

and the resistor, the fields in  $S'$  due to remote sources are  $\mathbf{B}' = \mathbf{j}B'_0$  and  $\mathbf{E}' = 0$  for all finite values of  $x'$ ,  $y'$ , and  $z'$ .

#### IV. CONCLUSIONS

The results summarized in Table I confirm that consistent solutions for the induced current can be obtained with the aid of Faraday's law for the simple situations considered here. The induced current is interpreted as the conduction current in the resistor. The effects of self-inductance have been neglected. In each case, the magnetic flux density between the tracks in  $S$  is greater than the magnetic flux density between the tracks in  $S'$  by the factor  $\gamma$  (because the electric field between the tracks in  $S'$  is always zero). The resistor current  $I$  in  $S$ , the system in which the resistor is at rest, is related to the resistor current  $I'$  in  $S'$  by  $I = \gamma I'$ . Similarly, the bar current  $I'_b$  in  $S'$ , the system in which the bar is at rest, is related to the bar current  $I_b$  in  $S$  by  $I'_b = \gamma I_b$ . Also,  $P$ , the power dissipation in the resistor in  $S$ , is related to  $P'$ , the power dissipation in the  $S'$ , by  $P = \gamma^2 P'$ . An observer in motion with respect to the tracks may perceive a convection current and a charge density due to the induced current in the tracks, in addition to the induced conduction current.

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<sup>10</sup>If the self-inductance of the circuit is included, the current in  $S$  is

$$I \cong \frac{vB_0 l}{R(1 + \mu_0 v l / R w)}$$

In this paper it will be assumed that the resistance  $R$  is so large that  $\mu_0 v l / R w \ll 1$  and, consequently, that effects due to self-inductance can be neglected.

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## Undergraduate experiment in critical phenomena. II. The coexistence curve of a binary fluid mixture

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An undergraduate experiment is described that uses meniscus heights to determine the coexistence curve of a binary fluid mixture. The data can be obtained with a minimum of equipment and yield results that are easily interpreted by the theory also presented. Data taken on the binary liquid mixture methanol–isooctane are presented and analyzed. The critical temperature and composition were found to be  $(42.5 \pm 0.5)^\circ\text{C}$  and  $(67.3 \pm 0.2)\%$  by volume isooctane, respectively.

### I. INTRODUCTION

Critical phenomena occur in a very diverse set of systems when they approach a second-order phase transition. The behavior of different systems close to their critical points can be described with the same mathematics: a universality that provides a powerful insight into a system's behavior. Thus the behavior of many events across the disciplines of physics can be viewed as part of a common process. Such

events occur<sup>1,2</sup> in many-particle production in high energy physics, isotopic yields in nuclear physics, liquid helium, mixtures of metals in alloys, mixtures of fluids, a one-component gas at its critical point, ferromagnetism, structural phase transitions, polymers in solution, biophysics, and others.

That so many disparate fields can have similar behavior near a systems' "critical point" indicates an overall symmetry in the interaction which masks the identity of the objects. Wilson showed<sup>3</sup> in 1971 that critical phenomena

obey a scale symmetry called the renormalization group; he won the Nobel prize for this work in 1982. This symmetry approach can give relationships between quantities, but not predict an actual value unless a model is introduced. The discussion below is for a system falling under the Ising model which describes liquid-gas systems, ferromagnetism, and binary fluid mixtures.

The type of phenomena considered here is a binary fluid mixture—two fluid components which are only partially miscible below a certain temperature, but completely miscible in all proportions above that temperature called the critical temperature. (A few mixtures mix below the critical temperature, but not above. These will not be considered here, although they are trivially related.) A binary fluid mixture is chosen for study due to the simplicity of sample preparation and the ease of temperature control. Binary fluid mixtures exhibiting a second-order phase transition (mixing to partial mixing) have small pressure effects so that the sample can be prepared at atmospheric pressure. Many mixtures can be prepared from commercially available, already purified fluids. Finally, many binary fluid mixtures have a critical temperature only slightly above room temperature. The insight obtained from studying a near-critical binary fluid mixture can give information on how other systems behave near their critical points because of universality.

The property studied here is the degree of miscibility of the two components below the critical point and is called the coexistence curve. This curve is universal<sup>4</sup> when scaled variables are used. For a binary fluid mixture, the proper variables are the fluid temperature as a function of the order parameter. The order parameter usually chosen in binary fluid mixtures is volume fraction.<sup>2</sup> Each parameter is scaled by dividing by its value at the critical point.

Most coexistence curves are studied by one of three techniques: (1) Many vials can be prepared with different compositions of the two components. The vials are placed in a temperature controlled bath and the temperature where each vial changes from two phases to one is noted.<sup>5</sup> The locus of these transition temperatures forms the coexistence curve, with the maximum temperature closest to the critical temperature. (2) One sample can be prepared and the density of each phase can be monitored to determine the relative composition as the temperature is varied.<sup>6</sup> If the sample is prepared close to the critical composition, then the system can closely approach the critical point. (3) One sample can be prepared and the refractive index, a nonintrusive technique, can be used to determine the composition of each phase at various temperatures.<sup>7</sup>

This paper's procedure, described more fully below, differs from these other techniques by directly using the motion of the meniscus to infer the mutual miscibility. Although the meniscus motion is not as accurate as density or refractive index measurements, its ease and simplicity make it ideal for an undergraduate experiment.

The meniscus motion provides a very simple experiment on a binary fluid mixture below its critical point. The degree of mixing of the two components can be determined by measuring the height of the liquid-liquid and liquid-gas menisci as the composition and temperature are varied. This is a very easy measurement, yet it provides information on the shape of the coexistence curve. The experiment presented here complements another experiment describing the approach to the critical point from above the critical temperature.<sup>8</sup>

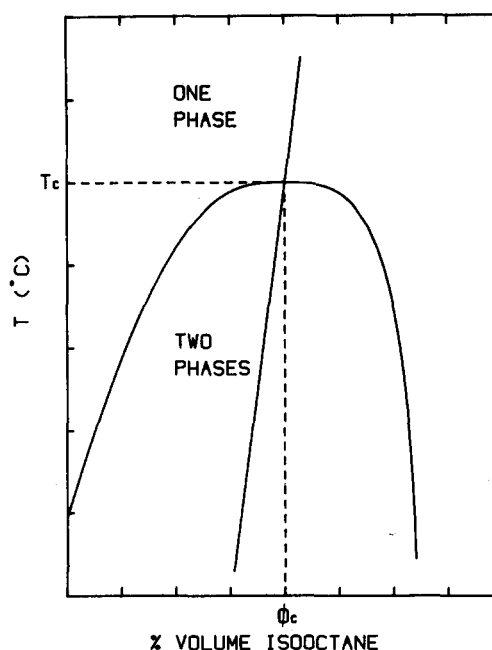


Fig. 1. The coexistence curve of a binary fluid mixture. The system is a homogeneous one-phase mixture at temperatures  $T$ , higher than the critical temperature  $T_c$ , for any composition  $\phi_A$ . The system is two-phase for compositions and temperatures within the (roughly) cubic boundary that is the coexistence curve. For systems where  $\phi_A$  is the composition of the more dense phase, then the right-hand branch of the cubic boundary is the locus of compositions of the upper phase. The maximum of the coexistence curve is the critical point defined by the critical composition  $\phi_c$ , and by  $T_c$ . The straight line above the critical point is the one-phase composition as a function of temperature; a finite slope exists because of volume expansion of the fluids. The solid straight line below the critical point is the average composition  $\bar{\phi}$  of the upper and lower phases.

## II. THEORY

The coexistence curve measures the degree of mixing of the two components in the mixture and is illustrated in Fig. 1. Above the critical temperature the two components mix completely in any proportion and provide a one-phase sample. Below this temperature two phases form—an upper phase over a lower phase. The lower phase will be rich in the more dense component while the upper phase is rich in the other component. Each phase has some of each component in it. The relative amount indicates the degree of mixing or coexistence of the two components.

As the temperature of this two-phase system is increased, the two phases become more similar in composition until a transition temperature resulting in a one-phase system is reached. The transition temperature is less than or equal to the critical temperature; there is a unique composition called the critical composition which results in the highest transition temperature. The point on the top of the coexistence curve is called the critical point and is characterized by the critical composition  $\phi_c$  and critical temperature  $T_c$ . These parameters are unique to a given system; however, by studying the behavior around the critical point, universal quantities can be observed.

An example is the shape of the coexistence curve. The Ising model in a renormalization group setting predicts the shape when close to the critical point as given by<sup>2</sup>

$$\phi_U - \phi_L = B [(T_c - T)/T_c]^\beta, \quad (1)$$

where  $\phi_{U(L)}$  is the composition of component  $A$  in the upper (lower) phase at a temperature  $T$ ,  $T_c$  is the critical temperature,  $B$  is an amplitude dependent on the sample, and  $\beta$  is a universal critical exponent predicted<sup>2</sup> to be  $0.327 \pm 0.003$ .

The average composition of the upper and lower phase as a function of temperature is called the diameter of the curve. This diameter is expected to be linear in temperature and have only a very small anomaly when the system is very close to the critical point.<sup>2</sup> This anomaly in the diameter will be neglected in this treatment. Thus

$$\phi_U + \phi_L = 2\bar{\phi}, \quad (2)$$

where  $\bar{\phi}$  is the average composition. Equations (1) and (2) can be combined to give

$$\bar{\phi} - \phi_L = Bt^\beta/2. \quad (3)$$

The volume fraction of the upper phase,  $\phi_U$ , is defined as the volume of component  $A$  in the upper phase  $V_U^A$ , divided by the total volume of the upper phase  $V_U$ . A similar definition can be given for the volume fraction of the lower phase  $\phi_L$ :

$$\phi_L = V_L^A/V_L. \quad (4)$$

A negligible loss of volume upon mixing is assumed so that

$$V_U^A + V_L^A = V^A$$

and

$$V_U + V_L = V,$$

where  $V^A$  is the total volume of component  $A$  placed in the cell out of the total fluid volume  $V$ . The prepared composition  $\phi_A$  is just  $\phi_A = V^A/V$ .

For a cell of constant cross-sectional area, the height  $h_m$ , measured from the bottom of the cell to the meniscus between the phases, divided by the total height of fluid  $h_t$ , is just  $h_m/h_t = V_L/V$ .

This can be used to develop a relation between the measured meniscus heights and the prepared composition as a function of temperature. From Eq. (2),  $\phi_U$  can just be written as

$$2\bar{\phi} - \phi_L = V_U^A/V_U,$$

which, using Eq. (4), becomes

$$\begin{aligned} 2\bar{\phi} - \phi_L &= \frac{V_U^A - V_L^A}{V - V_L} \\ &= \left[ \left( \frac{V^A}{V} \right) \left( \frac{V}{V_L} \right) - \phi_L \right] / \left( \frac{V}{V_L} - 1 \right). \end{aligned}$$

Using  $h_m/h_t = V_L/V$  and Eq. (3), the final result is obtained:

$$h_m/h_t = t^{-\beta}(\phi_A - \bar{\phi})/B + \frac{1}{2}. \quad (5)$$

The term  $\bar{\phi}$  is expected to vary, at most, linearly with temperature (neglecting the small anomaly discussed earlier) so that the critical composition can be determined by extrapolating  $\bar{\phi}$  to  $T_c$ . Equation (5) will be used to understand the data described in Sec. III.

### III. THE EXPERIMENT

The assumptions leading to Eq. (5) have been well verified experimentally.<sup>2</sup> Equation (1), which is often described as simple scaling, quite adequately describes coexistence curves of binary fluid mixtures when within 10 °C of

critical. A linear diameter has also been observed to hold for such systems over a similar range of temperatures.

This experiment will involve a simple technique for determining the critical exponent  $\beta$  and the critical parameters  $T_c$  and  $\phi_c$ . Several cylindrical vials are filled with different compositions of a binary mixture and then sealed. A length scale is affixed to each vial and they are immersed in a temperature controlled water bath. The meniscus heights in each vial are recorded at different temperatures.

The cells are simple cylindrical, 8-dram (30 ml), vials with polypropylene coned caps. Five vials were filled with varying compositions of the binary fluid mixture and sealed. The cells stayed sealed and provided reproducible results after immersion in the water bath for two days. A commercially available adhesive tape with millimeter scribes was placed on the side of each vial to determine menisci heights. Alignment errors were taken into account in recording the heights.

The system studied was the binary fluid mixture methanol-isooctane. This system was chosen to provide essential data for a separate experiment being studied. These fluids are readily available in a pure form ("spectroscopic" quality) and were used without further purification. The samples reported here were prepared simultaneously in a dry box to insure a uniformity of components. However, a dry box is not essential, provided all the vials have equal access to moisture in the air which can shift the critical temperature and composition.<sup>9</sup> The composition  $\phi_A$  of isooctane in the isooctane-methanol mixtures varied from 50%–66.7% by volume over the five vials.

The sealed vials were then placed in a temperature controlled water bath. The bath was a rectangularly shaped glass container, while the temperature control was provided by a HAAKE R21 unit. Temperatures below ambient were obtained by simultaneously using a FTS LC-20 cold finger.

The procedure for taking a data point required the bath

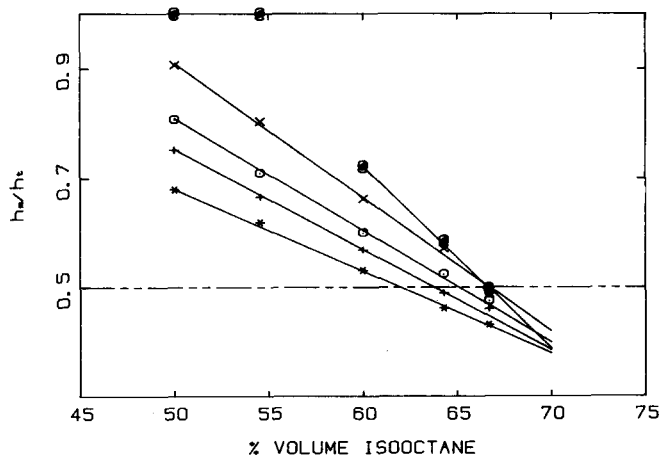


Fig. 2. The ratio of the height of the meniscus between the upper and lower phases  $h_m$  to the total height of fluid  $h_t$  is plotted as a function of composition  $\phi_A$  of isooctance in the binary fluid mixture methanol-isooctane. Data point errors are contained within the symbols used in this plot. Straight lines fit the points at a fixed temperature, as predicted in Eq. (5). The value of  $\phi_A$  when  $h_m/h_t = 0.5$  is the average composition  $\bar{\phi}$ , and values taken from this graph are used in Fig. 3. The slopes of the lines are used to form Fig. 4. \*, 13.0 °C; +, 23.5 °C; O, 30.0 °C; X, 36.5 °C; @, 40.0 °C.

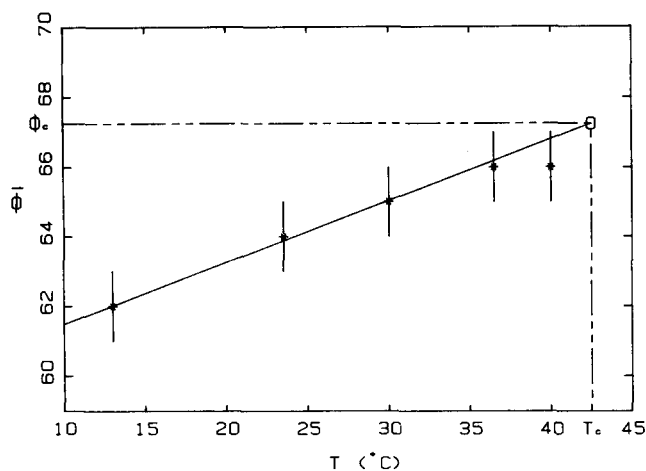


Fig. 3. The average composition  $\bar{\phi}$  as determined from Fig. 2 are plotted as a function of temperature  $T$ . The linearity of these points is consistent with theoretical assumptions used in the text and shown in Fig. 1. The endpoint of the line is the critical point and determines  $T_c$  and  $\phi_c$ .

to be stable in temperature and then to shake the vials to assure uniform mixing. The phases were allowed to form and clear before the menisci heights were read off the scale attached to each vial. The temperature was measured with a mercury thermometer. The temperature was then changed and the process repeated. The ratio of the menisci heights in each vial is presented in Fig. 2.

#### IV. DISCUSSION AND ANALYSIS

The data shown in Fig. 2 have error that include both systematic and random errors. Sources of systematic error include the nonuniform diameter of the vials, scale placement and calibration, and temperature accuracy.

As can be seen in Fig. 2, the theory agrees quite well with the data. The qualitative dependence shows a height ratio of 1 or 0 when the system is in the one-phase region. (See Fig. 1.) This changes abruptly as the two-phase region is encountered. In the two-phase region, each temperature shows the expected linear behavior of  $h_m/h_t$  versus  $\phi_A$ , with slopes increasing as the critical temperature is approached. The lines do not intersect at a common point, which indicates that the diameter of the coexistence curve has a temperature dependence and that the average composition,  $\bar{\phi}$ , will be the critical composition only at the critical temperature. This is shown in Fig. 3, where  $\bar{\phi}$  is determined from the value of  $\phi_A$  when  $h_m/h_t$  is  $\frac{1}{2}$ . [See Eq. (5).] If one vial has a composition close to critical, then an upper limit on the critical temperature can be obtained by observing the lowest temperature where all vials are one phase; a lower limit is the largest transition temperature. If the critical composition is unknown, as was the case here, then the critical temperature can be determined from an analysis similar to the one below.

The slopes of the isothermal lines in Fig. 2 provide information on the critical exponent  $\beta$ . Differentiating Eq. (5) gives the relationship between these slopes and  $T_c$  (through  $t$ ),  $\beta$ , and  $B$ :

$$\frac{dH}{d\phi_A} \equiv d\left(\frac{h_m}{h_t}\right) / d\phi_A = \frac{t^{-\beta}}{B} \quad (6)$$

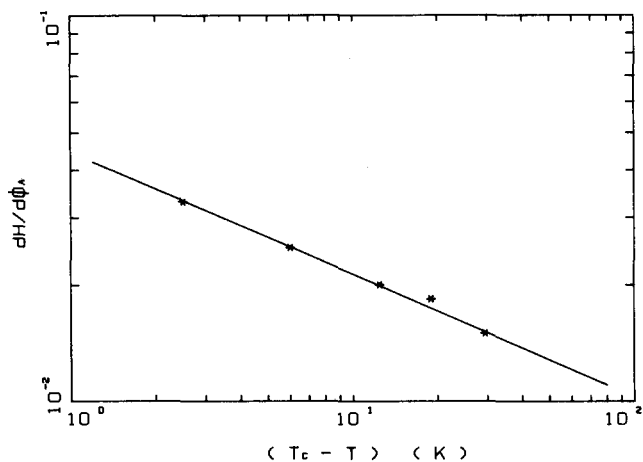


Fig. 4. The values of the slopes from the isothermal lines in Fig. 2 exhibit the expected dependence [Eq. (7)] on temperature away from critical,  $T_c - T$ .  $H$  is defined as the ratio  $h_m/h_t$ . The slope of the straight line through these points represents the critical exponent  $\beta$ . The critical temperature was chosen to be  $42.5^\circ\text{C}$  so that  $\beta$  would be the known value of 0.327. The intercept determines the coexistence curve amplitude to be  $B = (142 \pm 7)\%$  by volume isooctane.

Taking the log of Eq. (6) gives

$$\log\left(\frac{dH}{d\phi_A}\right) = -\beta \log(T_c - T) + \log\left(\frac{T_c^\beta}{B}\right), \quad (7)$$

so that a log-log plot of  $dH/d\phi_A$  versus  $(T_c - T)$  should provide a straight line of slope  $\beta$  (the critical exponent) and intercept  $\log(T_c^\beta/B)$  (see Fig. 4). Thus if  $T_c$  is known, then  $\beta$  can be determined. Since we did not know  $\phi_c$  (and hence could not determine  $T_c$  from Fig. 3), then the critical temperature was chosen in Fig. 4 to give the critical exponent  $\beta$  a value of 0.327, which is the current theoretical and experimental value.<sup>2</sup>

The value of  $T_c$  and  $\beta$  are correlated in this experiment, but they can be determined precisely by taking more data at temperatures closer to critical than was attempted here. The critical temperature  $T_c$  was thus determined to be  $(42.5 \pm 0.5)^\circ\text{C}$  with a corresponding critical composition of  $\phi_c = (67.3 \pm 0.2)\%$  by volume isooctane. The amplitude of the coexistence curve,  $B$ , is determined from the intercept of the line fitting the points in Fig. 4 and has a value  $(142 \pm 7)\%$  by volume isooctane.

#### V. CONCLUSION

This experiment provided data that corresponded well with current theory and allowed a critical point to be determined in the binary fluid mixture methanol-isooctane. The data were easily obtained and required little equipment. The results provide insight into critical phenomena and gave the first determination of the critical parameters  $T_c$  and  $\phi_c$  for this mixture.

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## Uniform solutions for scattering by a potential barrier and bound states of a potential well

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The one-dimensional Schrödinger equation is solved asymptotically for scattering of a particle by a potential barrier and for bound states of a potential well, when the potentials change little in a wavelength. Both solutions are represented uniformly in space, rather than nonuniformly as in the WKB method. This avoids matching expansions and using connection formulas. The scattering solution and the complex reflection and transmission coefficients are also uniform in the particle energy.

### I. INTRODUCTION

One-dimensional scattering and bound state problems in quantum mechanics are often solved approximately by the WKB method. This method has an intrinsic defect which makes it inconvenient or difficult to use. It is that different expressions for the solution must be used on each side of a turning point, and they must be matched to a third expression which is valid near the turning point. Thus in a typical bound state or scattering problem with two turning points, five different expressions for the solution must be used and matched to one another.

We shall show how to overcome this defect by using one spatially uniform asymptotic representation of the solution instead of the WKB five-part nonuniform representation. For scattering the spatially uniform representation and the corresponding complex reflection and transmission coefficients are also uniform in the energy of the incident particle. That is, they are valid for the particle energy above, at, or below the peak of the potential. These results are not available in textbooks and they do not appear to be given in the literature either.

To gain these advantages one must use Hermite polynomials for bound state problems and parabolic cylinder functions for scattering problems. Hermite polynomials are already used to treat bound states of a harmonic oscillator, and the present method provides an additional use for them. Parabolic cylinder functions can be used to exactly solve scattering by a parabolic potential barrier, and then used for the approximate solution of scattering by any potential. In fact, in Sec. II we shall treat first the bound states of a harmonic oscillator and then those of a general poten-

tial. Similarly, in Sec. III we shall treat scattering by a parabolic potential barrier and then in Sec. IV we shall treat scattering by a general potential.

The idea of using uniform representations was introduced by Langer<sup>1</sup> in 1934, and in a modified form by Chery<sup>2</sup> in 1950, to treat problems with one simple turning point. McKelvey<sup>3</sup> and Kazarinoff<sup>4</sup> applied it to a second-order turning point and to two simple turning points, respectively. All these authors proved that the uniform representation is asymptotic to the exact solution as the wavelength divided by a typical scale length of the potential tends to zero. Their results have been refined and extended by various authors, especially Olver.<sup>5</sup> The formal aspects of the method have been described by Miller and Good,<sup>6</sup> and developed further by Lynn and Keller,<sup>7</sup> Zauderer,<sup>8</sup> and Anyanwu and Keller.<sup>9</sup>

In Sec. II we shall write the Schrödinger equation in the form

$$\psi_{xx} + [E - V(x)]\psi = 0. \quad (1)$$

Here  $\psi(x)$  is the wavefunction  $E = 2mE'/h^2$ , where  $E'$  is the particle energy,  $m$  is its mass,  $h$  is Planck's constant divided by  $2\pi$ , and  $V(x) = 2mV(x)/h^2$ , where  $V'(x)$  is the potential energy function. In Secs. III and IV we shall set  $E = k^2$ .

### II. BOUND STATES OF A POTENTIAL WELL

Let us begin with the harmonic oscillator, for which we write the potential as  $V(x) = x^2/4$  so that Eq. (1) becomes

$$\psi_{xx} + [E - (x^2/4)]\psi = 0. \quad (2)$$