

Table III. Comparison of the Value of " ω " the Interaction Constant Parameter Obtained from Different Measurements at 30° C.

Systems	" ω " Cal. Mole ⁻¹		
	Heats of mixing	Boiling points	Surface tension
Benzyl acetate and dioxane	-118	894	104
Benzyl acetate and aniline	-64	24	924
Benzyl acetate and <i>m</i> -cresol	-1064		463

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LITERATURE CITED

- (1) Chaudhri, M.M., Katti, P.K., Baliga M.N., *Trans. Faraday Soc.* **55**, 2013 (1959).
- (2) Errera, J., Gaspard, R., Sack, H., *J. Chem. Phys.* **8**, 63, (1940).
- (3) Gordy, W., Neilsen, A.H., *Ibid.*, **6**, 12 (1938).
- (4) Guggenheim, E.A., "Mixtures," Oxford University Press, New York, 1952.
- (5) Katti, P.K., Chaudhri, M.M., *Proc. Natl. Inst. Sci. India* **24**, 330, (1958).
- (6) Katti, P.K., Chaudhri, M.M., *J. Chem. Phys.* **35**, 756, (1961).
- (7) Mathot, V., Desmyter, A., *Ibid.*, **21**, 782, (1953).
- (8) Moore, W.R., Russell, J., *J. Appl. Chem.* **4**, 369, (1954).
- (9) Moore, W.R., Styant, G.E., *Trans. Faraday Soc.* **52**, 1556, (1956).
- (10) Smith, R.P., *J. Am. Chem. Soc.* **54**, 2626 (1932).
- (11) Thacker, R., Rowlinson, J.S., *Trans. Faraday Soc.* **50**, 1036 (1954).

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Densities of Binary Mercury-Rich Amalgams of Cadmium and Zinc

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Densities have been measured in binary mercury-rich amalgams containing 0 to 10 atomic per cent cadmium and 0 to 5.6 atomic per cent zinc. Measurements were obtained over a temperature range from 50° to 150° C. Using the method of least squares, the density values were used to determine a linear expression for zinc amalgam densities and a quadratic expression for cadmium amalgam densities as a function of the atomic fraction of the solute.

DENSITIES FOR MERCURY-RICH AMALGAMS of cadmium and of zinc at temperatures from 50° to 150° C. have been measured as part of an investigation of liquid diffusion behavior in these systems. The density data previously available for these systems consisted of measurements at 25° C. by Hulett and De Lury (2) for cadmium amalgams and by Crenshaw (1) for zinc amalgams.

EXPERIMENTAL

Materials and Apparatus. The materials and chemicals used in this work were ACS Reagent Grade except for the cadmium which was obtained from the Consolidated Mining and Smelting Co. of Canada, Ltd., and contained 99.999% Cd.

Dilute amalgams were prepared by dissolving the solute

zinc or cadmium directly in the mercury. The technique of Hulett and De Lury (2) was used in the production of the more concentrated amalgams. In this technique, mercury is made the cathode of a cell, and a platinum anode is placed in distilled water over the mercury; the solute material is placed on the mercury surface, and a 12-volt potential applied to the cell in order to enhance the amalgam formation. This type of cell also provided a convenient method for storing the prepared amalgams to avoid the preferential oxidation of the solute. Amalgams were in some instances stored under a deoxygenated glycerol layer.

The pycnometers used in the density measurements were made using a T/S No. 19/38 borosilicate glass ground joint as shown in Figure 1. The capillary section of the pycnometer was approximately 0.5 mm. inside diameter. The pycnometer volumes were approximately 14.5 cc. and the weight of the pycnometer and amalgam charge was approximately 190 grams. The apparatus shown at the right in Figure 1 was used in the preparation of some

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amalgams under an argon atmosphere and for loading the pycnometers. The arrangement of stopcocks permitted the pycnometer, when attached to the bottom end, to be evacuated before the filling operation. Density measurements were made in constant temperature bath facilities. As many as four calibrated thermocouples were located in the baths at various positions to measure temperature and check for gradients. The temperature variation in the baths was no more than $\pm 0.01^\circ\text{C}$. during data measurements.

Amalgams of the compositions listed in Table I were prepared by gravimetric techniques. In each case, the amount of solute added was completely dissolved. The accuracy of the reported values of composition is estimated as better than $\pm 0.0001\%$.

Procedure. Densities for cadmium and zinc amalgams were measured in pycnometers that were calibrated by using pure

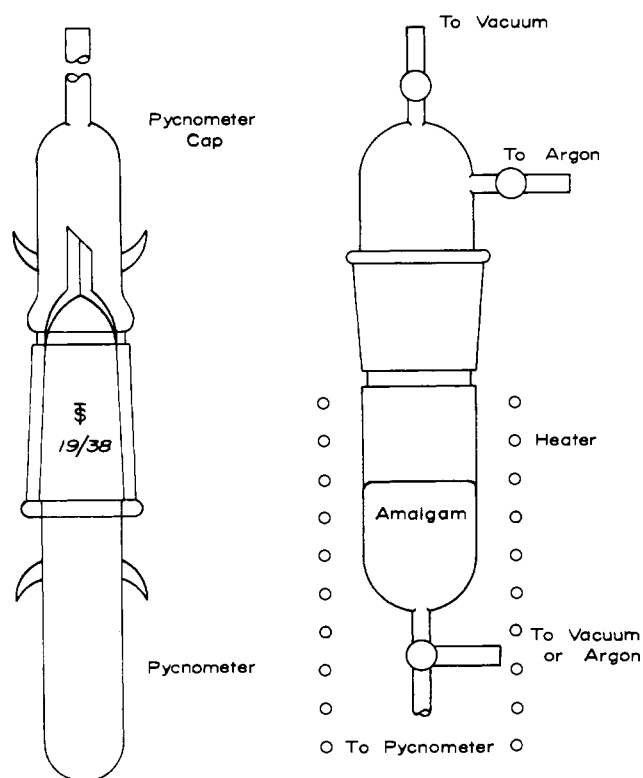


Figure 1. Pycnometer and pycnometer filling apparatus

Table I. Densities of Various Cadmium or Zinc Amalgams vs. Temperature, Average of Five Measured Values

Atomic Per Cent Solute	Amalgam Density, Gram/Cc., at Temperature $^\circ\text{C}$.				
	50.0	70.2	93.2	119.1	150.0
Cadmium Amalgams					
0.1047	13.4689	13.4199	13.3626	13.3001	13.2269
0.5250	13.4550	13.4066	13.3511	13.2885	13.2162
2.625	13.3852	13.3382	13.2832	13.2206	13.1500
5.169	13.2979	13.2515	13.1983	13.1375	13.0688
9.998	13.1206	13.0760	13.0253	12.9695	12.9035
Zinc Amalgams					
0.0583	13.4698	13.4211	13.3630	13.2987	13.2247
0.350	13.4625	13.4140	13.3581	13.2943	13.2140
1.750	13.4345	13.3765	13.3194	13.2572	13.1831
3.446	13.3705	13.3246	13.2701	13.2102	13.1399
5.609	13.3136	13.2672	13.2137	13.1517	13.0828
Mercury (3)					
	13.4729	13.4238	13.3682	13.3059	13.2319

mercury. The procedure was to fill a pycnometer with amalgam and then place it in the constant temperature bath. As thermal equilibrium was reached, the excess amalgam (which was present because of the lower filling temperature) overflowed from the pycnometer and was caught in the cavity between the capillary section of the pycnometer and the top piece. After the pycnometer was removed from the bath and all oil cleaned from the outside, the pycnometer and contents were weighed on a standard analytical balance using an empty pycnometer as a counterpoise. The weight of the pycnometer when empty (measured against the same counterpoise) was subtracted from the weight of the pycnometer plus amalgam. This quantity was then divided by the pycnometer volume to give the amalgam density.

Each pycnometer volume was determined as a function of temperature from the pure mercury calibration data. The calibration procedure was exactly as described above for the amalgam measurements to the point of calculating the density. The average weight of mercury in the pycnometer from five measurements was divided by the density of mercury (3) to obtain the pycnometer volume. The values of volume were then used with each measured weight to calculate the experimental densities of pure mercury. These experimental mercury densities were then used to analyze statistically for pycnometer bias and to establish the precision of this technique. The statistical tests showed that the pycnometer bias was not significant at a confidence level of 0.999.

RESULTS

Amalgam densities for solutions of up to 10 atomic per cent cadmium in mercury and up to 5.6 atomic per cent zinc in mercury were obtained. These data, obtained in the temperature interval from 50.0° to 150.0°C ., are shown as Figures 2 and 3. The average values from five determinations at each condition are presented in Table I. The standard deviation of these measurements was about ± 0.00055 gram/cc., and the standard deviation of the average would be ± 0.00024 gram/cc.

The zinc amalgam density data were least square fitted to the linear relationship

$$\rho_a = A N_{\text{Zn}} + \rho_T \quad (1)$$

where

ρ_a = density of amalgam

A = a constant

N_{Zn} = atomic fraction of zinc

ρ_T = density of pure mercury at temperature

Since the intercept was fixed as the value for pure mercury, only the slopes were determined by the method of least squares. The values for A as a function of temperature are summarized in Table II.

A quadratic expression was selected for least square fitting density data for cadmium amalgams:

$$\rho_a = A N_{\text{Cd}}^2 + B N_{\text{Cd}} + \rho_T \quad (2)$$

The values of the constants A and B are also given in Table II. The curves shown in Figures 2 and 3 are those calculated from Equations 1 and 2, respectively.

Table II. Least Square Fit Constants for Cadmium and Zinc Amalgam Densities

Temp., $^\circ\text{C}$.	Zinc Amalgams		Cadmium Amalgams	
	A	B	A	B
50.0	-2.866	-2.658	-3.257	
70.2	-2.806	-2.949	-3.184	
93.2	-2.786	-2.807	-3.149	
119.1	-2.758	-1.877	-3.176	
150.0	-2.681	-2.495	-3.035	

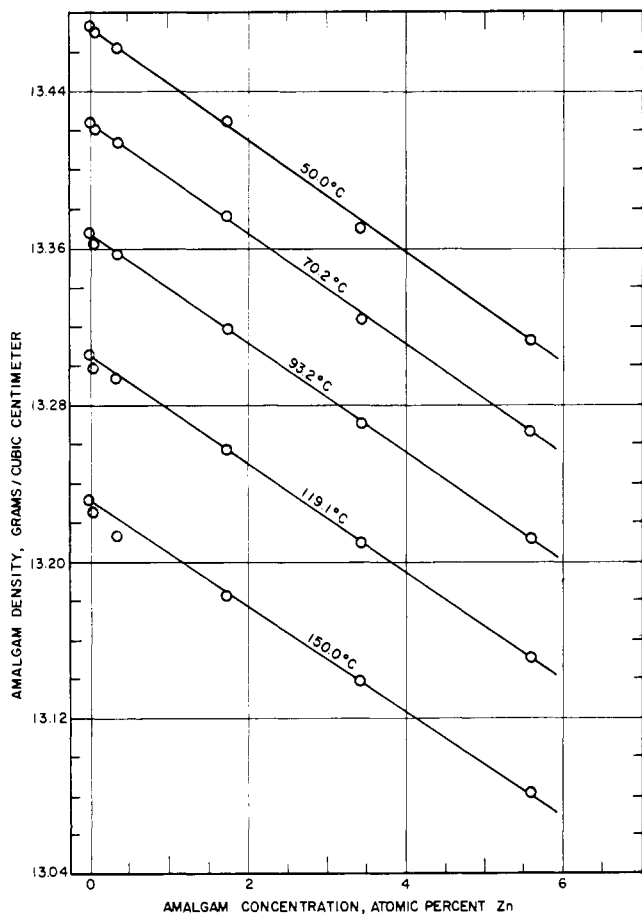


Figure 2. Density of zinc amalgams
(Curves calculated from Equation 1 with values from Table II)

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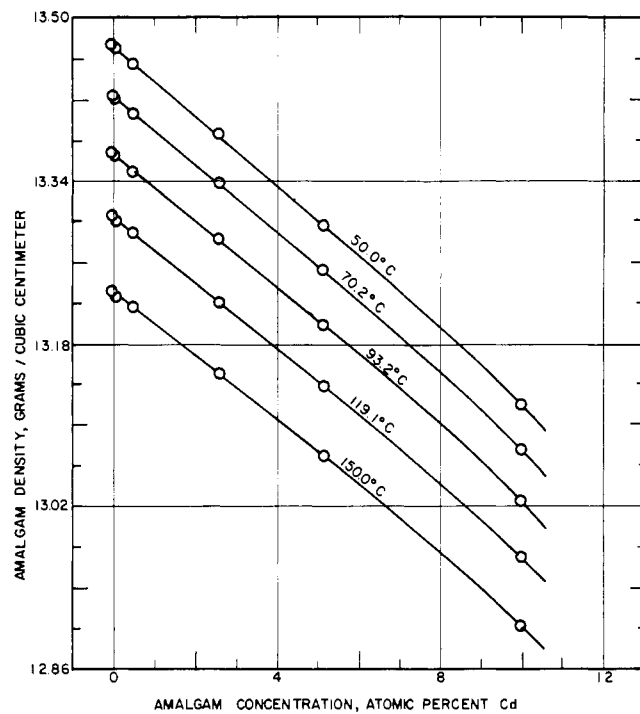


Figure 3. Density of cadmium amalgams
(Curves calculated from Equation 2 with values from Table II)

LITERATURE CITED

- (1) Crenshaw, J.L., *J. Phys. Chem.* **14**, 158 (1910).
- (2) Hulett, G.A., De Lury, R.E., *J. Amer. Chem. Soc.* **30**, 1805 (1908).
- (3) International Critical Tables, Vol II, p. 458, McGraw-Hill, New York, 1933.

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