difference between the Ps and Ps* binding energies.

At the present time, the search for a greater Ps* formation efficiency with other target materials and methods of sample preparation is in progress. A new target assembly incorporating an rf cavity is being built to attempt a measurement of the $2S$-$2P$ fine structure.

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Gravitationally Induced Density Gradients near the Liquid-Liquid Critical Solution Point*

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Analysis of sedimentation in a binary mixutre near a liquid-liquid critical solution point shows that, as a result of the divergence of the sedimentation rate, a density inversion occurs. At high gravitational fields (10^5 normal gravity) the inversion can occur as much as 1–3 K above T_c. Turbulence associated with the inversion gives the appearance of phase separation.

Recently there has been considerable interest in the effect of concentration gradients upon thermodynamic and transport properties in the critical solution region. Of particular interest is the rate at which gradients form.

Unfortunately there are no clear-cut experiments concerning these gradients reported in the literature. However, measurements of the effect of a centrifugal field upon the upper critical solution temperature T_c of binary mixtures which were reported in 1954 by Hildebrand, Alder, Beams, and Dixon[1] have bearing on this problem. They studied two systems—(1) carbon tetrachloride + perfluoromethylcyclohexane and (2) 2, 2, 3-trimethylpentane + perfluoro-n-heptane—and observed in both cases that the apparent T_c increased linearly with centrifugal field. Moreover, after correction for, or the elimination of, the contribution of hydrostatic pressure to a change in T_c, system (2)—in which the densities of the pure components differ by a factor of 2.5 —was found to exhibit a residual increase in T_c (1.9 K at the highest fields), while system (1) —in which the ratio of the densities is only 1.1 —showed no such effect, at least within an experimental uncertainty of not more than 0.2 K. These results Hildebrand et al. attributed to "sedimentation" of incipient clusters of markedly different densities.

The equations of equilibrium thermodynamics can describe the effect of gravitational or centrifugal fields on the equilibrium properties of critical systems,[2] but they cannot account for these results. A large difference in density between the two components leads to a substantial concentration gradient in the system, as Fannin and Knobler[3] have shown. The equilibrium critical solution temperature T_c depends upon the magni-

tude of the graviational field only in the sense
that this determines the hydrostatic pressure p
at the position in the tube where the critical phe-
nomena occur.

Since it appeared impossible to account for the
1954 observations reported as equilibrium phe-
nomena, we turned to a consideration of the way
in which concentration gradients develop as a
function of time. This note reporte results of
some extensive numerical integrations of the
sedimentation equation and of an approximate
analytic solution. Details of the calculations will
be given elsewhere.

At any point in the real mixture, the mass flux
(in the direction of the field) of component 1 rela-
tive to the average mass velocity is given by[4]

$$j_1 = -j_2 = -Lx_1[(\partial \mu_1/\partial x_1)_{p,T}\nabla x_1$$
$$+ (\overline{V}_1 - M_1/\rho)\nabla p], \quad (1)$$

where L is the Onsager phenomenological coeffi-
cient for diffusion; μ_1, x_1, $\overline{V}_1$, and M_1 are the
chemical potential, molar volume, and molar
mass of component 1, respectively; and ρ is the
overall mass density. The first term in the
square brackets of Eq. (1) is proportional to a
flux due to concentration diffusion; the second
is proportional to a flux due to sedimentation
("pressure diffusion"). At equilibrium the net
mass flow is zero and the two terms within
square brackets exactly cancel.

Under normal circumstances the coefficient L
is only weakly temperature dependent. However,
in the critical region the theory of dynamic scal-
ing requires that it diverge according to the
equation[5]

$$L = L_0[(T - T_c)/T_c]^{-\psi}, \quad (2)$$

where L_0 is a constant and ψ is a critical expo-
nent.[6] $(\partial \mu_1/\partial x_1)_{p,T}$ vanishes at the critical point
with an exponent $\gamma = 1.2$–1.3, but the product
$L(\partial \mu_1/\partial x_1)_{p,T}$ vanishes with a much smaller ex-
ponent $\gamma^* = 0.6$–0.7. It follows then that $\psi = 0.6$–
0.7, and that L diverges at T_c. Since in Eq. (1)
the sedimentation factor $(\overline{V}_1 - M_1/\rho)\nabla p$ is well
behaved at T_c, the flux due to sedimentation be-
comes very large as the critical point is ap-
proached, in sharp contrast to the flux due to
concentration diffusion which tends to zero in the
same region.

For most binary mixtures, including the two in
question, dT_c/dp is positive. Consequently, in
an isothermal system, the bottom of the tube is
closer to T_c and the sedimentation flux is great-

est there. This leads to the unexpected, but in-
escapable, conclusion that there are intermedi-
ate layers in the system where the flux of the
denser component leaving through a lower bound-
ary plane exceeds the flux entering through the
upper boundary. This is confirmed by the com-
puter calculations in which Eq. (1) was numerical-
ly integrated over a series of fifty discrete layers
and over a series of short time intervals.

If one starts with a system in which the mole
fraction x_1 is uniform and equal to the critical
composition x_c at all heights (i.e., no gravitation-
al field, $\nabla p = 0$) and then "turns on" a field or
pressure gradient, the large sedimentation fluxes
in the critical region quickly remove the denser
component from layers near the bottom of the
tube and produce reverse composition gradients
in the intermediate range of height (S-shaped
curves of x versus height), Fig. 1. Concentra-
tion inversions are not *per se* unstable, but den-
sity inversions are. The point at which these in-
stabilities, which produce turbulence and give
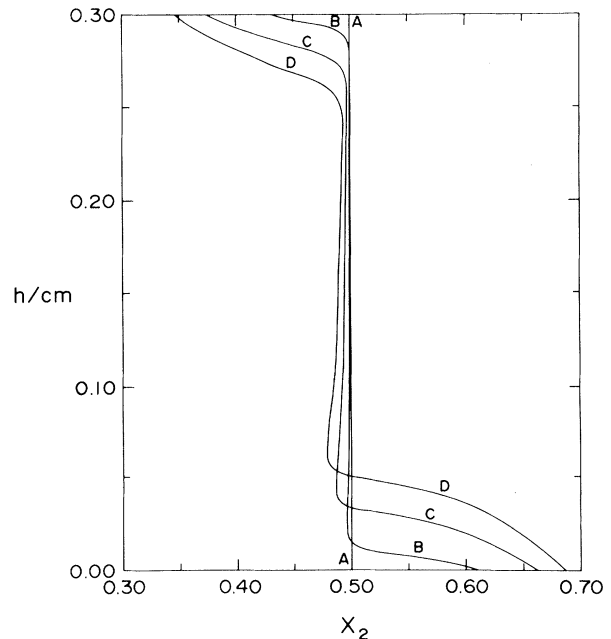the appearance of phase separation, may occur

FIG. 1. Computer calculation of sedimentation at g
$= 10^6$ m sec^{-2}. The curves marked A, B, C, and D
represent gradients computed for times $t = 0$, 10, 50,
and 100 sec, respectively. The temperature is 300 K,
$\psi = 0.56$, $\overline{V}_1 = \overline{V}_2 = 200$ cm^3 mol^{-1}; $M_1 = 144$ g mol^{-1}; M_2
$= 388$ g mol^{-1}; $L_0 = 3.5 \times 10^{-4}$ mol cm^{-3} sec. Because
of the hydrostatic head, T_c varies from 296.8 K at the
top of the liquid to 299.4 K at the bottom. The density
inversion appears at 8 sec if $(\partial \rho/\partial x)_{p,T}/(\partial \rho/\partial p)_{x,T}$
$= 3.4 \times 10^3$ atm.

in the actual system depends upon the compressibility of the mixture. This density inversion is inevitable when $dT_c/d\phi$ is large and when the sedimentation is large by comparison with the diffusion rate (i.e., when g is large and when the system is near its critical solution point). Just when and where it occurs will depend upon the precise values of the parameters for a particular system. If it occurs at all, it will occur where the reverse slope dx/dh has its maximum value; it is evident from Fig. 1 that this is near the bottom of the tube.

Although Eq. (1) cannot be solved analytically, a tractable relation can be obtained if several approximations are made. Under conditions where diffusion is negligible compared to sedimentation, as at short times at temperatures close to T_c and compositions close to x_c, the substitution of Eq. (2) into Eq. (1) yields a proportionality between dx/dt and d^2L/dh^2. Integration then yields an expression for the mole fraction gradient at time t:

$$\frac{dx_1}{dh} \cong - C x_1 (\overline{V}_1 \rho - M_1)\psi(\psi+1)$$
$$\times \int_0^t \frac{[g(t)]^3 dt}{[(T - T_c)/T_c]^{2+\psi}} , \tag{3}$$

where

$$C = \frac{L_0(x_1 M_1 + x_2 M_2)^2}{(M_1\overline{V}_2 + M_2\overline{V}_1)} \left(\frac{\partial \ln T_c}{\partial p}\right)^2 . \tag{4}$$

The parameter C, indeed the entire factor preceding the integral in Eq. (3), depends only upon nondivergent properties of the mixture and is constant within a few percent over the range of temperature, composition, and pressure of interest to this problem. The acceleration of gravity g has been written as time dependent since the rotor speed may be varied during the experiment.

The condition for the onset of the density inversion, $d\rho/dh = 0$, leads to the equation

$$\frac{dx}{dh} = \frac{(\partial\rho/\partial p)_{x,T} \rho g}{(\partial\rho/\partial x)_{p,T}} . \tag{5}$$

If diffusion is neglected, the maximum inverse gradient dx/dh occurs at the bottom of the cell where the hydrostatic pressure is greatest and T_c is closest to T. In general this T_c will be a function of g and of the height l of the fluid, and thus, if g varies, T_c is a function of t. However, in the limit that l is negligibly small (negligible hydrostatic pressure), T_c is independent of g and integration in Eq. (3) reduces to the integration

of $g^3 dt$.

In the usual experimental situation it is convenient to increase the rotor speed ω linearly with time; then, since g is proportional to ω^2,

$$g = kt^2 . \tag{6}$$

When, after substitution from Eq. (6), Eq. (3) is integrated and combined with Eq. (5), we obtain

$$\left(\frac{T - T_c}{T_c}\right)^{2+\psi}$$
$$= -\frac{C x_1(\overline{V}_1\rho - M_1)(\partial\rho/\partial x)_{p,T}\,\psi(\psi+1)g_f^{2.5}}{7\rho(\partial\rho/\partial p)_{x,T}k^{0.5}} , \tag{7}$$

where g_f is the (final) value of the gravitational acceleration at which the density inversion appears, and $T - T_c$ is the increase over the expected (true) critical solution temperature. We note that $2 + \psi \approx 2.6$, so Eq. (6) predicts that within the usual experimental error a linear relation between $T - T_c$ and g would be observed. This conclusion is insensitive to the precise manner in which g increases with time; it is not important that Eq. (6) be exactly satisfied.

Equation (7) can be compared directly with the experimental results of Hildebrand et al.[1] who reported the linear relation between the "critical temperature" (in our model the inversion temperature) and g. Moreover, when parameters appropriate for the mixture i-$C_8H_{18} + C_7F_{16}$ (substantially the same as those cited in the legend for Fig. 1) are inserted into Eq. (7), a value of $T - T_c \approx 1$–2 K is obtained at $g_f = 10^6$ m sec^{-2}, a value of the same order of magnitude as that which they observed.

In our view the mechanism by which these concentration gradients develop and the unexpected concentration inversions found should be general features of mixtures in the critical solution region.

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Domain of Two-Dimensional Excitations in Superfluid Helium Films*

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Using third-sound resonance, we find for helium film thickness less than 2.8 atomic layers that there exist excitations which are phononlike and two dimensional, obeying a T^3 law, that their areal density is independent of film thickness, and that their velocity (using Landau theory) is 76 ± 2 m/sec. This velocity is slightly above the maximum third-sound velocity, 69 m/sec, that can be attained by ^{4}He on argon. For thicker films the areal density of these excitations becomes smaller.

A central problem in the study of thin ^{4}He films is whether "two-dimensional superfluidity" is simply a limiting case approached as film thickness and hence T_c vanish[1] or a domain of film thickness with finite T_c's.[2] Our interpretation of measurements given below is that there does exist such a domain.

The measurements of Pobell *et al.*[3] have demonstrated that reducing the dimensionality by confining helium in small pores has a profound effect on the magnitude and temperature dependence of the excitation density. Using the Landau quasiparticle theory for reduced dimensions, Padmore[4] and Haug[5] have provided a framework to understand this class of experiments. We believe that the measurements presented below provide an accurate characterization of these size effects for two dimensions.

In the first part of the analysis we will characterize our helium films by a superfluid film thickness through an analysis similar to the work of Scholtz, McLean, and Rudnick.[6] Next, we will analyze the temperature dependence of the third-sound velocities to produce an areal excitation density. Finally we will try to fit these results with the various Landau quasiparticle models.

Third-sound resonance[7,8] can produce measurements of third-sound velocity C with 1 part in 10^5 resolution. Fortunately, for the films described here, the linewidths are often less than 10^{-4} of the resonant frequencies (which range from 400 to 1800 Hz). The resonator consists of two thin sheets of quartz flame-sealed together. The substrate is a 15-atomic-layer film of crystallized argon which has sublimed just below liquid-nitro-gen temperature. The argon gas is permanently sealed within the quartz resonator. Any amount of ^{4}He may be diffused into the resonator at room temperature with an 8-h time constant. Capacitor plates within the resonator provide a means of measuring the gas pressure, to a resolution of 2×10^{-4} Torr, through the flexing of the resonator walls. Total film thicknesses are established by comparing the chemical potentials, as measured by gas pressure, of various film thicknesses instead of by using the vapor pressure of saturated ^{4}He:

$$T \ln\left(\frac{P'}{P}\right) = \frac{\Gamma(d)}{d^3} - \frac{\Gamma(d')}{d'^3}. \tag{1}$$

P is the pressure well above a film of thickness d and P' is the pressure well above a film of thickness d'. In addition we use conservation of atoms since we are dealing with a sealed system. This method of analysis minimizes errors due to temperature scale and pressure calibration. The Van der Waals coefficient $\Gamma(0)$ has been calculated by Sabisky and Anderson[9] to be 14.5 K (atomic layers)^3 for a helium film adsorbed on an argon substrate. As the adsorbed film thickness increases, $\Gamma(d)$ decreases slowly. These calculations have been checked against direct measurements on CaF$_2$ substrates by Sabisky and Anderson.

Two-fluid hydrodynamics permits us to use measured values of C to determine the density of the excitations that comprise the normal part of the fluid. The equation for velocity V of surface waves of wavelength λ on a liquid with surface