

## Approaches to the Tricritical Point in Quasibinary Fluid Mixtures

Roland Lindh,<sup>(a)</sup> Ian L. Pegg, Charles M. Knobler, and Robert L. Scott  
*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024*  
 (Received 19 October 1983)

When the Griffiths theory of tricritical points is extended to the eighth power of the order parameter, certain composition differences preserve the limiting behavior far from the tricritical point, an unexpected result that had been overlooked in earlier van der Waals model calculations. New calculations show that, along a path of constant tricritical composition and density and increasing temperature, a quasibinary system goes from two phases to one at the tricritical point, with no appearance of the third phase.

PACS numbers: 64.60.Kw

Simple phenomenological theories of tricritical phenomena, e.g., that of Griffiths,<sup>1</sup> have proved very useful in understanding the limiting behavior as the tricritical point is approached. However, our measurements and our model calculations both suggest that for some properties the limiting behavior is found only very close to the tricritical point. In particular the *S*-shaped three-phase coexistence curves that we have measured for quasibinary hydrocarbon mixtures,<sup>2,3</sup> even those closest to the tricritical point, are rather asymmetric, whereas the simple theory predicts that such plots of temperature versus order parameter should be symmetric with respect to a twofold rotation around the midpoint. Recently<sup>4,5</sup> we reported some model calcula-

tions using the van der Waals equation that also showed this asymmetry and we were able to deduce a power-series form for the corrections to the limiting behavior at the upper and lower critical end points. This encouraged us to look for a more general mean-field derivation.

Griffiths<sup>1</sup> has shown that the simplest expression (for the molar Gibbs free energy  $G_m$ ) that yields tricritical behavior is one that is sixth order in the order parameter, which we have taken to be the difference between the mole fraction  $x$  and its tricritical value  $x_t$ ,  $\Delta x = x - x_t$ . In order to find the nature of deviations from limiting behavior we have extended the free-energy expression to eighth order:

$$G_m(\Delta\zeta, T, p, \Delta x) = a_0 + a_1(\Delta x) + a_2(\Delta x)^2 + a_3(\Delta x)^3 + a_4(\Delta x)^4 + a_5(\Delta x)^5 + (\Delta x)^6 + a_7(\Delta x)^7 + a_8(\Delta x)^8 + \dots, \quad (1)$$

where the coefficients  $a_n$  are smooth functions of three independent field variables, the temperature  $T$ , the pressure  $p$ , and  $\zeta$ , a measure of the binary interaction. (The fourth field variable, the difference of chemical potentials,  $\mu_1 - \mu_2$ , is the conjugate of the order parameter  $\Delta$ .) The coefficients  $a_0$  and  $a_1$  are arbitrary and may be chosen to fit one's convenience, but in the three-phase region the coefficients  $a_2$  to  $a_5$  must scale properly with respect to the distance  $y$  from the tricritical point, expressed in terms of the three field variables (e.g.,  $\Delta T$ ,  $\Delta p$ , or  $\Delta\zeta$ ); we choose  $y$  to be proportional to  $\Delta\zeta$ . Then  $\Delta x$  scales as  $y^{1/2}$ ,  $a_2$  as  $y^2$ ,  $a_3$  as  $y^{3/2}$ ,  $a_4$  as  $y$ , and  $a_5$  as (at least)  $y^{1/2}$ ; the correction coefficients  $a_7$  and  $a_8$  are nonzero at the tricritical point and thus substantially independent of  $y$ . However, since the coefficients  $a_n$  must be smooth functions of the three fields and thus in the tricritical region essentially only linear combinations of them, it is impossible for any coefficient to be proportional to a power of  $y$  less than 1. Thus we take  $a_5$  as proportional to  $y$  rather than to  $y^{1/2}$ ; this is in accord with the van der Waals calculations and, within some uncertainty, with our experimental results.

One can rewrite (1) in terms of the compositions of the three coexisting phases ( $\Delta x = \alpha$ ,  $\beta$ , and  $\gamma$ ):

$$G_m(\Delta\zeta, T, p, \Delta x) = (\alpha - \Delta x)^2(\beta - \Delta x)^2(\gamma - \Delta x)^2[f_0 + f_1(\Delta x) + f_2(\Delta x)^2 + \dots], \quad (2)$$

where the quantities  $\alpha\beta\gamma$ ,  $\alpha\beta + \beta\gamma + \gamma\alpha$ ,  $\alpha + \beta + \gamma$ ,  $f_0$ ,  $f_1$ , and  $f_2$  can be identified as functions of the coefficients in (1). Once these new coefficients have been identified, the third-order equation for the coexisting phases,  $(\alpha - \Delta x)(\beta - \Delta x)(\gamma - \Delta x) = 0$ , can be transformed into a reduced equation:

$$z^3 + (Ay^{1/2} - 2\theta By)z^2 + (-3 + 2\theta Cy^{1/2} + Dy)z + (-2\theta + Ey^{1/2} + 2\theta Fy) = 0, \quad (3)$$

where the coefficients  $A$ ,  $B$ , etc., are functions of the original coefficients  $a_n$  and substantially independent

of  $y$ ;  $z = x/y^{1/2}$  is a reduced composition, and  $\theta = (2T - T_U - T_L)/(T_U - T_L)$ , a reduced temperature that varies from  $-1$  at the lower critical end point to  $+1$  at the upper critical end point. At the critical end point  $d\theta/dz$  must be exactly zero, so that this generates two relations between the coefficients in (3):

$$A - 2C + E = 0; \text{ and } 6B - 3D + 6F + (A - C)^2 = 0. \quad (4)$$

With an extended equation including higher powers of  $y^{1/2}$ , the coefficients  $a_n$  themselves may be polynomials in  $y^{1/2}$ ; this produces some ambiguity in relating them to the coefficients  $A$ ,  $B$ ,  $C$ , and  $D$ . However, if we set  $a_4$  exactly equal to  $-6y$ , which then leaves  $a_3$  equal to  $-4\theta y^{3/2}$  plus higher terms, we obtain

$$A = 3[a_7 - a_5/a_4]; \quad B = a_8 - a_7^2; \quad C = a_7; \quad D = [27a_8 - 25a_7^2 - 6a_7(a_5/a_4) - 9(a_5/a_4)^2]/2. \quad (5)$$

One can easily obtain from (3) an expression for the roots of the extended equation as a perturbation upon the limiting equation:

$$z = z_0 - [Cz_0^2 + (A - 2C)]y^{1/2}/3 - [6Bz_0^3 + (-18B + 3D - A^2 + C^2)z_0]y/18, \quad (6)$$

where  $z_0$  is a root ( $\alpha_0/y^{1/2}$ ,  $\beta_0/y^{1/2}$ , or  $\gamma_0/y^{1/2}$ ) of the unperturbed equation  $z_0^3 - 3z_0 - 2\theta = 0$ . Since, from the unperturbed equation  $\alpha_0(\theta) = -\gamma_0(-\theta)$ , it follows from (6) that  $\alpha(\theta) - \gamma(-\theta)$  is a function only of half-integral powers of  $y$ . Two such differences are that between the critical phases at the two end points ( $z_0 = \pm 1$ ) and that between the two noncritical phases at the two end points ( $z_0 = \pm 2$ ):

$$\Delta x_c = x_{Lc} - x_{Uc} = 2y^{1/2} + (12B - 3D + A^2 - C^2)y^{3/2}/9; \quad (7)$$

$$\Delta x' = x_{U'} - x_{L'} = 4y^{1/2} + 2(-6B - 3D + A^2 - C^2)y^{3/2}/9. \quad (8)$$

Especially simple is the ratio  $R_{l/c}$ :

$$R_{l/c} = (\Delta x')/(\Delta x_c) = 2 - 2By + O(y^2). \quad (9)$$

To no surprise, these new simple results can be found in the van der Waals calculations; however, we had not recognized them when we wrote our earlier paper.

The ratio we have reported<sup>4,5</sup> in the past, that of the lengths of the tie lines at the upper and lower critical end points, is not so simple:

$$R_{U/L} = (x_{U'} - x_{Uc})/(x_{Lc} - x_{L'}) = 1 - 2Cy^{1/2}/3 - 2C^2y/9 + O(y^{3/2}). \quad (10)$$

It is now clear that a better test of the limiting behavior is the new ratio  $R_{l/c}$ , which by suppressing the half-integral powers of  $y$  emphasizes the underlying symmetry, while the other ratio  $R_{U/L}$  is a measure of the asymmetry.

Alternative order parameters, such as the molar volume  $V_m$  or the molar concentrations, can be used in equations like (1) and will have roots given by equations like (3); only the numerical coefficients are different. Thus, for any order parameter, the ratios  $R_{l/c}$  and  $R_{U/L}$  have the form of (9) and (10). In our recent paper<sup>5</sup> we raised the question of the appropriate choice of order parameter for tricritical systems. In the present formulation a particular linear combination of  $x$  and  $V$  will make  $C$  equal to zero and thus suppress the  $y^{1/2}$  term in  $R_{U/L}$ , but this corresponds to no physically obvious order parameter, and we doubt if it is of much significance.

These predictions about the shape of the S-shaped coexistence curve are borne out by all the experimental measurements we have made on

binary and quasibinary mixtures of hydrocarbons. As an example we cite the molar concentration of the second component in the binary system ethane + *n*-octadecane. For this system, for which  $\Delta T = 160$  mK, we find  $R_{l/c} = 2.1$ , within experimental uncertainty the limiting value, while  $R_{U/L} = 1.5$ .

Finally from (1) and (3) one can also derive the susceptibilities  $\chi = [(\partial^2 G_m / \partial x^2)_{T,p}]^{-1}$  for the three conjugate phases, and permit an examination of the so-called Griffiths first sum rule.<sup>6</sup> We find for the Griffiths ratio  $R_\chi$ , which should be unity in the limit, the result

$$R_\chi = (\chi_\alpha^{1/2} + \chi_\gamma^{1/2})/\chi_\beta^{1/2} \\ = 1 + (4B + C^2)(2\beta^2 + \alpha\gamma)/8 + \dots \quad (11)$$

The correction term scales as  $(\Delta x)^2$ , i.e., as  $y$  or  $\Delta\zeta$ , and has a temperature dependence that is roughly proportional to  $(1 - \theta^2)^{1/2}$ . The prediction that the change in  $R_\chi$  is proportional to  $\Delta\zeta$  is not yet supported by any convincing experimental evi-

dence. Our own light-scattering measurements<sup>7</sup> on the quasibinary system ethane + *n*-heptadecane + *n*-octadecane seem to yield values of  $R_x$  around 1.2–1.3, in agreement with earlier measurements on another system,<sup>8,9</sup> with no strong dependence on  $\Delta\zeta$ .

The experimental evidence about the limiting behavior at a tricritical point is, at least in most respects, in agreement with the mean-field theory of Griffiths,<sup>1</sup> so that detailed calculations based upon a mean-field equation of state, which can handle changes in both temperature and pressure, should yield qualitatively correct results concerning the approach to the tricritical point. We have long been using the van der Waals equation to calculate phase equilibria in binary systems.<sup>10–12</sup> By continuously varying an intermolecular interaction parameter we can approach the tricritical point in a series of truly binary systems which should be similar to the quasibinary ternary mixtures we have been studying in the laboratory.

In the van Konynenburg and Scott formulation<sup>12</sup> there are three parameters:  $\xi$ , a measure of the difference in size of the two molecules;  $\zeta$ , a measure of the difference in internal pressure (or critical pressure) of the two components; and  $\Lambda$ , a measure of the interchange energy on mixing the two substances. In most of our calculations we have, for simplicity, set  $\xi=0$  (equal sizes) and  $\Lambda=0$ . Then the “distance” from the tricritical point is measured by a single parameter  $\Delta\zeta = \zeta - \zeta_t$ , where  $\zeta_t$  is the value of  $\zeta$  at the tricritical point; this is proportional to the  $y$  used in the eighth-order treatment developed earlier in this paper. This quantity  $\Delta\zeta$  is substantially equivalent to the  $\Delta Z$  we use to define the mixture of two very similar substances that is the “second component” in our experimental quasibinary mixtures.

As reported earlier,<sup>5</sup> we have been able to fit our van der Waals calculations in the vicinity of the tricritical point to various power series in  $(\Delta\zeta)^{1/2}$ . All these fits are, without exception, of exactly the same form as those we have now derived from the eighth-order free energy equation (1).

Our computer programs include the ability to calculate the compositions of the three conjugate phases, and thus to delimit the region of the phase diagram in which three phases can coexist. If one takes  $x$  and  $V_m$  as the variables (by eliminating temperature from the  $T, x$  and  $T, V_m$  plots) one finds that the locus of the three-phase line is now approximately a parabola. If one constructs the various three-phase triangles, a second parabola is the outer envelope. For an overall loading of a constant-

volume cell with mole fraction  $x$  and density  $1/V_m$ , three phases can occur only if the coordinates of the loading lie within the small “crescent-moon” area so defined. For each of these loadings one can derive the relative volumes of the three phases as a function of temperature and determine the points at which one phase disappears; this has been a great help in planning and interpreting the experimental measurements. As the distance from the tricritical point, as measured by  $\Delta\zeta$ , decreases, the crescent shrinks and becomes more and more symmetrical.

Of particular interest is what we call the tricritical path; if one fills a sealed tube with a ternary mixture at exactly the tricritical composition and exactly the tricritical density, what will be observed as one heats the tube to and beyond the tricritical temperature? (A similar question can be posed for a four-component system at constant pressure.) Three alternatives have been suggested:

(a) At the tricritical temperature three phases go to one phase (as at the tricritical temperature in symmetrical magnetic systems). Efremova and Shvarts<sup>13</sup> claim to have observed 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 another appears. Efremova and Shvarts<sup>13</sup> reported having seen this behavior in the system carbon dioxide + methanol + water.

(c) Kaufman and Griffiths,<sup>14</sup> on the basis of a model designed to fit the experimental data on water + ethanol + benzene + ammonium sulfate,

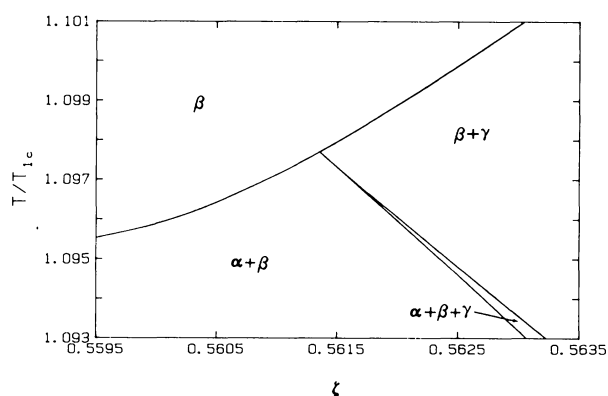


FIG. 1.  $T, \zeta$  “phase diagram” in the vicinity of the tricritical point for a sealed tube at fixed tricritical density and composition. The tricritical point is at the confluence of the three lines.  $T/T_{1c}$  is the ratio of the temperature to the gas-liquid critical temperature of pure component 1. (Calculated from the van der Waals equation for  $\xi=0$ ,  $\Lambda=0$ .)

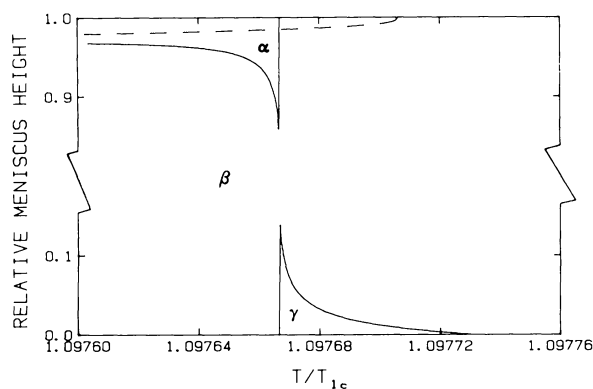


FIG. 2. Relative meniscus heights as a function of temperature for a sealed tube at fixed tricritical density and composition and two values of  $\zeta$ : the tricritical value  $\zeta_t = 0.5613551$  (dashed curve) and  $\zeta = 0.56137$  (solid curve), slightly greater than the tricritical value.  $T/T_{1c}$  is the ratio of the temperature to the gas-liquid critical temperature of pure component 1. (Calculated from the van der Waals equation for  $\xi = 0$ ,  $\Lambda = 0$ .)

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 "we have not been able to confirm that this situation . . . , two phases coexisting just below and only one phase just above the tricritical temperature, is a general feature of the classical model, nor to show the opposite, that other situations are possible by an alternative choice of the parameters."

Our calculations on the van der Waals binary mixture at  $\zeta_t$  yield behavior substantially identical to that found by Kaufman and Griffiths for the four-component system, suggesting that this result is a fairly general one. A phase diagram for fixed tricritical density  $\rho_t$  and mole fraction  $x_t$ , and variable temperature and  $\zeta$ , is shown in Fig. 1; we believe it to be typical of all such binary or quasibinary systems. Experimental paths are at fixed values of  $\zeta$ , and only for  $\zeta$  greater than  $\zeta_t$  does one pass through the three-phase region. At  $\zeta$  equal to or less than  $\zeta_t$ , one passes directly from two phases to one; if  $\zeta$  is exactly  $\zeta_t$ , the  $\alpha$  phase disappears precipitously at the tricritical temperature  $T_t$  (infinite slope of the phase volume versus temperature).

However, for a  $\zeta$  infinitesimally larger than  $\zeta_t$ ,

there is a very narrow three-phase region and a substantially larger two-phase region above it. Figure 2 shows our calculated phase volumes along a very nearly tricritical path, which looks quite different from the exactly tricritical path. It is possible that what Efremova and Shvarts saw in the system carbon dioxide + methanol + water was a slightly off-tricritical mixture with a three-phase region as narrow as a few millikelvins and a two-phase region above as wide as 1 K; if so, it is entirely understandable that they interpreted their results the way they did.

This research was supported in part by the National Science Foundation.

(a) Present address: Physical Chemistry 2, Chemistry Center, University of Lund, Lund 7, Sweden.

<sup>1</sup>R. B. Griffiths, *J. Chem. Phys.* **60**, 195 (1974).

<sup>2</sup>J. L. Creek, C. M. Knobler, and R. L. Scott, *J. Chem. Phys.* **74**, 3489 (1981).

<sup>3</sup>J. Specovius, M. Leiva, C. M. Knobler, and R. L. Scott, *J. Phys. Chem.* **85**, 2313 (1981).

<sup>4</sup>J. L. Creek, A. Sivaraman, J. Specovius, C. Goh, I. L. Pegg, C. M. Knobler, and R. L. Scott, in Proceedings of the Symposium on Phase Equilibria, American Institute of Chemical Engineers Meeting, Los Angeles, California, November 1982 (to be published).

<sup>5</sup>I. L. Pegg, C. M. Knobler, and R. L. Scott, *J. Phys. Chem.* **87**, 2866 (1983).

<sup>6</sup>M. Kaufman, K. K. Bardhan, and R. B. Griffiths, *Phys. Rev. Lett.* **44**, 77 (1980).

<sup>7</sup>A. Kumar, D. S. Cannell, C. Goh, C. M. Knobler, and R. L. Scott, to be published.

<sup>8</sup>M. W. Kim, W. I. Goldberg, P. Esfandiari, and J. M. H. Levelt Sengers, *J. Chem. Phys.* **71**, 4888 (1979).

<sup>9</sup>M. W. Kim, W. I. Goldberg, P. Esfandiari, J. M. H. Levelt Sengers, and E.-S. Wu, *Phys. Rev. Lett.* **44**, 80 (1980).

<sup>10</sup>P. H. van Konynenburg, Ph.D. dissertation, University of California at Los Angeles, 1968 (unpublished).

<sup>11</sup>R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.* **49**, 87 (1970).

<sup>12</sup>P. H. van Konynenburg and R. L. Scott, *Philos. Trans. Roy. Soc. London, Ser. A* **298**, 495 (1980).

<sup>13</sup>G. D. Efremova and A. V. Shvarts, *Zh. Fiz. Khim.* **40**, 907 (1969) [*Russ. J. Phys. Chem.* **40**, 486 (1969)].

<sup>14</sup>M. Kaufman and R. B. Griffiths, *J. Chem. Phys.* **76**, 1508 (1982).