Shape of the Coexistence Curve of the Ga-Hg System Near T_c

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A new method is presented to study the coexistence curve near the critical point. We applied it to the Ga-Hg system and found $\beta = 0.373 \pm 0.005$.

Recently[1] it has been pointed out that the available experimental results, which are indeed very scarce, on the behavior of conducting fluids near their critical point indicate that the critical indices are much more similar to the classical ones than to those of the Ising type. This has been related to the range of interatomic forces. However, in the case of the binary mixture Ga-Hg, a new measurement[2,3] reports $\beta = 0.335 \pm 0.005$. Unfortunately, in this experiment, although very accurate and rich in points for T near T_c, the concentration is not measured directly, but a resistivity measurement has been done and the resistivity is connected to the concentration via phenomenological relationships. Moreover the use of these relationships near the critical point is to some extent in conflict with a previous work[4] where it is shown that the resistivity has a small anomalous behavior near T_c. To obtain more information on the critical behavior we studied the shape of the coexistence curve of the Ga-Hg system near the critical mixing point by means of a new method giving directly the concentration of the component liquids. This method, essentially a neutron radiography, is very promising for the general study of critical behavior. The idea underlying the method is the following: The total cross sections of Ga and Hg for thermal neutrons are very different (for a neutron energy of 0.075 eV, Ga has $\sigma_{\mathrm{Ga}} = 8.3$ b whereas Hg has $\sigma_{\mathrm{Hg}} = 236$ b[5]); in addition the Hg cross section is almost entirely an absorption cross section. Therefore, if we have a sample of Ga-Hg in which the Hg concentration varies along the vertical axis z of the sample, the neutron transmission T will be a function of z. Let us consider now the case in which our mixture is at a temperature lower than the critical mixing temperature. In this case a meniscus will exist and two phases will be present in our sample, the upper one rich in Ga and the lower one rich in Hg. If we measure the neutron tramsmission through each phase we will have

$$T^{(u)} = \exp[-(\sigma_{\mathrm{Hg}} x_{\mathrm{Hg}}{}^{(u)} + \sigma_{\mathrm{Ga}} x_{\mathrm{Ga}}{}^{(u)})d] \qquad (1)$$
$$T^{(l)} = \exp[-(\sigma_{\mathrm{Hg}} x_{\mathrm{Hg}}{}^{(l)} + \sigma_{\mathrm{Ga}} x_{\mathrm{Ga}}{}^{(l)})d],$$

where the superscripts (u) and (l) refer, respectively, to the upper and lower phases, $x_A{}^{(i)}$ is the number of atoms A per unit volume in the phase i,[6] and d is the thickness of the sample.

Multiple scattering can be neglected since in our mixture the absorption cross section is much higher than the scattering cross section. From Eqs. (1) we can easily derive

$$(x_{\mathrm{Hg}}{}^{(l)} - x_{\mathrm{Hg}}{}^{(u)}) + \frac{\sigma_{\mathrm{Ga}}}{\sigma_{\mathrm{Hg}}}(x_{\mathrm{Ga}}{}^{(l)} - x_{\mathrm{Ga}}{}^{(u)}) = \frac{1}{d}\ln\left(\frac{T^{(u)}}{T^{(l)}}\right). \qquad (2)$$

If we define $C^{(i)}$ from $x_{\mathrm{Hg}}{}^{(i)}/x_{\mathrm{Hg}}{}^{(0)} + x_{\mathrm{Ga}}{}^{(i)}/x_{\mathrm{Ga}}{}^{(0)} = C^{(i)}$, where $x_A{}^{(0)}$ is the number of atoms A per unit volume in the pure liquid A, we have

$$\Delta\varphi = \frac{x_{\mathrm{Hg}}{}^{(l)} - x_{\mathrm{Hg}}{}^{(u)}}{x_{\mathrm{Hg}}{}^{(0)}} = \frac{1}{(x_{\mathrm{Hg}}{}^{(0)}\sigma_{\mathrm{Hg}} - x_{\mathrm{Ga}}{}^{(0)}\sigma_{\mathrm{Ga}})d}\left[\ln\left(\frac{T^{(u)}}{T^{(l)}}\right) + x_{\mathrm{Ga}}{}^{(0)}\sigma_{\mathrm{Ga}} d(C^{(l)} - C^{(u)})\right]. \qquad (3)$$

In our case (since $d = 0.31$ cm and $x_{\mathrm{Ga}}{}^{(0)}\sigma_{\mathrm{Ga}} = 0.047 x_{\mathrm{Hg}}{}^{(0)}\sigma_{\mathrm{Hg}}$), $d x_{\mathrm{Ga}}{}^{(0)}\sigma_{\mathrm{Ga}}(C^{(l)} - C^{(u)})$ is less than the error with which we know $\ln(T^{(u)}/T^{(l)})$ (due to the statistical error of the transmission which is $\simeq 1\%$), assuming $C^{(l)} - C^{(u)} = 0.10$ for $(T_c - T)/T_c = 3 \times 10^{-4}$ (i.e., $\Delta\varphi = 0.083$), and $C^{(l)} - C^{(u)} = 0.20$ for $(T_c - T)/T_c$

$=3\times10^{-2}$ (i.e., $\Delta\varphi=0.48$). Both these limits for $C^{(l)}-C^{(u)}$ are clearly safe enough[7] to enable us to write

$$\Delta\varphi=\frac{1}{d(x_{\mathrm{Hg}}^{(0)}\sigma_{\mathrm{Hg}}-x_{\mathrm{Ga}}^{(0)}\sigma_{\mathrm{Ga}})}\ln\left(\frac{T^{(u)}}{T^{(l)}}\right). \qquad (4)$$

Now the index β is determined by the relationship[8] $\Delta\varphi=B[(T_c-T)/T_c]^\beta$ which holds in the critical region. Therefore the transmission measurements as a function of temperature give us the possibility to derive β and B.

Our experimental setup is the following: A monochromatic, collimated (within ± 2°) neutron beam of 0.075 eV is obtained from the reactor, by reflection on a Ge single crystal. The dimension of the beam (3 mm high × 7 mm wide) is determined by a Cd window on which a stainless steel box containing the sample (3 mm thick × 20 mm wide × 25 mm high) can slide. The position of the sample with respect to the beam is read on a graduated scale, fixed with respect to the Cd window, with a precision of ± 0.5 mm. The detector is a BF_3 counter. The stainless steel box is in a frame of copper containing the heaters, in such a geometry as to reduce the thermal gradients to less than 0.01°C. Teflon and aluminium radiation shieldings are all around the sample. The temperature is read by a Pt thermometer,[9] imbedded in the sample box, with a sensitivity of 0.01°C. The temperature stability is obtained within ± 0.01°C, by controling the current in the heaters by means of the signal from the Pt thermometer. A mechanical stirrer is placed in the sample box outside of the neutron path. This stirrer is very important in order to reach the equilibrium state when the temperature is raised (in fact the mass diffusion is a very slow process). The measurements proceed as follows: (1) A mixture[10] of nearly critical composition ($\simeq 75\%$ in weight of Hg) is enclosed in the stainless steel box. (2) The temperature is raised at least 10°C above T_c and the mixture is mechanically stirred. (3) At this fixed temperature, transmission measurements are performed as a function of the position of the sample with respect to the Cd window. We are sure that the sample is at equilibrium since the neutron transmission is constant at every level. (4) We lower the temperature and we stabilize it at a new value. We repeat the transmission measurements as a function of the level; to be sure about equilibrium, we stir the mixture and we check, through the transmission measurement, to see that nothing has changed. When we are at $T<T_c$ we find a sharp change in the transmission as a function of the level and this indicates the meniscus position. Outside the meniscus region we find the transmission in each phase to be independent of the level and we choose these transmission values to derive the $\Delta\varphi$ value at this temperature. At our working temperatures the effect of gravity for $T<T_c$ was undetectable, as was expected by comparison with the case of CO_2.[11]

The experimental results are shown in Fig. 1. It we fit the experimental points with the relationship $\Delta\varphi=B[(T_c-T)/T_c]^\beta$ we derive $T_c=475.48$°K, $B=1.74\pm0.04$, and $\beta=0.373\pm0.005$; the errors are those given by the least-squares fit. We choose the T_c value which gives the lower χ^2 value; this value also agrees with our experimen-

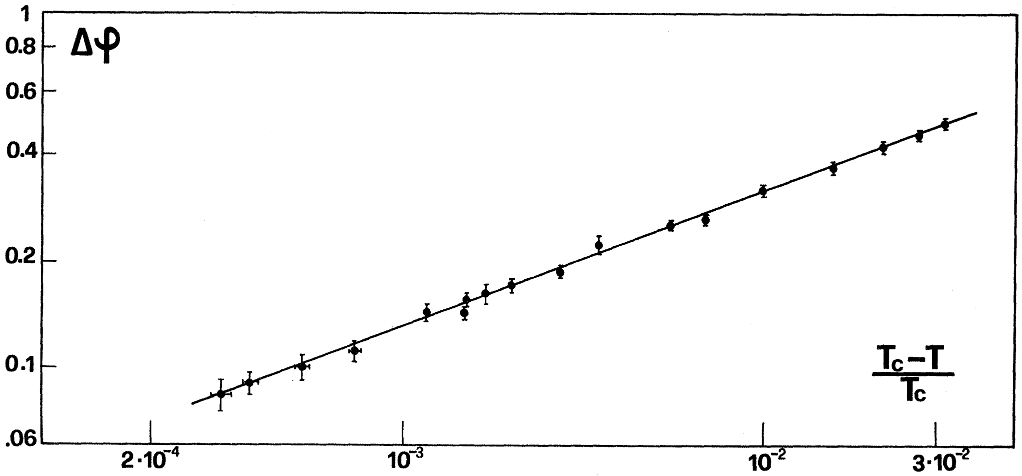

FIG. 1. Log-log plot of our experimental results: the volume fraction difference, $\Delta\varphi$, for Hg in the two phases versus $(T_c-T)/T_c$ (the temperature is given in °K). When the error bars are not shown they are smaller than the dimension of the dots. The solid line represents the equation $\Delta\varphi=1.74[(475.48-T)/475.48]^{0.373}$.

tal results giving an upper bound to T_c, since we found that the sample is homogeneous at $T = 475.48$°K, and a lower bound since at $T = 475.32$° K the meniscus is already present.

Finally, we comment on the values derived from our experiment:

(1) The experimental points in the range $3\times10^{-4} \leq (T_c - T)/T_c \leq 2\times10^{-2}$ fit the simple power law very well (see Fig. 1).

(2) The value of β is the same as that found in ordinary liquids.[12] It is a little higher than the Ising-type but certainly different from the classical value. Compared to previous measurements, we are closer to the Schürmann and Parks result than to that of Predel. The small but definite discrepancy between our β and the β derived through the resistivity measurements is, in our opinion, due to the inaccuracy of the two phenomenological relationships $\partial R/\partial x = AR_c$ and $\partial R/\partial T|_x = BR_c/T_c$ used by Schürmann and Parks.

(3) We are able to derive the B value also, whereas this is not possible from resistivity measurements, and again this value turns out to be very close to those reported for nonmetallic mixtures.[8]

(4) Our T_c value is a little lower than the values previously reported.[1,2] However we wish to point out that for $T = 475.58$°K we found by scanning that our sample was really homogeneous in Hg concentration, and to note that our thermometer was calibrated with a precision of ± 0.01°C.

We would like to underline the power of our method (of course limited to atoms with high neutron-absorption cross sections such as Xe, ^{3}He, Hg, etc.) which is complementary to the optical isotherm method.[11]

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[6] The densities of pure Hg and Ga as a function of temperature have been taken from the *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (Chemical Rubber Publishing Co., Cleveland, Ohio, 1969), 50th ed.

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[9] The Pt thermometer is a Rosemount 118L and has $R(0°\text{C}) = 501.93$.

[10] Ga, 99.99% pure, from Fluka AG; Hg, 99.9% pure, from Rudipont. For the pure liquids we measured the neutron transmission and we found them in good agreement with Ref. 5.

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