# Part I

## CHEMICAL ENGINEERING

## INORGANIC CHEMISTRY

## PHYSICAL CHEMISTRY

# Densities and Molal Volumes of Molten Magnesium Chloride, Potassium Chloride, and Barium Chloride Mixtures

J. N. REDING
Metallurgical Laboratory, Dow Metal Products Company, Midland, Mich.

**Results obtained from density determinations of molten mixtures of $MgCl_2$, KCl, and $BaCl_2$ by the buoyancy method are reported. The densities and molal volumes at 800° C. and the temperature coefficients of the densities, as determined by interpolation of the plotted data, are presented for each composition studied.**

PHYSICAL PROPERTIES of molten salts pertinent to the magnesium industry are being determined to develop a better understanding of magnesium-molten salt processes. This paper presents the density and molal volume data obtained on the ternary system $MgCl_2$-KCl-$BaCl_2$. These salts are the basic constituents of many of the magnesium melting fluxes.

The densities were determined by the buoyancy method using a tungsten sinker. Because of the hygroscopic nature of magnesium chloride, the determinations were made under an argon atmosphere.

The results are presented in tabular and plot form for a series of binary systems. In each binary system, the ratio of barium chloride to potassium chloride is maintained constant while the ratio of the two salts to magnesium chloride is varied. The data incorporated in the paper for the $BaCl_2$-KCl system were not determined under this work but were taken from the paper of Bothwell and Peake (*2*). Other investigators have reported density data for the $MgCl_2$-KCl and $MgCl_2$-$BaCl_2$ binary systems. Some of their data are presented here for comparison.

## PROCEDURE

In the buoyancy method, the density of a liquid is calculated from a knowledge of the buoyant force exerted by the liquid on a totally submerged sinker of known volume. A sketch of the apparatus is presented in Figure 1. The tungsten sinker is hung from an analytical balance and hangs freely in the system. To prevent salt vapors from condensing on the sinker wire during a run, argon gas is continually passed through the guide tube that surrounds the wire. This tube is fixed in space and extends through a bearing in the top flange to just above the crucible. The stainless steel

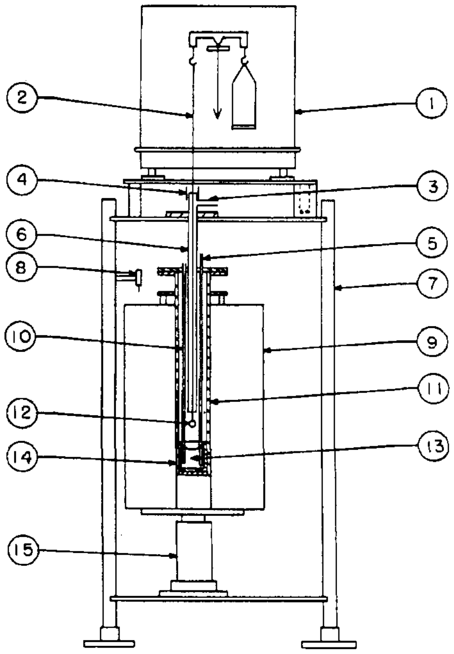

Figure 1. Schematic and density apparatus
1. Balance. 2. Platinum suspension wire. 3. Argon inlet. 4. Rubber tubing. 5. Argon mixing tube. 6. Guide tube. 7. Stand. 8. Dial indicator. 9. Electric resistance furnace. 10. Stainless steel thermocouple well. 11. Stainless steel shell. 12. Tungsten sinker. 13. Salt melt. 14. Stainless steel crucible. 15. Hydraulic jack

shell and crucible move with the electrical resistance furnace which can be raised or lowered with a hydraulic jack. A stainless steel thermocouple well and argon mixing tube extend from the top flange of the shell into the crucible. A chromel-alumel thermocouple is used to measure the temperature of the melt. The argon gas is purified by passing it through a bed of titanium sponge maintained at 1400° F.

The potassium chloride used in this investigation was Baker and Adamson reagent grade material. The salt was dried under vacuum at 400° C. for 12 hours or more. The barium chloride was obtained by drying the Baker and Adamson reagent grade barium chloride dihydrate under vacuum for 12 hours at 200° C. and then for 5 hours at 500° C. The magnesium chloride was obtained from the core of anhydrous magnesium chloride cakes purchased from titanium and zirconium producers. The magnesium chloride was given the same drying treatment as the barium chloride. Only that magnesium chloride which contained less than 1.0% MgO and more than 99.0% $MgCl_2$ after drying was accepted for the experiments. All of the dried salts were stored in tightly sealed Mason jars that had been previously flushed with argon and dried. The mixes for the experiments were formulated by adding the ingredients to the crucible in their proper proportions. No further attempt was made to check the composition of the melt after the density determination.

Prior to placement of the sinker within the guide tube, the system with the crucible and its charge was maintained at 300° C. for 16 hours and then brought to 900° C. while being continually flushed with argon. After the charge had been mixed at 900° C. for 2 minutes by bubbling argon through the melt, the sinker and wire assembly were placed in position. The weight of the sinker assembly in argon was determined, and then the sinker was immersed in the usual fashion (*2*) to a known depth in the melt. The temperature of the melt was maintained constant for 15 minutes, and the weight of the sinker was determined. Then the system was brought to the next temperature without moving the sinker, and the weight of the sinker was determined again. Before each measurement, the temperature of the melt was maintained constant within ±2° C. for 15 minutes by controlling the power input to the furnace through a manually operated variable transformer. Normally the measurements were determined at 900° C., then at 50° C. intervals until reaching 750° C., and again at 50° C. intervals until reaching 925° C.

This method provided a good check on the measurements and made it possible to determine if there were any gradual build up of salt on the wire or change in salt composition owing to vaporization or hydrolysis.

The density of the melt, $\rho$, was calculated from the data by using the well known equation:

$$\rho = \frac{W_a - [W_m - (\pi D_w \gamma_m)/g]}{V_b}$$

$W_a$ = weight of the sinker in argon, grams.

$W_m$ = weight of the sinker in the melt, grams.

$D_w$ = diameter of the wire properly corrected for temperature, cm.

$\gamma_m$ = surface tension of the melt. In most cases, we assumed that it was directly proportional to the molar composition of the melt and the surface tension of the pure components, dynes/cm.

$g$ = gravity, cm./sec.$^2$

$V_b$ = volume of the sinker properly corrected for temperature, cm.$^3$ (The volume of the sinker was periodically determined at room temperature by solving the above equation for $V_b$ after taking the data for a liquid of known density—*i.e.*, $CCl_4$ and $H_2O$.)

## EXPERIMENTAL RESULTS

The results of this investigation are presented in Table I. The experimental data for $MgCl_2$ and KCl are plotted in Figure 2 and are compared with those of other investigators (*2, 4, 5*). Figure 3 is a presentation of the molal volume data for the pseudobinary systems studied as a function of $MgCl_2$ concentration. Molal volume values calculated from the

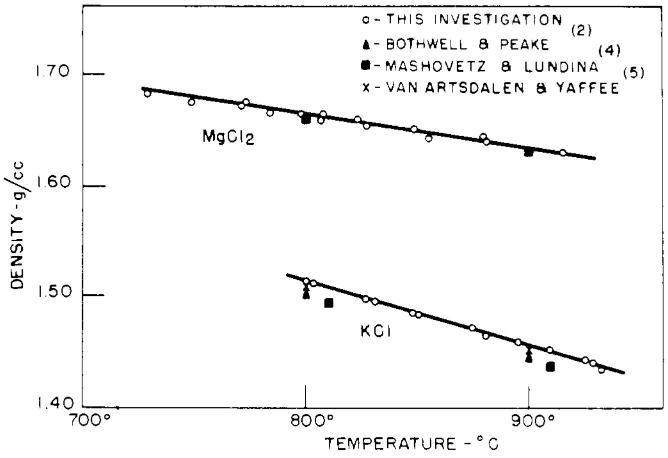

Figure 2. Density of KCl and $MgCl_2$ vs. temperature

Table I. Densities and Temperature Coefficients of Density of $MgCl_2$–KCl–$BaCl_2$ Mixtures at 800°

$$d_4^t = d^{800} - K\,(t - 800°)$$

| Mole % | | | $d^{800°}$ (G./Ml.) | $K \times 10^3$ (G./Ml., °C.) |
|---|---|---|---|---|
| $MgCl_2$ | KCl | $BaCl_2$ | | |
| ... | 100.0 | ... | 1.514 | 0.58 |
| 8.0 | 92.0 | ... | 1.509 | 0.55 |
| 16.4 | 83.6 | ... | 1.508 | 0.49 |
| 35.5 | 64.5 | ... | 1.520 | 0.47 |
| 54.0 | 46.0 | ... | 1.572 | 0.50 |
| 64.8 | 35.2 | ... | 1.630 | 0.50 |
| 75.8 | 24.2 | ... | 1.643 | 0.49 |
| 87.6 | 12.4 | ... | 1.665 | 0.43 |
| 100.0 | ... | ... | 1.666 | 0.30 |
| ... | 96.2[a] | 3.8 | 1.578 | ... |
| 17.3 | 79.6 | 3.1 | 1.584 | 0.53 |
| 31.1 | 66.3 | 2.6 | 1.576 | 0.52 |
| 45.5 | 52.4 | 2.1 | 1.594 | 0.53 |
| 60.8 | 37.7 | 1.5 | 1.629 | 0.53 |
| 77.1 | 22.0 | 0.9 | 1.659 | 0.47 |
| ... | 89.3[a] | 10.7 | 1.727 | ... |
| 14.3 | 76.9 | 8.8 | 1.698 | 0.55 |
| 28.5 | 63.9 | 7.6 | 1.682 | 0.54 |
| 38.4 | 55.0 | 6.6 | 1.672 | 0.53 |
| 48.3 | 46.2 | 5.5 | 1.697 | 0.51 |
| 63.3 | 32.8 | 3.9 | 1.694 | 0.53 |
| ... | 80.7[a] | 19.3 | 1.910 | ... |
| 20.9 | 63.8 | 15.3 | 1.847 | 0.61 |
| 36.2 | 51.5 | 12.3 | 1.804 | 0.56 |
| 51.3 | 39.3 | 9.4 | 1.780 | 0.58 |
| 66.2 | 27.3 | 6.5 | 1.758 | 0.53 |
| 80.8 | 15.5 | 3.7 | 1.743 | 0.47 |
| ... | 65.0[a] | 35.0 | 2.240 | ... |
| 29.9 | 45.6 | 24.5 | 2.067 | 0.61 |
| 56.0 | 28.6 | 15.4 | 1.940 | 0.58 |
| 65.6 | 22.4 | 12.0 | 1.892 | 0.53 |
| 74.9 | 16.4 | 8.7 | 1.853 | 0.54 |
| 87.8 | 8.0 | 4.2 | 1.759 | 0.41 |
| ... | 41.2[a] | 58.8 | 2.671 | ... |
| 28.7 | 29.4 | 41.9 | 2.414 | 0.71 |
| 40.9 | 24.4 | 34.7 | 2.300 | 0.65 |
| 61.6 | 15.8 | 22.6 | 2.110 | 0.53 |
| 70.7 | 12.0 | 17.3 | 2.011 | 0.53 |
| 86.5 | 5.6 | 7.9 | 1.846 | 0.42 |
| ... | ... | 100.0[a] | 3.257[b] | 0.69 |
| 19.6 | ... | 80.4 | 3.074[b] | 0.71 |
| 42.2 | ... | 57.8 | 2.802 | 0.75 |
| 68.6 | ... | 31.4 | 2.323 | 0.64 |
| 86.8 | ... | 13.2 | 1.957 | 0.47 |
| 95.2 | ... | 4.8 | 1.785 | 0.36 |

[a] Data for KCl–$BaCl_2$ from Bothwell and Peake.
[b] Extrapolated values.

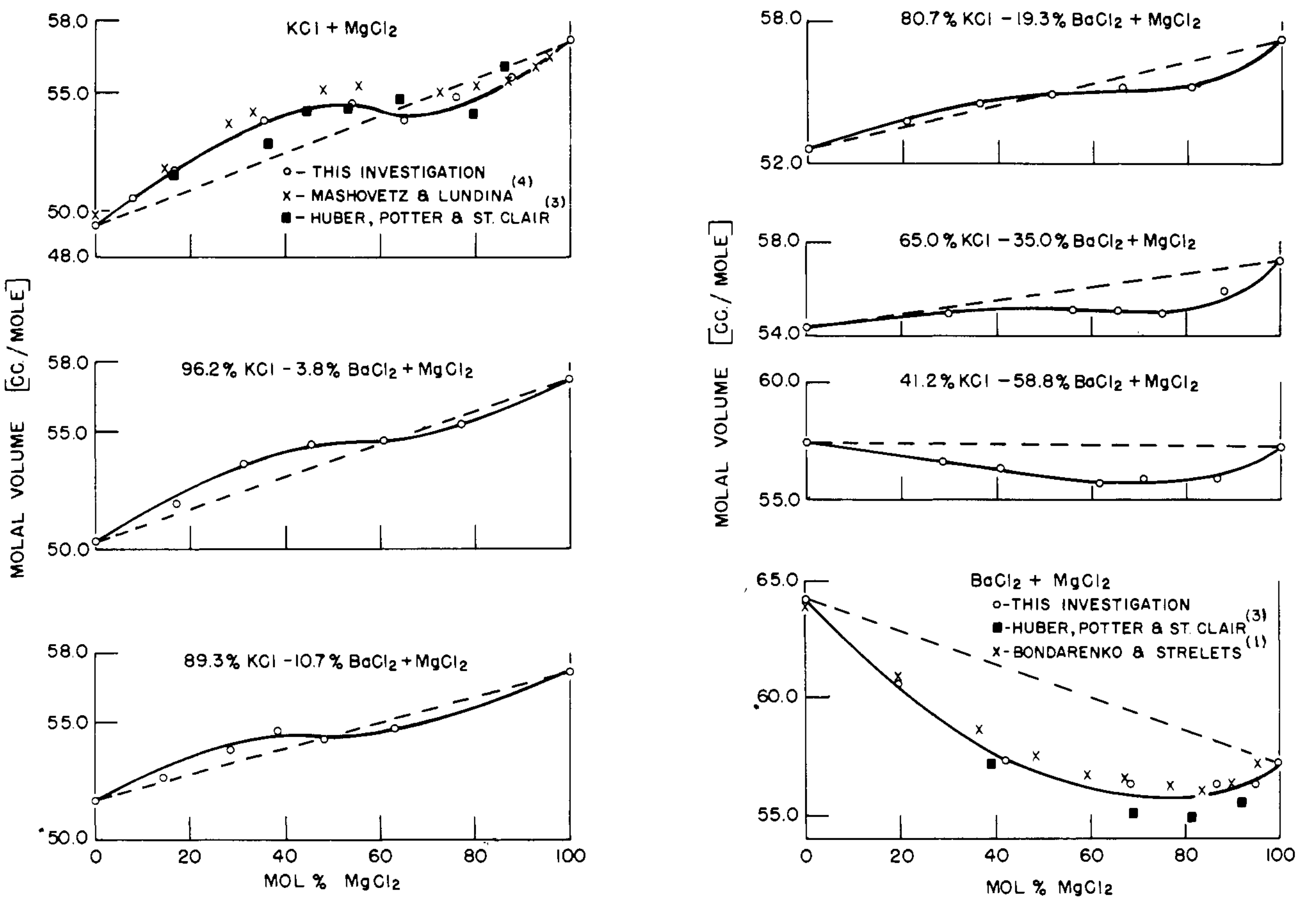

Figure 3. Molal volume *vs.* $MgCl_2$ concentration at 800° C.

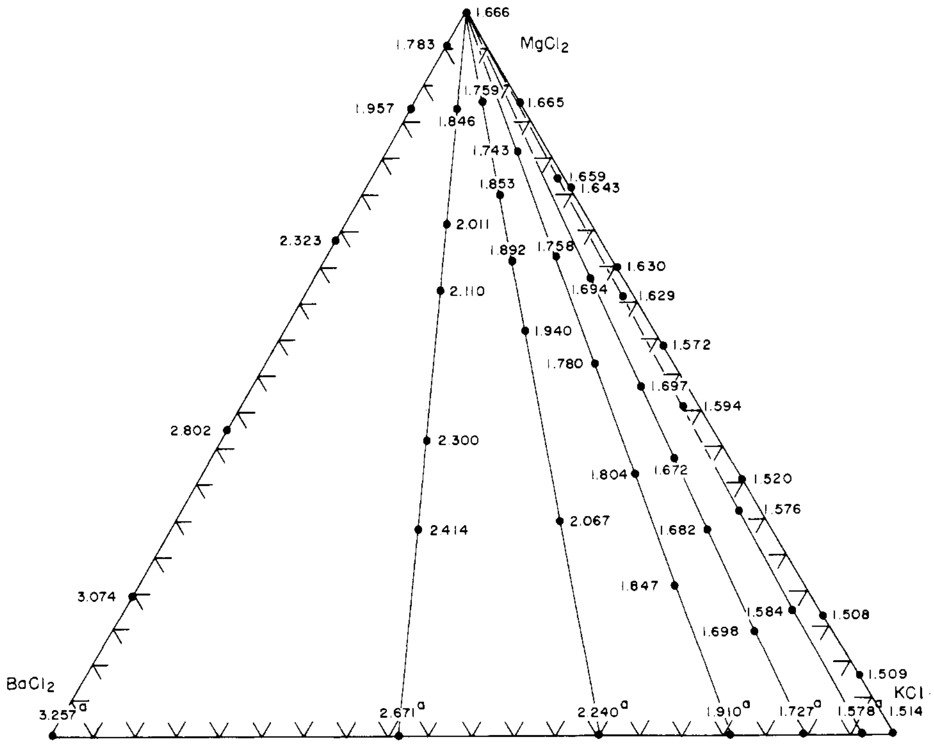

Figure 4. Density of $MgCl_2$–KCl–$BaCl_2$ system at 800° C.
a. Data for KCl–$BaCl_2$ from Bothwell and Peake

data reported by other investigators (*1*, *3*, *4*) for the $MgCl_2$–KCl and $MgCl_2$–$BaCl_2$ binaries are also included for comparison. Figure 4 is a ternary diagram presenting the density at 800° C. as a function of composition.

## DISCUSSION

The density data for pure KCl are in excellent agreement with those of Yaffee and Van Artsdalen but are slightly higher than those of Mashovetz and Lundina and Peake and Bothwell. The density data for $MgCl_2$ are also slightly higher than those of Mashovetz and Lundina. The molal volume plots for the binaries, KCl-$MgCl_2$ and $BaCl_2$-$MgCl_2$, exhibit the same general shape as that reported by other investigators and fall within their range of results.

The molal volume plots of the series of pseudobinary systems presented in Figure 3 indicate that there is a progressive transition from the KCl–$MgCl_2$ type plot to that of the $BaCl_2$–$MgCl_2$ type as the $BaCl_2$ content is increased. Indeed the convex-concave curve of the KCl–$MgCl_2$ system is still evident in the plot for the 65% KCl–35% $BaCl_2$ + $MgCl_2$ system.

## ACKNOWLEDGMENT

The author acknowledges with gratitude the help of R. O. Bolenbaugh, W. E. Eden, and H. C. Kent who performed most of the experiments and collected the data reported in this paper.

## LITERATURE CITED

(1) Bondarenko, N.V., Strelets, K.L., *Zh. Prikl. Khim.* **35**, 1271–6 (1962).

(2) Bothwell, M.R., Peake, J.S., *J. Am. Chem. Soc.* **76**, 2653 (1954).

(3) Huber, R.W., Potter, E.V., St. Clair, H.W., *U.S. Bur. Mines, Rept. Invest.* **4858**, 14pp., 1952.

(4) Mashovetz, V. P., Lundina, Z. F., *Proc. 1st All-Union Conf. Non-aqueous Solutions*, 191–212, 1935.

(5) Van Artsdalen, E.R., Yaffee, I.S., *J. Phys. Chem.* **59**, 118–27 (1955).

RECEIVED for review June 5, 1964. Accepted August 17, 1964.

---

# Solubility of Carbon Dioxide in Cyclohexanol, 1,2-Dibromoethane, a Mixture of 1-Chloro-2-bromopropane and 2-Chloro-1-bromopropane, and Mineral Oil

JOHN W. BEGLEY[1], HENRI J. R. MAGET[2] and BRYMER WILLIAMS
University of Michigan, Ann Arbor, Mich.

**The solubilities of carbon dioxide in cyclohexanol, 1,2-dibromoethane (ethylene bromide), a mixture of 1-chloro-2-bromopropane and 2-chloro-1-bromopropane (propylene chlorobromide), and mineral oil have been determined at atmospheric pressure in the temperature range of 20° to 50° C. For all four solvents, the solubilities decrease with increasing temperature. For cyclohexanol, the Ostwald absorption coefficient was compared with values for alcohols ranging from $C_1$ to $C_6$.**

DURING the bubble-cap plate efficiency research program at the University of Michigan (1953–58), the solubilities of carbon dioxide in various solvents were needed to determine the equilibrium conditions for mass transfer experiments.

Solubility measurements were used to determine Henry's law constant. This is possible because at very dilute solutions

$$p = H \cdot c \qquad (1)$$

where $p$ represents the partial pressure of one component in the vapor phase, $c$ represents the concentration of the same component in the liquid phase, and $H$ is Henry's law constant. Equation 1 can be rewritten as,

$$\frac{RT}{v} = \frac{H}{V} \qquad (2)$$

where $v$ represents the volume of gas dissolved in the liquid phase and $V$ the volume of the liquid phase. Equation 2 becomes,

$$\frac{v}{V} = \frac{RT}{H} = \alpha \qquad (3)$$

which is often independent of pressure.

Thus, to calculate the constant, $H$, it was only necessary to determine the volume of gas absorbed per unit volume of liquid at atmospheric pressure.

---

[1] Present address: Phillips Petroleum Co., Bartlesville, Okla.

[2] Present address: General Electric Co., West Lynn, Mass.