[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF LIBERAL ARTS, UNIVERSITY OF CINCINNATI]

# Partial Molal Volumes of Cobalt Sulfate and of Cadmium Iodide

BY R. C. CANTELO AND H. E. PHIFER

Masson[1] discovered the empirical linear relation connecting the apparent molal volume, $\phi$, of a solute and the square root of the volume molar concentration, $c$.

$$\phi = ac^{1/2} + b \qquad (1)$$

$a$ and $b$ are constants characteristic of the substance dissolved. Of twenty-four strong electrolytes studied, Masson found that twenty-two of them conformed to equation (1). Geffcken[2] and Scott[3] elaborated upon Masson's work, for uni-univalent electrolytes.

Geffcken found that equation (1) held with great accuracy for a given temperature, for a wide temperature and concentration interval. Scott discussed the constant, $b$, of equation (1) with respect to the additivity in infinitely dilute solution, of the apparent molal volumes of the ions. He suggested that the constant, $a$, is a measure of the interionic forces existing in the solution.

Redlich and Rosenfeld[4] derived as a necessary consequence of the Debye–Hückel interionic attraction theory, an equation for the partial molal volume of a strong electrolyte:[5]

$$\bar{V}_1 - \bar{V}_1^0 = qw^{3/2}c^{1/2} - \frac{2qgaw^{3/2}}{\frac{3}{D}\frac{\partial D}{\partial P} - \beta}\left(\frac{2}{D}\frac{\partial D}{\partial P} - \beta\right)c \qquad (2)$$

As a limiting law for dilute solutions, equation (2) becomes

$$\bar{V}_1 = qw^{3/2}c^{1/2} + \bar{V}_1^0 \qquad (3)$$

According to Geffcken[2] and Masson,[1] the linear relation (1) held for a given electrolyte up to fairly high concentrations, but the slope of the curves for electrolytes of the same valence type varied from solute to solute in an apparently characteristic manner. Redlich and Rosenfeld[6] upon examining the best experimental data for uni-univalent electrolytes

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(1) Masson, *Phil. Mag.*, **8**, 218 (1928).

(2) Geffcken, *Naturwissenschaften*, **19**, 321 (1931); *Z. physik. Chem.*, **A155**, 1 (1931).

(3) Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

(4) Redlich, *Naturwissenschaften*, **19**, 251 (1931); Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

(5) $\bar{V}_1$ = partial molal volume of solute; $\bar{V}_1^0$ = partial molal volume at infinite dilution; $q = 2.303\ RTh\left(\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right)$; $w = \frac{\Sigma \nu_i z_i^2}{2}$; $\nu_i$ = number of ions of the $i^{th}$ kind which are formed from a molecule of electrolyte; $z_i$ = valence of ion of the $i^{th}$ kind; $g = 0.328 \times 10^8$; $a$ = ion radius; $D$ = dielectric constant of solution; $P$ = pressure; $\beta$ = compressibility of the solution; $h = \frac{1}{2.303}\left(\frac{\epsilon^2}{DkT}\right)^{3/2}\left(\frac{2\pi N}{1000}\right)^{1/2}$; $\epsilon = 4.774 \times 10^{-10}$ e. s. u.; $k$ = Boltzmann constant $= 1.371 \times 10^{-6}$ ergs deg.$^{-1}$; $N$ = Avogadro's number $= 6.062 \times 10^{23}$; $T$ = absolute temperature.

(6) Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).

came to the conclusion that at high concentrations the lines were really curved, and that at great dilution the curves all have the same slope, this slope being approximately that required by theory.

The object of the present investigation was to determine whether the partial molal volumes of cobalt sulfate and of cadmium iodide could be represented by equations of the form of (2) or (3).

Cantelo and Payne[7] explained the decrease in the transference numbers of cobalt sulfate, in the concentration range 0.1 to 2 molar, on the basis of formation of complex ions. The presence of complex ions in solutions of cadmium iodide has been postulated by McBain, Van Rysselberghe and Squance,[8] by Tesche and Van Rysselberghe,[9] by Gooding and Walton[10] and by other investigators.

Since equations (2) and (3) have been derived from a theory of complete dissociation of strong electrolytes, it is to be expected that solutions containing complex ions will deviate considerably in behavior from that required by these equations. Again, if the partial molal volumes can be represented by an equation, $\bar{V}_1 = kc^{1/2} + \bar{V}_1^0$, the numerical value of $k$ should give a measure of the extent of the deviation, and a possible explanation for this deviation on the basis of complex ions. Finally, the numerical value of $\bar{V}_1^0$ will give, to some extent at least, a measure of the net volume change in infinitely dilute solution due to (a) the breaking down of the crystal lattice, (b) the effect of the ionic field upon the dipole water molecules.

## Experimental Part

**Cobalt Sulfate.**—"International Critical Tables" gives values for the densities, 25°/4°, of cobalt sulfate solutions for the range 0.065 to 0.558 molar only. Accordingly, we have used the complete density determinations, 25°/4°, of Payne for the range 0.01 to 2.4 molar.[11]

The partial molal volumes of water, $\bar{V}_2$, in this range of concentration were determined according to the "method of intercepts" described by Lewis and Randall;[12] the corresponding partial molal volumes of cobalt sulfate, $\bar{V}_1$, were calculated from the equation

$$\bar{V}_1 = \frac{v - \bar{V}_2(1 - x)}{x} \tag{4}$$

$v = V/(n_1 + n_2)$, where $V$ is the volume of the solution containing $n_1$ and $n_2$ moles of solute and solvent, respectively, $x$ is the mole fraction of solute. The results obtained are given in Column 3 of the data for cobalt sulfate given in Table I.

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(7) Cantelo and Payne, *J. Phys. Chem.*, **36**, 1045 (1932).

(8) McBain, Van Rysselberghe and Squance, *ibid.*, **35**, 999 (1931).

(9) Tesche and Van Rysselberghe, *Trans. Am. Electrochem. Soc.*, **59**, 333 (1931).

(10) Gooding and Walton, *J. Phys. Chem.*, **35**, 3612 (1931).

(11) Payne, Dissertation, University of Cincinnati, 1931.

(12) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., 1923, p. 38

**Cadmium Iodide.**—Density determinations, 25°/4°, are given in "International Critical Tables" for the concentration range 2 to 45% $CdI_2$. However, on account of the straight line relationship obtained, when the values of V calculated from these data were plotted against the mole fraction, $x$, of cadmium iodide, we determined densities for thirteen interpolated concentrations. Finally, twenty-five points were used to determine the functional dependence of V on $x$. It is definitely linear. The "least squares" equation to the straight line obtained was found to be

$$V = 49.09x + 18.07 \tag{5}$$

$\bar{V}_1$ is thus constant for the whole range of concentration and is found by substituting $x = 1$ in equation (5). $\bar{V}_1 = 67.16$ (see Table I).

**Potassium Chloride.**—For purposes of comparison, particularly with respect to the $w$ factor of equations (2), (3), we have calculated the partial molal volumes of potassium chloride from the equation given for this salt by Gronwall and La Mer[13]

$$\bar{V}_1 = 27.02 + 4.234\ m - 1.4706\ m^2 + 0.20767\ m^3 \tag{6}$$

$m$ = molality. The results obtained are given in Column 3 of the data for potassium chloride in Table I.

**Results Obtained.**—Table I contains the complete results for the three salts.

TABLE I

PARTIAL MOLAL VOLUMES AT 25° AND 1 ATM.

| Cobalt Sulfate | | | | Potassium Chloride | | | |
|---|---|---|---|---|---|---|---|
| $c$ | $c^{1/2}$ | $\bar{V}_1$ exptl. | $\bar{V}_1$ calcd. | $c$ | $c^{1/2}$ | $\bar{V}_1$ G. & L. eqn. | $\bar{V}_1$ calcd. |
| 2.250 | 1.500 | 16.82 | 17.57 | 2.2926 | 1.5141 | 31.76 | 31.63 |
| 1.954 | 1.397 | 16.29 | 16.13 | 1.6694 | 1.2921 | 30.95 | 31.05 |
| 1.827 | 1.352 | 15.73 | 15.49 | 0.9187 | 0.9585 | 29.73 | 29.88 |
| 1.731 | 1.315 | 15.12 | 14.98 | .6689 | .8179 | 28.22 | 29.29 |
| 1.615 | 1.271 | 14.47 | 14.35 | .3342 | .5781 | 28.34 | 28.29 |
| 1.511 | 1.229 | 13.76 | 13.77 | .2713 | .5209 | 28.13 | 28.07 |
| 1.389 | 1.179 | 13.01 | 13.06 | | | | |
| 1.265 | 1.125 | 12.18 | 12.30 | Cadmium Iodide | | | |
| 1.121 | 1.059 | 11.27 | 11.38 | $c$, 0.005 to 1 molar, | | | |
| 0.9721 | 0.9858 | 10.23 | 10.35 | $\bar{V}_1$ = 67.16 | | | |
| .8752 | .9354 | 8.976 | 9.64 | | | | |
| .7261 | .8521 | 8.264 | 8.47 | | | | |
| .6473 | .8044 | 7.473 | 7.80 | | | | |
| .5301 | .7280 | 6.498 | 6.72 | | | | |
| .3587 | .5988 | 5.271 | 4.90 | | | | |

The values of $\bar{V}_1$ given in Column 3 of Table I have been plotted against $c^{1/2}$ in Fig. 1. The $\bar{V}_1 - c^{1/2}$ curves are evidently linear for these salts. The best equations for the lines were determined by the method of "least squares." These equations are

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(13) Gronwall and La Mer, *J. Phys. Chem.*, **31**, 393 (1927).

$$\text{For CoSO}_4 \qquad \bar{V}_1 = 14.06\, c^{1/2} - 3.514 \tag{7}$$

$$\text{For KCl} \qquad \bar{V}_1 = 3.652\, c^{1/2} + 26.23 \tag{8}$$

$$\text{For CdI}_2 \qquad \bar{V}_1 = 67.16 \tag{9}$$

Values for the respective $\bar{V}_1$'s calculated from equations (7) and (8) are given in Column 4, Table I. The respective molal volumes for the three solid salts, cobalt sulfate, potassium chloride, cadmium iodide are 44.64 cc., 37.58 cc., 64.88 cc.

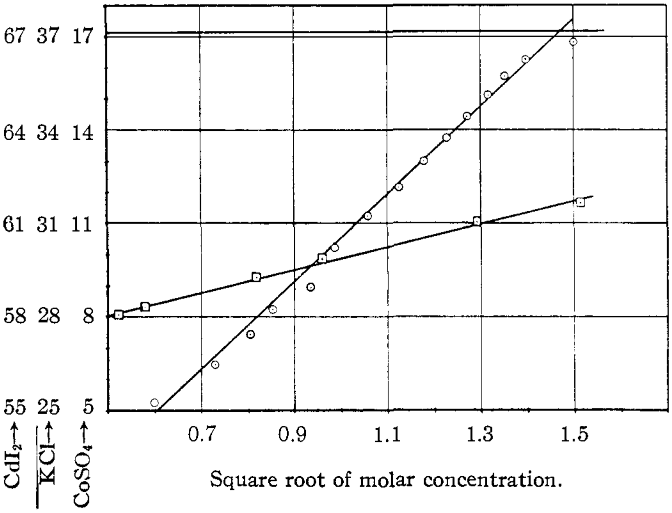

Fig. 1.—Plot of partial molal volumes at 25°: ⊙, $CoSO_4$; ⊡, KCl.

## Discussion of Results

**Potassium Chloride.**—The factor, $q$, in equations (2) and (3), calculated from Falckenberg's measurements at 16.3° of $\frac{1}{D}\frac{\Delta D}{\Delta P} = 46 \times 10^{-9}$ for the interval 7 to 200 atmospheres, and from $\beta = 49.2 \times 10^{-6}$ and $h = 0.497$, has the value 2.7 (for 16.3°). Hence the Redlich equation for potassium chloride may be written

$$\bar{V}_1 = 2.7\, c^{1/2} + \bar{V}_1^0 \tag{10}$$

The agreement of the coefficients of $c^{1/2}$ in equations (8) and (10) can be considered satisfactory, in view of the fact pointed out by Redlich and Rosenfeld[4] that an accuracy of only about 30% can be assigned to the numerical value of $q$.

If we integrate equation (6) we obtain $V$, the total volume of solution per 1000 grams of water.

$$V = 0.05192\, m^4 - 0.4902\, m^3 + 2.117\, m^2 + 27.02\, m + 1003 \tag{11}$$

From equation (11) and the other necessary data, we can calculate the contraction per mole of potassium chloride for a solution of molality, $m$. When this is done we find that this contraction per mole is 7.56 cc. for 2.50 $m$ solution and increases to 11.35 cc. for zero concentration.

In a recent paper Pearce and Nelson[14] showed that the fractional vapor pressure lowerings produced by potassium chloride differed least, of all the alkali halides, from the theoretical fractional vapor pressure lowerings calculated on the assumptions that the salts are completely dissociated and that the ions behave as perfect solutes. According to their interpretation this means that in the case of potassium chloride solutions, the ionic field has little effect in causing the dipole water molecules to lose a part of their fugacity.

Since the ionic field in potassium chloride solutions has little effect upon so characteristic a property as the fugacity of the water molecules, it seems plausible to suggest that this field has but little effect also in distorting the dipole water molecules.

In other words, the above decreases in volume produced upon solution of solid potassium chloride can be assigned to the volume change accompanying the physical change, solid to liquid.

We shall, therefore, look upon potassium chloride as an electrolyte whose behavior in solution does not exhibit abnormalities.

**Cobalt Sulfate.**—The Redlich equation for cobalt sulfate is

$$\bar{V}_1 = 21.6\, c^{1/} + \bar{V}_1^0 \qquad (12)$$

The discrepancy in the coefficients of $c^{1/2}$ in equations (7) and (12) is in the right direction to be explained by the existence of complex ions. According to equation (3), the coefficients of $c^{1/2}$ for potassium chloride and for cobalt sulfate should be in the ratio 1:8. Actually, they are in the ratio 1:4. No definite conclusion can be drawn, however, from this investigation, as to whether cobalt sulfate does or does not form complex ions.

When we examine the $\bar{V}_1^0$ value in (7), we find a tremendous discrepancy between it and the value, 44.64 cc., for the solid salt. Masson[1] explains a discrepancy of this kind by assuming hydration of the ions. He says: "The true solute is a hydrate whose molecular volume is $\phi' = \phi + (18.016/d_w)x = b' + ac^{1/2}$." Since actually $\phi = b + ac^{1/2}$ is the relation plotted, $b' = b + (18.016/d_w)x$. Even though $b = \phi^0 = \bar{V}_1^0$ may be negative, the correction added is sufficient to make $b'$ positive. $x$ is "an integer indicated by the composition of the hydrate in question."

For cobalt sulfate, in terms of molality, we have

$$\bar{V}_1 = 13.48\, m^{1/2} - 3.164 \qquad (13)$$

Upon integration we obtain $V$, the total volume of solution per 1000 grams of water.

$$V = 8.987\, m^{3/2} - 3.164\, m + 1003 \qquad (14)$$

From this equation, and the other necessary data, we obtain for the contraction per mole of cobalt sulfate, 34.2 cc. for 2.30 $m$ and 48.15 cc. for zero concentration.

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[14] Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932).

Evidently in the case of cobalt sulfate we have to consider that the volume changes upon solution are due to the two effects (a) the change from crystal lattice to solution, (b) the effect of the ion field upon the configuration and volume of the water molecules. Measurements of the fractional vapor pressure lowerings produced by cobalt sulfate might give some information as to the relative importance of these two effects.

**Cadmium Iodide.**—The coefficient of $c^{1/2}$ for cadmium iodide is zero. In other words, cadmium iodide solutions do not conform at all to equations (2) and (3), derived from a theory of complete dissociation. This is one more abnormality to be added to the many exhibited by this salt.[8]

The $\bar{V}_1^0 = \bar{V}_1$ values of cadmium iodide differ little from the molal volume of the solid salt. Evidently, the two effects considered above in the case of cobalt sulfate must be negligible or must neutralize each other in the case of cadmium iodide.

It is interesting to note here the equation given by Longsworth for $\bar{V}_1$ for cadmium chloride[15]

$$\bar{V}_1 = 8.82\,m^{1/2} + 23.24 \qquad (15)$$

The coefficients of $m^{1/2}$ and $c^{1/2}$ will not differ much. $qw^{3/2}$ for cadmium chloride is 14.03; the ratio of the coefficients of equations (8) and (15) is a little over 1:2. Theoretically this ratio should be about 1:5.

## Summary

1 The partial molal volumes of cobalt sulfate at 25°, within the range 0.3 to 2.25 molar, have been determined.

2. The partial molal volumes of potassium chloride at 25°, within the range 0.27 to 2.29 molar, have been calculated from the Gronwall–La Mer equation.

3. The partial molal volumes of cadmium iodide at 25°, within the range 0.005 molar to 1 molar, have been determined.

4. Empirical equations have been derived, governing the linear relation between the partial molal volume and the square root of the molar concentration, for potassium chloride, cadmium iodide and cobalt sulfate; and the constants of these equations have been compared with those of the corresponding theoretical equations.

5. A theoretical discussion of the partial molal volume relations of the three salts has been given.

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[15] Longsworth, **This Journal, 54,** 2741 (1932).