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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Caput, R. W. , Rodriguez, S. E. and Pings, C. J.(1968) 'Structure of Liquids. VIII. An X-Ray Diffraction Study of Liquid Mercury-Gallium Systems', *Physics and Chemistry of Liquids*, 1: 2, 121 — 128

To link to this Article: DOI: 10.1080/00319106808083792

URL: <http://dx.doi.org/10.1080/00319106808083792>

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Structure of Liquids. VIII. An X-Ray Diffraction Study of Liquid Mercury-Gallium Systems*

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(Received January 18, 1968)

Abstract—X-ray diffraction measurements were made at 0°, 30°, and 50°C on pure mercury and on two mercury-gallium systems of composition 0.9658 and 0.0197 mole fraction of mercury. Peak positions of the radial distribution functions for all samples show no significant change with temperature; the average position of the first and second peaks of the mercury curves are 3.01 Å and 5.80 Å, respectively. Coordination numbers for mercury as determined by the symmetrical curve method are 7.5, 7.3, and 7.0 atoms for 0°, 30°, and 50°C. The scattering function and the features of the structure obtained for the Ga-in-Hg solution are not significantly different from those of pure mercury; for the Hg-in-Ga solution, however, the coordination numbers are smaller than those for pure gallium, and the scattering functions are significantly different.

Mercury (m.p. — 38.9°C) and gallium (m.p. 29.8°C) are relatively convenient choices for determinations of liquid structure, as in the original work by Debye and Menke^{1, 2}. Pure liquid mercury has been the subject of at least 13 such structural investigations, the most recent being by Rivlin *et al.*³ for temperatures between — 36° and 27°C. Pure gallium was recently investigated in this laboratory⁴ between 0°C and 50°C to compare the structures of the stable and supercooled liquids. In the work now reported, the same apparatus and techniques were used to obtain x-ray diffraction data and structural inversions for a gallium-in-mercury and a mercury-in-gallium liquid solutions at temperatures of 0° C, 30° C,

* Research supported by Directorate of Chemical Sciences of the Air Force Office of Scientific Research under Contract AF 49(638)-1273 and by the Metallurgy Branch of the Office of Naval Research under Contract Nonr-220(40).

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and 50°C. In addition, pure mercury was investigated in the same manner to provide internally consistent data for comparison.

The two gallium-mercury solutions investigated were 0.9658 and 0.0197 mole fraction in mercury. These were made up from Ballard's triply-distilled mercury and Alcoa's 99.9999% pure gallium following the procedure of preparation and analysis given by Spicer and Bartholomay.⁵ Diffraction measurements were made in "reflection" geometry with a fixed silver K- α x-ray source and scintillation counter. The apparatus for sample containment and temperature support, as well as the x-ray diffraction instrumentation and techniques, were essentially the same as for the work on gallium.^{4, 6}

The reported temperatures for the free liquid surface were uniform and steady to well within 0.5°C. In the present case, the beta filter was rhodium. Gallium fluorescence counts were practically eliminated by inherent absorption effects, but a narrower pulseheight analyzer window was required to avoid fluorescence counts from the pure mercury and the mercury-rich solution. The independent scatter data chosen for gallium were the same as before;⁴ for mercury, atomic scattering factors were taken from Ibers,⁷ and the incoherent scattering, which is a relatively minor effect, was estimated from the early data by Compton and Allison⁸ and from extrapolations on the calculations by Freeman^{9, 10, 11} on other elements. The detailed data of this investigation are available.¹²

In reducing the diffraction data, the scattering function $i(S)$ for a polyatomic liquid was defined here as

$$i(S) = \frac{I_{\text{coh}} - \sum x_i f_i^2}{(\sum x_i f_i)^2} \quad (1)$$

where I_{coh} is the coherent scattered intensity per atom, x_i and f_i are, respectively, the mole fraction and scattering factor of i -type atoms, and the summation covers all atom species. This definition differs from the traditional forms (e.g. Kruh¹³) in the denominator, which is usually f_e^2 , the function $f_e(S)$ being a sort of average scattering factor per electron chosen to satisfy the assumption

$$f_i = K_i f_e \quad (2)$$

as well as possible for each component; K_i is a constant coefficient on the order of the atomic number of i -type atoms.

Without any assumptions regarding the scattering factors, the formal Fourier inversion of $i(S)$ may be carried out,

$$\bar{\rho}rH(r) = \frac{1}{2\pi^2} \int_0^{\infty} si(s) \sin sr ds \quad (3)$$

where $H(r)$ can be shown to be a weighted sum of functions $H_{ij}(r)$, each of which is a convolution of $h_{ij}(r)$ with a particular function of the scattering factors. Details are discussed by Pings and Waser.¹⁴ The function $h_{ij}(r) = g_{ij}(r) - 1$ where $g_{ij}(r) = \rho_{ij}(r)/\bar{\rho}_j$ and $\rho_{ij}(r)$ is the density of

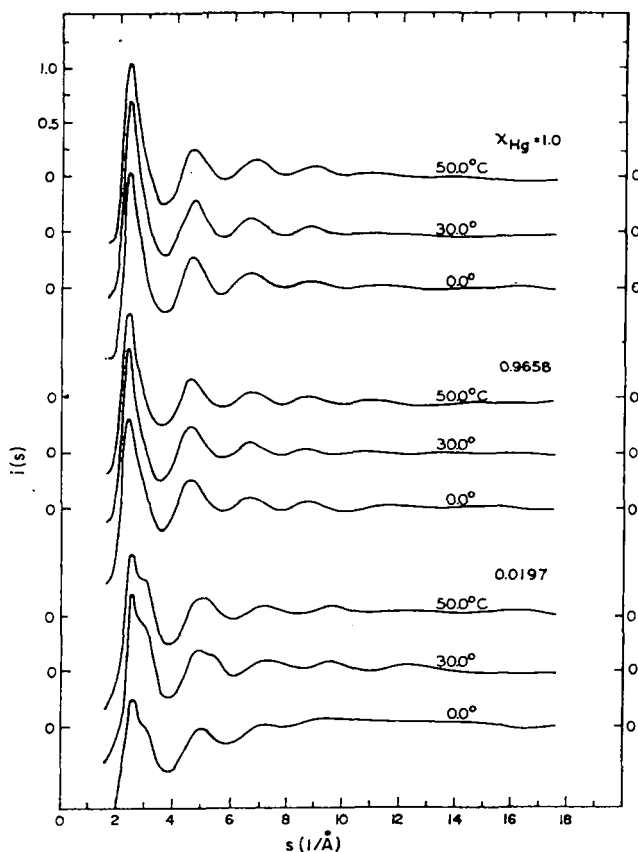


Figure 1. Analytical approximation to $i(S)$ curves for pure mercury and the two mixtures.

j -type atoms at a distance r from an i -type atom. Now if the assumption of Eq. (2) is employed $H(r)$ may be expressed as

$$H(r) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \frac{K_i K_j}{[\sum x_i K_i]^2} h_{ij}(r) \quad (4)$$

The function $f_e(S)$ is never explicitly defined in this type of development, though the denominator in Eq. (1) may be said to correspond to choosing an $f_e(S)$ depending on composition. The particular advantage of the $i(S)$ definition and inversion given here is their close relation to the standard forms for a monatomic liquid, which arise simply and exactly when one of the mole fractions is set to unity.

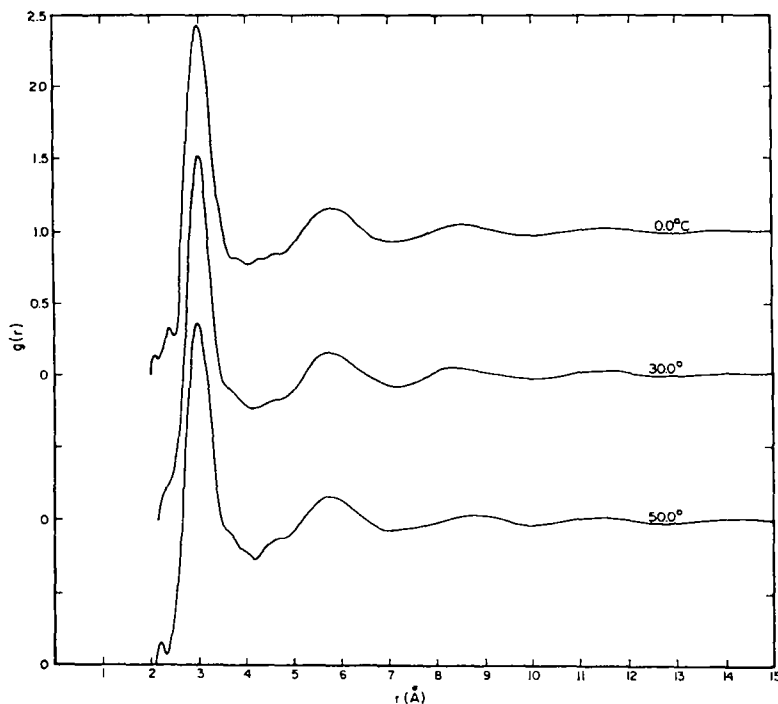


Figure 2. Radial distribution function for pure mercury.

Figure 1 shows the $i(S)$ curves obtained for the two solutions and pure mercury at 0°C, 30°C, and 50°C. These curves are plotted from piecewise polynomial approximations to the experimental points; the approxi-

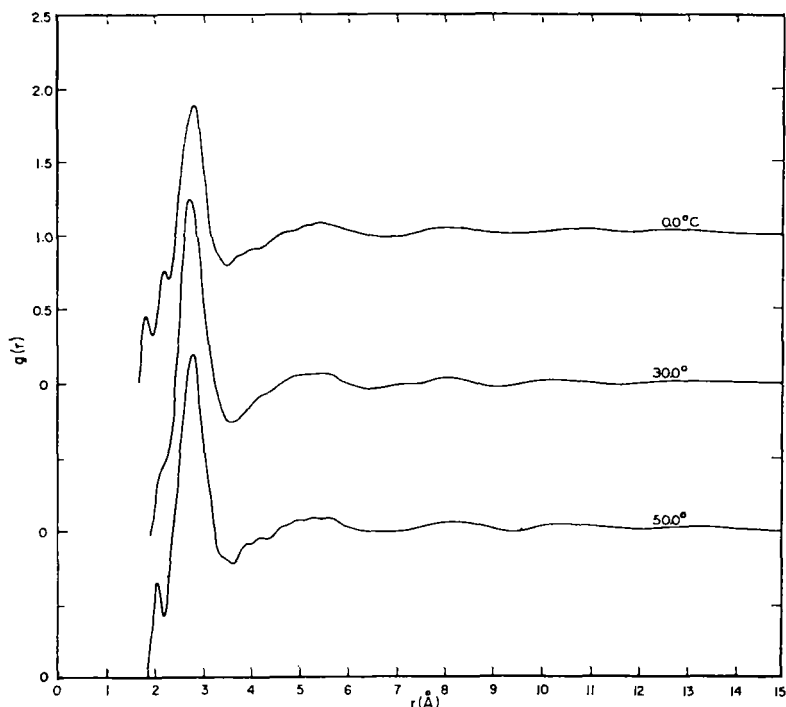


Figure 3. Radial distribution function for mercury-gallium mixture containing 0.97 mole fraction mercury.

mations were used to evaluate the inversion integral. Figures 2, 3, and 4 show the radial distribution functions $g(r) = H(r) + 1$ obtained from the inversions. Table 1 summarizes the positions of the first three peaks in the $g(R)$ curves and gives estimated coordination numbers for the near-neighbor shell by three methods of integrating the corresponding $4\pi^2(R)$ distributions. Method A postulates a high- R side of the first peak symmetric with the calculated low- R side; for method B the integration is taken to the high- R minimum defining the first peak; in method C the peak integrated is the residual from extrapolating the low- R side of the second peak to the R abscissa.

As indicated by Eq. (4), these $g(r)$ curves and the computed coordination numbers have a complex meaning for the polyatomic liquids. The possible pair interactions are weighted not only by relative concentration, but also according to scattering power. In the case of the system

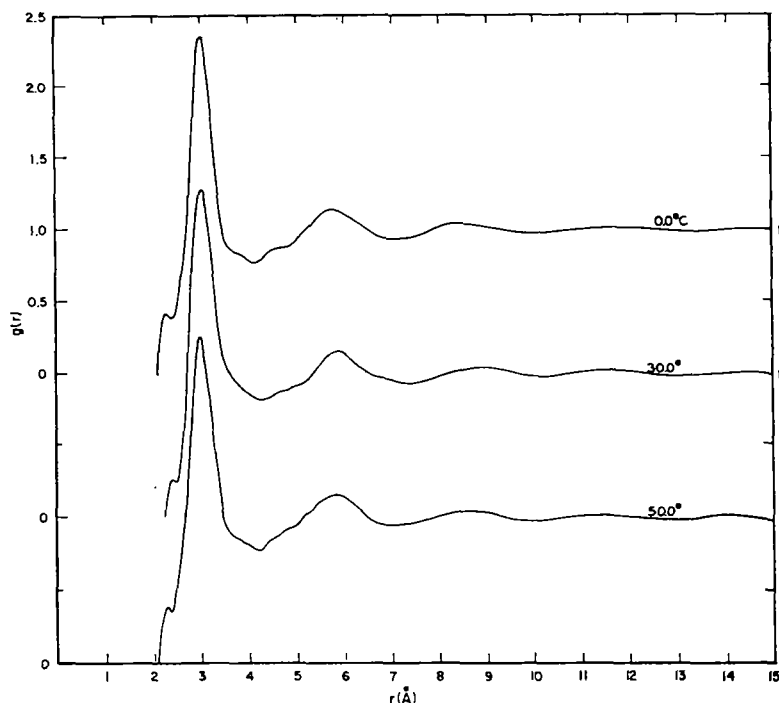


Figure 4. Radial distribution function for mercury-gallium mixture containing 0.02 mole fraction mercury.

containing a low concentration of mercury in gallium, the computed function $g(r)$ corresponds essentially to the distribution of the gallium pairs.

The structural interpretation for pure mercury essentially corroborates the results recently obtained by Kruh.¹⁵ The scattering function and structural distribution obtained for the gallium-in-mercury solution are not significantly different from those for pure mercury. The result appears reasonable in view of the low gallium solubility and the considerably greater scattering cross section of mercury. In the case of the mercury-in-gallium solution, however, the measured $i(S)$ curves in all three cases are significantly different than those obtained for pure gallium; the most striking feature for the mixture scattering function is an exaggerated shoulder on the right hand side of the first peak. Also, the coordination numbers are significantly smaller than those obtained for pure gallium.⁴

TABLE I Features of the radial distribution curves and coordination number

State		Peak distance			Coordination number		
Temp. °C	Comp. X_{Hg}	1st peak (Å)	2nd peak (Å)	3rd peak (Å)	(atoms) ^a (±.1)	(atoms) ^b (±.5)	(atoms) ^c (±.5)
0	1.0	3.02	5.82	8.60	7.5	8.7	8.5
30	1.0	3.02	5.80	8.50	7.3	8.4	8.3
50	1.0	2.98	5.80	8.70	7.0	8.4	8.1
0	0.9658	2.98	5.78	8.44	7.8	8.3	10.0
30	0.9658	3.00	5.86	8.84	7.0	8.5	9.0
50	0.9658	2.98	5.82	8.62	7.1	7.7	8.4
0	0.0197	2.86	5.47	8.12	8.5	8.3	9.9
30	0.0197	2.74	5.45	8.14	7.7	8.7	8.8
50	0.0197	2.75	5.48	8.14	7.9	8.4	9.3
0	0.0 ^d	2.83	5.52	8.27	9.2	11.1	10.8
30	0.0	2.80	5.47	8.41	8.4	10.8	10.7
50	0.0	2.81	5.47	8.33	8.0	10.8	10.6

^a Symmetrical curve method

^b Vertical boundary method

^c Second peak extrapolating method

^d The pure Ga data are from S. E. Rodriguez and C. J. Pings, *J. Chem. Phys.*, **42**, 2435 (1965)

For the Au-Sn system, Kaplow, Strong, and Averbach¹⁶ conjectured that the liquid mixture was not totally random, and accounted for the experimentally observed coordination numbers with a model involving Au-Sn complex in the liquid phase. The decrease discussed above for Hg-Ga probably cannot be as simply explained since the Hg atoms are present only in a ratio of about 1 in 50. However, previous work⁴ has suggested the existence of a Ga-Ga complex in the liquid, and it may be that only a few Hg atoms adversely effect the packing of such relatively bulky dimers.

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