[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

# The Boiling Point Elevation. IV. Potassium Bromide in Water[1]

BY GEORGE C. JOHNSON[2] AND RODNEY P. SMITH[3]

The work reported here is a continuation of the study reported in the first three papers of this series.[4,5,6] The earlier reports were on the boiling point elevations of sodium chloride in water; these are on potassium bromide in water in concentrations to 5.0 $M$ and over the temperature range 60 to 100°.

**Apparatus and Procedure.**—The apparatus and procedure were similar to that already described.[4] The following changes were made.

1. In the former apparatus the salt solutions, particularly the more concentrated ones, did not boil smoothly. This difficulty was minimized in the present apparatus by heating the solution flask with an oil-bath, rather than with a direct gas flame. The oil level was kept equal to or slightly below the level of the solution.

2. The concentrations were determined from the weight of dry potassium bromide recovered from a weighed sample of the solution. To prevent creeping during the evaporation the samples were dried by heating from above with a stream of hot air. The last traces of water were removed by heating in a muffle furnace for thirty minutes at 450–500°.

3. In the previous work the apparatus constant[4] was determined for a fixed rate of boiling. The constant proved to be quite sensitive to the rate of boiling and a calibration was made to account for this variation.

**Materials.**—The water was obtained from the laboratory distilled water supply. J. T. Baker analyzed potassium bromide was used, the main impurity being potassium chloride. It was assumed that in small amounts, formula weight for formula weight, the two salts were the same in their property of raising the boiling point. The problem then became not to purify the salt further but to determine its formula weight. Atomic weight determinations were carried out on the anion, assuming the cation to be potassium. The formula weight thus obtained was 118.62, while that for pure potassium bromide would be 119.01. In all subsequent calculations of molality from the weight composition, the formula weight of 118.62 was used.

**Results.**—Values of $\theta$, the boiling point elevation, at round concentrations and temperatures are given in Table I. The differences between the smoothed results and the experimental results were of the order of ±0.0002° up to 1.0 $M$ ±0.0005° from 1.0 to 2.0 $M$ and ±0.001° from 2.0 to 4.0 $M$.

TABLE I

BOILING POINT ELEVATIONS (°C.)

| $m$ | 60° | 70° | 80° | 90° | 100° |
|---|---|---|---|---|---|
| 0.1 | 0.0724 | 0.0774 | 0.0828 | 0.0884 | 0.0944 |
| .2 | .1430 | .1532 | .1639 | .1751 | .1868 |
| .3 | .2137 | .2291 | .2452 | .2619 | .2794 |
| .4 | .2848 | .3054 | .3267 | .3491 | .3723 |
| .5 | .3563 | .3820 | .4088 | .4367 | .4657 |
| .6 | .4284 | .4594 | .4915 | .5250 | .5598 |
| .8 | .5741 | .6156 | .6587 | .7038 | .7507 |
| 1.0 | .7220 | .7746 | .8293 | .8861 | .9453 |
| 1.5 | 1.104 | 1.185 | 1.269 | 1.356 | 1.447 |
| 2.0 | 1.501 | 1.612 | 1.727 | 1.846 | 1.970 |
| 2.5 | 1.914 | 2.057 | 2.204 | 2.357 | 2.516 |
| 3.0 | 2.341 | 2.517 | 2.698 | 2.886 | 3.081 |
| 3.5 | 2.783 | 2.994 | 3.210 | 3.435 | 3.668 |
| 4.0 | 3.241 | 3.487 | 3.741 | 4.004 | 4.276 |
| 5.0 | 4.208 | 4.531 | 4.862 | 5.206 | 5.563 |

**Free Energies.**—For the reaction

$$\begin{array}{lcl} \text{Water} & \longrightarrow & \text{Water in Salt Solution} \\ (T_0+\theta),\ P_0 & & m,\ (T_0+\theta),\ P_0 \end{array} \qquad (1)$$

the change in the partial molal free energy of the water, $\Delta\bar{F}_1$, is given by the equation

$$\Delta\bar{F}_1 = \bar{F}_1 - \bar{F}_1^0 = -(T_0+\theta)\int_{T_0}^{T_0+\theta}(\Delta H_v/T^2)\,\mathrm{d}T \qquad (2)$$

where $T_0$ is the boiling point of pure water at the saturation pressure $P_0$, $\theta$ is the boiling point elevation, $m$ is the molality of the solute, $\Delta H_v$ is the heat of vaporization of water at $P_0$ and $\Delta\bar{F}_1$ is the Gibbs free energy involved in transferring one mole of water from one body to the other keeping the concentration, temperature and pressure of each body constant. The heat of vaporization of water in international joules per gram at the temperature $(T_0 + \theta)$ and at a pressure corresponding to saturation at $T_0$, is given in Table II. These values have been recalculated in order to include new data.[7] The difference between the values given in Table II and those previously published[5] would not cause an appreciable change in the calculated quantities.

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[1] This communication embodies part of the material contained in the thesis submitted by George C. Johnson to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1940. [Original manuscript received October 28, 1940.]

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[4] Smith, THIS JOURNAL, **61**, 497 (1939).

[5] Smith, *ibid.*, **61**, 500 (1939).

[6] Smith and Hirtle, *ibid.*, **61**, 1123 (1939).

[7] These values were evaluated from data of Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939); **23**, 261 (1939); Collins and Keyes, *Proc. Am. Acad. Arts Sci.*, **72**, 283 (1938); Keenan and Keyes, "Thermodynamic Properties of Steam," Table IV, John Wiley and Sons, Inc., New York, N. Y., 1936.

TABLE II

HEAT OF VAPORIZATION OF WATER

| $T_0$, °C. | $\Delta H_v$, int. j./g. |
|---|---|
| 60 | $2357.45 - 2.2475\theta - 0.00006\theta^2 - 0.00021\theta^3$ |
| 70 | $2332.84 - 2.2241\theta - 0.00031\theta^2 - 0.00024\theta^3$ |
| 80 | $2307.83 - 2.1996\theta - 0.00080\theta^2 - 0.00027\theta^3$ |
| 90 | $2282.35 - 2.1741\theta - 0.00122\theta^2 - 0.00030\theta^3$ |
| 100 | $2256.32 - 2.1417\theta - 0.00169\theta^2 - 0.00034\theta^3$ |

The corresponding values for $\Delta\bar{F}_2$ may be found from the Gibbs–Duhem relation

$$\sum n_i\,\partial\bar{F}_i = 0 \ (P,\ T \text{ constant}) \tag{3}$$

$\Delta\bar{F}_1$ may be expressed

$$\Delta\bar{F}_1 = \bar{F}_1'' - \bar{F}_1^0 = RT_0 \ln X_1'' + (\Delta\bar{F}_1)_{\text{non-ideal}} \tag{4}$$

$$X_1'' = 55.506/(55.506 + 2m) \tag{5}$$

and $\Delta\bar{F}_2$ becomes

$$\Delta\bar{F}_2 = \bar{F}_2'' - \bar{F}_2' = 2RT_0 \ln X_2''/X_2' + (\Delta\bar{F}_2)_{\text{non-ideal}} \tag{6}$$

$$(\Delta\bar{F}_2)_{\text{non-ideal}} = -n_1 \int_{m'}^{m''} \frac{1}{m}\,(\Delta\bar{F}_1)_{\text{non-ideal}} \tag{7}$$

It will be seen that as $X_2' \rightarrow 0$, $\Delta\bar{F}_2$ becomes infinite. However, $(\Delta\bar{F}_2)_{\text{non-ideal}}$ approaches zero.

From equations (2) and (7) together with interpolation to round values of temperature and concentrations the values of Tables III and IV were calculated. This was done as follows.

(1) Values of $\Delta F_1$ were calculated from the data of Table I by equation (2). These values of $\Delta F_1$ are at a pressure $P_0$; however, in this case they may be considered equivalent to the corresponding values of $\Delta F_1$ for a pressure of one atmosphere. The error due to this assumption is not greater than 0.0003 int. j./g. which is less than the accuracy to which the data are reported.

2. The values of $\Delta F_1$ were converted to round values of temperature by the equation

$$\Delta F_1 = (\Delta F_1)_{\text{ideal}} + (\Delta F_1)_{\text{DH}} + (\Delta F_1)_{\text{empirical}} + (\Delta F_1)_{\text{graphical}}$$

where $(\Delta F_1)_{\text{ideal}}$ is that given by the ideal relation, $(\Delta F_1)_{\text{DH}}$ that given by the Debye–Hückel equation and $(\Delta F_1)_{\text{empirical}}$ that given by $k_1m^2$ where $k_1$ depends on temperature. For each $m$, $(\Delta F_1)$ was calculated at five temperatures and values at round temperatures read from a graph. Back calculations were made at each of the five round temperatures and the values of Table III obtained.

TABLE III

$(\bar{F}_1 - \bar{F}_1)$, INT. J./FORMULA WEIGHT

| $m$ | 60° | 70° | 80° | 90° | 100° |
|---|---|---|---|---|---|
| 0 | | | | | |
| 0.1 | − 9.22 | − 9.48 | − 9.75 | − 10.01 | − 10.28 |
| .2 | − 18.22 | − 18.76 | − 19.29 | − 19.81 | − 20.34 |
| .3 | − 27.22 | − 28.03 | − 28.84 | − 29.63 | − 30.41 |
| .4 | − 36.25 | − 37.35 | − 38.43 | − 39.48 | − 40.51 |
| .5 | − 45.37 | − 46.73 | − 48.07 | − 49.38 | − 50.66 |
| .6 | − 54.53 | − 56.17 | − 57.78 | − 59.35 | − 60.89 |
| .8 | − 73.03 | − 75.23 | − 77.40 | − 79.51 | − 81.59 |
| 1.0 | − 91.81 | − 94.61 | − 97.36 | −100.04 | −102.68 |
| 1.5 | −140.1 | −144.5 | −148.7 | −152.9 | −156.9 |
| 2.0 | −190.3 | −196.4 | −202.2 | −207.8 | −213.4 |
| 2.5 | −242.2 | −250.1 | −257.6 | −264.9 | −271.9 |
| 3.0 | −295.7 | −305.5 | −314.8 | −323.8 | −332.5 |
| 3.5 | −351.0 | −362.7 | −373.9 | −384.6 | −395.1 |
| 4.0 | −407.9 | −421.8 | −434.8 | −447.5 | −459.7 |

TABLE IV

$(\bar{F}_2 - \bar{F}_2^0)_{\text{non-ideal}}$, INT. J./FORMULA WEIGHT

| $m$ | 60° | 70° | 80° | 90° | 100° |
|---|---|---|---|---|---|
| 0 | | | | | |
| 0.1 | −1508 | −1579 | −1652 | −1734 | −1818 |
| .2 | −1855 | −1936 | −2021 | −2117 | −2213 |
| .3 | −2050 | −2137 | −2226 | −2329 | −2440 |
| .4 | −2175 | −2265 | −2359 | −2467 | −2585 |
| .5 | −2261 | −2354 | −2450 | −2563 | −2687 |
| .6 | −2321 | −2416 | −2515 | −2630 | −2758 |
| .8 | −2395 | −2491 | −2592 | −2711 | −2841 |
| 1.0 | −2426 | −2521 | −2622 | −2742 | −2874 |
| 1.5 | −2400 | −2488 | −2587 | −2705 | −2839 |
| 2.0 | −2295 | −2374 | −2467 | −2583 | −2713 |
| 2.5 | −2150 | −2220 | −2305 | −2414 | −2540 |
| 3.0 | −1985 | −2042 | −2119 | −2222 | −2343 |
| 3.5 | −1803 | −1849 | −1917 | −2007 | −2127 |
| 4.0 | −1609 | −1644 | −1703 | −1789 | −1897 |

3. $(\Delta F_2)_{\text{non-ideal}}$ was then calculated by equation (7) using the form in paragraph (2) above so that

$$(\Delta F_2)_{\text{non-ideal}} = (\Delta F_2)_{\text{DH}} + (\Delta F_2)_{\text{empirical}} + (\Delta F_2)_{\text{graphical}}$$

where

$$(\Delta F_2)_{\text{graphcial}} = -1000 \int_0^m \frac{\mathrm{d}(\Delta F_1)_{\text{graphical}}}{m}$$

**Osmotic and Activity Coefficients.**—These quantities are defined by the equations

$$\Delta\bar{F}_1 = \bar{F}_1 - \bar{F}_1^0 = gRT\ln X_1 = -\frac{\varphi RT\,2m}{1000/M_1} \qquad (8)$$

$$(\Delta\bar{F}_2)_{\text{non-ideal}} = 2RT\ln f \qquad (9)$$

$$\log\gamma = \log f - \log(1 + 2mM_1/1000) \qquad (10)$$

where $g$ is the rational osmotic coefficient, $\varphi$ is the practical osmotic coefficient, $f$ is the rational activity coefficient, $\gamma$ is the practical activity coefficient, $m$ is the molality, and $M_1$ is the formula weight of the solvent. These quantities may be calculated readily from the values of Tables III and IV.

A comparison of these results for osmotic and activity coefficients with those obtained from freezing point data by Scatchard and Prentiss,[8] isopiestic vapor pressure data at 25° by R. A. Robinson[9] and unpublished isopiestic vapor pressure data at 30 and 40° by R. A. Robinson shows the same type of agreement as in the case of solutions of sodium chloride.[5,6] The agreement is satisfactory for concentrations to 1.5 molal; at higher concentrations and at temperatures near 60°, the activity coefficients determined from the boiling point elevations are high relative to those obtained by the other methods.

## Summary

1. Boiling point elevations of solutions of potassium bromide in water have been determined to 5.0 molal over the range 60–100°.

2. Partial molal free energies have been calculated from these boiling point values. The method of calculating activity and osmotic coefficients has been indicated.

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[8] Scatchard and Prentiss, THIS JOURNAL, **55**, 4355 (1933).

[9] R. A. Robinson, *ibid.*, **57**, 1161 (1935).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# The Exchange of Oxalates of Some Complex Trioxalate Ions of Trivalent Metals

BY F. A. LONG

Many trivalent metal ions form complex salts with alkali oxalates of the general formula $\mathrm{Alk_3M(C_2O_4)_3}$. These complex oxalate salts are similar in many properties. They are very soluble in water, ionize to give alkali and complex oxalate ions, and show similar crystal forms.[1] In 1912 Werner[2] was able to resolve potassium chromium trioxalate into its optical isomers. Since then attempts have been made to resolve other analogous oxalate salts and in most cases the attempts have been successful. Complex oxalate salts of the following trivalent metal ions have been reported as capable of resolution into optical isomers: chromic,[2] cobaltic,[3] ferric,[4] aluminum,[5] rhodium,[6] iridium,[7] and gallium.[8] In addition resolutions have been reported for complex salts involving dibasic acid ions other than oxalate.

For many years the assumption was tacitly made that any similar salt could be resolved into its optical isomers. Recently this assumption was challenged by C. H. Johnson[9] from the standpoint of the types of bonds involved in coördination compounds.

Pauling[10] has discussed the bond type for various coördination compounds and has shown that for many such compounds the bonds approach rather closely to one or the other of the two types, covalent bonds or ionic bonds. If there are available for bonding two *d*, three *p* and one *s* orbital, then strong *s*-*p*-*d* hybrid bonds directed toward the apices of a regular octahedron can be formed provided that the increased bonding energy can more than offset any loss of energy due to change of multiplicity. Magnetic susceptibility measurements will often give an indication of the bond type but this criterion is, of course, useful only when a change of multiplicity occurs as the bond type changes from primarily ionic to primarily covalent. For instance chromic ion complexes will give the same susceptibility whether the bonding is covalent or ionic, as may

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[1] Jaeger, "Optical Activity and High Temperature Measurements," Chapter VIII, McGraw-Hill Co., New York, N. Y., 1930.

[2] Werner, *Ber.*, **45**, 3061 (1912).

[3] Jaeger and Thomas, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **21**, 693 (1919). Johnson and Mead, *Trans. Faraday Soc.*, **29**, 626 (1933).

[4] Thomas, *J. Chem. Soc.*, **119**, 1140 (1921). See, however, Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

[5] Wahl, *Ber.*, **60**, 399 (1927). Burrows and Lauder, THIS JOURNAL, **53**, 3600 (1931).

[6] Werner, *Ber.*, **47**, 1954 (1914).

[7] Delépine and Bruhat, *Bull. soc. chim.*, [4] **17**, 223 (1915); Jaeger, *Rec. Trav. Chim.*, **38**, 270 (1919).

[8] Neogi and Dutt, *J. Indian Chem. Soc.*, **15**, 83 (1938).

[9] Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

[10] "The Nature of the Chemical Bond," Chapters II and III, Cornell University Press, Ithaca, N. Y., 1939.