f_i	fugacity of component i, atm
H	Henry's constant, atm
$\hat{H}$	mean of experimental Henry's constants, atm
n_i	moles of component i
P	pressure, atm
P_i	partial pressure of component i, y_iP, atm
R	gas constant, 82.056 cm^3 atm K^{-1} g-mol^{-1}
T	absolute temperature, K
V^i	volume of phase i, cm^3
V_1	saturated liquid molar volume of solvent, cm^3 g-mol^{-1}
$\bar{V}_i$	partial molar volume of component i, cm^3 g-mol^{-1}
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Greek

α	isothermal compressibility of liquid phase, $-(1/V)(\partial V/\partial P)_T$, atm^{-1}
ρ	molar density, g-mol cm^{-3}
$\hat{\sigma}_H$	standard root-mean-square error of experimental Henry's constant
ϕ_i	fugacity coefficient of component i

Subscripts

1	of the solvent (liquid)
2	of the solute (gas)
M	of the mixture

Superscripts

T	total in system (added to bomb)
L	in the liquid phase
V	in the vapor phase
sat	pure saturated solvent, component 1
∞	at infinite dilution

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Received for review November 12, 1976. Accepted April 4, 1977.

Densities of the Molten Salt System Cesium Bromide–Cuprous Bromide

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Densities of the molten salt system cesium bromide–cuprous bromide have been measured at nine mole fractions over the complete composition range and in the temperature range 507–950 °C using the method of Archimedean displacement. The temperature coefficients of the densities have been evaluated from these measurements.

The present work was undertaken as part of a research project of the above mentioned department on the properties of molten cuprous halide–alkali halide systems.

Experimental Section

Materials. Cesium bromide (Merck/Suprapur) was dried under dynamic vacuum at 300 °C for 24 h and used without further purification. Cuprous bromide (Riedel-de Haën, 99%) was further purified (*4, 5*) by dissolving it in the minimum amount of 47% hydrobromic acid (Merck/Suprapur) and reprecipitating by dilution with deaerated distilled water containing 1 g of anhydrous sodium sulfite per liter. The white precipitate was washed successively with water (as described for the dilution process) and acetone and then vacuum dried as specified for the cesium bromide. To minimize oxidation of the purified cuprous bromide during subsequent handling it was melted under vacuum and formed a light green crystalline substance upon cooling. All storage and handling of the purified salts took place under an atmosphere of nitrogen, purified and dried by passing it through columns containing silica gel (Merck) and Type 5A molecular sieve (BDH Chemicals Limited).

Apparatus and Procedure. The furnace, balance, sample assembly, and experimental procedure were similar to those described by Brookes and Paul (*1*), except for the following respects.

The nichrome suspension wire hanging from the stirrup of the balance to the sinker (bob) went through a short length (2 cm) of a Silicone rubber tube attached to the top of the Pyrex tube enclosing the suspension wire. The Silicone tube could be clamped vacuum tight which enabled the system to be evacuated or kept under a completely closed inert atmosphere. During the short time an actual mass measurement was conducted the clamp on the Silicone tube was released and dry purified nitrogen escaped through the Silicone tube to the atmosphere. The nitrogen was released at a fixed pressure during each mass measurement to ensure a constant upthrust by the gas on the suspension wire. Prior to each mass measurement the system was subjected to a vacuum to remove possible nitrogen bubbles from the sinker.

The relatively high vapor pressure of cuprous bromide (*3*) leads to condensation on the suspension wire. To correct for the condensation the wetting of the sinker, after immersion in a molten salt mixture, was determined at the beginning of each run before condensation occurred on the suspension wire. The wetting of the sinker as a function of temperature at a given mole fraction was determined by duplicate runs beginning at various temperatures. Once the wetting of the sinker was known it was possible to make a correction for the condensation on the sus-

Table I. Least-Squares Fits for the Densities Fitted to Equation 1

Mole fraction of CsBr	a, g cm^{-3}	$10^3 b$, g cm^{-3} K^{-1}	Std dev	Temp range, °K
85.097	4.283_4	1.232	0.0019	918–1226
74.239	4.451_0	1.326	0.0020	880–1223
58.763	4.586_4	1.377	0.0028	870–1222
40.543	4.617_3	1.231	0.0021	850–1226
30.000	4.932_2	1.400	0.0027	861–1223
19.961	5.021_7	1.300	0.0035	849–1227
10.467	5.085_8	1.141	0.0058	840–1224
0.000 (pure CuBr)	5.282_8	0.916	0.0067	780–1224

pension wire. The mass of the sinker was measured inside (to a known depth) and outside the melt at each temperature. Results of density calculations from heating and cooling cycles of duplicated runs justified this correction procedure.

Room-temperature sinker volumes were determined by mass measurements in air of a known density and to a known depth in deaerated distilled water and in benzene and chloroform of spectroscopic purity. There were no significant changes in the sinker volumes before and after each run.

Corrections were made for the positive effect of surface tension (*6*). The surface tension of cuprous bromide is not known and was taken as 150 ± 100 dyn cm^{-1}. By using a heavy sinker of approximately 17 g and a 0.15 mm diameter platinum wire fastened to the sinker, the uncertainty in the surface tension of cuprous bromide leads to a maximum error of ±0.06% in the density values on the cuprous bromide rich side of the composition rage. This uncertainty is incorporated in the standard deviations reported in Table I.

Results and Discussion

The densities of pure cesium bromide, determined at eight temperatures between 645 and 950 °C, agreed to within 0.03% with the densities recommended by Janz (*2*), namely

$$\rho(\mathrm{g\ cm^{-3}}) = 4.2449 - (1.2234 \times 10^{-3})T\,(°\mathrm{K})$$

All the experimental density data were linearly dependent upon temperature and fitted to equations of the form

$$\rho = a - bT$$

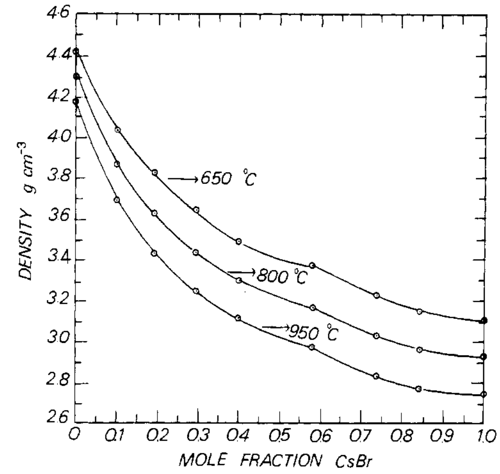

Figure 1. Densities of the CsBr–CuBr system as calculated at 650, 800, and 950 °C, from the data in Table I.

where ρ is in grams per cubic centimeter and T in Kelvin. The constants for the temperature-density equations were calculated using the method of least squares and are listed together with the standard deviations of the densities in Table I. The increase in the standard deviations toward the cuprous bromide rich side may be attributed to the relative high volatility of cuprous bromide under the present experimental conditions and to the uncertainty in the surface tension of cuprous bromide.

Figure 1 gives overview of the densities, calculated from the data in Table I, over the entire composition range at three chosen temperatures.

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Received for review November 22, 1976. Accepted April 6, 1977. Financial assistance from the University of Zululand is acknowledged.