Critical Exponent of Phase Separation in Metallic Binary Liquids

H. K. Schürmann and R. D. Parks
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

(Received 5 August 1970)

The first detailed study of the critical exponent of phase separation, β_{BM}, in a metallic binary liquid is reported. High-precision electrical resistivity measurements made on a Ga-Hg mixture of critical composition allowed the determination of β_{BM}, which was found to be 0.335 ± 0.005 in the reduced temperature interval $10^{-4} \leq \epsilon \leq 10^{-2}$.

Critical phenomena appear in liquids in two instances: the liquid-gas transition of one-component systems and the phase separation of liquid binary mixtures which exhibit a miscibility gap. The first class can be divided into metallic and nonmetallic substances; the second also includes their combinations (ammonia-alkali mixtures). Because of experimental difficulties it is not surprising that metallic systems have been given only scant attention.[1] Density ρ and temperature T in the liquid-gas critical system have concentration x and temperature T as their analogs in the binary-liquid critical system, thus the equivalent equations[2]

$$(\rho_L-\rho_G) \sim \epsilon^{\beta_{LG}}, \tag{1a}$$

$$(x_A-x_B) \sim \epsilon^{\beta_{BM}}, \tag{1b}$$

where $\epsilon = (T_c-T)/T_c$.

For every liquid-gas system measured the exponent β_{LG} is, close to the critical temperature T_c, equal to $\frac{1}{3}$ within experimental error,[3] except for the quantum liquids which appear to follow an equation proposed by Fisher.[4] The limited data available on the coexistence curve for metals would indicate a value of β_{LG} between 0.42 and 0.45 for the alkali metals,[5] but the lowest ϵ attained was about 10^{-1} as compared with 10^{-5} for Xe or CO_2.

In the binary fluid mixtures the situation is somewhat similar. For a number of nonmetallic combinations β_{BM} has been found to be $\frac{1}{3}$ within experimental error.[3,6] No metallic system has yet been experimentally investigated with the determination of β_{BM} as the primary objective. Some of the best determinations of miscibility gaps[7-10] have uncertainties of at least ±1 K at the critical point and are therefore not very suitable for an analysis of critical indices. Egelstaff and Ring[1] give curves prepared from the data of Predel[8,9] which would indicate a whole range of values for β_{BM} (0.3 for Ga-Pb, 0.35 for Ga-Tl, 0.5 for Al-In and Ga-Hg) in the range $10^{-3} < \epsilon < 10^{-2}$ with a decrease of all β_{BM} to the low value of 0.3 for all systems near $\epsilon = 10^{-1}$. The experimental methods employed are either density-temperature curves[7] or cooling curves,[8-10] since a visual observation such as employed by Thompson and Rice[6] proves impractical if not impossible for metallic mixtures.

We have used a method of determining the coexistence curve in the Ga-Hg system which makes use of only one sample. The fact that most determinations of the coexistence curve in binary liquids had to be made on different samples for every point is probably the main reason for the relatively large scatter in the results. The notable exception is the work by Thompson and Rice[6] who measured the density of one of the liquid phases of the CCl_4-C_7F_{14} system and calculated its composition under the assumption that the density of the mixture is a linear function of the composition near the critical composition; thus, they could show that previous point-by-point determinations of the phase boundary were in error. We measured the electrical resistance of different sections of a column of a mixture of Ga-Hg while decreasing the temperature very slowly. Resistivity measurements have long been used for point-by-point determinations of phase diagrams and are in some instances inferior to other methods, such as differential thermal analysis. However, the present method uses not only the discontinuities of R-vs-T curves but the curves themselves, and thus we are able to determine a whole phase boundary, as opposed to one point on a phase boundary, from data on a single sample. This is clearly an advantage since it eliminates errors inherent in different runs on different samples.

For the change of resistance with temperature we can write

$$\frac{dR}{dT} = \left.\frac{\partial R}{\partial T}\right|_x + \frac{\partial R}{\partial x}\frac{\partial x}{\partial T}, \tag{2}$$

where $\partial x/\partial T = 0$ for $T > T_c$.

Assuming that

$$\partial R/\partial x = AR_c \tag{3a}$$

near T_c and

$$\left.\frac{\partial R}{\partial T}\right|_x = \frac{BR_c}{T_c} \tag{3b}$$

to be constant near the critical composition x_c (the experimental basis for these assumptions is discussed below), we can integrate Eq. (2) and obtain the resistance near x_c and for some temperature interval below the critical temperature (with subscripts H for Hg-rich, G for Ga-rich):

$$R_{H,G} = R_c + BR_c(T-T_c)/T_c + AR_c(x_c - x) \tag{4a}$$

or, dividing by R_c,

$$r_{H,G} = R_{H,G}/R_c = 1 - B\epsilon + A(x_c - x). \tag{4b}$$

With x representing atomic percent gallium, Eqs. (4) can be written as

$$r_H - 1 + B\epsilon = A(x_c - x) \sim \epsilon^\beta, \tag{5a}$$

$$1 - B\epsilon - r_G = A(x - x_c) \sim \epsilon^\beta, \tag{5b}$$

where both sides are positive at all temperatures below T_c.

Weighed amounts of Ga and Hg were mixed in a 9-mm-i.d. Pyrex tube that had been provided with ten tungsten electrodes at intervals of about 15 mm, the lowest and highest of which being used as current leads, those between to measure the voltage drop across subsequent layers. The composition was nominally 50% Hg (Ga: 99.999+% pure from Eagle-Picher Co., Hg: 99.999 99+% pure from Beckman Instruments), which is, according to Predel,[9] the critical composition. The sample tube, contained in a calorimeter, was placed vertically in a molten salt bath and its temperature was monitored at the top and bottom of the liquid mixture by Chromel-Alumel thermocouples placed outside the Pyrex tube. A small heater wound on the tube allowed us to keep the temperature difference over the length of the sample smaller than 0.01 K. Argon gas at atmospheric pressure protected the metal mixture during the run. The mixture was mechanically stirred at about 250°C, i.e., about 50°C above the critical temperature, until the resistances of all the sections on the tube did not change any more. The temperature of the whole furnace was then slowly lowered and monitored with a K-5 Leeds & Northrup potentiometer which also monitored the measuring current of ~1 A, while the voltages across the different sections were measured by a 7556 Leeds & Northrup potentiometer. Between successive voltage measurements the measuring current was interrupted, i.e., switched through a shunt bypassing the sample, and the zero-current voltage was measured and later subtracted from the voltage measurements. In the vicinity of the transition the rate of cooling was about 2 K/hr and it nowhere exceeded 5 K/hr.

Figures 1 and 2 show the behavior of the resistances of two different layers of the mixture with temperature. Since the geometrical shapes of the two sections were not exactly equal, we plot reduced resistances $r = R/R_c$, where R is the measured resistance and R_c the critical resistance. Our measured critical temperature is (203.32 ± 0.50)°C (we have not made a special effort to establish the absolute temperature very accurately), which agrees well with Predel's value[9] of (204 ± 1)°C. Due to the changes of the density of the mixture with composition, and therefore with temperature, the interface between the Ga-rich and the Hg-rich layer moves vertically in the tube. In a preliminary run we monitored more than two sections and then made sure that the interface would always stay somewhere between the two sections measured in the final run. In another paper[13] we demonstrate that the two layers separate very rapidly and there-

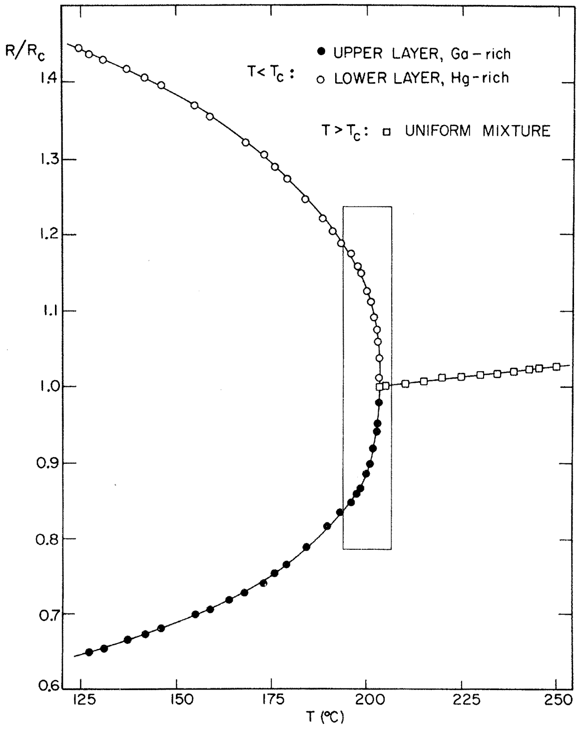

FIG. 1. Reduced electrical resistivity $r = R/R_c$ as a function of temperature in the region of the critical temperature T_c. The solid line is a smooth fit through the points, only a small fraction of which have been plotted.

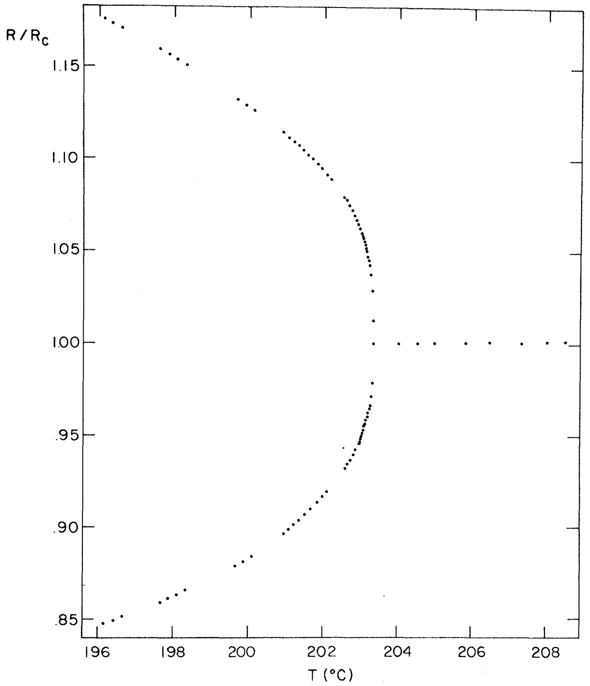

FIG. 2. Blowup of the resistivity in the temperature region indicated in Fig. 1. The points with $T<T_c$ shown here were used in calculating β_{BM}.

fore we are working under equilibrium conditions.

If the composition of our sample were not critical, the points for $T>T_c$ would hit the curve for $T<T_c$ off center; e.g., for $x_c+2\%$ and $x_c-2\%$ these interactions would be lower and higher, respectively, by about 1.2% of the critical value and thus the plot for $T<T_c$ would be quite unsymmetrical.

Alternatively, one might argue that the sample composition is not critical and that the near-perfect symmetry of the curves in Figs. 1 and 2 results from an asymmetry in the coexistence curve cancelling exactly the asymmetry of the curve of resistivity versus concentration. However, plausibility arguments would clearly disfavor this explanation.

In Fig. 3 we show the results of Predel[9] as given by Egelstaff and Ring[1] and log-log plots of the three functions

$$(1-B\epsilon-r_G) \text{ vs } \epsilon, \tag{6a}$$

$$(r_H-1+B\epsilon) \text{ vs } \epsilon, \tag{6b}$$

$$(r_H-r_G) \text{ vs } \epsilon, \tag{6c}$$

where $B=T_c(\partial r/\partial T)_x$ is the coefficient of the linear, temperature-dependent background. Assuming that $(\partial r/\partial T)|_{x,\,T>T_c}=(\partial r/\partial T)|_{x,\,T<T_c}$ we take for B the value determined above T_c, viz. $B=0.25$. Since $B\epsilon\leqslant 2.5\times10^{-3}$ in the temperature region considered, inclusion of the factor $B\epsilon$ has negligible effect on the results; it changes the slopes of the lines (6a) and (6b) in Fig. 3, and therefore

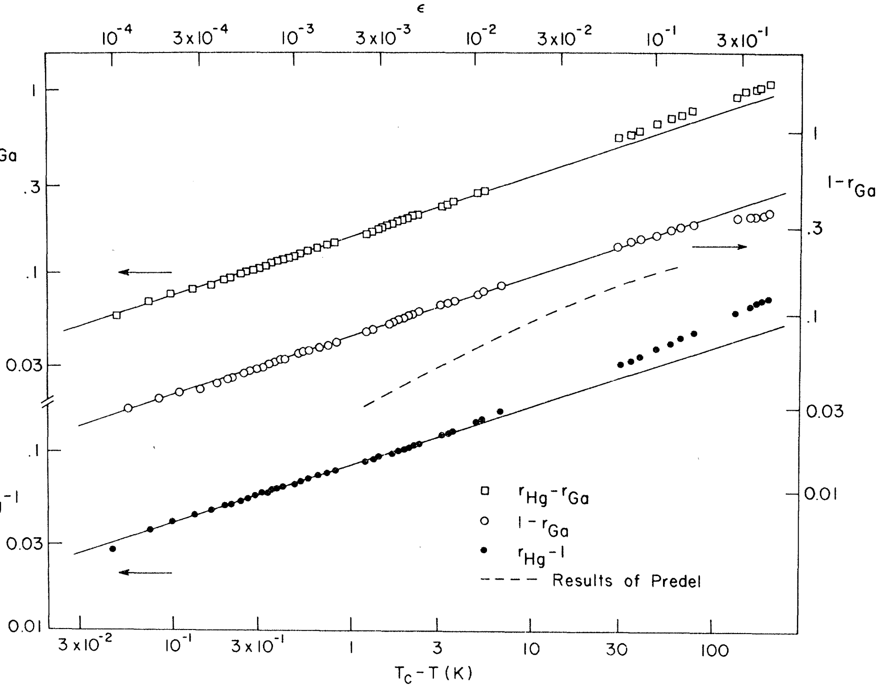

FIG. 3. Log-log plot of the functions in Eq. (6) and results of Predel, displaced vertically by an arbitrary amount. The solid lines all have a slope of $\frac{1}{3}$.

the determined exponents, by approximately 1%. In the range $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ the three sets of data have the slopes 0.329 (6a), 0.342 (6b), and 0.335 (6c), all of them ±0.005. These slopes were determined by linear least-sqaures fits to the points plotted: The individual points were not weighted in any way. The plots of relations (6a) and (6b) show that the resistivity is to a very good approximation a symmetrical function of composition, which demonstrates the law of rectilinear diameters.[11] The fact that the exponents of relations (6a) and (6b) are symmetrically displaced from the exponent of relation (6c) implies that the disparity between the former two exponents arises from the quadratic term in a Taylor series expansion of $r(x)$ about x_c. The influence of this quadratic term can be demonstrated as follows: Assume that $r=1+B\Delta x+C\Delta x^2$ for a Taylor series of the resistivity around r_c. A typical plot of r vs x for the system[12] Hg-In shows the slopes at $x=0.4$ and $x=0.6$ to be 0.8 and 0.5, respectively (in arbitrary units). Then we determine $B=0.65$ and $C=0.75$, and the relative contribution of the quadratic term at these compositions is roughly 12%. The presence of a quadratic term of this magnitude has the effect of decreasing the slope of relation (6a) and increasing the slope of relation (6b) by roughly the amounts observed; viz. $\beta_{BM}(6a)=0.329$ and $\beta_{BM}(6b)=0.342$ as compared with the value $\beta_{BM}(6c)=0.335$, which is insensitive to the presence of the quadratic term.

The systematic deviations of the points from the straight lines at large values of (T_c-T), viz. $>5°C$, seen in all three curves of Fig. 3, reflect the presence of higher-than-quadratic terms in the Taylor series expansion of $r(x)$. These higher order deviations can be dealt with only if the curvature of $r(x)$ is known to high precision. In the absence of such knowledge the region $T_c-T>5°C$, or $\epsilon>10^{-2}$, is outside the domain of applicability of the present method.

The difference between our results (top curve of Fig. 3) and those of Predel,[9] as analyzed by Egelstaff and Ring[1] (dashed curve of Fig. 3) could easily result from the relatively poor accuracy of the Predel data (±1°C); especially if the critical temperature were chosen as 203.6°C, the lower part of the curve would straighten considerably and would make the whole curve nearly parallel to our curves.

In conclusion we can say that the critical exponent of phase separation in the metal binary system Ga-Hg is $\beta_{BM}=0.335\pm0.005$ for the temperature interval $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ [determined from a least-squares analysis of relation (6c)].[14] This value is considerably different from that reported earlier for this system,[1] but agrees with the values for nonmetallic liquid binary systems and the liquid-gas critical systems.

---

[1] P. A. Egelstaff and J. W. Ring, in *Physics of Simple Liquids*, edited by H. N. V. Temperley (North-Holland, Amsterdam, 1968), Chap. 7.

[2] J. S. Rowlinson, *Liquids and Liquid Mixtures* (Plenum, New York, 1969), 2nd ed., Chap. 5.

[3] E.g., L. P. Kadnoff *et al.*, Rev. Mod. Phys. 39, 395 (1967).

[4] M. E. Fisher, Phys. Rev. Lett. 16, 11 (1966).

[5] I. G. Dillon, P. A. Nelson, and B. S. Swanson, J. Chem. Phys. 44, 4229 (1966).

[6] D. R. Thompson and O. K. Rice, J. Amer. Chem. Soc. 86, 3547 (1964).

[7] R. C. Faxon, thesis, Syracuse University, 1966 (unpublished).

[8] B. Predel, Z. Phys. Chem. (Frankfurt am Main) 20, 150 (1959).

[9] B. Predel, Z. Phys. Chem. (Frankfurt am Main) 24, 206 (1960).

[10] B. Predel, Z. Metallk. 49, 90 (1958).

[11] Ref. 2, Chap. 3.

[12] N. E. Cusack, P. Kendall, and M. Fielder, Phil. Mag. 10, 871 (1964).

[13] H. K. Schürmann and R. D. Parks, to be published.

[14] The determination of β_{BM} by any of the relations (6a), (6b), or (6c) is consistent with the value $\beta_{BM}=0.335\pm0.012$; this larger error would then reflect experimental scatter and as well deviations from condition (3b) which is relaxed, as discussed above, if we use only relation (6c).