the carbonium cluster ions, and the boranes. At the same time, the versatility inherent in boron cage chemistry is continually creating new opportunities to explore structural features and phenomena that are difficult to approach otherwise; for example, the construction and study of very large polyhedra, the thermal mobility of metal atoms on polyhedral surfaces, and the low-energy fusion of cage frameworks. The unfolding of these and many other facets of polyhedral metal-loborane chemistry, along with the developing ties to other areas, will be fascinating to watch.

Liquid-Liquid Critical Phenomena

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Over the last decade or so, theoreticians and experimentalists have developed a framework for understanding the behavior of matter near critical points which promises to encompass an amazing medley of phenomena.[1] The mixing and unmixing of two liquids as temperature and composition are varied is one of these phenomena—one which is of particular interest to chemists.

In thinking of liquid-liquid critical phenomena, it is useful to keep in mind the analogous liquid-gas critical phenomena. Figure 1a shows the phase diagram of a system of one component. By Gibb's phase rule for one component, there is a pressure-volume-temperature surface (shown shaded) where one phase exists and a coexistence curve (shown dashed) along which two phases (a "gas" and a "liquid") exist. As the temperature increases, the coexistence region narrows and the coexisting phases become more and more alike until, at the critical point, the two phases are indistinguishable. Figure 1b shows the projection of the coexistence curve onto the TV plane; it is this projection which we will find convenient for our analogy with liquid-liquid critical phenomena.

When another component is added, the phase rule tells us that an additional degree of freedom is gained. Thus, for a binary mixture a coexistence curve becomes a coexistence surface and a critical point becomes a line of critical points. Figure 2a shows a temperature-composition-pressure diagram for a binary liquid mixture with liquid-liquid immiscibility. We will be concerned here with constant pressure sections of this diagram, such as that shown in Figure 2b, which is analogous to Figure 1b. Below the critical point, the system consists of two coexisting liquid phases of different composition. As the temperature is raised, the two phases become more and more alike until, at the critical point, the two liquid phases are indistinguishable.

The liquid-liquid critical solution point shown in Figure 2b has an *upper* critical solution temperature (UCST)—the mixture mixes at higher temperatures and unmixes at lower temperatures. When the opposite happens—mixing at lower temperatures and unmixing at higher temperatures—the associated critical point has a *lower* critical solution temperature (LCST). Both kinds of critical points can occur in the same system, forming a closed miscibility gap. As examples, the mixture aniline + cyclohexane has an UCST at 29.5 °C, triethylamine + water has a LCST at 18.5 °C, and 2,6-lutidine + water shows both an UCST at 231 °C and a LCST at 34 °C.[2]

Let us think about what is happening at a liquid-liquid phase transition. Consider a liquid mixture at the critical composition and above its UCST: a homogeneous mixture of one liquid phase (see Figure 2b). Suppose now that the temperature is lowered toward critical. Near the critical point, the two phases are very nearly identical, so it takes little energy for small regions of one phase or the other to form in the "homogeneous" liquid. The nearer the system is to the critical point, the larger these "fluctuations" become. Within millidegrees of the critical point, the size of these fluctuation regions, termed the "correlation length" and denoted by ξ, becomes thousands of angstroms. In fact, the correlation length diverges toward infinity very close to the critical point.

This divergence of the correlation length causes the intense light scattering near critical points known as "critical opalescence". It has been found that many thermodynamic properties—compressibility, heat ca-

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(1) Reviews of critical phenomena in general can be found in: M. E. Fisher, *Rep. Prog. Phys.*, **30**, 615 (1967); P. Heller, *ibid.*, **30**, 731 (1967); L. P. Kadanoff, W. Gotze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, and J. Swift, *Rev. Mod. Phys.*, **39**, 395 (1967); H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena", Oxford University Press, New York, N.Y., 1971.

(2) Liquid-liquid miscibility gaps have been catalogued by A. W. Francis in "Liquid-Liquid Equilibrium", Interscience, New York, N.Y., 1963, and in "Critical Solution Temperatures", American Chemical Society, Washington, D.C., 1961.

Table I
Critical Exponents Describing Thermodynamic Anomalies[a]

	liquid–liquid transition	liquid–gas transition
specific heat	$C_{px} \sim \epsilon^{-\alpha}$ $\alpha_{px} \sim \epsilon^{-\alpha}$	$C_v \sim \epsilon^{-\alpha}$
order parameter	$\Delta\rho_N{}^A \sim \epsilon^\beta$	$\Delta\rho \sim \epsilon^\beta$
compressibility	$(\partial x_A/\partial\mu_A)_{p,T} \sim \epsilon^{-\gamma}$	$K_T \sim \epsilon^{-\gamma}$
pair correlation function	$G(r) \sim \dfrac{1}{r^{d-2+\eta}}$	$G(r) \sim \dfrac{1}{r^{d-2+\eta}}$
correlation length	$\xi \sim \epsilon^{-\nu}$	$\xi \sim \epsilon^{-\nu}$

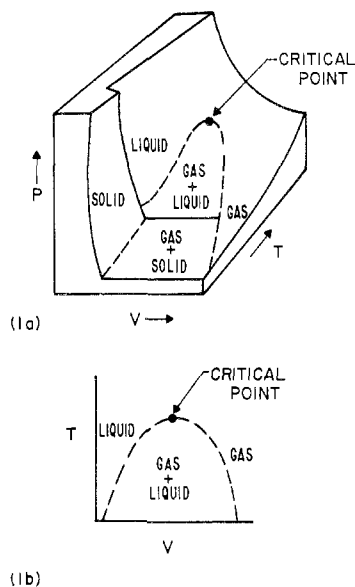[a] $\epsilon = |T - T_c|/T_c$, where T_c is the critical temperature.

Figure 1. (a) Pressure–volume–temperature surface for a pure fluid. (b) Temperature–volume projection of a pure fluid PVT surface.
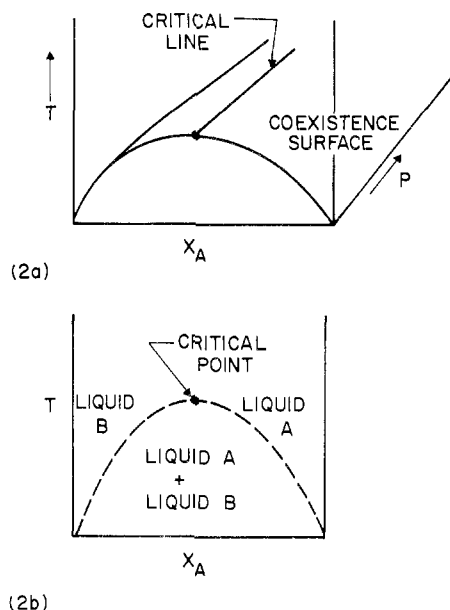

Figure 2. (a) Temperature–composition–pressure surface at a liquid–liquid phase transition. (b) Constant pressure phase diagram for a liquid–liquid phase separation. The temperature and composition at the critical point are termed the critical temperature and critical composition.

pacity, etc.—behave anomalously at critical points. *It is the postulate of the modern theories of critical phenomena that all the peculiar behavior at critical points is traceable to the divergence of the correlation*

length. From this postulate have come very successful predictions of critical behavior for a variety of types of phase transitions.

We can describe the thermodynamic anomalies near critical points by equations in which the divergence of a given property enters as a "critical exponent". These exponents are defined in Table I both for liquid–gas and for liquid–liquid transitions.[3,4] We use a reduced temperature ϵ, $\epsilon = |T_c - T|/T_c$, where T_c is the critical temperature. The "order parameter" is some quantity chosen as a measure of what is different about the two coexisting phases. As the phases become more and more alike, the order parameter gets smaller and smaller. The other quantities in the table are:

C_v	heat capacity at constant volume
C_{px}	heat capacity at constant pressure and composition
α_{px}	thermal expansion at constant pressure and composition
$\Delta\rho$	difference in mass density of coexisting phases
$\Delta\rho_N{}^A$	difference in number density of component A between coexisting phases
K_T	isothermal compressibility
$(\partial x_A/\partial\mu_A)_{P,T}$	derivative of composition with respect to chemical potential for component A
$G(r)$	pair correlation function: probability of finding a molecule at a distance r from a given molecule
d	spatial dimensionality
ξ	correlation length

Two aspects of these definitions of critical exponents must be emphasized. First, these definitions are valid close to the critical point and are not intended to apply over a large region. In order to describe behavior over an extended region, it will be necessary to add other terms in an expansion for each thermodynamic property. We must determine the range in which the exponents have their limiting values by analyzing the data for various choices of range and for various numbers of terms in the expansions.

Second, the choice of thermodynamic properties—variables—to use in these definitions is somewhat arbitrary. For example, it is possible to choose various variables or "order parameters" to describe the liq-

(3) Liquid–liquid critical phenomena have been comprehensively reviewed by R. L. Scott, *Ber. Bunsenges. Phys. Chem.*, **76**, 296 (1972), and in *Spec. Period. Rep. Chem. Thermodyn.*, **2**, in press. See also B. Chu, *J. Stat. Phys.*, **6**, 173 (1972), and *Ber. Bunsenges. Phys. Chem.*, **76**, 202 (1972).

(4) Fluid critical phenomena in general have been reviewed by J. V. Sengers and J. M. H. Levelt Sengers, *Prog. Liquid Phys.*, 103–174 (1978). A "popular" exposition was given by A. L. Sengers, R. Hocken, and J. V. Sengers, *Phys. Today*, **30**, 42 (1977).

Table II
Comparison of Experiment and Theory for Equilibrium Critical Exponents[a]

	theory		experiment	binary liquid mixtures	
exponent	RG[b]	series[c]	pure fluids[d]	nitroethane + 3-methylpentane	isobutyric acid + water
α	(0.1098 ± 0.0022)	0.125 ± 0.020	$(0.08-0.11)$	0.12 ± 0.06^e	$0.08-0.14^h$
β	(0.325 ± 0.001)	0.312 ± 0.005	$0.321-0.329$	0.330 ± 0.018^f	0.328 ± 0.004^i
γ	1.2402 ± 0.0009	$1.250 + 0.003, -0.007$	$1.23-1.28$	$(1.241 \pm 0.023)^g$	1.24 ± 0.05^j
ν	0.6300 ± 0.008	$0.638 + 0.002, -0.008$	$(0.62-0.64)$	0.625 ± 0.009^g	0.615 ± 0.015^h
η	0.0315 ± 0.0024	$(0.041 + 0.017, -0.030)$	$(0.0-0.05)$	0.016 ± 0.021^g	(0.016 ± 0.10)
asymptotic range			$e < 10^{-4}$	$e < 10^{-3}-10^{-2}$	

[a] Values in parentheses were calculated from the other exponent values using scaling relations. Experimental uncertainties are given as three standard deviations. Theoretical values refer to renormalization group (RG) methods and series estimates for lattice models. [b] Le Guillou and Zinn-Justin, ref 11. [c] Domb, Camp, et al., ref 10. [d] Hocken and Moldover, ref 12. [e] Greer and Hocken, ref 13. [f] Wims et al., ref 14. [g] Chang et al., ref 15. [h] Morrison and Knobler, ref 16. [i] Greer, ref 17. [j] Chu et al., ref 18. [k] Chu et al., ref 19.

uid–liquid coexistence curve, including the difference between coexisting phases in mole fraction of component A, Δx_A, or the difference in mass density, $\Delta \rho$. In some region close to the critical point, the exponent describing a given property should be the same regardless of the choice of variables. Some variables, however, can be expected to show the limiting behavior over a larger region than others and are therefore to be preferred. The effort has been to choose those variables which seem to give the simplest, most symmetric behavior over the largest region of the phase diagram, while one is guided by the theories[5] in that choice.

The theoretical approach to the understanding of critical phenomena has developed at a fast pace over the last 10 years[6] and reached a new plateau in 1971 in the renormalization group (RG) theory of Kenneth G. Wilson.[7] The RG theory is a truly statistical mechanical theory of critical phenomena, which starts with a microscopic Hamiltonian for the system.[8] The theory then assumes that, close enough to a critical point, the correlation length becomes so large that the behavior of the system is independent of the choice of the length scale. Group operations are applied to find the circumstances under which this scale invariance is obtained. The equations for these operations then contain a phenomenal amount of information about the critical behavior.

The first result of the RG theory is that critical phenomena in isotropic systems can be grouped into classes—"universality classes"—which are determined, quite simply, by the spatial dimension, d, and the spin dimension, D. The "spin dimension" is, in the language of magnets, the dimension of a vector representing the possible values of the spin. As a magnetic spin can either be "up" or "down", a mixture molecule can either be "A" or "B". Thus, for liquid–gas critical points and

for liquid–liquid critical points, $d = 3$ and $D = 1$, and these cases belong to the same universality class. Moreover, even a lattice model[9,10] for these phase transitions will belong to this universality class.

Second, for all systems in a given universality class, the critical exponents are predicted to be the same and, with certain mathematical approximations, can actually be calculated with the RG theory. The most recent such calculations of exponent values[11] are given in the second column of Table II. We note that these values are not quite the same as those calculated for the lattice models by series expansion techniques[10] (third column, Table II).

Third, RG theory shows (as had earlier phenomenological theories[20]) that the critical exponents are related to one another:

$$\alpha = \alpha'$$

$$\gamma = \gamma'$$

$$\nu = \nu'$$

$$2 - \alpha = \gamma + 2\beta$$

(5) J. J. Rehr and N. D. Mermin, *Phys. Rev. A*, 8, 472 (1973); R. B. Griffiths and J. C. Wheeler, *ibid.*, 2, 1047 (1970).
(6) The "Bible" for the theory of critical phenomena is the series of volumes "Phase Transitions and Critical Phenomena", C. Domb and M. S. Green, Ed., Academic Press, New York, N.Y.
(7) K. G. Wilson, *Phys. Rev. B*, 4, 3174 (1971); K. G. Wilson, *ibid.*, 4, 3184 (1971); K. G. Wilson and J. Kogut, *Phys. Rep.*, 12, 75 (1974).
(8) Among the most readable accounts of RG theory are S.-K. Ma, "Modern Theory of Critical Phenomena", W. A. Benjamin, Reading, Mass., 1976, and R. Balescu, "Equilirium and Nonequilibrium Statistical Mechanics", Wiley, New York, N.Y., 1975.
(9) T. D. Lee and C. N. Yang, *Phys. Rev.*, 87, 410 (1952).
(10) C. Domb in ref 6, Vol. 3, 1974, p 434; W. J. Camp, D. M. Saul, J. P. Van Dyke, and M. Wortis, *Phys. Rev. B*, 14, 3990 (1976); P. H. E. Meijer and R. A. Farrell, *ibid.*, 12, 243 (1975); M. A. Moore, D. Jasnow, and M. Wortis, *Phys. Rev. Lett.*, 22, 940 (1969).
(11) J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. Lett.*, 39, 95 (1977). See also G. A. Baker, Jr., B. G. Nickel, M. S. Green, and D. I. Meiron, 36, 1351 (1976); G. R. Golner and E. R. Riedel, *Phys. Lett. A*, 58, 11 (1976); L. P. Kadanoff, A. Houghton, and M. C. Yalabik, *J. Stat. Phys.*, 14, 171 (1976).
(12) R. Hocken and M. R. Moldover, *Phys. Rev. Lett.*, 37, 29 (1976).
(13) S. C. Greer and R. Hocken, *J. Chem. Phys.*, 63, 5067 (1975).
(14) A. M. Wims, D. McIntyre, and F. Hynne, *J. Chem. Phys.*, 50, 616 (1969). The data were reanalyzed by J. Reeder, T. E. Block, and C. M. Knobler, *J. Chem. Thermodyn.*, 8, 133 (1976).
(15) R. F. Chang, H. Burstyn, J. V. Sengers, and A. J. Bray, *Phys. Rev. Lett.*, 37, 1481 (1976). The errors given in this paper are probably overestimated; the authors are preparing a more detailed data analysis.
(16) G. Morrison and C. M. Knobler, *J. Chem. Phys.*, 65, 5507 (1976). See also H. Klein and D. Woermann, *ibid.*, 62, 2913 (1975).
(17) S. C. Greer, *Phys. Rev.*, 14, 1770 (1976); T. S. Venkataraman and L. M. Narducci, *J. Phys. C*, 10, 2849 (1977), report measurements on the same system which are less precise and are in the variable mass fraction. The work has been extended to a deuterated mixture in S. C. Greer, *Ber. Bunsenges. Phys. Chem.*, 81, 1079 (1977).
(18) B. Chu, F. J. Schoenes, and W. P. Kao, *J. Am. Chem. Soc.*, 90, 3042 (1968).
(19) B. Chu, S. P. Lee, and W. T. Scharnuter, *Phys. Rev. A*, 7, 353 (1973).
(20) B. Widom, *J. Chem. Phys.*, 43, 3892 (1965); B. Widom, *ibid.*, 43, 3898 (1965); L. P. Kadanoff, *Physics*, 2, 263 (1966).

$$(2 - \eta)\nu = \gamma$$

$$d\nu = 2 - \alpha$$

The "primed" numbers refer to temperatures such that $T < T_c$ and the "unprimed" to $T > T_c$. Two exponents from the set α, β, and γ are sufficient to describe the thermodynamic anomalies. The exponents η and ν describe the correlation function; the sixth equality given above relates γ to η and ν. The last equation, the "hyperscaling" relation,[20,21] relates a thermodynamic exponent, a correlation function exponent, and the spatial dimensionality.

Fourth, RG theory can be used to calculate the values of exponents for correction terms outside the "asymptotic" critical region. The universal exponential behavior pertains only to an "asymptotic" region (of theoretically undetermined size) very near the critical point. Beyond that region, correction terms are needed to describe the physical behavior. The exponents of these terms (but not yet their coefficients) can be calculated by RG theory.[11,22]

Recent Experimental Work

It has been the aim in our laboratory in the last few years to seek to test these theoretical predictions against the critical behavior of binary liquid mixtures. Let us first list here the criteria for selecting those experiments which will give the most reliable comparison with theory.

First, the measurements should not be susceptible to spurious effects due to gravity. It has long been understood[1] that gravity effects are significant at the liquid–gas critical point. The divergence of the compressibility of a fluid near the liquid–gas critical point results in a variation of fluid density along the height of a sample. The inhomogeneity of the sample is, then, a major factor in the experimental design and analysis. At equilibrium near a liquid–liquid critical point, similar density and composition gradients should develop due to the divergence of $(\partial x_A/\partial \mu_A)_{P,T}$[23,24] and have, in fact, been reported.[23,25,26] However, most investigators have ignored the gradients in binary liquid mixtures, assuming that the slow diffusion and long equilibrium times near a critical point would mean that no significant gradients develop on an experimental time scale.

More recently, it has been learned that significant *nonequilibrium* gradients can develop at liquid–liquid critical points in the time it takes to do an experiment.[26–28] These nonequilibrium gradients are due to pressure diffusion or sedimentation in the earth's gravitational field. The method we used for studying sedimentation was magnetic densimetry,[29] a technique
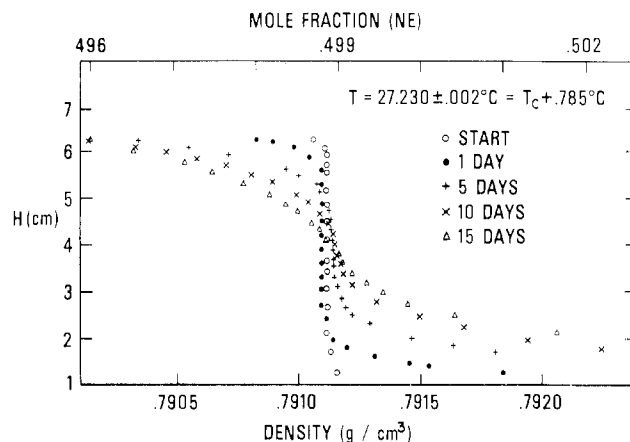
Figure 3. The development of density gradients due to sedimentation in the mixture nitroethane (NE) + 3-methylpentane. The vertical axis is the height in a sample with a total height of 7.6 cm. See text and ref 28.

which we have found valuable not only for studies of gravity effects but also for studying thermal expansions[13] and coexistence curves[17] in these liquid mixtures. In this technique, a magnetic buoy is suspended in the liquid by means of a servocontrolled solenoid. The solenoid current required to suspend the buoy is a very precise measure of the fluid density. The liquid sample can then be moved relative to the buoy and density measured as a function of sample height. Figure 3 shows are measurements of sedimentation in the mixture nitroethane + 3-methylpentane at an average composition which is the critical one and at a temperature about 0.8 °C above critical.[28] The sample was stirred until homogeneous, then its mass density as a function of height was monitored over 2 weeks. The nature of the sedimentation profile can be explained by consideration of the flux equation, including terms due to a composition gradient and due to a pressure gradient.[26–28] Such inhomogeneities can certainly affect experimental results, as we saw in our measurement of the thermal expansion anomaly in nitroethane + 3-methylpentane.[13] The measurement of this anomaly depended upon the sample history and ultimately was limited by gravity effects. (In fact, difficulties in our thermal expansion measurement led us *accidentally* to a discovery of the sedimentation phenomenon!)

For binary liquid mixtures there is a solution to the gravity problem—as much of a solution as one could hope for on this earth. Namely, the magnitude of the gravity effects (equilibrium and nonequilibrium) can be minimized by a judicious choice of the mixture.[24] We can, therefore, choose for examination systems for which the gravity effects are smaller than the experimental resolution. For some techniques (e.g., light scattering), the measurement can be made near the middle of the sample and over a sufficiently small height that gravity effects are negligible.

The second criterion for experiments is that the data extend into the "asymptotic" region. As was mentioned above, the critical exponents can be expected to have their theoretical values only very close to the critical point and the size of the region of limiting behavior can

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(24) A. A. Fannin, Jr., and C. M. Knobler, *Chem. Phys. Lett.*, **25**, 92 (1974); L. Mistura, *J. Chem. Phys.*, **55**, 2375 (1971).

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be expected to depend upon the variables chosen. So far we do not know how to choose the best variables a priori, but must depend on trial and error. For coexistence curves, for example, we try to find those variables which give the most symmetric curve. For liquid–liquid critical points we have found[17,30,31] that the experimental variable which gives the most symmetric coexistence curve is the volume fraction[30] $\phi_A = V_A/(V_A + V_B)$, where V_A is the volume of component A and V_B that of component B. We choose volume fraction, therefore, because any other order parameter for a liquid–liquid coexistence curve produces a less symmetric coexistence curve, exponents which do not have the limiting values, and a need for more terms to fit the data satisfactorily.

Before we consider the experimental results for liquid mixtures, let us briefly mention the experimental evidence on liquid–gas critical points. Most data within 0.01–10 °C of pure fluid critical points have yielded exponents distinctly different from the theoretical values, either by series or RG calculations.[32] For example, the usual value obtained for β has been 0.35. More recent work has revealed that the typical measurements are outside the "asymptotic" region, that when the data are within $\epsilon < 10^{-4}$, the RG values are indeed obtained. This work was pioneered by L. R. Wilcox and his collaborators[33] with an interferometric technique which uses the density gradient due to gravity as a measure of the fluid equation-of-state. This technique, which *takes advantage* of the gravity effect, combined with remarkably fine temperature control, has resulted in the exponents shown[12] in the fourth column of Table II. We can see that these experiments are in quite good agreement with the theory, especially with the RG theory. Thus for liquid–gas critical points, while the series values and the "older" experiments were in clear disagreement, the RG values and the newest experiments agree quite nicely.

The experimental investigation of liquid–liquid critical phenomena is in some ways simpler than that of liquid–gas critical phenomena. First, as was described above, gravity effects can be minimized. Second, the phase transitions can be studied at near room temperature and at atmospheric or vapor pressure. Third, we have some evidence that the range of "asymptotic" critical behavior is somewhat larger in temperature ($\epsilon < 10^{-2}$) for liquid–liquid critical points than for liquid–gas critical points.[17]

Two binary mixtures—nitroethane + 3-methylpentane and isobutyric acid + water—have been studied extensively enough that several exponents have been independently determined. The exponent values for these systems are given in the last two columns of Table II. These are the data which best satisfy our criteria with respect to gravity effects and choice of variables and which, in addition, have sufficient precision to make their comparison with theory mean-
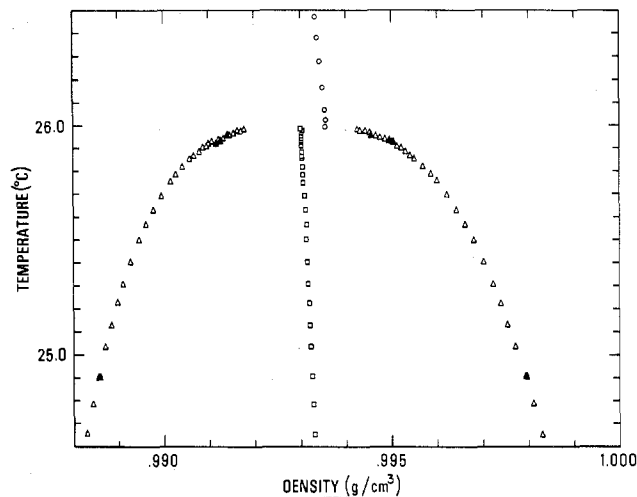
Figure 4. Coexistence curve of isobutyric acid + water: coexisting mass densities (▲, △), average densities of coexisting phases ("diameter" of the coexistence curve) (□), and densities in the one-phase region (○). The diameter and the densities in the one-phase region would coincide at the critical point if the sample were precisely at the critical composition. See ref 17.

ingful. Let us consider each of these exponent determinations.

The determination of the exponent α has always been difficult because the heat capacity is hard to measure.[3,34] The most successful measures of α—those given in Table II—were made by measuring instead the thermal expansion, by magnetic densimetry[13] and by dilatometry.[16] The values for α agree within error with both series and RG calculations.

The exponent β is the best determined exponent for binary mixtures in that it has been measured with precision for several mixtures by several methods. Both values given in Table II were obtained from magnetic densimeter measurements of coexisting mass densities which were then converted to volume fractions. Figure 4 shows our data on the coexistence curve of isobutyric acid + water. The coexistence curve can also be determined by visual observation of the transition temperatures of a number of mixture samples of different compositions[35] or by optical techniques in which the refractive index serves as a measure of volume fraction.[36,37] Several reliable β determinations are available other than the two in Table II: carbon disulfide + nitroethane[17,35] 0.316 ± 0.008; aniline + cyclohexane[36] 0.328 ± 0.007; methanol + cyclohexane[37] 0.326 ± 0.003. Altogether, the β determinations for binary liquid mixtures agree well with the RG calculations and do not agree with the series calculation.

The exponents γ, ν, and η are obtained from measurements of the intensity of radiation (usually light)

(30) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions", Van Nostrand Reinhold, New York, N.Y., 1970, pp 169–172, and references therein.

(31) A. Stein and G. F. Allen, *J. Phys. Chem. Ref. Data*, **2**, 443 (1974).

(32) J. M. H. Levelt Sengers, *Physica*, **73**, 73 (1974); J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, *J. Phys. Chem. Ref. Data*, **5**, 1 (1976); J. M. H. Levelt Sengers and J. V. Sengers, *Phys. Rev. A*, **12**, 2622 (1975).

(33) L. R. Wilcox and D. Balzarini, *J. Chem. Phys.*, **48**, 753 (1968); W. T. Estler, R. Hocken, T. Charlton, and L. R. Wilcox, *Phys. Rev. A*, **12**, 2118 (1975).

(34) P. Calmettes and C. Laj (*Phys. Rev. Lett.*, **36**, 1372 (1976)) determined α from the relaxation time of entropy fluctuations in nitroethane + 3-methylpentane to be 0.059 ± 0.006. This value is low compared to other experiments and to the theory. The exponent was determined in a fit of a two-term exponential with both exponents free, whereas a better technique would have been to fix the other exponent (see F. S. Acton, "Numerical Methods That Work", Harper and Row, New York, N.Y., 1970, p 253).

(35) E. S. R. Gopal, R. Ramachandra, and P. Chandra Sekhan, *Pramana*, **1**, 260 (1973); E. S. R. Gopal, R. Ramachandra, P Chandra Sekhan, K. Govindarajun, and S. V. Subramanyam, *Phys. Rev. Lett.*, **32**, 284 (1974); E. S. R. Gopal, P. Chandra Sekhar, G. Ananthakrishna, R. Ramachandra, and S. V. Subramanyam, *Proc. R. Soc. London, Ser. A.*, **350**, 91 (1976).

(36) D. A. Balzarini, *Can. J. Chem.*, **52**, 499 (1974).

(37) D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, *Chem. Phys.*, **20**, 219 (1977).

scattered by composition fluctuations near the critical point.[3,4] Many such measurements have been made on liquid mixtures;[3] we choose to include in Table II only some which meet our selection criteria with regard to precision and to the absence of, or correction for, gravity effects. One other notable measurement, in addition to those in Table II, is: nitrobenzene + *n*-hexane[38] ν = 0.630 ± 0.005, γ = 1.228 ± 0.006. The exponent η is the one for which we have the least experimental information, even for pure fluids.[39] Because it is so small, its determination is difficult. We see from Table II that the evidence on γ, ν, and η is consistent with the theoretical values and is somewhat closer to the RG values than to the series values.

In summary, Table II shows that pure fluid liquid–gas critical points and binary mixture liquid–liquid critical points have the exponents predicted by the renormalization group theory. We can also see that, where we have independent measurements of exponents, the exponent values are consistent within probable error with the scaling relations predicted to hold between them.

Having confirmed the validity of the RG theory in the "asymptotic" critical region, we can consider the extension of the analysis to a region further from the critical point. Wegner[22] has worked out an asymptotic series expansion for critical behavior, and Ley-Coo and Green[40] have translated Wegner's expansion into the terminology of fluids. Ley-Coo and Green tested this expansion on the coexistence curve data of SF$_6$,[41] and the expansion has been successfully applied to the equation of state of H$_2$O.[42] The only liquid–liquid data set for which there is sufficient range and precision to test the Wegner expansion is that of Gopal et al. on the coexistence curve of carbon disulfide + nitromethane,[35] which extends 60 °C from T_c. We[17] have fitted Gopal's data to Wegner's series. When terms with similar exponents are collected, the Wegner expansion for a coexistence curve can be written:

$$\frac{\Delta\rho}{2\rho_c} = B_0\epsilon^\beta[1 + B_1\epsilon^{\Delta_1} + B_2\epsilon^{2\Delta_1} + \cdots]$$

Here $\Delta\rho$ is the difference in order parameter between

Table III
Parameters to Fits to the Wegner Expansion for the Coexistence Curves of SF$_6$ and Carbon Disulfide + Nitroethane[a]

	SF$_6$[b]	carbon disulfide + nitromethane[c]
range	$\epsilon < 0.002$	$\epsilon < 0.2$
β	0.327 ± 0.009	0.316 ± 0.008
B_0	1.72 ± 0.06	1.63 ± 0.09
B_1	0.48 ± 0.12	0.47 ± 0.19
B_2	−0.84 ± 0.72	−1.5 ± 0.3

[a] The expansion is: $\Delta\rho/2\rho_c = B_0\epsilon^\beta[1 + B_1\epsilon^{\Delta_1} + B_2\epsilon^{2\Delta_1} + \ldots]$, where $\Delta_1 = 0.50$. Errors are given as 3σ. [b] Ley-Coo and Green, ref 40. [c] Greer, ref 17.

coexisting phases (mass density for a liquid–gas critical point and volume fraction for a liquid–liquid critical point), ρ_c is the critical value of the order parameter, and Δ_1 is a correction exponent, the value of which is very close to 0.5.[11] For $\Delta_1 = 0.5$, β and the remaining coefficients can be found by a least-squares analysis. The results for SF$_6$ and for carbon disulfide + nitromethane are given in Table III. The data for both systems can be fitted within their uncertainty to the Wegner expansion and the values obtained for β are consistent with RG theory.

Conclusions

We conclude that the experimental data on liquid–liquid critical points confirm the renormalization group theory and support the assumption that, very close to a critical point, the behavior is determined by the long-range nature of the correlation length. Furthermore, the experimental evidence is consistent with the theoretical predictions for extensions beyond the "asymptotic" region.

Several questions remain unresolved. We need a better understanding of the size of the region of Ising-like behavior in real fluids. We require both theoretical attacks on the calculation of this regime and careful consideration of the experimental evidence, especially as to differences between liquid–gas and liquid–liquid critical regions. We have no logical approach to the choice of liquid–liquid order parameter. There is already considerable interest in developing better expansions for analyzing the behavior over a broad range.[43] We can also expect further work to resolve the discrepancies between series and RG calculations of exponent values.

It seems that we now know a great deal about what is *alike* for various critical points and we are beginning to focus on what is *different* about various critical points. This is evidence of the maturation that has occurred in the field of critical phenomena.

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