solution. Many of these questions could be probed by electrochemical methods, which as yet have been underexploited.

Little is known of the reaction of radical cations with other reagents, but the examples described here in which cyclobutadiene radical cations are formed from acetylenes, the biphenyl radical cation from benzene, azulene radical cations from arylacetylenes, and Diels–Alder dimers from dienes suggest that they may have a considerable potential in organic synthesis, and it may be possible to take advantage here of differences in the orbital symmetry requirements of pericyclic reactions involving RH and RH$^{\bullet+}$.

Models for Phase Equilibria in Fluid Mixtures[†]

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Received May 26, 1986 (Revised Manuscript Received November 10, 1986)

Introduction

First, I want to express my appreciation for the unexpected honor of receiving the 1984 Hildebrand Award. Any American Chemical Society award is a great honor, but for me with my long association with Joel Hildebrand this one is especially pleasing and appropriate.

My own interest in phase equilibria started with my Princeton Ph.D. research on high polymer solutions.[1] Unlike most scientists, I progressed (or retrogressed) from polymers to simpler and simpler systems, like mixtures of methane and krypton.[2]

My long association with Joel Hildebrand started in 1946, when I started what became 2 years of a postdoctoral appointment; that association covered nearly all of my scientific life, but only a small fraction of his! Working with him on the third edition of *Solubility of Nonelectrolytes* whetted my interest in phase diagrams.

Hildebrand used his "regular solution" model to interpret the behavior of solutions and, in particular, to explain solubility of nonelectrolytes,[3-7] an important example of phase equilibrium. This model combines the assumption of an ideal entropy of mixing at constant volume with a kind of volume-fraction random-mixing formulation of the constant-volume energy of mixing, resulting in a simple equation for the molar Gibbs free energy of mixing ΔG_m^M of a binary mixture

$$\Delta G_m^M = -T\Delta S_{m,ideal} + \Delta E_{m,constant\ volume,random}$$
$$= RT(x_1 \ln x_1 + x_2 \ln x_2) + V_m^\circ K\phi_1\phi_2 \quad (1)$$

where x_1 and x_2 are the mole fractions of the two components in the mixture and ϕ_1 and ϕ_2 are the corresponding volume fractions, defined as $x_1 V_1^\circ / V_m^\circ$ and $x_2 V_2^\circ / V_m^\circ$, respectively. V_1° and V_2° are the molar volumes of the two pure liquids, and $V_m^\circ = x_1 V_1^\circ + x_2 V_2^\circ$. The factor K is a constant, essentially the energy (per unit volume) of making 1–2 pair interactions by breaking 1–1 and 2–2 pair interactions. If the unlike (1–2) interaction energy can be written as the geometric mean of the like (1–1 and 2–2) interaction energies, a further simplification results:

$$K = (\delta_1 - \delta_2)^2; \qquad \delta_i = (\Delta E_i^\circ / V_i^\circ)^{1/2} \quad (2)$$

Here the δ_i's are the Hildebrand "solubility parameters", calculated as the square roots of the energies of vaporization per unit volume of the pure liquids.

It has long been recognized that eq 1 is not entirely self-consistent. In order to produce a nonzero energy of mixing, there have to be differences in the energies of interaction of 1–1, 1–2, and 2–2 nearest-neighbor pairs; if so, the probabilities of finding the different pairs will not be exactly random, and the entropy of mixing cannot be exactly ideal. The corrections necessary to make eq 1 self-consistent are frequently relatively small and are therefore often neglected. The simple eq 1, even with the further simplification of eq 2, fits approximately a wide variety of nonpolar nonelectrolyte mixtures.

The earliest substantial attempts to account for equilibrium between phases came from van der Waals and other members of the Dutch school of chemical

[†] Adapted from the Hildebrand Award Address, American Chemical Society Meeting, St. Louis, April 9, 1984.

(1) Scott, R. L. Ph.D. Dissertation, Princeton University, 1945.
(2) Thorp, N.; Scott, R. L. *J. Phys. Chem.* **1956,** *60,* 670.
(3) Hildebrand, J. H.; *Solubility;* ACS Monograph; Chemical Catalog Co.: New York, 1924.
(4) Hildebrand, J. H. *Solubility of Non-electrolytes,* 2nd ed.; ACS Monograph No. 17; Reinhold: New York, 1936.
(5) Hildebrand, J. H.; Scott, R. L. *Solubility of Nonelectrolytes,* 3rd ed.; ACS Monograph No. 17; Reinhold: New York, 1950 [reprinted as a paperback (with new preface and corrections of 1950 edition) by Dover Publications, 1964].
(6) Hildebrand, J. H.; Scott, R. L. *Regular Solutions;* Prentice-Hall: Englewood Cliffs, NJ, 1962.
(7) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions;* Van Nostrand Reinhold: New York, 1970.

physics and physical chemistry, with applications to binary mixtures starting in the first decade of the 20th century. van der Waals[8] seems not to have actually calculated many binary phase diagrams; most of his papers lack useful figures. van Laar,[9] on the other hand, reported many calculations of phase diagrams, covering many of the types that have been rediscovered by others since. The calculations were all by hand, so the diagrams lacked detail and were sometimes inaccurate. Everything was based upon the van der Waals equation of state; with the eclipse of that equation, discarded by some as "utterly worthless", much of this fine early work was almost universally forgotten.

However, my interest in what Griffiths[10] has called "global phase diagrams" really started only about 1961 when I learned about lower critical solution phenomena in hydrocarbon mixtures (e.g., methane + hexane, first studied by Davenport and Rowlinson[11]). For a short time a satisfactory explanation for these unexpected observations seemed elusive, and during this period I tried to account for them using corresponding-states theories, but the conclusions to be drawn depended much too sensitively upon the way in which the reduced quantities were generated.

Somewhat discouraged, I asked John Rowlinson whether it might be worthwhile to see if the van der Waals equation for mixtures, which would yield unambiguous results given a set of a's and b's, might yield such lower critical solution temperatures. He encouraged me; I tried it and found what I was looking for. In fact, van Laar[9c] had found it already in 1906 as I would have discovered if I had known then where to look and how to interpret what he said!

A Slightly Generalized van der Waals Equation for Fluid Mixtures

A few years ago I always had to preface a talk by trying to answer the question "Why the van der Waals equation? Isn't it utterly outdated and useless?" That introduction is no longer necessary now that the equation has undergone a renaissance, primarily because of the belated recognition that the structure of liquids and liquid mixtures, and hence their entropy, is determined primarily by the repulsive forces between molecules. Joel Hildebrand, with his great physical intuition, had known this all along.

The original van der Waals equation is

$$p = RT/(V_m - b) - a/V_m^2 \qquad (3)$$

where the ideal-gas relation between the pressure p, the molar volume V_m, and the thermodynamic temperature T is modified to allow for the hard-core volume of the molecules (i.e., their repulsion), expressed in the constant b, and the attraction between molecules, expressed in the constant a.

There are now far more complicated equations of state for liquids, ones that fit the thermodynamic properties of liquids, or at least those of liquid argon,

far better than does the van der Waals equation. One may fit each isotherm by varying the hard-sphere diameter in a perturbation treatment of the hard-sphere fluid. (van der Waals and van Laar played this game too, with temperature-dependent a's and b's.)

I do not quarrel with these treatments or with the even more empirical methods used by engineers. But Joel Hildebrand taught me to try to keep things simple. I try to apply the principle of Occam's razor in attempting to develop global models of phase equilibria. I am not interested in fitting the fine details of any particular system; it will be a long time before we have theories of liquids and liquid mixtures so good that the experimental thermodynamicist can shut up shop. I want to see how far the simplest reasonable models can account *qualitatively* for what one observes.

We have only started to understand the enormous diversity of phase equilibria in mixtures that can be deduced from what we call a "generalized van der Waals-like equation", written in the form

$$pV_m/RT = 1 + cf(b/V_m) - a/(RTV_m) \qquad (4)$$

The parameters a and b have the usual van der Waals meaning, except that for mixtures they are functions of the mole fractions. The parameter c, first introduced by Prigogine[12] but appearing here in a form suggested by Beret and Prausnitz,[13] adds a third dimension to a corresponding-states treatment; it allows for the entropy differences produced by a chain molecule with internal degrees of freedom.

The equation for the pressure can be integrated to yield the Helmholtz free energy; then, by adding a term for ideal mixing, one obtains an equation for the molar Helmholtz free energy A_m of a binary mixture:

$$A_m(T,V_m,x) - x_1 A_1°(T,V_m°) - x_2 A_2°(T,V_m°) = \\ -RT \ln (V_m/V_m°) - RTcg(b/V_m) - a/V_m + \\ RT(x_1 \ln x_1 + x_2 \ln x_2) \qquad (5)$$

Here the $A_i°$'s are the molar Helmholtz free energies of the pure fluids in their ideal-gas state at molar volume $V_m°$, x_1 and x_2 are the mole fractions of the two components, and the function $g(b/V_m)$ is just an integral of the function f in eq 4. The final term in eq 5 is the combinatorial free energy of ideal mixing. An alternative for this in the dense fluid mixture would be to substitute the Flory expression[14] for mixing chains of different length; one can do this by adding to eq 5 the extra term $RT[x_1 \ln b_1 + x_2 \ln b_2 - \ln (x_1 b_1 + x_2 b_2)]$.

Two of the simplest forms for $g(b/V_m)$ are that of the original van der Waals equation and a modification that I suggested some years ago;[15] a third is that derived from the widely used equation of Carnahan and Starling:[16]

van der Waals: $g = \ln (1 - b/V_m) \qquad (6a)$

Scott: $g = 2 \ln (1 - b/2V_m) \qquad (6b)$

Carnahan and Starling:

$$g = (b/V_m)(1 - 3b/16V_m)/(1 - b/4V_m)^2 \qquad (6c)$$

(8) van der Waals, J. D. *Proc. Sect. Sci., K. Ned. Akad. Wet.* 1906-1907, 9, 621, 727, 826; 1907-1908, 10, 56, 123, 183; 1908-1909, 11, 146, 187, 201, 317, 426, 477, 698, 816, 890; 1911-1912 14, 504, 655, 875, 1049, 1217; 1912-1913, 15, 602.

(9) van Laar, J. J. *Proc. Sect. Sci., K. Ned. Akad. Wet.* (a) 1904-1905, 7, 517, 636, 646; (b) 1905-1906, 8, 33; (c) 1906-1907, 9, 226.

(10) Furman, D.; Dattagupta, S.; Griffiths, R. B. *Phys. Rev. B: Solid State* 1977, 15, 441.

(11) Davenport, A. J.; Rowlinson, J. S. *Trans. Faraday Soc.* 1963, 59, 78.

(12) Prigogine, I. *The Molecular Theory of Solutions;* North-Holland: Amsterdam, 1957; Chapter XVI.

(13) Beret, S.; Prausnitz, J. M. *AIChE J.* 1975, 21, 1123.

(14) Flory, P. J. *J. Chem. Phys.* 1942, 10, 51.

(15) Scott, R. L. In *Physical Chemistry, An Advanced Treatise;* Henderson, D., Ed.; Academic: New York, 1971; Vol. 8A, Chapter 1, p 1.

Equation 6b has no real theoretical justification what-soever; it does, however, fit the properties of the hard-sphere fluid ($a = 0$) and those of real fluids like argon much better than the van der Waals eq 6a does. (Indeed, although eq 6c fits the hard-sphere fluid very well, when it is substituted into eq 4 and 5 it fits some of the properties of argon less well than eq 6b does.)

One final feature remains to be added, a set of pre-scriptions for a, b, and c. The usual ones are either linear or quadratic:

$$a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \qquad (7)$$

$$b = x_1 b_1 + x_2 b_2 \qquad (8a)$$

or

$$b = x_1^2 b_1 + 2x_1 x_2 (b_1^{1/3} + b_2^{1/3})^3/8 + x_2^2 b_2 \quad (8b)$$

$$c = x_1 c_1 + x_2 c_2 \qquad (9)$$

Equation 8a for b is that originally suggested by van der Waals and seems appropriate for rods or chain molecules; eq 8b incorporates the "Lorentz combining rule" (addition of radii of spheres) and is more nearly appropriate for globular molecules. Most of our exploration of global phase diagrams has utilized the simpler combining rule eq 8a with the c's set equal to 1. (It is worth noting that the Hildebrand equation (1) reduces to a van der Waals binary-mixture equation with eq 8a if one sets the V_i°'s equal to the b_i's.)

In our treatment of van der Waals phase diagrams[17-19] Peter van Konynenburg and I introduced some reduced parameters to describe the binary interactions:

$$\xi = (b_2 - b_1)/(b_2 + b_1) = (V_{c2} - V_{c1})/(V_{c2} + V_{c1}) \qquad (10)$$

$$\zeta = (a_{22}/b_2^2 - a_{11}/b_1^2)/(a_{22}/b_2^2 + a_{11}/b_1^2) = \\ (p_{c2} - p_{c1})/(p_{c2} + p_{c1}) \quad (11)$$

$$\Lambda = \\ (a_{22}/b_2^2 - 2a_{12}/b_1 b_2 + a_{11}/b_1^2)/(a_{22}/b_2^2 + a_{11}/b_1^2) \\ (12)$$

For van der Waals-like equations, the parameter ξ measures the relative difference in size of the two molecules and is related to the difference in critical volumes of the two pure fluid components; similarly, the parameter ζ measures the relative differences in "internal pressures" and is related to the difference in critical pressures of the two fluids. The parameter Λ is a measure of the magnitude of the (low-temperature high-density) enthalpy of mixing; in the absence of a nonideal configurational term, it is a measure of the magnitude of the deviation from ideal-solution behavior at low temperatures and high densities.

Figure 1 shows what we call the "master diagram" for mixtures of molecules of equal size ($\xi = 0$). First, we see the usefulness of the definitions of ζ and Λ; as long as all the a's and b's are positive (and negative values seem physically unreasonable), the diagram is bounded at the top by $\Lambda = 1$ and on the sides by $\zeta = \pm 1$. For

(16) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.
(17) van Konynenburg, P. H. Ph.D Dissertation, UCLA, 1968.
(18) Scott, R. L.; van Konynenburg, P. H. *Discuss. Faraday Soc.* **1970**, *49*, 87.
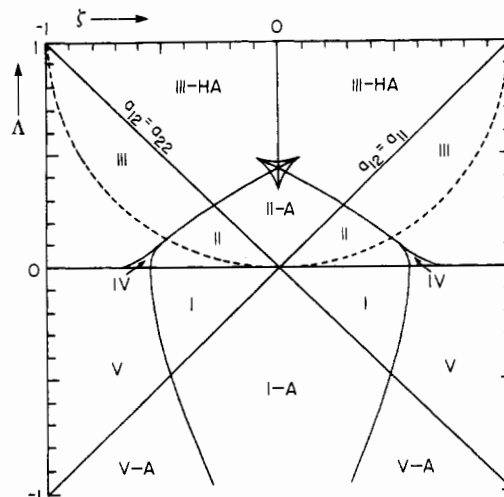(19) van Konynenburg, P. H.; Scott, R. L. *Philos. Trans. R. Soc. London* **1980**, *298*, 495.

Figure 1. "Master diagram" for types of phase diagrams for binary mixtures of molecules of equal size ($\xi = 0$). For explanation of types I–V, see text and Figure 2. The dashed half-circle is the locus of the geometric mean $a_{12} = (a_{11}a_{22})^{1/2}$.
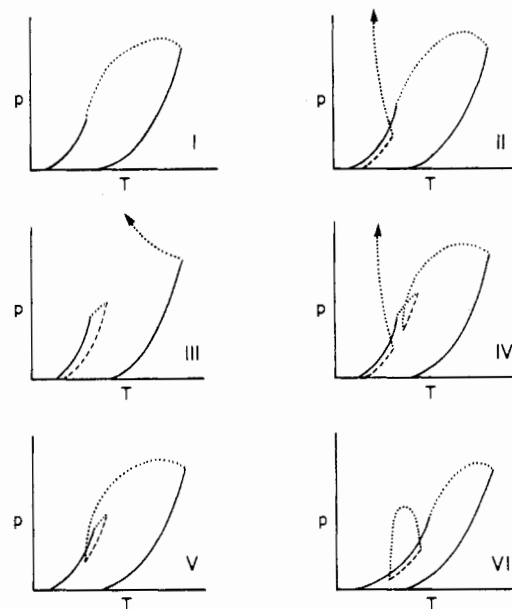

Figure 2. Pressure–temperature projections of p,T,x phase diagrams for the five types of van der Waals phase diagrams shown on the "master diagram" of Figure 1. The solid lines are the vapor pressure curves of the pure components, the dashed lines are three-phase (L_1–L_2–G) lines, and the dotted lines are critical lines. For a discussion of type VI, see text.

$\xi = 0$ the diagram is symmetrical around the $\zeta = 0$ vertical axis. The diagram shows the range of values of ζ and Λ over which five major types of binary-fluid phase diagrams may occur. These five types are most easily distinguished by the number and character of the critical lines, shown in their p,T projections in Figure 2. Critical lines may end in various ways, at the one-component gas–liquid critical points C_1 and C_2 or at the limiting upper critical solution point C_m (at $p = \infty$ and, for $\xi = 0$, at $x = \frac{1}{2}$) of a close-packed ($V_m = b$) "liquid–liquid" system at infinite pressure. In addition, critical lines may terminate on the ends of three-phase lines (L_1–L_2–G) at upper or lower critical end points.

These five types, and subdivisions thereof based upon the presence or absence of azeotropes or heteroazeotropes and the presence or absence of a minimum

pressure along a critical line, include all but one of the kinds of binary-fluid phase diagrams known to the chemist or chemical engineer. Moreover, although neither the phase diagrams nor the boundaries on the master diagram are quantitatively correct, they are in surprisingly good qualitative agreement with what is known from experiment.

The exception is the binary-fluid phase diagram for systems with low-temperature, lower critical solution phenomena (e.g., water + triethylamine), a type that has since[20,21] been labeled VI. All such systems involve hydrogen bonding and obviously violate the spirit of a "random-mixing" model like the van der Waals one. (An example of a p,T projection for type VI is shown in Figure 2; there are several variants.)

Of special importance in Figure 1 is the half-circle dashed line representing the locus of the geometric mean for a_{12} [i.e., $(a_{11}a_{22})^{1/2}$]; this Berthelot "combining rule" (substantially equivalent to that which yields the Hildebrand solubility parameter eq 2) fits, although only approximately, many binary mixtures. The majority of systems will be found in a band around this line, and systems with coordinates far from this line will be rare.

In the center of the master diagram, far from this geometric-mean line, is an especially complex "shield region", where the phase diagrams have additional critical lines and three-phase lines. This was first discovered in a three-component system by Furman, Dattagupta, and Griffiths[10] and later found by Furman and Griffiths[22] for a van der Waals binary mixture; we missed this feature in our earlier description of the master diagram. Whether such systems will ever be found experimentally may depend upon how far the shield region moves toward the geometric-mean line for systems of unequal size.

In real systems at low temperatures solid phases intervene to obscure the (metastable) fluid behavior of binary systems. Because of this, it is not always certain whether a system is really type I; it may have a type II phase diagram that is truncated by a solid phase that appears above the temperature of the liquid–liquid phase separation. A similar ambiguity exists with apparent type V systems thay may really be type IV. In 1973 Eric Dickinson[23] used the van der Waals equation to support our inference that close below the melting curve in the system methane + n-hexane lies a metastable liquid–liquid critical point (near $x_{hexane} = 0.8$ and $T = 150$ K); in our view this mixture corresponds to a positive Λ and should thus be classed as type IV.

Tricritical Phenomena

I turn now to a special class of phase equilibria, that found at or near tricritical points, phenomena that my colleague Chuck Knobler and I, with our two research groups, have been studying experimentally for nearly a decade. In principle, a tricritical point is a point at which three phases simultaneously merge into one phase, just as an ordinary critical point is where two
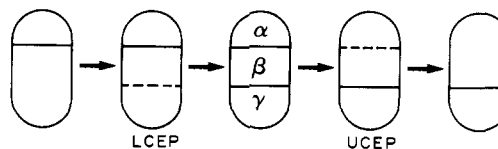
(20) Clancy, P.; Gubbins, K. E.; Gray, C. G. *Faraday Discuss. Chem. Soc.* 1978, *66*, 116.
(21) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworths: London, 1982; Chapters 6 and 8.
(22) Furman, D.; Griffiths, R. B. *Phys. Rev. B: Solid State* 1978, *17*, 1139.
(23) Dickinson, E.; Knobler, C. M.; Scott, R. L. *J. Chem. Soc., Faraday Trans. 1*, 1973, *69*, 2179.

Figure 3. Schematic representation of the behavior of a closed binary or ternary system in the vicinity of a tricritical point. As the temperature is raised, the system goes from two phases ($\alpha + \beta\gamma$) to three phases ($\alpha + \beta + \gamma$) to two phases ($\alpha\beta + \gamma$). The dashed line is the critical interface.

phases merge into one. However, that is not what one observes in the laboratory if one increases the temperature of a closed system along a path that passes through a tricritical point.

It is easier to explain an unsymmetrical tricritical point (the commoner kind in fluid mixtures) by showing what happens along a constant-composition, constant-density path *near* a tricritical point. If one fills a constant-volume vessel with a type IV mixture (for example, methane + n-hexane) at an appropriate composition and density, one observes at low temperatures two phases with one interface separating them (Figure 3). With increasing temperature a second interface appears (at a lower critical end point, an LCEP) as one goes from two phases to three. At a higher temperature the first interface disappears (at an upper critical end point, a UCEP), and one is back to two phases. If one could vary the magnitude of the binary interaction continuously (by changing Λ or ζ in the master diagram, Figure 1), one could move to the boundary between the type IV and type II regions. That boundary is in fact the locus of tricritical points; in terms of the p,T projections of Figure 2 and the schematic diagrams in Figure 3, the tricritical point is precisely where the three-phase region has just shrunk to nothing.

We had in fact calculated tricritical points, and had even made experimental studies in the vicinity of a tricritical point, before we had ever heard of the concept. Figure 4 is a diagram from Peter van Konynenburg's 1968 dissertation,[17] illustrating the disappearance of the three-phase region as one varies the ratio a_{22}/a_{11} (along a particular Λ,ζ path in the calculated van der Waals master diagram). Figure 5 is a plot of the experimental measurements he made of the locus of upper and lower critical end points in a series of methane + C_6–hydrocarbon binary and ternary systems.[17,24]

Figure 6 is from the experimental study by Jeff Creek[24] of tricritical phenomena in methane + 2,2-dimethylbutane + 2,3-dimethylbutane. This system is one we call "quasi-binary" because the two "solute" components are so similar that we can regard them as constituting a single "solute" of average properties. The Phase Rule imposes the thermodynamic condition that an unsymmetrical tricritical point can occur only in systems of three or more components. We can in effect "cheat" on this requirement with our quasi-binary systems because the relative proportions of the two "solutes" are almost exactly the same in all coexisting phases. Not only does this make the preparation of near-tricritical mixtures much easier, but it permits us to model tricritical behavior with van der Waals or van der Waals-like binary mixtures by simply varying the parameter ζ or Λ.

(24) Creek, J. L.; Knobler, C. M.; Scott, R. L. *J. Chem. Phys.* 1981, *74*, 3489.

Figure 5. Upper and lower critical-end-point temperatures for binary mixtures of methane with various C_6 hydrocarbons as a function of the solubility parameter δ of the higher hydrocarbon. The solid line is the locus of the experimental critical end points of the quasi-binary mixture methane + (2-methylpentane + 2-ethyl-1-butene). The dashed line approximates the locus of upper critical end points. From ref 24, and based upon measurements by van Konynenburg[17] and by Creek.[24]
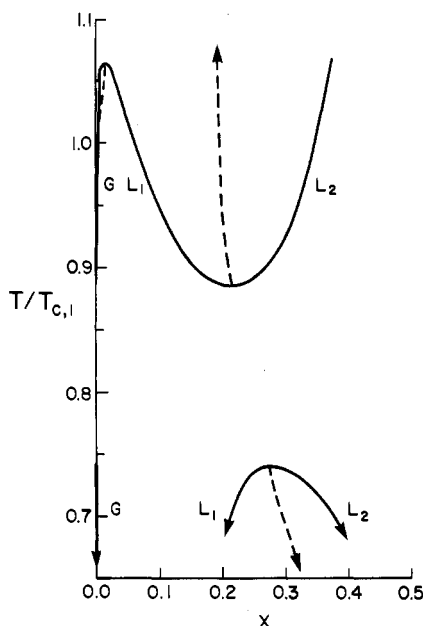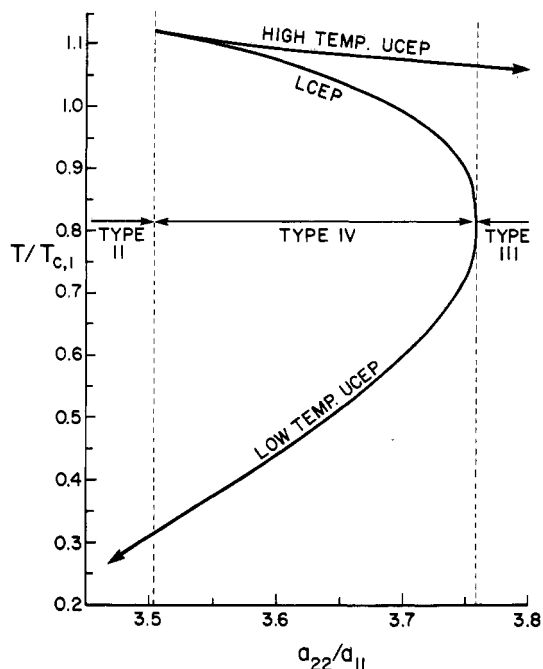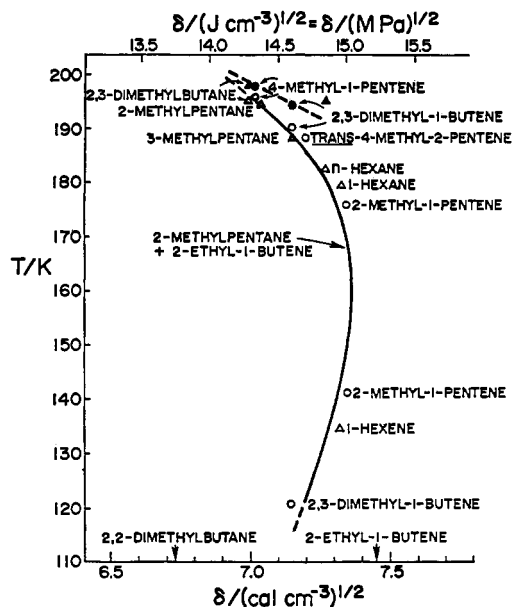

Figure 4. van der Waals calculated phase diagrams: (a, top) The disappearance of the three-phase region characteristic of type IV binary systems as a function of the ratio a_{22}/a_{11} (effectively equivalent to the parameter ζ). (b, bottom) T,x projections of the two three-phase lines and the critical lines occurring in a type IV binary system. From ref 17. Reprinted with permission from ref 24. Copyright 1981 American Institute of Physics.

Our modeling of tricritical phenomena started of course with van Konynenburg's work,[17,19] but recently we have resumed making similar calculations and in much greater detail. Our basic understanding of unsymmetrical tricritical points in fluid mixtures derives from a very important paper by Griffiths[25] in 1974. His phenomenological theory, a mean-field Landau-type treatment, utilizes a sixth-order polynomial for the free energy, the simplest form that yields three coexisting phases and tricritical points.

The crossover between normal ("classical") and anomalous ("nonclassical") behavior occurs at a di-

(25) Griffiths, R. B. *J. Chem. Phys.* **1974**, *60*, 195.
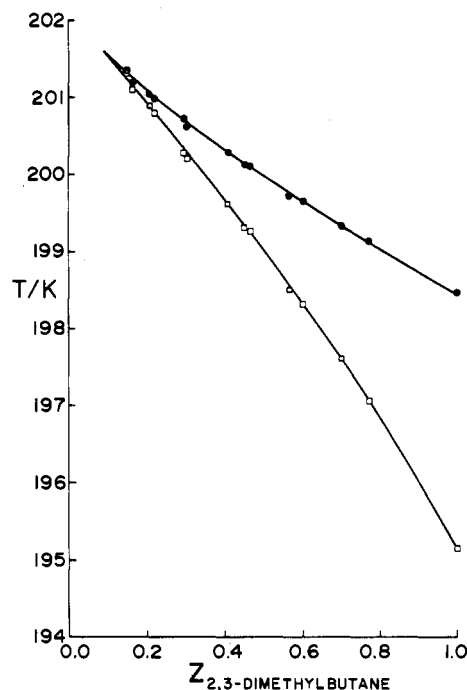

Figure 6. Upper and lower critical-end-point temperatures for the quasi-binary system methane + (2,2-dimethylbutane + 2,3-dimethylbutane). The abscissa is the relative mole fraction of 2,3-dimethylbutane in the "solute", $Z_{23} = x_{23}/(x_{22} + x_{23})$. Reprinted with permission from ref 24. Copyright 1981 American Institute of Physics.

mensionality of three for tricritical points rather than that of four for ordinary critical points; consequently, mean-field theory should yield the correct asymptotic behavior (i.e., the approach to the tricritical point should be governed by normal mean-field exponents), except possibly for some logarithmic corrections and
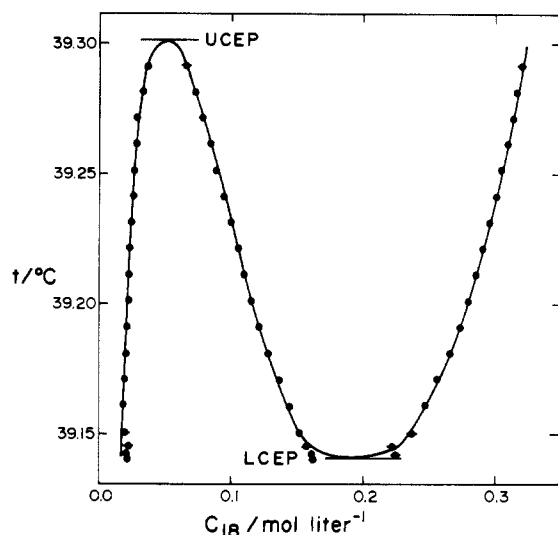
Figure 7. Three-phase coexistence curve T,c_{18} for the binary system ethane + n-octadecane. Reproduced from ref 26.

some nonclassical amplitude ratios. The predictions of the Griffiths theory about the asymptotic region are now confirmed by experiment, at least in most respects (an important remaining problem will be discussed later), but the asymptotic theory says nothing about more complex behavior outside the asymptotic region.

This can be illustrated by the three-phase coexistence curve (Figure 7) that Jürgen Specovius[26] measured for the binary system ethane + n-octadecane. In the asymptotic theory this should have twofold rotational symmetry about its midpoint, but the curve for the real system is obviously rather unsymmetrical. Such unsymmetrical curves appear in our van der Waals calculations, the asymmetry increasing with the distance from the tricritical point (as measured by $\Delta \zeta = \zeta - \zeta_t$ on the master diagram); indeed the first such curve (Figure 4b) appeared in van Konynenburg's dissertation.[17]

For any type IV binary or quasi-binary mixture with a particular set of intermolecular interactions (i.e., fixed ξ, ζ, Λ for the van der Waals model), the three-phase region appears as an isolated "monohedron" in a three-dimensional T,x,V_m diagram or the equivalent T,c_1,c_2 diagram with molar concentrations (Figure 8). The three projections of the coexistence curve are two S-shaped curves (T,c_1 and T,c_2) and one approximately parabolic curve (c_1,c_2). In the asymptotic sixth-order theory the S-shaped curves are symmetrical and the parabola reduces to a straight line.

Ian Pegg[27] calculated a large number of these three-phase curves and has fitted the temperature, pressure, and composition differences to power series in $(\Delta \zeta)^{1/2}$. The success of these fits encouraged me to try to extend the Griffiths phenomenological theory to higher terms, specifically[28,29] with the Gibbs free energy expressed as a polynomial truncated at the eighth power of the mole fraction x. (An expansion of the appropriate thermo-
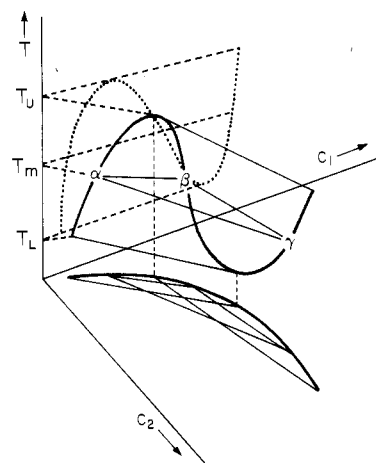
(26) Specovius, J.; Leiva, M.; Scott, R. L.; Knobler, C. M. *J. Phys. Chem.* **1981**, *85*, 2313.

(27) Pegg, I. L.; Knobler, C. M.; Scott, R. L. *J. Phys. Chem.* **1983**, *87*, 2866.

(28) Lindh, R.; Pegg, I. L.; Knobler, C. M.; Scott, R. L. *Phys. Rev. Lett.* **1984**, *52*, 839.

(29) Scott, R. L. *J. Chem. Phys.*, in press.

Figure 8. A schematic three-phase monohedron in T,c_1,c_2 space, showing two projections T,c_1 and c_1,c_2. The third projection T,c_2 is omitted for reasons of clarity.

dynamic potential in powers of c_1 leads to entirely equivalent results.)

Griffiths: $G_m =$

$$K[a_0 + a_1\Delta x + a_2(\Delta x)^2 + a_3(\Delta x)^3 + a_4(\Delta x)^4 + (\Delta x)^6] \quad (13)$$

extended:

$$G_m = K[a_0 + a_1\Delta x + a_2(\Delta x)^2 + a_3(\Delta x)^3 + a_4(\Delta x)^4 + a_5(\Delta x)^5 + (\Delta x)^6 + a_7(\Delta x)^7 + a_8(\Delta x)^8 + ...] \quad (14)$$

From this eighth-order polynomial one obtains a cubic equation for the composition of the three coexisting phases

$$(\Delta x)^3 - 3(\Delta x)^2[(b_{01} + 2b_{20})y^{1/2} + 2b_{30}\theta y^2 + ...]y^{1/2} - 3\Delta x[1 + 2b_{20}\theta y^{1/2} + (2b_{11} + 6b_{30} - b_{01}^2 - 4b_{01}b_{20} - 3b_{20}^2)y + ...]y - [2\theta - 3b_{01}y^{1/2} + 6(b_{11} + 2b_{30} - b_{01}b_{20} - b_{20}^2)\theta y + ...]y^{3/2} = 0 \quad (15)$$

where y is proportional to $\Delta \zeta$, and $\theta = (2T - T_U - T_L)/(T_U - T_L)$, a relative temperature that ranges from -1 to $+1$ across the three-phase region between the two critical end points (T_U and T_L). The parameters b_{ij} are uniquely related to ratios of the coefficients a_i in eq 14. The extended theory's eq 15 accounts almost quantitatively for the shapes of the unsymmetrical coexistence curves.

Much of what we have observed can be accounted for with only one extra correction (i.e., by adding only the seventh power of the order parameter to the original Griffiths phenomenological expression for the free energy). Figure 9a,b shows the fits to the coexistence curve for the binary system methane + 2,3-dimethylbutane recently remeasured by Enrique Fernandez-Fassnacht and Arthur Williamson.[30] [Here the compositions ("densities") are expressed not as mole fraction x and molar volume V_m but rather in terms of the alternative pair, the molar concentrations c_1 and c_6.]

The smooth curves shown were constructed by fitting compositions of the three conjugate phases at the midtemperature T_m and, of course, imposing the condition that the curves end at the critical end-point temperatures (but the compositions at the end points were *not* fitted). The only nonzero correction parameter is b_{20}. The curvature at the end points is not quite

(30) Fernandez-Fassnacht, E.; Williamson, A. G.; Sivaraman, A.; Scott, R. L.; Knobler, C. M. *J. Chem. Phys.*, in press.
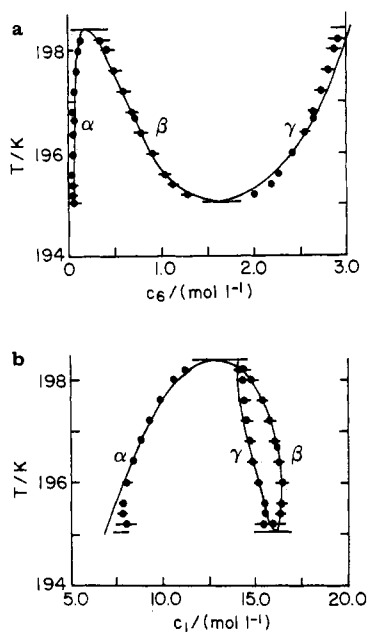
Figure 9. Three-phase coexistence curves for the binary system methane + 2,3-dimethylbutane: (a) T,c_6; (b) T,c_1 (measurements of Fernandez-Fassnacht and Williamson[30]). The solid curves are fits with the single extra parameter required by the seventh-order free energy polynomial.

Figure 10. The T,ζ "phase diagram" in the vicinity of the tricritical point for a sealed tube at fixed tricritical density ρ_t and mole fraction x_t. The tricritical point is at the confluence of the three lines. T/T_{1c} is the ratio of the temperature to the gas–liquid critical temperature of pure component 1. Calculated from the van der Waals equation for $\xi = 0$, $\Lambda = 0$. Reprinted with permission from ref 28. Copyright 1984 American Institute of Physics.

right, nor should it be; these are *ordinary* critical points where the coexistence curve is nonanalytic, having an approximately cubic shape rather than the parabolic shape predicted by any classical (mean-field) treatment.

Otherwise the fit is remarkably good, considering the experimental error bars and the neglect of any second-order corrections (arising from the coefficient b_{30} in eq 15), especially so for the T,c_1 curve where, for most of the temperature range, the concentration (although not the mole fraction) of methane in the intermediate β phase exceeds that in the γ phase. The agreement between the theoretical eq 15 and the experimental coexistence curve for the quasi-binary system ethane + (n-heptadecane + n-octadecane), studied in detail by Cynthia Goh,[31,32] is even more impressive. (All of these temperature–composition curves are of course projections of the original monohedron in T,x,V_m or T,c_1,c_6 space. A particular projection in the direction of a linear combination of x and V_m or of c_1 and c_6 generates an almost symmetrical curve like that predicted by the asymptotic theory.)

Another feature of interest is what we call the tricritical path. If we fill a sealed tube with a ternary mixture at exactly the tricritical composition and exactly the tricritical density (i.e., for our quasi-binary mixtures, selecting exactly ζ_t, x_t, and V_{mt}), what will be observed as the system is heated to the tricritical temperature and beyond? Three alternatives have been suggested:

(a) At the tricritical temperature three phases go to one phase. Efremova and Shvarts[33] reported having seen this in the system n-butane + acetic acid + water.

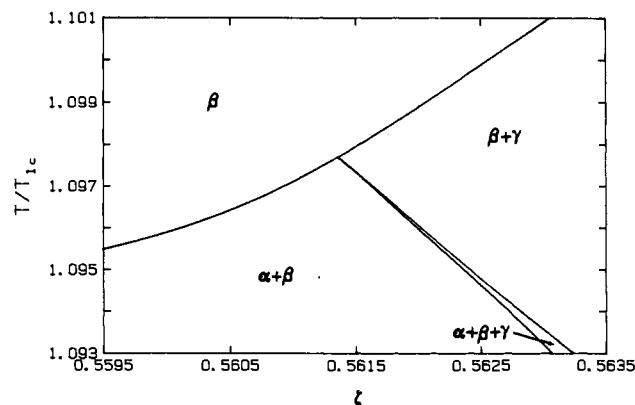(b) At the tricritical temperature two phases go to two different phases; one meniscus disappears just as an-

other appears. Efremova and Shvarts[33] reported having seen this behavior in the system carbon dioxide + methanol + water.

(c) Kaufman and Griffiths[34] on the basis of a model (designed to fit the experimental data on the system water + ethanol + benzene + ammonium sulfate) suggest that below T_t two phases coexist and that the volume of one shrinks precipitously to zero at T_t. However, they reported that they "have not been able to confirm that this ... is a general feature of the classical model".

van der Waals calculations[28,35] by Roland Lindh and Ian Pegg on a binary mixture at ζ_t,x_t,ρ_t yield the third alternative, suggesting that the Kaufman and Griffiths result is a fairly general one. Figure 10 shows the T,ζ "phase diagram" for fixed x_t and ρ_t. At the tricritical ζ_t the system goes from two phases to one; only for ζ greater than ζ_t does one encounter a three-phase region. However, for a ζ very slightly larger than ζ_t, the three-phase region is very narrow and a substantially larger two-phase region lies above it (see Figure 10). It is possible that the other two kinds of behavior, reported by Efremova and Shvarts, are slightly misinterpreted observations for slightly off-tricritical paths. In our experiments on the C_2H_6 + (n-$C_{17}H_{36}$ + n-$C_{18}H_{38}$) system we have found the one-phase region above the two-phase regions, but we have not attempted the almost impossible feat of producing in the laboratory an exactly tricritical path.

Before leaving the subject of unsymmetrical tricritical points, I should report on some of our recent work, a combination of experimental studies and modeling, that casts doubt upon the validity of the "Griffiths first sum rule" for light scattering in the region of a tricritical point. According to this rule[36] the light scattering from the three conjugate phases α, β, and γ should satisfy the following relationship

$$\Sigma_1 = \chi_\alpha^{1/2} + \chi_\gamma^{1/2} - \chi_\beta^{1/2} = 0 \qquad (16)$$

where χ is the susceptibility or "osmotic

(31) Goh, M. C. Ph.D. Dissertation, UCLA, 1985.
(32) Goh, M. C.; Specovius, J.; Scott, R. L.; Knobler, C. M. *J. Chem. Phys.*, in press.
(33) Efremova, G. D.; Shvarts, A. V. *Zh. Fiz. Khim.* **1969**, *40*, 907 [*Russ. J. Phys. Chem.* **1969**, *40*, 486].

(34) Kaufman, M.; Griffiths, R. B. *J. Chem. Phys.* **1982**, *76*, 1508.
(35) Lindh, R.; Pegg, I. L.; Knobler, C. M.; Scott, R. L., to be submitted for publication.
(36) Kaufman, M.; Bardhan, K. K.; Griffiths, R. B. *Phys. Rev. Lett.* **1980**, *44*, 77.

compressibility", $1/(\partial^2 G_m/\partial x^2)_{T,p}$. This result, obtained from the asymptotic theory, i.e., from the sixth-order polynomial (eq 13) for the free energy G_m, is modified when this classical theory is extended[29,37] to eighth order; the sum is now *not* zero, but a constant. On carrying the derivation to still higher order, one finds

$$\Sigma_1 = d_8 + d_{10}(\Delta\zeta) + d_{11}\theta(\Delta\zeta)^{3/2} + d_{12}(\Delta\zeta)^2 + O[(\Delta\zeta)^{5/2}] \tag{17}$$

Here the coefficients d_n are all strictly constant over the entire three-phase region; their subscripts denote the order of the free-energy polynomial required to produce them. Not only is the sixth-order coefficient exactly zero (hence the zero of the original Griffiths derivation), but so also are those from the seventh and ninth orders. Note that the first dependence upon temperature (that is, θ) occurs in the eleventh-order term.

The experimental intensities and the experimental correlation lengths are directly related to the susceptibilities by factors (coupling "constants") that are at most power series in Δx. If one derives the experimental intensity sum Σ_I or the experimental correlation length sum Σ_ξ by including these factors, these sums have exactly the same form as eq 17; only the numerical values of the constant coefficients change.

Experimental measurements of the light scattering from the system ethane + n-heptadecane + n-octadecane near its tricritical point, carried out by Anil Kumar[37] in David Cannell's laboratory at the University of California, Santa Barbara, in cooperation with our groups in Los Angeles, show a strikingly large variation of the experimental sums over a range of $\Delta\zeta$ where the seventh-order extension of the asymptotic theory seems sufficient to account reasonably well for the thermodynamic measurements. The correlation length sum Σ_ξ is reasonably linear in $\Delta\zeta$, but the intensity sum Σ_I shows a substantial curvature (Figure 11) that may indicate a divergence at ζ_t. The earlier measurements[38] on the four-component mixture indicated similar difficulties with the sum rule, but those results were perhaps less conclusive than ours because of the nature of the thermodynamic path that the measurements covered.

It seems hard to avoid the conclusion that these results show either that the classical theory—even when extended—has failed or that, even as close to the tricritical point as we have come, several terms in eq 17 are important, at least as high as $d_{12}(\Delta\zeta)^2$. The latter alternative seems very unlikely.

I have already mentioned that for tricritical phenomena the boundary between classical (mean-field) behavior and nonclassical (nonanalytic) behavior occurs at a dimensionality of three; the tricritical exponents should be those deduced from a mean-field theory, except very close to the tricritical point where logarithmic corrections[39] should be evident. Outside this very close region certain amplitude ratios should depart from their classically predicted values.[40] My UCLA

Figure 11. Light-scattering results on quasi-binary systems of ethane with mixtures of n-heptadecane, n-octadecane, and n-nonadecane: (a) intensity sums Σ_I; (b) correlation length sums Σ_ξ. $\langle n \rangle$ is the average carbon number in the quasi-binary "solute". Reprinted with permission from ref 37. Copyright 1985 American Institute of Physics.

collaborators and I believe that these light-scattering measurements provide strong evidence for these nonclassical amplitude ratios, a view buttressed by a very recent nonclassical theoretical treatment by Rudnick and Jasnow.[41,42]

[We have twice reviewed[43,44] the experimental studies on multicritical points in fluid mixtures (including the symmetrical tricritical points to be discussed in the next section). The second review brought the literature to 1983, but later studies, like our new light-scattering measurements, are not included.]

Symmetrical Tricritical Points

The last models I want to mention are those for what we call symmetrical tricritical points. They bear a mathematical relationship to the unsymmetrical tricritical points just described, but the relationships between the physical variables are sufficiently different that, for the purpose of this discussion, it is not worth trying to make the connection. Let us simply consider

(37) Kumar, A.; Chamberlin, R.; Cannell, D. S.; Pegg, I. L.; Knobler, C. M.; Scott, R. L. *Phys. Rev. Lett.* **1985**, *54*, 2234.

(38) Kim, W.; Goldburg, W. I.; Esfandiari, P.; Levelt Sengers, J. M. H. *J. Chem. Phys.* **1979**, *71*, 4888. Kim, M. W.; Goldburg, W. I.; Esfandiari, P.; Levelt Sengers, J. M. H.; Wu, E.-S. *Phys. Rev. Lett.* **1980**, *44*, 80.

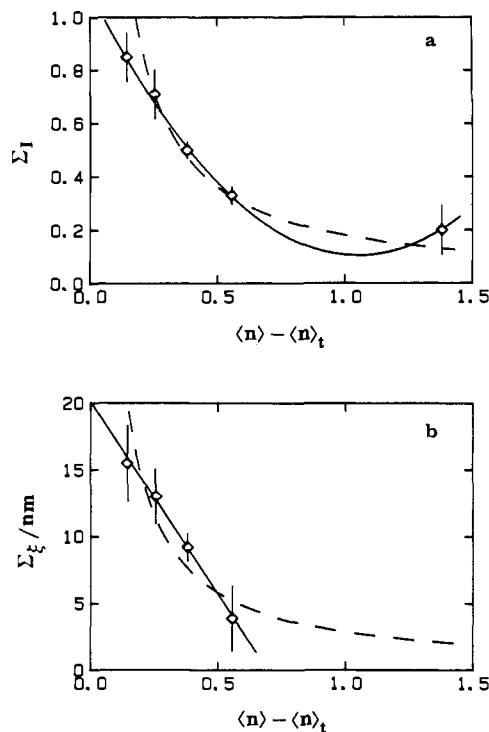(39) Stephen, M. J. *Phys. Rev. B: Solid State* **1975**, *12*, 1015.

(40) Fisher, M. E.; Sarbach, S. *Phys. Rev. Lett.* **1978**, *41*, 1127. Sarbach, S.; Fisher, M. E. *Phys. Rev. B: Condens. Matter* **1978**, *18*, 2350; **1980**, *20*, 2797.

(41) Rudnick, J.; Jasnow, D. *Phys. Rev. B: Condens. Matter* **1985**, *32*, 6087.

(42) This paragraph contains the only substantive change in our thinking since the presentation of the award address in April 1984. At that time we already believed that the light-scattering results showed evidence that the Griffiths sum diverged, presumably as a consequence of nonclassical effects, but at that time we attributed the discrepancies to the logarithmic corrections, not to the corrections in amplitude ratios.

(43) Scott, R. L. In *Proceedings of the Eighth Symposium on Thermophysical Properties, June 1981*; American Society of Mechanical Engineers: New York, 1982; Vol. I, p 397.

(44) Knobler, C. M.; Scott, R. L. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic: London, 1984; Vol. 9, pp 163–231.
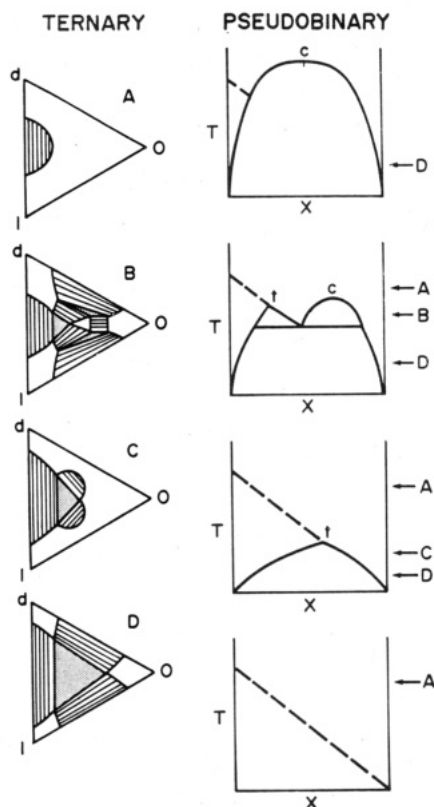
TERNARY   PSEUDOBINARY

Figure 12. Hypothetical phase diagrams for ternary fluid mixtures of d and l enantiomers with a third optically inactive fluid: (left) ternary diagrams; (right) pseudobinary diagrams for the racemic mixture plus the third component. Reprinted with permission from ref 43. Copyright 1982 ASME.
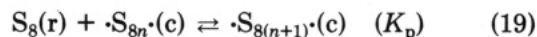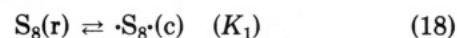
these a different phenomenon in phase equilibria.

I find it easiest to explain symmetrical tricritical points with a hypothetical ternary system composed of a pair of enantiomers (optically active d and l isomers) together with a third optically inert substance. One can imagine triangular phase diagrams like those shown in Figure 12, necessarily symmetrical around a horizontal axis that represents equal amounts of the two enantiomers. Depending upon the temperature and upon the interaction energies, various kinds of phase diagrams can occur, but any symmetrical three-phase region will have to shrink in a symmetrical way, so it *must* disappear at a tricritical point.

Now suppose that we have a racemic mixture of this enantiomer pair so that the overall composition lies on the symmetry axis. A pair of mirror-image conjugate phases cannot physically separate or even become turbid. (They have exactly the same density and exactly the same index of refraction.) Unless we look for thermodynamic anomalies, we will conclude that the system is a binary mixture with phase diagrams like those on the right-hand side of Figure 12, in which the two-phase coexistence curve ends at a sharp corner (essentially the intersection of two straight lines), a symmetrical tricritical point.

These unusual "pseudobinary" phase diagrams were derived initially by Meijering[45] from a very simple "regular solution" model for ternary mixtures. Much later Blume, Emery, and Griffiths[46] deduced the iden-

(45) Meijering, J. L. *Philips Res. Rep.* **1950**, *5*, 333; **1951**, *6*, 183; **1963**, *18*, 318.

(46) Blume, M.; Emery, V. J.; Griffiths, R. B. *Phys. Rev. A* **1971**, *4*, 1071.

tical diagrams from a three-spin model of helium mixtures; the third diagram on the right is substantially that found experimentally for the fluid mixture ^{4}He + ^{3}He.

Symmetrical tricritical points are also found in the fluid mixtures of sulfur with certain solvents. The unusual properties of sulfur and its solutions at elevated temperatures have been known since the past century, but an understanding of them had to wait for the development of an adequate treatment of polymer solutions. In pure liquid sulfur at a temperature of 432 K (159 °C) there is a remarkably sudden onset of the formation of very long sulfur chains from the S_8 rings that predominate at lower temperatures. The simple model of Tobolsky and Eisenberg[47] assumes two chemical equilibria, one for ring opening and a second for chain growth (polymerization):

$$S_8(r) \rightleftarrows \cdot S_8 \cdot (c) \quad (K_1) \tag{18}$$

$$S_8(r) + \cdot S_{8n} \cdot (c) \rightleftarrows \cdot S_{8(n+1)} \cdot (c) \quad (K_p) \tag{19}$$

Essential to this treatment is its use of the Flory–Huggins free energy for mixing polymers with monomers (solvent); this requires that, for the equilibrium "constant" K_p to be reasonably constant, it must be expressed in terms of molar concentrations or volume fractions, *not* in terms of mole fractions. If K_p is expressed in terms of molar concentrations, it becomes appropriate to assume that it is the same number for all n. At 432 K the ring-opening constant is very small (ca. 10^{-12}), but K_p changes continuously from a value slightly less than 1 to one slightly greater than 1, and it is this that produces the sudden, almost catastrophic, appearance of long chains, with thermodynamic behavior very close to that expected for a second-order transition.

In 1965 I extended[48] this theory for pure liquid sulfur to liquid mixtures of sulfur, adding to the chemical equilibria and the Flory–Huggins free energy a Hildebrand "regular-solution" interaction between the solvent and the sulfur. The equation $K_p \phi_S = 1$, where ϕ_S is the volume fraction of total sulfur, defines a "critical polymerization line" in the solvent + sulfur phase diagram, a temperature at which long chains start forming in quantity and at which the viscosity of the solution increases sharply (Figure 13). If the solvent–sulfur interaction is large enough, there will be an upper critical solution temperature lying below the critical polymerization line and at a higher temperature a lower critical solution point that lies on the critical polymerization line. For still larger interactions the two two-phase regions merge and there is no temperature range of complete miscibility.

In most qualitative respects these predictions agreed with the then-existing experimental data and with the new measurements that we reported 2 years later[49] (Figure 14). In two annoying respects, however, theory and experiment were not in agreement: (1) for certain values of the interaction parameters the theory predicted three-phase equilibria (Figure 13d) that have never been found, and (2) the calculated coexistence curves were sharply pointed at their junctions with the critical polymerization line (i.e., the lower critical so-

(47) Tobolsky, A. V.; Eisenberg, A. *J. Am. Chem. Soc.* **1959**, *81*, 780.
(48) Scott, R. L. *J. Phys. Chem.* **1965**, *69*, 261.
(49) Larkin, J. A.; Katz, J.; Scott, R. L. *J. Phys. Chem.* **1967**, *71*, 352.
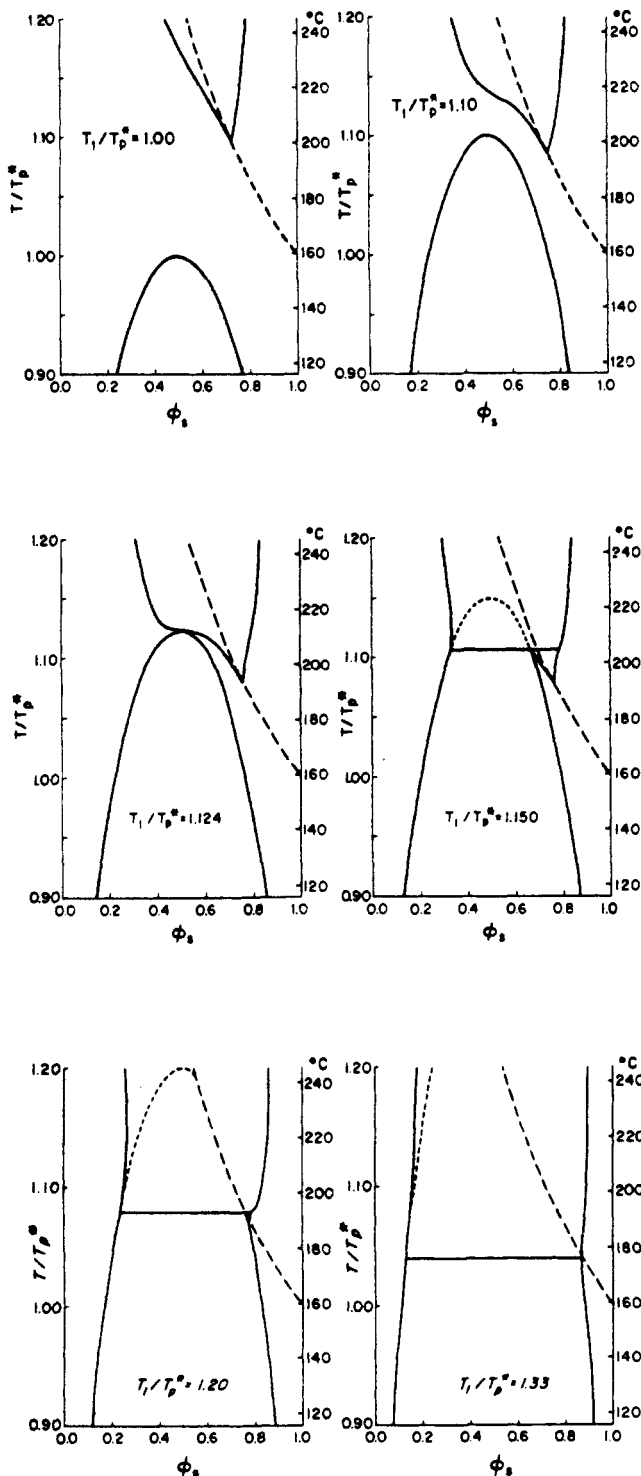
Figure 13. Calculated phase diagrams for solvent + sulfur systems. T_1 is the (low-temperature) upper critical solution temperature, while T_p^* is the critical polymerization temperature for pure sulfur; ϕ_S is the volume fraction of total sulfur. The dashed line is the critical polymerization line. The different values of the ratio T_1/T_p^* correspond to different values of the solvent–sulfur interchange energy. Reproduced from ref 48.

Figure 14. Experimental phase diagrams for solvent + sulfur systems: (a) triphenylmethane + sulfur; (b) *cis*-decalin + sulfur. The critical polymerization line, unlike that in Figure 13, is here drawn solid rather than dashed. Reproduced from ref 49.

lution point) while the experimental coexistence curves (Figure 14) were rather flat. Of course, the theory was a classical (mean-field) treatment and K_1 was taken as negligibly small, but these simplifications did not seem to be responsible for the discrepancies.

Anyone who compares Figures 12 and 13 should be struck by the similarity; the phase diagrams in the latter resemble those in the former, except that the temper-
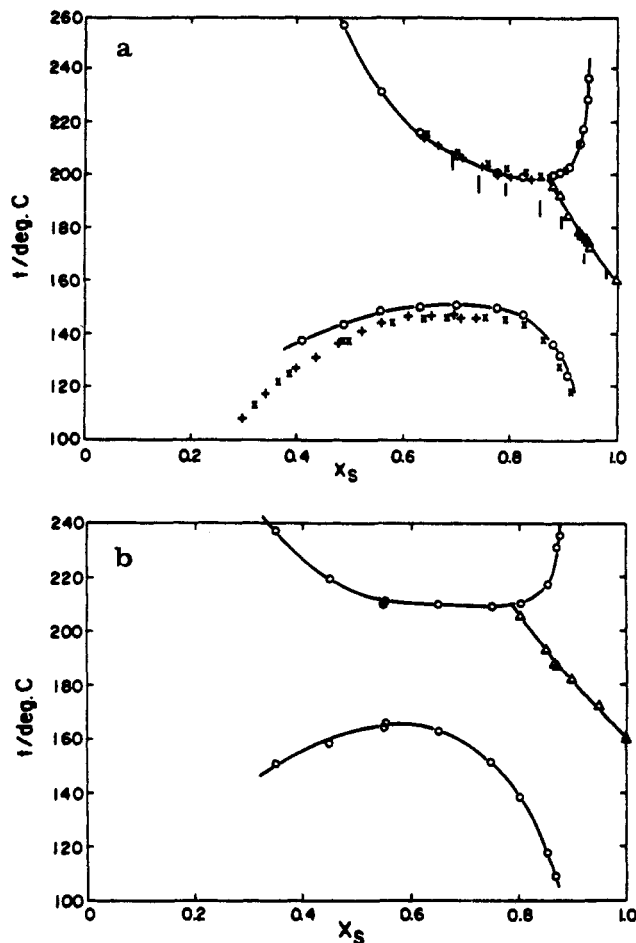
ature scale is upside down. However, in 1965 we had never heard of a tricritical point and, although I was familiar with some of Meijering's work, I never saw the relationship. It took John Wheeler to make the connection. He, together with Kennedy and Pfeuty,[50] had just found an exact mathematical analogy between the formulation of the equilibrium polymerization of sulfur and the $n \rightarrow 0$ vector model of magnetism. They promptly extended[51] this $n \rightarrow 0$ vector model to sulfur solutions, and the mean-field approximation to it proved to be *identical* with my earlier thermodynamic theory.

Since then they have introduced a number of refinements[52] to their theory including (a) the formation of very large rings as well as long chains in the region above the critical polymerization line and (b) the effect of impurities produced by slow chemical reactions between solvent and sulfur (which certainly take place in the systems we studied experimentally). The effect of the impurities is similar to that of greatly increasing K_1; it can eliminate the three-phase equilibrium, flatten the coexistence curve, and even introduce an unsymmetrical tricritical point. The flattening of the coexistence curve

(50) Wheeler, J. C.; Kennedy, S. J.; Pfeuty, P. *Phys. Rev. Lett.* **1980**, *45*, 1748. Wheeler, J. C.; Pfeuty, P. *Phys. Rev. A* **1981**, *24*, 1050.

(51) Wheeler, J. C.; Pfeuty, P. *Phys. Rev. Lett.* **1981**, *46*, 1409; *J. Chem. Phys.* **1981**, *74*, 6415.

(52) Wheeler, J. C.; Petschek, R. G.; Pfeuty, P. *Phys. Rev. Lett.* **1983**, *50*, 1633. Wheeler, J. C. *Phys. Rev. Lett.* **1984**, *53*, 174; *J. Chem. Phys.* **1984**, *81*, 3635.

depends upon the amount of impurity, i.e., the extent of the reaction; the degree of flattening that we observed in our experiments does seem to correlate qualitatively with our estimates of the reactivity.

It is interesting to note that the experimental discovery of symmetrical tricritical points in fluid mixtures dates from 1967, when Graf, Lee, and Reppy[53] established the correct phase diagram for the helium mixture and when we[49] determined the phase diagram for triphenylmethane + sulfur (Figure 14a), including the critical polymerization line (which is analogous to the superfluid transition line). Neither paper called the phenomenon a tricritical point.

I conclude by returning to the enantiomer diagrams. Before anyone can find these pseudobinary ternary diagrams, one has to find fluid–fluid phase separation in racemic mixtures. It is only very recently that thermodynamic measurements have finally given convincing evidence[54] of deviations from ideal-solution behavior in fluid mixtures of d–l isomers. Systems with much larger and positive deviations must be found. The model exists; substances that will fit it need to be

found. Some think this virtually impossible. But macroscopic phase separation has to involve the whole molecule, not just a few segments, so I hope that construction of polymer chains from appropriate optically active monomers will amplify the monomer effect sufficiently to produce incompatibility. Only time will tell, and it is likely to be a rather long time; but what fun it will be to find it!

It has often been suggested that the study of phase equilibria, like the classical thermodynamics upon which it is based, is really a 19th century subject far from the frontier of modern science. I hope that this presentation shows that this is not so, that there is still much excitement in this field. Moreover, many new types of phase equilibria that are just beginning to be understood have not even been mentioned—areas to which I have made no contributions at all, but ones that are exciting and will continue to excite the next generation of physical chemists: liquid crystals, microemulsions, phase equilibria in two dimensions (surface films), and many others.

(53) Graf, E. H.; Lee, D. M.; Reppy, J. D. *Phys. Rev. Lett.* **1967**, *19*, 417.

(54) Atick, Z.; Ewing, M. B.; McGlashan, M. L. *J. Phys. Chem.* **1981**, *85*, 3300; *J. Chem. Thermodyn.* **1983**, *15*, 159.

Organic Photochemistry with Far-Ultraviolet Photons. The Photochemistry of Allyl-, Vinyl-, and Alkylidenecyclopropanes

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Received March 14, 1986 (Revised Manuscript Received October 24, 1986)

The past 3 decades have witnessed a tremendous surge of interest in the photochemistry of organic compounds in solution. The studies that have been undertaken have encompassed a wide variety of chromophores which absorb in the near-ultraviolet (>300 nm) and the mid-ultraviolet (200–300 nm) regions of the spectrum. As a result, there is general understanding of the photochemical behavior of chromophores (e.g., carbonyl, phenyl) whose lowest electronic transitions lie in these spectral regions. Compounds such as alkenes, acetylenes, cyclopropanes, alcohols, ethers, and amines whose chromophores do not absorb in this region have been studied by extending their absorption by suitable conjugating groups or, where possible, by

promotion to their lowest triplet states by sensitization.

Organic photochemistry in the far-ultraviolet (185–214 nm) offers opportunities to study the behavior of simple, unsubstituted chromophores in their singlet excited states in solution. It also makes possible excitation of the second upper singlet states of those chromophores (e.g., carbonyl) which absorb at longer wavelengths as well.

Photons of wavelengths in the far-ultraviolet region correspond to energies greater than 143 kcal/einstein, which is more than adequate to break almost any bond in a typical organic molecule. In the gas phase, secondary bond homolysis does occur, often randomly, as a result of the primary photoproducts being formed with excess vibrational energy.[1] In solution, however, irradiation with far-UV light usually results in highly

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(1) See, for example: (a) McNesby, J. R.; Okabe, H. *Adv. Photochem.* **1964**, *3*, 157 and references cited therein. (b) Currie, C. L.; Okabe, H.; McNesby, J. R. *J. Phys. Chem.* **1963**, *67*, 1494. (c) Lopez, E.; Doepker, R. D. *Ibid.* **1978**, *82*, 753.

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