB = \frac{NAB}{NB-NBA+NAB}$$

If we now use the additional relationships: XAA + XBA = 1 and XBB+XAB=1, the solution of (2) and (3) for NAB and NBA gives

$$(4) \qquad NAB = \frac{NB\cdot\frac{XAB}{XBB} - NA\cdot\frac{XBA\cdot XAB}{XAA\cdot XBB}}{1 - \frac{XAB\cdot XBA}{XAA\cdot XBB}}$$

$$(5) \qquad NBA = \frac{NA\cdot\frac{XBA}{XAA} - NB\cdot\frac{XAB\cdot XBA}{XAA\cdot XBB}}{1 - \frac{XAB\cdot XBA}{XAA\cdot XBB}}$$

Since XAA, XBB, XAB and XBA are functions of temperature and pressure only, we can simplify (4) and (5) by defining

$$(6) \qquad F1(T,P) = \frac{\frac{XAB}{XBB}}{1-\frac{XAB\cdot XBA}{XAA\cdot XBB}}$$

$$(7) \qquad F2(T,P) = \frac{\frac{XBA}{XAA}}{1-\frac{XAB\cdot XBA}{XAA\cdot XBB}}$$

$$(8) \qquad F3(T,P) = \frac{\frac{XAB\cdot XBA}{XAA\cdot XBB}}{1-\frac{XAB\cdot XBA}{XAA\cdot XBB}}$$

When we substitute (6)-(8) into (3) and (4) we obtain

$$(9) \qquad NAB = NB\cdot F1(T,P) - NA\cdot F3(T,P)$$

$$(10) \qquad NBA = NA\cdot F2(T,P) - NB\cdot F3(T,P)$$

We can express F3(T,P) in terms of F1(T,P) and F2(T,P) by making use of the combinatorial identity

$$(11)\quad \sum_{k=0}^{n} \binom{n}{k} \cdot \left[\frac{Y0\cdots Yn}{1-Y0\cdots Yn}\right]^{k+1} = \prod_{k=0}^{n} \frac{Yk}{1-Y0\cdots Yn}$$

For the case n=1 we obtain

$$(12)\quad \left[\frac{Y0\cdot Y1}{1-Y0\cdot Y1}\right]^{1} + \left[\frac{Y0\cdot Y1}{1-Y0\cdot Y1}\right]^{2} = \frac{Y0}{1-Y0\cdot Y1} \cdot \frac{Y1}{1-Y0\cdot Y1}$$

If we let

$$(13)\quad Y0 = \frac{XAB}{XBB}$$

$$(14)\quad Y1 = \frac{XBA}{XAA}$$

We obtain upon substituting (13) and (14) into (12)

$$(15)\quad \left[\frac{\frac{XAB\cdot XBA}{XBB\cdot XAA}}{1-\frac{XAB\cdot XBA}{XBB\cdot XAA}}\right]^{1} + \left[\frac{\frac{XAB\cdot XBA}{XBB\cdot XAA}}{1-\frac{XAB\cdot XBA}{XBB\cdot XAA}}\right]^{2} = \frac{\frac{XAB}{XBB}}{1-\frac{XAB\cdot XBA}{XBB\cdot XAA}} \cdot \frac{\frac{XBA}{XAA}}{1-\frac{XAB\cdot XBA}{XBB\cdot XAA}}$$

From (6)-(8) we obtain upon substitution

$$(16)\quad [F3(T,P)]^{1} + [F3(T,P)]^{2} = F1(T,P) \cdot F2(T,P)$$

If we express (16) as a quadratic equation in terms of F3(T,P), we obtain

$$(17)\quad [F3(T,P)]^{2} + [F3(T,P)]^{1} - F1(T,P)\cdot F2(T,P) = 0$$

Which upon substitution into the quadratic formula gives the result

$$(18)\quad F3(T,P) = -\tfrac{1}{2} + \sqrt{\tfrac{1}{4} + F1(T,P)\cdot F2(T,P)}$$

for the positive root. We must take the positive root when we recognize that the mole fractions and their functions are always positive or zero.

When (18) is substituted into (9) and (10) we obtain

$$(19)\quad NAB = NB\cdot F1(T,P) - NA\cdot\left[-\tfrac{1}{2}+\sqrt{\tfrac{1}{4}+F1(T,P)\cdot F2(T,P)}\right]$$

$$(20)\quad NBA = NA\cdot F2(T,P) - NB\cdot\left[-\tfrac{1}{2}+\sqrt{\tfrac{1}{4}+F1(T,P)\cdot F2(T,P)}\right]$$

If we then substitute (19) and (20) into (2) and (3) we obtain the form of the temperature and pressure dependence of the compositions of the conjugate phases. We remind the reader that we have not introduced any approximations up to this point.

From the point of view of numerical analysis, the value of F1(T,P) versus $\left[-\frac{1}{2}+\sqrt{\frac{1}{4}+F1(T,P)\cdot F2(T,P)}\right]$ and F2(T,P) " " has the following relationship. At low temperatures the expression in brackets is approximately equal to F1(T,P)•F2(T,P) which means that it is of the order of F1(T,P) times as small as F1(T,P), when F1(T,P) is a very small fraction of one. We assume that F1(T,P) and F2(T,P) are of the same order of magnitude. At high temperatures close to the critical temperature, the expression in brackets is approximately equal to the square root of F1(T,P) • F2(T,P) which means that it is of the same order of magnitude as F1(T,P). Thus, we can summarize this discussion by stating that at low temperatures NAB is a strong function of NB and a weak function of NA, whereas NBA is a strong function of NA and a weak function of NB. At high temperatures close to the critical temperature, NAB and NBA are both strong functions of NA and NB.

If we examine (19) and (20) we note that at a given temperature and presssure,variations in NAB and NBA depend upon variations in NA and NB only. We are led to the interesting conclusion from (19) that an increase in NA leads to a decrease in NAB. That is, the more A component that is added, the less A component that finds its way into the B-rich phase. Similarly, from (20) we are led to the conclusion that the more B component that is added, the less B component that finds its way into the A-rich phase. From this analysis we are led to the inescapable conclusion that the two components act as containers for each other. The concept of a vigorous penetration of one component into the other must be replaced by the concept of the containment of one component by the other. We shall develop this concept into a structural theory of liquids in the following chapters.

If the temperature and pressure dependence of the functions F1(T,P) and F2(T,P) were known, then the temperature and pressure dependence of the compositions of the conjugate phases could be derived from equations (2) and (3). If the functions F1(T,P) and F2(T,P) represent system characteristics of a more fundamental nature than the compositions of the conjugate phases, then the task of deriving the correct form of the temperature and pressure dependence of the compositions of the conjugate phases could be simplified by replacing this goal with the search for the pressure and temperature dependence of the functions F1(T,P) and F2(T,P).

This chapter will show the fundamental nature of these functions by examining experimental data from the coexistence curves of the three types of binary systems which show similar temperature-composition coexistence behavior.

These three systems are:

(1) Pure component vapor-liquid equilibria , in which the second component is taken to be the vacuum "holes."

(2) Liquid-liquid equilibria which exhibit the usual U.C.S.T.-curve (that is, exhibit no compositional extrema).

(3) Liquid-liquid equilibria which exhibit a L.C.S.T.(that is, exhibit compositional extrema).

Since,

$$F1(T,P) = \frac{\frac{XAB}{XBB}}{1 - \frac{XAB \cdot XBA}{XAA \cdot XBB}}$$

and

$$F2(T,P) = \frac{\frac{XBA}{XAA}}{1 - \frac{XAB \cdot XBA}{XAA \cdot XBB}}$$

the ratio $\frac{F1(T,P)}{F2(T,P)}$ simplifies to,

$$(21) \qquad \frac{F1(T,P)}{F2(T,P)} = \frac{XAB \cdot XAA}{XBB \cdot XBA} = \left[\frac{XA}{XB}\right]^2 \text{ at the critical point}$$

The small variation of this ratio over the entire temperature range of the coexistence curves for all three types of binary systems gives strong evidence of the fundamental nature of the functions F1(T,P) and F2(T,P).

The remainder of this chapter will review the experimental evidence as it relates to this ratio for the three types of binary systems.

$\frac{F1(T,P)}{F2(T,P)}$ in Pure Component Vapor-Liquid Equilibria

We are aided in our discussion by a paper by Guggenheim[1] in which the coexistence curves for the vapor-liquid equilibria of the pure components: Ne, A, Kr, Xe, N_2, O_2, CO and CH_4 are plotted on reduced temperature and density coordinates. The coincidence of the curves obtained for all of these systems is expected from the law of corresponding states. Guggenheim has aided us further by deriving expressions for the reduced densities of the liquid and vapor phase branches of this curve from the empirical shape of the curve. These expressions are:

$$(22)\quad \left[\frac{\rho}{\rho_{cr}}\right]_{\substack{\text{liquid}\\ \text{phase}}} = 1 + \frac{3}{4}\cdot\left[1-\frac{T}{T_{cr}}\right] + \frac{7}{4}\cdot\left[1-\frac{T}{T_{cr}}\right]^{\frac{1}{3}}$$

$$(23)\quad \left[\frac{\rho}{\rho_{cr}}\right]_{\substack{\text{vapor}\\ \text{phase}}} = 1 + \frac{3}{4}\cdot\left[1-\frac{T}{T_{cr}}\right] - \frac{7}{4}\cdot\left[1-\frac{T}{T_{cr}}\right]^{\frac{1}{3}}$$

In the generalized one component system which Guggenheim's reduced equations can be considered to represent, the critical density has the value of 1.0, the vapor phase density has the values 0.0 to 1.0, and the liquid phase density has the values 2.7 to 1.0 . We remind the reader that these are reduced densities.

1. Guggenheim,E.A., J. Chem. Phys., 13,253(1945).

Density is mass per unit volume. The only substance that has mass in our system is the pure component. The mass of an individual molecule of the pure component is essentially constant over the temperature range we are concerned with. Thus, in order to explain the variations in the densities of the vapor and liquid phases we conceptualize these phases to be composed of two species: (1) vacuum holes, and (2) hypothetical pure liquid . The experimental reduced density can be converted to mole fraction of hypothetical pure liquid (h.p.l.) and mole fraction of vacuum holes (v.h.) as follows:

$$\frac{\rho_{v.p.}}{\rho_{h.p.l.}} = X_{h.p.l.} \quad \text{in vapor phase}$$

$$1 - X_{h.p.l.} = X_{v.h.} \quad \text{in vapor phase}$$

$$\frac{\rho_{l.p.}}{\rho_{h.p.l.}} = X_{h.p.l.} \quad \text{in liquid phase}$$

$$1 - X_{h.p.l.} = X_{v.h.} \quad \text{in liquid phase}$$

We define the factor $\frac{1}{\rho_{h.p.l.}}$ in terms of the following equation:

$$\left[\frac{\frac{\rho_{v.p.}}{\rho_{h.p.l.}}}{1-\frac{\rho_{v.p.}}{\rho_{h.p.l.}}}\right]\bullet\left[\frac{\frac{\rho_{l.p.}}{\rho_{h.p.l.}}}{1-\frac{\rho_{l.p.}}{\rho_{h.p.l.}}}\right]=\left[\frac{\frac{1}{\rho_{h.p.l.}}}{1-\frac{1}{\rho_{h.p.l.}}}\right]^2$$

That is, $\frac{1}{\rho_{h.p.l.}}$ is defined to have the value that will balance the above equation. We can simplify the form of this equation by defining $\frac{1}{\rho_{h.p.l.}} \equiv f$. This simplification leads to equations (26)-(31) .

A Detailed Derivation of the Results Mentioned in the Preceeding Discussion

The ratio F1(T,P)/F2(T,P) was shown in equation (21) to be identical to the ratio $\frac{XAB}{XBB}\cdot\frac{XAA}{XBA}$, which can be set equal to $\left(\frac{XA}{XB}\right)^2_{cr}$ throughout the entire coexistence locus by the introduction of the f factor.

If we identify A as the hypothetical pure liquid and, B as the vacuum holes, then, since XAB + XBB =1 and XAA + XBA =1,

$$XAB = \rho_{\substack{vapor\\phase}} \cdot f \tag{26}$$

$$XBB = 1 - \rho_{\substack{vapor\\phase}} \cdot f \tag{27}$$

$$XAA = \rho_{\substack{liquid\\phase}} \cdot f \tag{28}$$

$$XBA = 1 - \rho_{\substack{liquid\\phase}} \cdot f \tag{29}$$

Thus, equation (21) becomes,

$$\frac{XAB}{XBB}\cdot\frac{XAA}{XBA} = \frac{\rho_{v.p.}\cdot f}{1-\rho_{v.p.}\cdot f} \cdot \frac{\rho_{l.p.}\cdot f}{1-\rho_{l.p.}\cdot f} \tag{30}$$

Clearly, at the critical point, $\rho_{v.p.} = \rho_{l.p.}$.

Thus, the right side of equation (21) becomes:

$$\left(\frac{\rho_{cr}\cdot f}{1-\rho_{cr}\cdot f}\right)^2 \tag{31}$$

The f factor is defined as a normalizing factor to insure the equality of equation (21). The slow variation of this normalizing factor shows the fundamental nature of the F1(T,P)/F2(T,P) ratio, and in addition, that this ratio contains the seeds of the critical ratio. That is,

$$\frac{F1(T,P)}{F2(T,P)} = \left(\frac{XA}{XB}\right)^2_{crit} \qquad (32)$$

Equation (32) is valid only at the critical point.

Sample Calculation of an f Factor

From equations (30) and (31)

$$(33)\quad \left(\frac{\rho_{v.p.}\cdot f}{1-\rho_{v.p.}\cdot f}\right)\cdot\left(\frac{\rho_{l.p.}\cdot f}{1-\rho_{l.p.}\cdot f}\right) = \left(\frac{\rho_{cr}\cdot f}{1-\rho_{cr}\cdot f}\right)^2$$

From Guggenheim's coexistence locus at reduced temperature and pressure we select the values of reduced density of the vapor and liquid phases corresponding to a reduced temperature of $0.85T_c$. These values are:

v.p. =0.183

l.p. =2.042

The reduced critical density is defined as = 1.

Substitution into equation (33) gives:

$$(34)\quad \left(\frac{0.183\cdot f}{1-\ 0.183\cdot f}\right)\cdot\left(\frac{2.042\cdot f}{1-2.042\cdot f}\right) = \left(\frac{f}{1-f}\right)^2$$

The solution of this equation gives $f=0.424$.

We can generalize this method of the calculation of f factors to arrive at the expression:

$$(35)\qquad f = \frac{1-\text{product}}{\text{sum}-2\cdot\text{product}}$$

In which ,

product= the product of the reduced densities of the vapor and liquid phases at a given reduced temperature

sum = the sum of the reduced densities of the vapor and liquid phases at a given reduced temperature

Generalization to the Entire Coexistence Locus

With the help of equations (22) and (23) we are able to express equation (35), and hence the value of f for the entire coexistence locus, from melting point to critical point. The product of the reduced densities in terms of equations (22) and (23) becomes:

$$\text{product} = 1 + \frac{3}{2}\left(1-\frac{T}{T_c}\right) + \frac{9}{16}\left(1-\frac{T}{T_c}\right)^2 - \frac{49}{16}\left(1-\frac{T}{T_c}\right)^{2/3} \qquad (36)$$

And the sum becomes:

$$\text{sum} = 2 + \frac{3}{2}\left(1-\frac{T}{T_c}\right) \qquad (37)$$

Thus, equation (35) becomes on substitution,

$$f = \frac{-\frac{3}{2}\left(1-\frac{T}{T_c}\right)^{1/3} - \frac{9}{16}\left(1-\frac{T}{T_c}\right)^{4/3} + \frac{49}{16}}{-\frac{3}{2}\left(1-\frac{T}{T_c}\right)^{1/3} - \frac{9}{8}\left(1-\frac{T}{T_c}\right)^{4/3} + \frac{49}{8}} \qquad (38)$$

Substitution of the extreme values that T can take, that is, $T=T_c$ at the critical and $T\approx 0.6T_c$ at the melting point, gives:

at $T=T_c$, $f = 0.500$

at $T=0.6T_c$, $f = 0.384$

Thus, $\frac{0.500 - 0.384}{0.384} \cdot (100)$ = % variation from melting point to critical point = 30%

The difference in the ratio of the densities of the coexistant phases changes from 2.7/0.1485 = 180 for the density ratio of the liquid and vapor phases at the melting point, to 1/1 =1 at the critical point. This variation represents a percentage change of 18,000 %. Thus the variation in the f factor versus the variation in the density ratio of the coexisting phases is 1:600 . We must stress that these computations were made from the corresponding states curve of reduced densities and temperatures so that we must conclude that the results are a general law for all pure component vapor-liquid equilibria which obey the corresponding states principle. Even stronger evidence of the importance of the F1(T,P)/F2(T,P) ratio is given by the study of liquid-liquid equilibria which exhibit the usual U.C.S.T.-curve(that is, exhibit no compositional extrema). Unfortunately,no one has done for this type of system what Guggenheim has done for pure component vapor-liquid equilibria. However, Hildebrand has stressed:highly asymmetric curves of mole fraction versus temperature become more symmetric when volume fractions versus temperature are used in place of mole fraction versus temperature.[2]

2.Hildebrand,J.H.,Prausnitz,J.M. and Scott,R.L. Regular and Related Solutions, Van Nostrand Reinhold,1970.

$\frac{F1(T,P)}{F2(T,P)}$ in Liquid-Liquid Equilibria Which Exhibit the Usual U.C.S.T.-Curve (No Compositional Extrema)

In terms of self-attractive intermolecular forces, the vacuum holes in the preceeding discussion would have none, and thus, the hypothetical pure liquid molecules would have a much greater (infinitely greater) self-attractive intermolecular force. In this context we choose to call the hypothetical pure liquid molecules the active component and the vacuum holes the passive component. A similar active-passive relationship can be shown to exist in all partially miscible liquid-liquid equilibria. However, before we transfer our attention to liquid-liquid equilibria, we shall examine vapor-liquid equlibria and the insights contained therein.

If we try to picture the processes involved in molecular movement between the vapor and liquid phases in pure component vapor-liquid equilibria, we see that the molecules escaping from the liquid phase cannot be physically blocked by the vacuum holes in the vapor phase. Thus, we are led to the inescapable conclusion that the movement of active molecules from the active-rich to the passive-rich phase must be limited by some quality of the active phase alone.

The primary characteristic of a liquid is that its molecules are sufficiently close together that the changes in the direction of movement that a molecule experiences are primarily the result of intermolecular attractive forces. In a gas, on the other hand, the changes in the movement of a molecule are primarily the result of intermolecular repulsive forces. At the critical point, we have a state in which the intermolecular attractive and repulsive forces are of equal importance.

When a liquid molecule leaves the liquid phase it must decontact from the bulk of the liquid. Its possible contacts are with its nearest neighbors. The number of nearest neighbors is continuously varying and we can only talk of an average number of nearest neighbors if we wish to make our discussion independent of time. However, the attractive contacts we are trying to visualize are varying in number from instant to instant. At higher temperatures, when the liquid is less dense, we would expect to observe a smaller average number of contacts. In addition, at higher temperatures the average kinetic energy would be greater. The overall result is that molecules have less contacts to break and more energy with which to break them. If we assume the process of contact formation and break up to be chaotic, then the simultaneous freeing of the several contacts a liquid molecule is likely to encounter from the presence of its nearest neighbors should be a function of the fraction of noncontacts(contacts whose potential energy is less than the connected molecules kinetic energy) raised to the power of the average number of contacts. That is, if a given liquid molecule has on average ten nearest neighbors, and if the state of the liquid is such that 30% = 0.3 of the contacts are decontacted, then the probability of ten given contacts being decontacted simultaneously is $(0.3)^{10}$. We shall devote a separate chapter to the quantitative description of contacts, decontacts, and the structure of nonrandom liquids. However, we choose not to digress in that direction at this point.

Our development has reached the point where we are able to state that when the active molecule goes into the passive-rich phase, the process is limited by decontacting from the active phase, and not by any hindrance the passive phase might offer.

The movement of passive molecules into the active-rich phase is not limited by the attractive forces of the passive phase as we can see from our study of pure component vapor-liquid equilibria. The holes that appear in the liquid phase are produced at the phase boundary of the vapor and liquid. They then move inward and distribute themselves in macroscopic uniformity throughout the liquid. The apparent movement of the passive component(the vacuum holes) into the active-rich phase is limited by the production of holes at the liquid interface. The holes we are referring to are vacuum holes.

However, in liquid-liquid equilibria these holes can be filled with passive molecules. The number and arrangement of the holes is constantly varying. Thus, the effect of a passive molecule is to act as a place holder(really a hole holder). The passive-active intermolecular attraction is assumed to be so much weaker than the active-active interaction that passive-active contacts represent effective decontacts. The effect of the passive is therefore seen as speeding up the decontact process in the active-rich phase. We would therefore expect liquid-liquid critical temperatures to be lower than the pure component vapor-liquid critical. This result is experimentally observed. If a passive molecule is very small then we would expect that its ability to act as a placeholder would be minimized. This would be caused by the small passive occupying the holes that exist in the active.

We can summarize our development by stating that decontact in the active controls both active into passive (via break-off of the active) and passive into active(via hole formation and containment of passive in the active).

In the case of vapor-liquid equilibria, if a given number of decontacts produce an average free volume which is linearly proportional to the total hypothetical pure liquid volume that is freed by the same number of average decontacts which allow an active molecule to break-off into the passive phase, then we would have an explanation of the relationship given by equation (32). In addition, we would be able to relate F1(T,P) and F2(T,P) to the relative tendencies for active break-off and passive containment, respectively. Thus,

F1(T,P) = The tendency for active molecules to leave the active-rich phase. It is a function of the fraction of contacts in the active which are broken (the decontact fraction) and the average number of simultaneous decontacts to effect an escape .

F2(T,P) = The tendency for passive molecules to enter the active-rich phase. It is a function of the fraction of contacts in the active which are broken (the decontact fraction) and the average number of simultaneous decontacts to effect an entrapment.

It appears that F1(T,P) and F2(T,P) are also related to the intermolecular attractive forces between the molecules. However, the relationship is not clear at the time of this writing.

Clearly, if the passive molecule is much larger than the active molecule we would expect F2(T,P) to be less than F1(T,P) . In addition, we would expect that the change in F2(T,P) with temperature would be a higher power of the (the number of decontacts needed is greater) fraction of molecules decontacted. Thus, the variation of the F1(T,P)/F2(T,P) ratio would be expected to show a decrease as the temperature increased(the fraction of decontacted molecules increases monotonically with the temperature). The following pages contain a detailed proof of this assertion. We point out here that experimental evidence is in agreement with this development and systems with a large passive to active molar volume ratio show the expected variation.

We can summarize our conception of active and passive molecules as follows:

active= The molecule which limits the movement of its own kind out of its phase and the movement of the other kind into its phase.

passive= The other molecule.

Although we can use critical temperatures of the pure components as a guide to determining which is the active, size considerations must also be taken into account.

A Detailed Derivation of the Expected Variation of the $\frac{F1(T,P)}{F2(T,P)}$ Ratio in Mixtures with a Large Passive/Active Molar Volume Ratio

At temperatures far removed from the critical NAB and NBA can be approximated by the expressions:

$$NAB \approx NB \cdot F1(T,P) \tag{39}$$

$$NBA \approx NA \cdot F2(T,P) \tag{40}$$

since, F1(T,P) and F2(T,P) are much larger than $-\frac{1}{2}+\sqrt{\frac{1}{4}+F1(T,P)\cdot F2(T,P)}$ as the numerical analysis treatment pointed out. Another way of looking at the same problem is to realize that the ratio of mole fractions expressed in equation (21) is approximated by XAB/XBA when XAA and XBB are close to one in value. If we let NA=NB, then

$$\frac{NAB}{NBA} \approx \frac{F1(T,P)}{F2(T,P)} \approx \frac{XAB}{XBA} \tag{41}$$

Therefore, if NAB represents the number of active molecules that are transferred to the passive-rich phase, and if NBA represents the number of passive molecules that are transferred into the active-rich phase, according to our previous development, we should expect XAB/XBA to decrease as the temperature increases.

If we let m equal the number of nearest neighbors to be decontacted for the break-off of an active molecule into the passive-rich phase, and if we let n equal the number of nearest neighbors to be decontacted for the containment of a passive molecule in the active-rich phase, then if fd equals the fraction of active molecules in the active-rich phase that are decontacted, we can write:

$$(fd)^{n} \approx F1(T,P) \tag{42}$$

$$(fd)^{m} \approx F2(T,P) \tag{43}$$

therefore,

$$(fd)^{n-m} \approx \frac{F1(T,P)}{F2(T,P)} \tag{44}$$

If the molar volume of the passive molecules is much larger than the molar volume of the active molecules, we would expect to find $m > n$. Therefore, n-m would be a negative number which we shall call -a, that is, $n-m = -a$. This gives

$$(fd)^{-a} \approx \frac{F1(T,P)}{F2(T,P)} \tag{45}$$

or,

$$\frac{1}{(fd)^{a}} \approx \frac{F1(T,P)}{F2(T,P)} \tag{46}$$

Since fd increases as the temperature increases for all liquid mixtures which exhibit the usual U.C.S.T., we would expect the denominator of the left side of equation (46) to increase. This increase in the denominator results in an overall decrease and so the right side of (46) decreases.

$\frac{F1(T,P)}{F2(T,P)}$ in Liquid-Liquid Equilibria which Exhibit the Phenomenon of a Lower Critical Solution Temperature

(Exhibit Compositional Extrema)

In terms of the F1(T,P)/F2(T,P) ratio in the lower half of the closed loop, mixtures which exhibit a lower critical solution temperature fall into three groups.

(I) Those mixtures which exhibit a large decrease in the ratio as the temperature is raised above the L.C.S.T..

(II) Those mixtures which exhibit a moderate decrease in the ratio.

(III)Those mixtures which exhibit a small decrease in the ratio.

The lower half of the closed solubility loop in Type(I) mixtures is highly asymmetric. This is in contrast to Type(II) mixtures which exhibit a moderate degree of asymmetry in the lower halves of their loops. In Type(III) mixtures the loop is symmetric throughout.

We can explain this variety of loop symmetry in terms of the following analysis from our Theory of Lower Critical Solution Temperatures.

The passive molecules which are involved in Type(I) mixtures (e.g.,2-Methylpiperidine) have a high saturated carbon to functional group ratio. The passive molecules involved in Type(III) mixtures (e.g., 2-Propoxy-propane-1-ol) have a relatively low saturated carbon to functional group ratio. The saturated carbon to functional group ratio of passive molecules involved in Type(II) mixtures (e.g., Nicotine) is found to lie between the ratios of Types(I) and (III).

It is widely known that the larger the number of functional groups and the smaller the number of saturated carbons, the more soluble a given organic compound is in water. On this basis, the order of increasing solubility of the three types of passive molecules involved in lower critical phenomena would be I < II < III.

Our previous analysis of variations in the $\frac{F1(T,P)}{F2(T,P)}$ ratio with respect to temperature involved liquid phases in which compound formation did not enter into consideration. The effect of compound formation, for example, the formation of a clathrate hydrate, is to lower the surface to volume ratio of the species in the phase in which the compound is found. Whereas in our previous analysis of the variation in the F1(T,P)/F2(T,P) ratio we were concerned with the fraction and number of decontacts in the active phase, in mixtures which exhibit a L.C.S.T. we must also take into account the variation with temperature of the free surface available to be decontacted in a phase. Thus, as the clusters break up with increasing temperature, the free surface available for a passive molecule, in the active phase, increases. This increase in free surface results in a random walk of longer time duration.

Since the variation of the free surface in a phase depends upon the variation of the surface to volume ratio of the species found in the phase, a phase in which there is only a small variation in the surface to volume ratio of the species which comprise the phase would be expected to show a small free surface variation. The species which we have identified with temperature variation of the surface to volume ratio are the clusters. If a phase is very poor in clusters then the free surface of the phase would be expected to change much less than a phase which is rich in clusters. In Type (I) mixtures the passive phase has a much smaller proportion of clusters in it than does the active phase. In Type (II) mixtures the passive phase has only a slightly smaller proportion of clusters in it than does the active phase. Finally, in Type(III) mixtures the phases have nearly equal proportions of clusters.

If we recall that the F1(T,P)/F2(T,P) ratio represents the relative tendency of active into passive divided by the relative tendency of passive into active, the variations of this ratio in the three types of mixtures we have considered means that we must expand the meaning of the ratio to: "relative tendency into and time of random walk inside of," for mixtures in which the free surface varies with temperature.

Therefore, in Type(I) mixtures, the F2(T,P) term, which in this case means:"relative tendency of passive into active and time of random walk inside of,"increases faster than the F1(T,P)term, due to the increase infree surface in the active phase vís a vís the increase in free surface in the passive phase. This difference in free surface variation with temperature is less pronounced in Type(II) mixtures and hardly detectable in type(III) mixtures.

In the upper halves of the three types of closed loops we would expect the sharp differences in behavior, of the F1(T,P)/F2(T,P) ratio, between the various mixtures, to be minimized . This result is observed experimentally. We conclude, therefore, that at the temperature of the upper critical solution temperature a large majority of the clusters have "melted." The slow variation of the F1(T,P)/F2(T,P) ratio in the upper halves of the closed loops of all three types of mixtures confirms this. Please consult Appendix E for representative systems.

CHAPTER II

A POSSIBLE FORM FOR THE FUNCTIONS F1(T,P) and F2(T,P)

Chapter I is concerned with the derivation of the fundamental equations governing the movement of molecular species between phases. The equations that are derived can be summarized as being complete except for two functions which are expressed in general terms. Molecular movement between phases is dependent upon factors such as size, shape and intermolecular forces. Our current incomplete knowledge concerning these factors necessitates a semiempirical approach to the construction of the correct form for the generalized functions mentioned above. If these functions are expressed in the form

$$F(T,P) = \frac{a}{(T_c - T)^b}$$

in which a and b are empirical parameters, a close fit between experimental data and theoretically calculated points is obtained only within approximately fifteen degrees of the critical temperature. At temperatures that are further removed from the critical temperature, the values of the functions are too large when calculated from the above form. This deficiency can be corrected by the following treatment.

In Chapter I it is developed that the liquid state represents a net attractive interaction, whereas the gaseous state represents a net repulsive interaction.

The critical point represents the transition between the dominance of these two interactions. That is, the critical point represents the point where there is an equality of importance, in terms of determining the changes in the direction of molecular trajectories, between the attractive and repulsive interactions. Of course, in a a partially miscible binary liquid mixture we are concerned with a liquid-liquid transition. In this case it is the energy and temperature of the system corresponding to the energy of"vaporization" of the active liquid into the passive liquid at the critical solution temperature.

It is a universal observation that the UCST of a partially miscible binary liquid mixture is always lower than the vapor-liquid critical temperature of the pure active component. We can explain this fact by viewing the passive molecules in the active phase as having a weakening effect on the intermolecular forces encountered in the active phase, since a passive-active interaction is,by definition,weaker than an active-active interaction. For a passive molecule to be effective in this weakening action it must gain admittance to the active phase and once present in the active phase, displace active-active contacts. If the passive molecule is much smaller than the active molecule it will gain easy entrance, however, the same factors that permit ease of entrance also tend to position it in the interstial spaces between the larger active molecules. If a passive molecule is in one of these spaces it cannot be effective in blocking active-active contacts. In contrast, if the passive molecule is much larger than the active molecule, it will be very effective in breaking active-active contacts, but it will be hindered in gaining admittance to the active phase. In the homologous series of alkanes, it would seem to be a logical deduction that a particular size molecule would combine these two antagonistic effects of size to the greatest possible advantage in accelerating the decrease in the number of active-active contacts. Thus, we would expect to find that the homologous series of alkanes, considered as passive components, would always have a member that would give a minimum UCST with respect to a given active component. Appendix C verifies this contention.

If $\exp(-E/kT_c)$ represents the critical fraction of pure active molecules that must have sufficient energy to "vaporize" into the passive phase in order to effect the liquid-liquid phase transition, then the ratio

$$\frac{\exp(-E/kT_c) - \exp(-E/kT)}{\exp(-E/kT)}$$

represents the difference between the critical decontact fraction and the actual decontact fraction divided by the actual decontact fraction. This ratio, called "D" in the following treatment, is, when normalized by division with E/kT_c^2 , approximately linear with T_c-T at temperatures near the UCST. That is,

$$\lim_{T \to T_c} \frac{\exp(-E/kT_c) - \exp(-E/kT)}{(E/kT_c^2).\exp(-E/kT)} \quad \text{is} \quad T_c - T \ .$$

Consult Appendix D for the proof.

The combination of equations (2),(3),(19) and (20) from Chapter I,leads to the following expressions:

$$XAB = \frac{NB\cdot F1-NA\cdot(-\frac{1}{2}+\sqrt{\frac{1}{4}+F1\cdot F2})}{NB+NB\cdot F1-NA\cdot F2+(NB-NA)\cdot(-\frac{1}{2}+\sqrt{\frac{1}{4}+F1\cdot F2})} \qquad (47)$$

$$XBA = \frac{NA\cdot F2-NB\cdot(-\frac{1}{2}+\sqrt{\frac{1}{4}+F1\cdot F2})}{NA+NA\cdot F2-NB\cdot F1+(NA-NB)\cdot(-\frac{1}{2}+\sqrt{\frac{1}{4}+F1\cdot F2})} \qquad (48)$$

The above expressions are a mathematical result free of any assumptions or approximations. We must now turn to the semiempirical treatment developed at the head of this chapter for the forms of F1(T,P) and F2(T,P) .

$$F1(T,P) = \frac{a_1}{(D)^{b_1}} \equiv \frac{a_1}{\left[\frac{\exp(-E/kT_c) - \exp(-E/kT)}{(E/kT_c^2)\exp(-E/kT)}\right]^{b_1}} \qquad (49)$$

$$F2(T,P) = \frac{a_2}{(D)^{b_2}} \equiv \frac{a_2}{\left[\frac{\exp(-E/kT_c) - \exp(-E/kT)}{(E/kT_c^2)\cdot\exp(-E/kT)}\right]^{b_2}} \qquad (50)$$

When equations (49) and (50) are substituted into equations (47) and (48) we obtain the forms that are used in this work to express the temperature and pressure dependency of XAB and XBA.

From the definition of the ratio of F1(T,P)/F2(T,P) , the value of this ratio must equal $(XA/XB)^2_{crit}$ at $T_c - T = 0$.

If $b_1 = b_2$, then $F1(T,P)/F2(T,P) = a_1/a_2$. If $b_1 \neq b_2$ the difference $b_2 - b_1$ must converge sufficiently rapidly that $(T_c - T)^{b_2 - b_1} \rightarrow 1$ as $(T_c - T) \rightarrow 0$. This can be accomplished by constructing b_2 as a function of b_1 and T/T_c . Thus, $b_2 = b_1 + \text{constant} \cdot \left[(1 - T/T_c)/(1 - T_{lev}/T_c)\right]$. In which, T_{lev} = the lowest experimental value used to fit the curve to the equation.

With this introduction we will show the application of this approach to two systems:

(1) Perfluoromethylcyclohexane—Benzene, a system in which $b_2 = b_1$. And,

(2) Pentaerythritol Tetraperfluorobutyrate—CCl_4, a system in which $b_2 \neq b_1$.

Parameters

System	E/kT_c	$T_c(^oK)$	b_1	b_2	a_1	a_2
(1)	11	358.55	0.52	0.52	3.35	0.353
(2)	11	345.25	0.42	$0.42+0.28\left[\frac{1-T/T_c}{.14482}\right]$	7.68	0.0760

Experimental Data

XAB = mole fraction Benzene in Perfluoromethylcyclohexane-rich phase. System (1).

T (°C)	XA	T(°C)	XA	T(°C)	XA	T(°C)	XA
61.1	0.956	84.7	0.814	82.7	0.593	69.3	0.397
76.1	0.916	85.1	0.785	79.2	0.523	58.9	0.305
81.6	0.876	85.3	0.767	75.7	0.467	35.0	0.190
83.9	0.845	84.9	0.687				

data from: J.H. Hildebrand and D.R.F. Cochran in the J.Am. Chem. Soc., 71,22(1949).

XBA = mole fraction Pentaerythritol Tetraperfluorobutyrate in CCl_4-rich phase. System (2).

T(°C)	XB	T(°C)	XB	T(°C)	XB	T(°C)	XB
25.0	.0023	69.95	.03944	71.68	.1370	57.1	.3213
56.6	1.292	71.82	.07094	69.90	.1829	25.00	52
65.8	2.524	72.09	.09116	62.7	.2706		

data from: K. Shinoda and J.H. Hildebrand in the J. Phys. Chem.,62,481(1958).

Theoretical Data

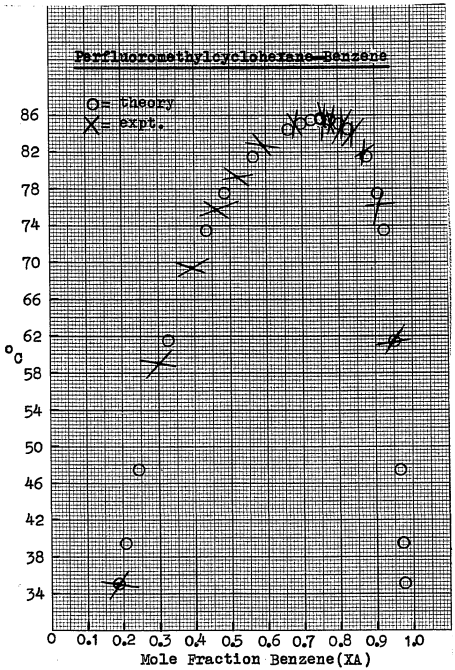
System (1)

T_c-T	D	F1	F2	XAB	1-XBA	T^oC
10^{-6}	0.000001	4416.	465.3	0.7549	0.7550	85.399999
0.1	0.100153	11.08	1.168	0.7284	0.7780	85.3
0.4	0.402830	5.375	0.5664	0.6990	0.8034	85.0
1.0	1.018205	3.319	0.3497	0.6629	0.8284	84.4
4.0	4.305982	1.568	0.1652	0.5637	0.8802	81.4
8.0	9.299488	1.051	0.1107	0.4873	0.9090	77.4
12.0	15.11021	0.8163	0.08601	0.4337	0.9253	73.4
24.0	39.15666	0.4975	0.05242	0.3267	0.9514	61.4
38.0	87.48102	0.3275	0.03451	0.2447	0.9670	47.4
46.0	131.9341	0.2645	0.02787	0.2080	0.9731	39.4
50.4	164.4223	0.2359	0.02486	0.1900	0.9759	35.0

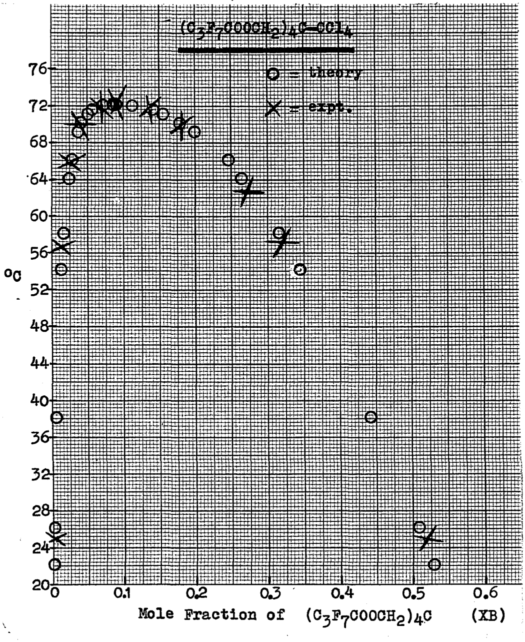
System (2)

T_c-T	D	F1	F2	XBA	1-XAB	T^oC
10^{-6}	0.000001	2543.	25.17	0.09031	0.09064	72.099999
0.001	0.001000	139.8	1.383	0.08756	0.09348	72.099
0.1	0.10019	20.18	0.2000	0.07219	0.1130	72.0
0.6	0.60683	9.473	0.09390	0.05652	0.1420	71.5
1.0	1.01911	7.619	0.07539	0.05080	0.1560	71.1
2.0	2.07751	5.781	0.05545	0.04230	0.1784	70.1
3.0	3.17696	4.726	0.04587	0.03732	0.2002	69.1
6.0	6.74045	3.370	0.03198	0.02830	0.2458	66.1
8.0	9.35750	3.003	0.02688	0.02439	0.2636	64.1
14.0	18.5762	2.251	0.01772	0.01677	0.3157	58.1
18.0	26.0920	1.952	0.01390	0.01337	0.3443	54.1
34.0	72.9864	1.267	0.005540	0.005471	0.4428	38.1
46.0	138.861	0.9670	0.002334	0.002323	0.5090	26.1
50.0	170.800	0.8870	0.002080	0.002072	0.5295	22.1

System (1)


Perfluoromethylcyclohexane-Benzene
O= theory
X= expt.
86
82
78
74
70
66
62
°C
58
54
50
46
42
38
34
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole Fraction Benzene(XA)

System (2)



$(C_3F_7COOCH_2)_4C—CCl_4$
○ = theory
X = expt.
°C
76
72
68
64
60
56
52
48
44
40
36
32
28
24
20
0
0.1
0.2
0.3
0.4
0.5
0.6
Mole Fraction of $(C_3F_7COOCH_2)_4C$ (XB)

COMPARISON WITH THE METHOD OF COX AND HERINGTON

You will recall, from the Historical Survey section of this work, that Cox and Herington used equations of the form

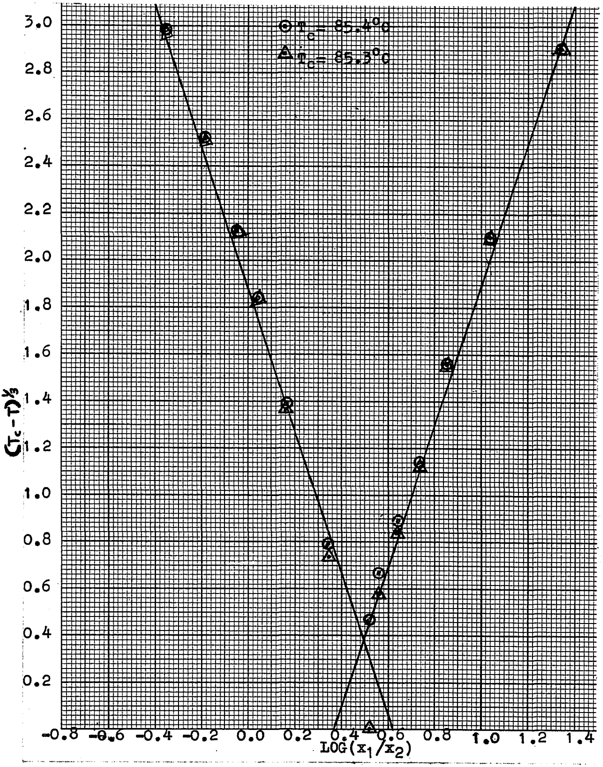
$$(T_c - T)^{1/3} = A \cdot \log_{10}(x_1/x_2) + B \quad ,$$

to express each branch of the coexistence locus for partially miscible binary liquid mixtures.

When the Perfluoromethylcyclohexane-Benzene system is plotted according to the method of Cox and Herington the figure on the following page represents the result. You will note that the two straight lines drawn through the data intersect at the same critical composition as that calculated by our method. However, they cross before $T_c-T = 0$ and hence their values at $T_c-T = 0$ are not the same. This internal inconsistency in the method of Cox and Herington is not found in our approach. We therefore conclude that our approach represents a significant improvement.

A Cox and Herington Plot of

Perfluoromethylcyclohexane—Benzene



CHAPTER III

The Theory of Lower Critical Solution Temperatures

Whereas it is logical to expect two partially miscible liquids to mix completely as the temperature is raised due to increased thermal agitation, it is surprising to find this mixing occuring when the temperature is lowered. The mystery surrounding this phenomenon has been shrouded in the thermodynamic formalism which defines phase splitting in terms of the second partial derivative with respect to mole fraction of the excess function of the Gibbs free energy. The excess function, by definition, was created to account for the difference between a real and an ideal mixture. The highly nonideal behavior of mixtures which exhibit phase splitting require excess functions of a high degree of complexity in order to accurately fit experimental data. These excess functions are, by necessity, of a semiempirical nature. More importantly, they are defined in terms of the mole fraction, volume fraction or local volume fraction of the original components. If compound formation occurs in a mixture, the extreme complexity of any semiempirical equation which could accurately fit the experimental data would by necessity mask the physical processes which occur. It is with this view of the limitations of the excess function approach to the understanding of the phenomenon of the lower critical solution temperature that we begin the introduction to our theory.

In all systems which exhibit a lower critical solution temperature the active component is always water or glycerol (or a deuterated analog). In addition, the passive component is always an amine, a nitrogen heterocycle or an alcoholic ether.[1] In ternary systems which exhibit a lower critical solution temperature, a mixture of tertiary amyl and butyl alcohols with water has been shown to exhibit a lower critical solution temperature.[2]

If we try to analyze the dominant physical property that both water and glycerol have in common, we would be confident in describing it as the ability to engage in extensive three-dimensional hydrogen-bonding. The dominant physical property of the passive species listed above would be their ability to engage in hydrogen-bonding via their nitrogen and oxygen atoms. Therefore, we can state, with some confidence at this point, that hydrogen-bonding is involved in the phenomenon of the lower critical solution temperature. However, we must remember, that of the thousands of potential passive molecules which contain oxygen and nitrogen atoms, only a small fraction exhibit a lower critical solution temperature with the above active species. Therefore, we must conclude that we are concerned with a relatively rare form of hydrogen-bonded structure.

In 1953 in an issue of The Discussions of the Faraday Society devoted to the equilibrium properties of solutions of non-electrolytes, Copp and Everett[1] in their paper on the thermodynamics of binary mixtures containing amines, concluded:

> "...The above discussion shows that the presence of lower consolute behavior in aqueous media is closely related to two important phenomena (i) association between the components usually by a hydrogen bonding mechanism, (ii) heat,entropy and heat capacity effects arising from the interaction of the"inert" hydrocarbon grouping of the second component with the water structure. A fuller understanding of the phenomenon is thus to be sought in a more fundamental study of these two effects separately; when they are understood then the explanation of lower consolute behavior will follow immediately..."

In the fifth edition of their book, Shriner, Fuson and Curtin[3] in their discussion of water solubility state:

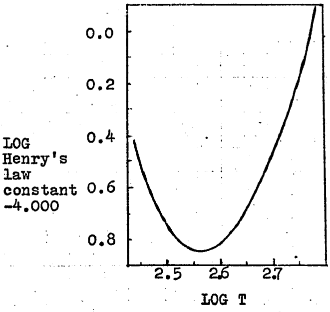
> "...The tendency of certain oxygen-containing compounds to form hydrates also contributes to water solubility. The stability of these hydrates is, therefore, a factor in determining water and ether solubility. Such compounds as chloral probably owe their great solubility in water to hydrate formation...."

> "...The amines probably owe their abnormally high solubility to their tendency to form hydrogen-bonded complexes with water molecules. This theory is in harmony with the fact that the solubility of amines deminishes as basicity decreases. It also explains the observation that many tertiary amines are more soluble in cold than in hot water. Apparently at lower temperatures the solubility of the hydrate is involved, whereas at higher temperatures the hydrate is unstable and the solubility measured is that of the free amine...."

In the same manner that the solubility of the passive component, in mixtures that exhibit a LCST, decreases as the temperature is raised above the LCST, to reach a minimum at the minimum at the widest point of the closed loop, the solubilty of gases in water decreases[4] as the temperature is raised until a minimum solubility is reached. At temperatures above the widest point of the closed loop the solubility of the passive component starts to increase in the same manner that the solubility of gases in water increases above the temperature of minimum solubility. This temperature dependence of gas solubility is illustrated in Figure 1.

The existence of gas hydrates has been known since the nineteenth century. The hydrates of the inert gases have been shown to have the formula $X.5.75H_2O$. Recent work by von Stackelberg[11] has shown that the gas hydrates are, in fact, clathrate compounds. Some of the gases which are known to form clathrate compounds are: Ar, CH_4, C_2H_2, PH_3, H_2S, CO_2, N_2O, H_2Se, C_2H_6, C_2H_4, C_2H_5F, SO_2, CH_3Cl, Cl_2 and Br_2. These clathrates fall into two groups of cubic crystals. The main difference between these groups is the length of the sides of the unit cell. The structure of the unit cell is illustrated in Figure 2. This picture of clathrate structure was developed from the complete structure determination of the chlorine clathrate by

Smoothed Solubility Data for O_2



after Himmelblau ref: 4.

Figure 1.

Pauling and Marsh.[5] There are three parts of the clathrate which we distinguish as separate components. These are: (see Figure 2.)

(i) the <u>solute</u> around which

(ii) the <u>clusters</u> form. The clusters are connected by the

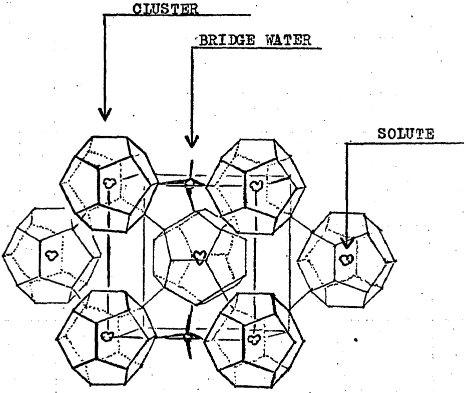
(iii) <u>bridge waters</u>.

In 1964 Glew[6] published a paper in which he inferred the existence of clathrate hydrates of soluble non-electrolytes from aqueous solution freezing curves. The existence of these clathrates was confirmed in 1967 by the X-ray diffraction studies of McMullan, Jordan and Jeffrey.[7] In their paper, in which nine amine clathrate hydrates were studied, they state:

> "...All the solutions studied became quite viscous as they were cooled toward their freezing points, but there were notable differences between them in the size and crystallinity of the specimens that were formed. The hydrates of $(CH_3)_2NH$, $(CH_3)_3N$, $(CH_3)_3CNH_2$, <u>n</u>-$C_3H_7NH_2$ (Type III), <u>iso</u>-$C_3H_7NH_2$, and $(C_2H_5)_2NH$ (Type V) formed readily, and frequently grew to several centimeters in size. The Type IV hydrate of $(C_2H_5)_2NH$ was observed only once after many attempts to prepare it under conditions where it was reported to be the stable phase...."

Only one of the amines studied exhibits a lower critical solution temperature when mixed with water. This amine is diethylamine. The composition of a diethylamine-water mixture at its lower critical solution temperature is 37.5% amine by weight.[8] This percentage of amine is the

Figure 2.



The structure of gas hydrates containing a hydrogen-bonded framework of 46 water molecules. Twenty molecules, arranged at the corners of a pentagonal dodecahedron, form a hydrogen-bonded complex (the cluster) about the corners of the unit cube, and another 20 form a similar complex, differently oriented, about the center of the cube. In addition, there are six hydrogen-bonded water molecules (the bridge waters), one of which is shown in the bottom face of the cube. In the proposed structure for water, additional water molecules, not forming hydrogen bonds, occupy the centers of the dodecahedra, and molecules, not forming hydrogen bonds, occupy the centers of the dodecahedra, and also other positions.

L. Pauling in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p.3.

exact stoichiometric composition of the Type IV hydrate of diethylamine which the authors considered to be so different in its crystallizability that they felt a special mention of the difficulties they encountered in its crystallization was called for in their paper. The above quote contains their statement.

At this point we have progressed to the point where we can summarize the evidence that we have gathered above.

1. The lower critical solution temperature composition represents the composition of a clathrate hydrate of the passive component.

2. The cluster-cluster interaction does not represent a strong interaction. It is assumed this is due to the configuration of the exterior waters in the clusters. That is, the configuration is such that a strong hydrogen-bonded interaction between clusters is a highly improbable orientation.

3. Individual water molecules not involved in clusters can bridge the space between clusters to serve as hydrogen-bonded linkages between the clusters.

4. The following equilibrium is shifted to the right with increasing temperature,

$$\text{clusters} \rightleftharpoons \text{bridge waters} + \text{passive}$$

5. At temperatures below the lower critical solution temperature the scarcity of bridge waters permits the clusters to move as independent entities. The passive component that is not inside a cluster is free to move in the volume between the disconnected clusters.

6. At the widest point in the closed loop (minimum solubility) the ratio of bridge waters to cluster molecules is such that the maximum intermolecular

attractive force exists between the clusters (via the bridge waters), simultaneously with the minimum amount of free volume for the free passive molecules.

9. At temperatures above the widest point in the closed loop the equilibrium between the active and passive phases becomes more like a normal binary mixture interaction with water as the active component.

10. At compositions to the passive side of the lower critical solution temperature composition the number of clusters formed is limited by the amount of active in the original mixture. Similarly, at compositions to the active side of the lower critical solution temperature composition the number of clusters formed is limited by the amount of passive in the original mixture. This analysis applies at a given temperature.

Frank and Quist's Statistical Thermodynamic Treatment

In 1961 Frank and Quist[9] published a paper titled: "Pauling's model and the Thermodynamic Properties of Water." The fundamental assumption of Pauling's model of water is that water is a water clathrate.[10] That is, the place of the solute molecule inside the cluster is taken up by water molecules. Without explanation, they assume that the following equilibrium is shifted to the right with increasing temperature,

$$\text{clusters} + \text{bridge waters} \rightleftharpoons \text{"solute" waters}$$

This is in contrast to our analysis which leads to the conclusion that the following equilibrium should be shifted to the right with increasing temperature,

$$\text{clusters} + \text{"solute" waters} \rightleftharpoons \text{bridge waters}$$

(see Figure 3.)

We cannot offer any explanation for their choice except to say that the concept of a clathrate involves the containment of a molecule in a void, therefore the equilibrium should involve the formation of this state of containment. On the other hand, the authors show their awareness of considering the cluster with enclosed solute molecule as a possible low temperature form:

> "...Another characteristic property of water is that nonpolar gases dissolved in it have unusually low partial molal entropies, a phenomenon which has been ascribed to the shifting of the water-structure equilibrium in the direction of greater 'ice-like-ness'...."

A Schematic Representation of the Difference in the Models

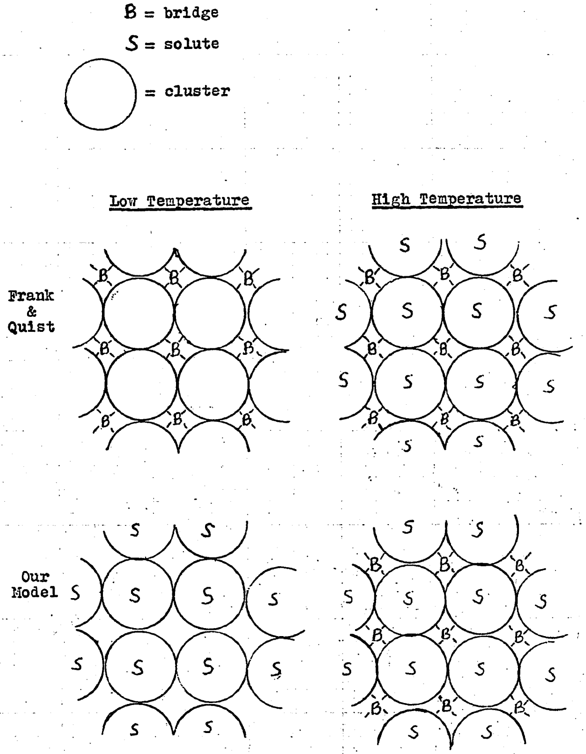


Figure 3.

In our treatment of mixtures exhibiting a lower critical solution temperature we shall be concerned with the following equilibrium which is shifted to the right as the temperature is increased,

$$\text{clusters} + \underset{\text{clusters}}{\overset{\text{solute}}{\text{in}}} \rightleftharpoons \text{bridge waters} + \underset{\text{clusters}}{\overset{\text{solute}}{\text{outside of}}}$$

It is interesting to note that Frank and Quist, although straddled with their original assumption of a completely formed framework of clusters and bridge waters at low temperatures, foreshadowed the possibility of the equilibrium which we consider to be the correct choice. They did this by postulating the existence of waters which were neither in the framework nor inside the clusters as "solute" waters. They called these other waters "State III" waters, and had the following to say about them:

> "...It seems possible to suppose that not much of 'State III' is present at 0°C, and that the success of the tests reported above arises in part from this circumstance...."

With this introduction to the approach of Frank and Quist we introduce the essential differences in the definitions of the terms in our model and theirs.

Frank and Quist's Model	Our Model
N_1=the total number of water molecules	same
N_2=the total number of solute molecules	N_2=the total number of solute molecules outside of the clusters
f=the fraction of the water molecules that form clusters and bridge waters	f=the fraction of the water molecules that form clusters
1-f=the fraction of the water molecules that are "solute" waters	1-f=the fraction of the water molecules that are bridge waters
v=the number of framework(cluster+bridge) waters per "solute" site inside a cluster	v=the number of cluster waters per "bridge" site outside a cluster
n_1=the number of moles of water	same
n_2=the number of moles of solute molecules outside of the clusters	same
$y=n_2/n_1$	same
F^o_{fr}=the hypothetical standard molal free energy of the (empty) framework	F^o_{fr}=the hypothetical standard molal free energy of the clusters (without bridge waters)
F^o_m=the hypothetical standard molal free energy of the "solute" waters	F^o_m=the hypothetical standard molal free energy of the bridge waters
$\Delta F^o=F^o_{fr} - F^o_m$	$\Delta F^o = F^o_{fr} - F^o_2 - F^o_m + F^o_{2fr}$
S^o_2=the standard molal entropy of the pure solute	same
S^o_{fr}= entropy equivalent of F^o_{fr}	S^o_{fr}= entropy equivalent of F^o_{fr}

Frank and Quist's Model	Our Model
S_m^o = entropy equivalent of F_m^o	S_m^o = entropy equivalent of F_m^o
no equivalent in this model	S_{2fr}^o = the hypothetical standard molal entropy of the solute molecules inside of the clusters
no equivalent in this model	n_2' = the number of moles of solute molecules inside of the clusters
no equivalent in this model	F_{2fr}^o = Gibbs free energy equivalent of S_{2fr}^o
ΔH^o = the standard enthalpy change, per mole of water, for the transformation of monomeric water into empty framework.	ΔH_1^o = the standard enthalpy change, per mole of water, for the transformation of cluster waters into bridge waters.
F_2^o = the standard molal free energy of the pure solute.	same

Frank and Quist's Derivation

Now that we have listed the differences in the equilibrium concepts contained in the two models we can review Frank and Quist's derivation keeping in mind the difference in meaning that we assign to the various symbols.

The first step in the derivation is the determination of the combinatorial factor. The combinatorial factor expresses the number of ways which the free solute molecules and bridge waters can occupy the bridge sites. We assume equal probability of occupancy. Thus,

$$(1) \quad W = (N_1 \cdot f/v)! / \left[N_1 \cdot (1-f)\right]! \; N_2! \; \left[N_1 \cdot f/v - N_1 \cdot (1-f) - N_2\right]!$$

Since, $S = k \cdot \ln W$, the logarithm of W times R will be , in this model, the counterpart of the entropy of mixing of a binary mixture per mole. Thus,

$$(2) \quad S^M = R \cdot \left[n_1 f/v \ln \frac{f/v}{f/v-(1-f)-y} - n_1 \cdot (1-f) \ln \frac{1-f}{f/v-(1-f)-y} - n_2 \ln \frac{y}{f/v-(1-f)-y} \right]$$

The total entropy of the solution is then,

$$(3) \quad S = n_1 f S^o_{fr} + n_1(1-f)S^o_m + n_2 S^o_2 + n_2' S^o_{2fr} + S^M$$

The molal Gibbs free energy of the liquid is therefore,

$$(4) \quad F = f\cdot\left\{F^o_{fr} + \alpha\cdot\left[(1-f)/f\right]\right\} + (1-f)\cdot F^o_m + \frac{n_2}{n_1+n_2+n_2'}\cdot F^o_2 + \frac{n_2'}{n_1+n_2+n_2'}\cdot F^o_{2fr} - RT\cdot\left[f/v \ln\frac{f/v}{f/v-(1-f)-y} - (1-f)\cdot\ln\frac{(1-f)}{f/v-(1-f)-y}\right]$$

Frank and Quist introduce the term $\alpha\cdot[(1-f)/f]$ to account for the alteration in the molal free energy of the framework as the sites on it become filled. Therefore, in our model this term would represent the alteration in the molal free energy of the clusters as bridge sites are filled.

If we let $\Delta F^o = F^o_{fr} - F^o_2 - F^o_m + F^o_{2fr}$

Then, equation (4) rearranges to:

$$(5) \quad F = F^o_m + F^o_2 + \; + f(\Delta F^o - \alpha) - RT(f/v)\cdot\ln\frac{f/v}{f/v-(1-f)-y} - (1-f)\cdot \ln\frac{(1-f)}{f/v-(1-f)-y}$$

Frank and Quist then relate ΔF^o to f by an equilibrium constant expression , which can be obtained by minimizing

F with respect to f, i.e., setting $(\partial F/\partial f)_{P,T} = 0$.

Carrying out this operation leads to,

(6) $(\Delta F^{o} - \alpha)/RT = (1/v)\cdot \ln \frac{f/v}{f/v-(1-f)-y} + \ln \frac{(1-f)}{f/v-(1-f)-y}$

Using this, the result of differentiating equation (3) with respect to n_2 is,

(7) $\bar{S}_2 = S_2^{o} - R\cdot \ln y + n_1(\partial f/\partial n_2)\left[(\Delta H_1^{o} - \alpha_1)/T\right]$

$$+ R\cdot \ln\left[f/v-(1-f)-y\right]$$

Frank and Quist then go on to show that since,

(8) $$(\partial f/\partial n_2) = (1/n_1)\cdot(\partial f/\partial y)$$

$$\frac{\partial f}{\partial y} = \frac{f\cdot(1-f)\cdot(v+1)}{1-y\cdot\left[vf-(1-f)\right]}$$

When equations (6) and (8) are combined.

The excess partial molal entropy is then given as,

(9) $\bar{S}_2^{E^{o}} = \bar{S}_2 - S_2^{o} + R\ln y = \frac{f\cdot(1-f)\cdot(v+1)}{1-y\cdot\left[vf-(1-f)\right]} \cdot \frac{\Delta H_1^{o} - \alpha_1}{T}$

$$+R\cdot \ln\left[f/v-(1-f)-y\right]$$

At infinite dilution, y approaches zero, therefore, the excess partial molal entropy at infinite dilution is,

$$(10) \qquad \bar{S}_2^{E\infty} = f\cdot(1-f)\cdot(v+1)\cdot\frac{\Delta H_1-\alpha_1}{T} + R\cdot\ln\left[f/v-(1-f)\right]$$

---

* Equation (7) is correct only as far as the simplification that $\frac{\partial}{\partial n_2}(n_2'\cdot S^o_{2fr}) = 0$ is correct. That is, this derivation assumes that the solute molecules inside of the clusters are not affected by the change in the number of solute molecules outside of the clusters.

The lower critical solution point may be defined thermodynamically in terms of the behavior of the excess functions. Thus, we require on thermodynamic grounds,

$$S^E < 0$$

and

$$\frac{\partial^2 S^E}{\partial x_2^2} > 0$$

Frank and Quist gave the value of $\Delta H^o - \alpha$ as -2210 cal/mole from the requirements of fitting the volume temperature curve of water.They use this value in their calculation involving a clathrate of a nonpolar solute. We therefore take the value of $\Delta H^o - \alpha$ as negative. All of the other terms are positive multipliers. Therefore,

$$f\cdot(1-f)\cdot(v+1)\cdot\frac{\Delta H_1^o - \alpha_1}{T} < 0$$

and, for $f/v-(1-f)$ to be less than one so that the logarithmic term is negative, requires:

$$f/v-(1-f) < 1$$
$$f/v + f < 2$$
$$f(1/v + 1) < 2$$
$$1/v + 1 < 2/f$$

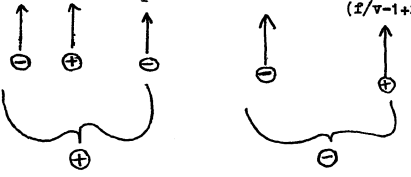
Since $v = \frac{\text{cluster}}{\text{bridge}}$ ratio at the widest point in the solubilty loop, and since f= the fraction of the waters that are in the clusters, when f approaches 1, v approaches 0/1 and so the left side of the inequality approaches 1 as the right side approaches 2. At the other extreme of f approaching 0, the right side of the inequality approaches infinity at twice the rate as the left side. Thus, from this analysis, the excess entropy is clearly negative in this model.

If we assume that all bridge sites not occupied by water molecules are occupied by solute molecules, then the variation in 1-f, the fraction of the water molecules at the bridge sites, is proportional to the mole fraction of the solute molecules at the bridge sites in the same manner as 1-f is proportional to f. Therefore,

$$\frac{\partial \bar{S}_2^{E\infty}}{\partial x_2^2} = \frac{\partial \bar{S}_2^{E\infty}}{\partial f^2}$$

And,

$$\frac{\partial \bar{S}_2^{E}}{\partial f^2} = (-2)\cdot(v+1)\cdot\frac{\Delta H_1-\alpha_1}{T} - R\cdot(1/v+1)^2\cdot\frac{1}{(f/v-1+f)^2}$$



According to our analysis, at the lower critical point the majority of the water molecules should be in the clusters, and therefore f should be close to one. If f is close to one, and if we assume v is approximately one, then f/v-1+f is certainly more than $\frac{1}{2}$. Therefore, the rightmost term is less than 4 and since $\frac{\Delta H_1 - \alpha_1}{T}$ is more than 4, with the other terms canceling the effect of each other, the overall value of the expression is positive as required.

1. J.L. Copp and D.H. Everett, Faraday Soc. Discussions, 15, 174(1953).

2. M.J.Blandamer, N.J.Hidden, M.C.R.Symons and N.C.Treloar, Trans. Fraraday Soc., 65, 2663(1969).

3. R.L.Shriner, R.C.Fuson and D.Y.Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, New York, N.Y., 1967, pp 80-81.

4. D.M.Himmelblau, J. Phys. Chem., 63, 1803(1959).

5. L.Pauling and R.E.Marsh, Proc. Natl. Acad. Sci. U.S., 38, 112(1952).

6. D.N.Glew, Nature, 201, 922(1964).

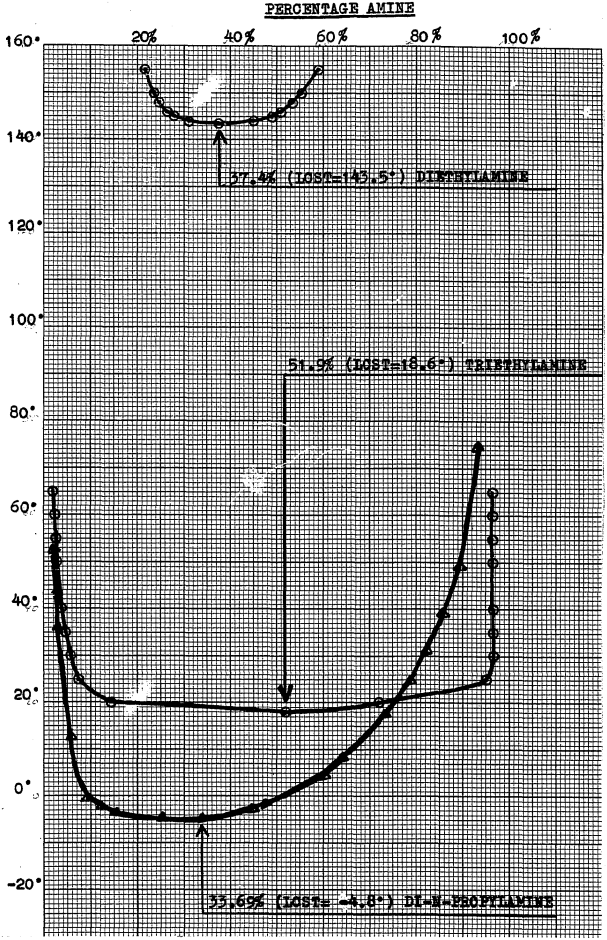
7. R.K.McMullan, T.H.Jordan and G.A.Jeffrey, J.Chem.Phys., 47, 1218(1967).

8. A.Seidell, Ed., "solubilities of Inorganic and Organic Compounds," D. Van Nostrand, New York, N.Y., 1919, p 294.

9. Frank, H.S., and Quist, A.S., J, Chem. Phys., 34, 604(1960).

10. L. Pauling in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p3.

11. von Stackelberg, M., Z. Elektrochem., 58, 104(1954).


PERCENTAGE AMINE
20%
40%
60%
80%
100%
160°
140°
120°
100°
80°
60°
40°
20°
0°
-20°
37.4% (LCST=143.5°) DIETHYLAMINE
51.9% (LCST=18.6°) TRIETHYLAMINE
33.69% (LCST= -4.8°) DI-N-PROPYLAMINE

EXPERIMENTAL DATA FOR THE ALKYLAMINES WITH LCST'S

DIETHYLAMINE

t^oC	%Amine(aq. ph.)	%Amine(am. ph.)	
155	21.7	59.0	
150	23.6	55.5	
148	24.8	53.5	
146	26.3	51.0	
145	28.0	49.0	
144	31.0	45.0	
143.5	37.4	37.4	LCST

TRIETHYLAMINE

65	1.97	96.3	
60	2.23	96.3	
55	2.57	96.3	
50	2.87	96.4	
40	3.65	96.48	
35	4.58	96.5	
30	5.80	96.60	
25	7.30	95.18	
20	14.24	72.0	
18.6	51.9	51.9	LCST

DI-N-PROPYLAMINE

74.8		93.25	
52.6	1.96		
49.0		89.26	
44.1	2.42		
39.0		85.83	
36.1	2.91		
31.2		82.15	
24.7		78.69	
17.5		73.33	
12.2	5.86		
8.0		64.06	
4.2		60.40	
-0.6	9.33		
-1.5		47.54	
-2.2	12.27		
-2.9		44.68	
-3.5	15.28		
-4.5	25.21		
-4.8	33.69	33.69	LCST

reference for Diethylamine and Triethylamine: Seidell,A.,"Solubilities of Organic Compounds," Vol. II, Van Nostrand, New York, 1941.

reference for Di-n-propylamine: R.J. Hartman & E.W. Kanning, J. Am. Chem. Soc. 63,2094(1941).

"...As to the general form of the figures representing the freezing point in the various cases, it may be noticed that with the methylamines the water curve extends a shorter distance, and the isolated hydrates contain more water as the number of methyl groups in the amine increases. Ethylamine and diethylamine show a similar behavior, but triethylamine is exceptional, water crystallising as far as a percentage composition of 30. The figure in the case of this amine is indeed strongly suggestive of the crystallising substance from 4 to 30 percent. molecules being a hydrate, but this cannot be so unless the hydrate resembles water very closely in its appearance , and is actually isomorphous with it,..."

S.U. Pickering, J.Chem. Soc., 63, 187 (1893).

What this quote says is that the method Pickering used to determine if his crystallizing substance was water or hydrate failed in triethylamine solutions that were up to 0.30 mole fraction triethylamine. Thus,the same seed crystal that triggered the crystallization of water triggered the crystallization of solutions of triethylamine that were up to 0.30 mole fraction triethylamine. The author concludes that since the freezing point curve for triethylamine is strongly suggestive of a hydrate curve, the only rational explanation he could think of was that water and triethylamine hydrate are isomorphous. Pauling came to the conclusion that water was a clathrate of itself more than sixty years later. The hydrates of the amines have been shown to be clathrates. Therefore, it appears that Pickering anticipated Pauling by more than sixty years.

(from Pickering) Water Molecules in Hydrates

◯ = corresponds to LCST composition

AMINE										
NH_3	-	-	-	3.5	-	-	-	11	-	-
Me	-	-	3	-	-	-	-	10	-	-
Me_2	-	-	-	-	-	7	-	-	-	-
Me_3	-	2	-	-	-	7	-	11	20	-
Et	0.5	-	-	-	5.5	-	-	-	-	-
Et_2	0.5	-	-	-	5.5	⊖	8	11	-	36
Et_3	-	2	-	-	⊖	-	8	-	-	31
Pr	0.5	-	-	3.5	-	-	8	-	-	-
Pr;iso	-	-	-	3.5	-	-	8	-	-	-
Pr_2	0.5	2	-	-	5.5	-	-	⊖	-	-
Am	-	-	-	-	5.5	-	-	-	-	37

According to the Theory of Lower Critical Solution Temperatures, the lower critical composition represents the composition of a clathrate hydrate. This hydrate should have unusually weak tendencies to crystallize. From the data presented on the previous pages, the lower critical composition of Diethylamine corresponds to an hydration number of 6.8, the lower critical composition of Di-n-propylamine corresponds to an hydration number of 11, and the lower critical composition of Triethylamine to 5.2 . According to Pickering, these hydrates were not discernible. However, recent work by Glew on Pickering's data predicted the existence of a hydrate with an hydration number of 6.8 for Diethylamine. The X-ray diffraction structure determination of this hydrate was performed by McMullan, Jordan and Jeffrey in 1966. We conclude, therefore, that the gaps in the number of waters of hydration in the above chart will eventually be filled in for the 11 hydrate of Di-n-propylamine and for the 5.5 hydrate of Triethylamine.

D.N.Glew, Nature 201, 922(1964).

D.N.Glew, Trans. Faraday Soc., 61, 30(1965).

R.K. McMullan, T.H. Jordan and G.A. Jeffrey, J.Chem. Phys., 47, 1218(1966)

APPENDIX A

The purpose of this appendix is to derive equation

$$(11) \qquad \sum_{k=0}^{n} \binom{n}{k} \cdot \left[\frac{YO...Yn}{1-YO...Yn}\right]^{k+1} = \prod_{k=0}^{n} \frac{Yk}{1-YO...Yn}$$

If we let y = YO...Yn, (11) becomes

$$(A1) \qquad \sum_{k=0}^{n} \binom{n}{k} \cdot \left[\frac{y}{1-y}\right]^{k+1} = y \cdot (1-y)^{-(n+1)}$$

Division of both sides of (A1) by y/(y-1) gives

$$(A2) \qquad \sum_{k=0}^{n} \binom{n}{k} \cdot \left[\frac{y}{1-y}\right]^{k} = (1-y)^{-n}$$

On substitution of x for y/(1-y) (A2) becomes

$$(A3) \qquad \sum_{k=0}^{n} \binom{n}{k} \cdot [x]^{k} = (1-y)^{-n}$$

The left side of (A3) is the binomial expansion of $(1+x)^n$

Therefore,

$$(A4) \qquad \sum_{k=0}^{n} \binom{n}{k} \cdot [x]^{k} = (1+x)^{n}$$

From the definition of x,substitution and rearrangement gives

$$(A5) \qquad 1+x = 1 + \frac{y}{1-y} = \frac{1-y}{1-y} + \frac{y}{1-y} = \frac{1}{1-y} = (1-y)^{-1}$$

Therefore,

$$(A6) \qquad (1+x)^{n} = (1-y)^{-n}$$

On combination of (A4), (A6) and the definition of x we obtain (A2) to complete our proof. Since divsion by zero is not defined, $y \neq 1$ is the only excluded value of y.

APPENDIX B

Certain liquids, for example, dibasic acids, form chains of linear hydrogen bonds. As energy is supplied to these liquids the average length of a chain is decreased. In the case of alcohols that form linear chains of hydrogen bonds , it is known that certain polymer lengths are favored because of the internal effects that hydrogen bonding has on the molecules involved in combination with the possibility of closed chain formation. In order to know to what extent a particular polymer length is preferred or hindered in its development, it is necessary to know the expected distribution of polymer lengths for a perfectly random break-up of an initial single chain consisting of all the monomer units. It is the purpose of this appendix to present the formula that applies to this problem.

L = total number of monomer units prior to chain formation

m = the length of a polymer chain

q = the number of random breaks in the initial single chain and its subdivisions

$$\text{the fraction of all segments that have length } m = \frac{(q)\cdot(L-m-1)\cdot(L-m-2)\cdots(L-m-q-1)}{(L-1)\cdot(L-2)\cdot(L-3)\cdots(L-q)}$$

Thus, after q breaks we have q terms in the numerator and in the denominator. For L = a large number, the above expression reduces to,

$$\begin{array}{l}\text{the} \\ \text{fraction of} \\ \text{all segments} \\ \text{that have length m} \\ \text{for L large}\end{array} = (1-q/L)^{m-1} \cdot (q/L)$$

In addition, the average length of a segment for L =large, is L/q, this holds for two and three dimensional clustering as well.

APPENDIX C

CRITICAL SOLUTION TEMPERATURES OF VARIOUS ORGANIC COMPOUNDS WITH THE NORMAL ALKANES

* indicates minimum

? indicates possible minimum

( ) indicates the critical temperature of the pure substance

# of C's in n-Alkane	ACTIVE COMPONENT			
	Aceto-nitrile (275)	Aceto-phenone	Benzyl Alcohol	2,2'-Dichloro-ethyl Ether
(96) 3	67			
(153) 4	?	11		13
(197) 5	60*	?	68	11*
(235) 6	77	3*	50.6*	13
(267) 7	85	4	50.7	16
(296) 8	92		55	20
9	100		57	24
10	108	10	62	
11	112		66	
12			72	
13			77	
14			82	
15			86	
16			90	
17			93	
18				

# of C's in n-Alkane	ACTIVE COMPONENT Ethyl Acetoacetate	2-Methoxy-4-Allylphenol	1-Naphthyl-amine
3	32		
4	25*	23	
5	28	?	
6	32	0*	117
7	43	3	113
8			?
9			?
10			?
11			?
12			104*
13			?
14			?
15			?
16			118
32			

# of C's in n-Alkane	Nitro-benzene	o-Nitro-toluene	Salicyl-aldehyde	Stannic Iodide
3		65		
4		13	59	
5	24	2	41	
6	20	0	31	149
7	18*	-1*	34	136
8	20	?		132*
9	22	?		?
10	24	?		?
11	25	?		?
12	27	?		?
13		?		?
14		?		?
15		?		?
16		18		?
17				?
18				?
32				194

Data from:

Francis, A.W., "Critical Solution Temperatures," American Chemical Society, Washington,D.C., (1961).

APPENDIX D

Proof that the limit as $T \rightarrow T_c$ of

$$(1) \qquad \frac{\exp(-E/kT_c) - \exp(-E/kT)}{E/kT_c^2 \cdot \exp(-E/kT)} \quad \text{is} \quad T_c - T \; .$$

Dividing numerator and denominator by $\exp(-E/kT)$ and factoring out E/k, gives

$$(2) \qquad \frac{\exp\left[(E/k)(1/T - 1/T_c)\right] - 1}{E/kT_c^2}$$

The series expansion of (2) is

$$(3) \qquad \frac{\frac{1}{0!} + \frac{(E/k)\cdot(1/T-1/T_c)}{1!} + \frac{(E/k)^2\cdot(1/T-1/T_c)^2}{2!} + \cdots - 1}{E/kT_c^2}$$

As $T \rightarrow T_c$ the terms $(1/T-1/T_c)^n$ become very small, and hence the higher order terms ($n=2,3,4,\ldots$) can be neglected. This gives for (2)

$$(4) \qquad \frac{(E/k)\cdot(1/T-1/T_c)}{E/kT_c^2} = (1/T-1/T_c)\cdot T_c^2$$

$$= \frac{T_c^2}{T} - \frac{T_c^2}{T_c}$$

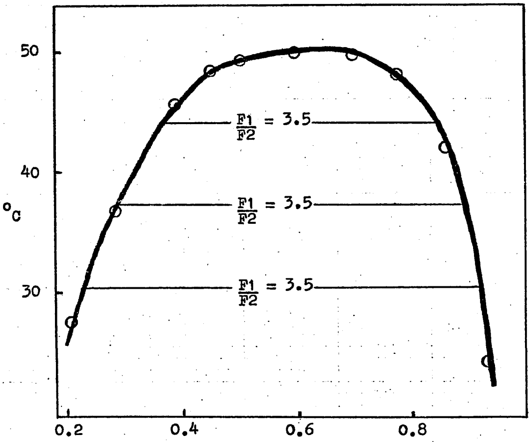
$$= \frac{T_c^2}{T} - T_c$$

$$= (T_c - T)\cdot\frac{T_c}{T}$$

In the limit as $T \rightarrow T_c$, $\frac{T_c}{T} \rightarrow 1$, hence $(T_c - T)\cdot 1 = T_c - T$.

Appendix E

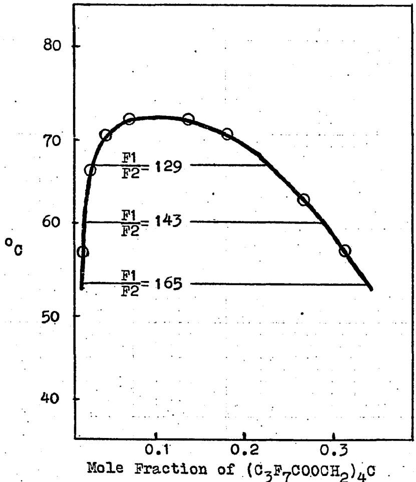
Perfluoro-n-heptane & C_7H_{16}



Mole Fraction of C_7H_{16}

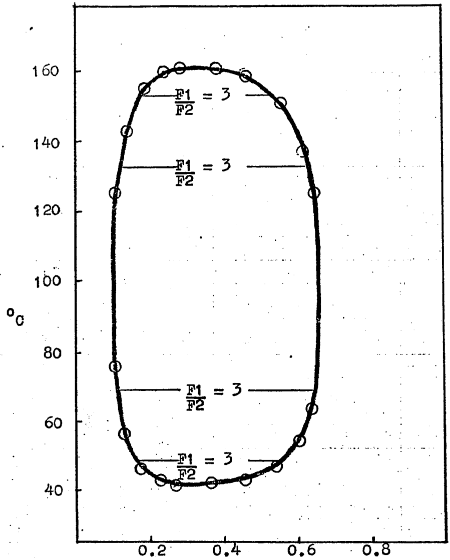
ref: Hildebrand, J. H., Fisher, B. B., and Benesi, H. A., J. Am. Chem. Soc., 72, 7348(1949).

CCl_4 & $(C_3F_7COOCH_2)_4C$



ref: Shinoda, K. and Hildebrand, J. H., J. Phys. Chem., 62, 481 (1958).

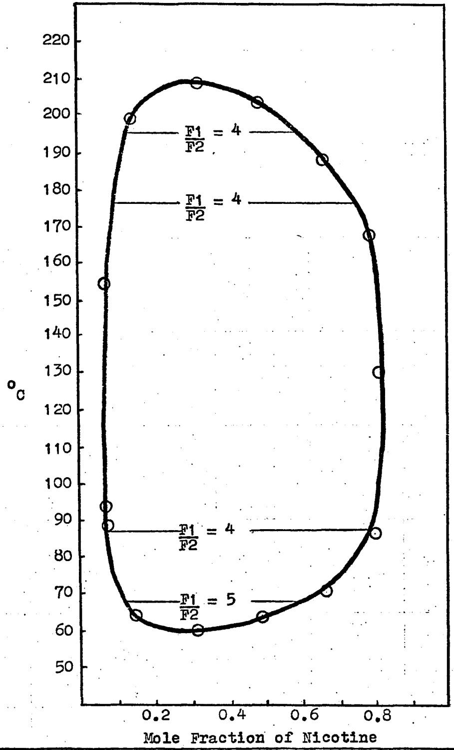
Water & 2-Propoxy-propane-1-ol



Mole Fraction of 2-Propoxy-propane-1-ol

ref: Cox, H. L., Nelson, W. L., Cretcher, L. H., J. Am. Chem. Soc., 49, 1080 (1927).

Water & Nicotine



ref: Hudson, C.S., Z. physik. Chem., 47, 113(1904).

Water & 2-Methylpiperidine

ref: Flaschner, O. and McEwen, B. C., J. Chem. Soc., 93, 1000(1908)