

Thermodynamics of Ion Association. Part I. Lead Chloride, Bromide, and Nitrate.

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[Reprint Order No. 5886.]

Conductivity measurements are reported for lead chloride, bromide, and nitrate at 25° and for lead bromide at 35°. ΔH , ΔG , and ΔS values are evaluated for the reaction $\text{Pb}^{2+} + \text{X}^- \rightleftharpoons \text{PbX}^+$, the entropy changes are compared with those calculated from an entropy cycle, and their significance is discussed.

ALTHOUGH there are a large number of complex species which have been identified and characterised by accurate determinations of stability constants, there are few for which temperature-coefficient data are available so that heat and entropy values can be calculated. The significance of many of the reported values is doubtful since the authors neglected to take into account variations in activity coefficients when the ionic strength was held constant. Empirical relations have been put forward in an attempt to correlate experimental association constants with properties of the metal ion involved. Such relationships, however, are of limited applicability.

The aim of the present work is a systematic study of the thermodynamic properties of ion-association reactions derived from thermodynamic equilibrium constants. This will enable more extensive correlations to be made than have hitherto been possible, and it is hoped that such a study will further clarify the factors affecting the values of K and provide some additional basis for a better understanding of the theory of ionic interactions in aqueous media.

EXPERIMENTAL

Conductivity measurements were made with a screened a.c. bridge described elsewhere (Jones and Joseph, *J. Amer. Chem. Soc.*, 1928, **50**, 1049; Shedlovsky, *ibid.*, 1930, **52**, 1793). The experimental technique and method of cell calibration have been described by Davies (*J.*, 1937, 432). Conductivity water was prepared by mixed-bed deionisation (Davies and Nancollas, *Chem. and Ind.*, 1950, **7**, 129) on the ion-exchange resins Nalcite SAR and Nalcite HCR: its specific conductivity was usually about 0.08×10^{-6} ohm⁻¹. During measurements at 35°, a stream of hot air prevented condensation on the cap of the cell.

Lead Nitrate.—The "AnalaR" salt was recrystallised three times from conductivity water and dried at 100–110°.

Lead Chloride.—Conductivity water at 100° was saturated with reagent-grade lead chloride. After filtration, a few drops of hydrochloric acid were added and the crystals formed on cooling were recrystallised three times in the same way. The salt was dried at 110° for 24 hr.

Lead Bromide.—Lead bromide was prepared by adding stoichiometric proportions of potassium bromide solution to boiling lead nitrate solution. The salt crystallised on cooling and was purified by three recrystallisations from conductivity water. Owing to the well-known difficulty in dissolving lead bromide, stock solutions were filtered before use and analysed gravimetrically ($\pm 0.02\%$) for bromide (Vogel, "A Test-Book of Quantitative Inorganic Analysis," Longmans, Green & Co., 1947, p. 475).

Conductivity figures at 25° and 35° are given in Table I, in which $c = \text{equiv./l.}$

TABLE I.

| Expt. | 10 ⁴ M | 10 ² c [‡] | Λ | 10 ⁴ I | α | K | Expt. | 10 ⁴ M | 10 ² c [‡] | Δ | 10 ⁴ I | α | K |
|---|-------------------|--------------------------------|-----------|-------------------|----------|------|-------|-------------------|--------------------------------|----------|-------------------|----------|------|
| <i>Conductivity of lead chloride at 25°</i> | | | | | | | | | | | | | |
| 1 | 2.2674 | 2.1295 | 140.21 | 6.728 | 0.984 | 38.3 | 2 | 5.1355 | 3.2050 | 136.78 | 15.05 | 0.965 | 40.6 |
| 1 | 3.0901 | 2.4860 | 139.12 | 9.140 | 0.979 | 40.1 | 2 | 15.162 | 5.505 | 130.10 | 43.15 | 0.923 | 38.0 |
| 1 | 4.3976 | 2.9660 | 137.41 | 12.91 | 0.968 | 39.8 | | | | | | | |
| <i>Conductivity of lead nitrate at 25°</i> | | | | | | | | | | | | | |
| 1 | 1.6163 | 1.7979 | 137.88 | 4.836 | 0.996 | 13.8 | 3 | 5.6395 | 3.3584 | 133.80 | 16.74 | 0.986 | 15.2 |
| 2 | 2.2514 | 2.1220 | 136.63 | 6.727 | 0.994 | 15.2 | 1 | 7.2992 | 3.8205 | 132.72 | 21.63 | 0.982 | 15.5 |
| 1 | 3.0988 | 2.4890 | 136.04 | 9.246 | 0.992 | 14.7 | 2 | 7.7788 | 3.9443 | 132.52 | 23.36 | 0.981 | 15.4 |
| 2 | 3.4628 | 2.6316 | 135.62 | 10.32 | 0.991 | 15.2 | 3 | 9.1574 | 4.2796 | 131.86 | 27.09 | 0.979 | 14.8 |
| 1 | 3.8364 | 2.7700 | 135.17 | 11.43 | 0.990 | 15.4 | 2 | 9.6221 | 4.387 | 131.55 | 28.42 | 0.977 | 15.5 |
| 1 | 4.4267 | 2.9755 | 134.74 | 13.18 | 0.989 | 14.9 | 3 | 22.617 | 6.725 | 126.39 | 65.82 | 0.955 | 15.4 |
| 2 | 4.6816 | 3.0599 | 134.51 | 13.93 | 0.988 | 15.3 | | | | | | | |
| <i>Conductivity of lead bromide at 25°</i> | | | | | | | | | | | | | |
| 1 | 1.5755 | 1.7751 | 143.86 | 4.700 | 0.992 | 29.8 | 2 | 4.5005 | 3.0002 | 140.60 | 13.31 | 0.978 | 29.7 |
| 2 | 1.9019 | 1.9503 | 143.40 | 5.667 | 0.990 | 29.7 | 1 | 6.3440 | 3.5620 | 138.97 | 18.65 | 0.970 | 29.9 |
| 1 | 2.5269 | 2.2481 | 142.64 | 7.517 | 0.987 | 29.1 | 2 | 8.1250 | 4.0310 | 137.54 | 23.76 | 0.962 | 30.5 |
| 2 | 3.4631 | 2.6317 | 141.63 | 10.27 | 0.983 | 29.0 | 1 | 11.370 | 4.7700 | 135.61 | 32.97 | 0.950 | 30.3 |
| 1 | 3.6200 | 2.6907 | 141.46 | 10.73 | 0.982 | 29.5 | | | | | | | |
| <i>Conductivity of lead bromide at 35°</i> | | | | | | | | | | | | | |
| 1 | 2.7053 | 2.2673 | 174.09 | 8.05 | 0.984 | 34.3 | 3 | 8.5790 | 4.1422 | 166.98 | 24.95 | 0.954 | 35.7 |
| 2 | 3.7503 | 2.7387 | 172.76 | 11.11 | 0.979 | 33.5 | 2 | 10.495 | 4.5810 | 165.20 | 30.31 | 0.945 | 35.5 |
| 1 | 4.8218 | 3.1054 | 171.36 | 14.22 | 0.974 | 33.1 | 3 | 12.560 | 4.9710 | 163.31 | 35.47 | 0.940 | 34.5 |
| 2 | 6.2880 | 3.5463 | 169.49 | 18.44 | 0.965 | 35.4 | 3 | 14.015 | 5.2940 | 161.63 | 40.08 | 0.930 | 36.7 |
| 1 | 7.5050 | 3.8740 | 168.16 | 22.52 | 0.960 | 34.7 | | | | | | | |

Results.—Thermodynamic association constants have been obtained from the conductivity data by the method of Righellato and Davies (*Trans. Faraday Soc.*, 1930, 26, 592) for 2 : 1 and 1 : 2 electrolytes. Mobility terms were evaluated from the empirical equations

$$[\Lambda_{(\text{Pb}^{2+})} + \Lambda_{(\text{X}^{-})}] = \Lambda^0 - bf_{(2-1)}(I)$$

$$[\Lambda_{(\text{PbX}^{+})} + \Lambda_{(\text{X}^{-})}] = \Lambda^0 - b'f_{(1-1)}(I)$$

where b and b' are the respective Onsager slopes, and I is the ionic strength. $f_{(1-1)}(I)$ values at 25° have been given by Robinson and Davies (*J.*, 1937, 574); $f_{(2-1)}(I)$ values at this temperature were calculated from the data of Shedlovsky and Brown (*J. Amer. Chem. Soc.*, 1934, 56, 1069) for calcium and magnesium chlorides, which are assumed to be completely dissociated. At 35°, Gunning and Gordon's data (*J. Chem. Phys.*, 1942, 10, 126; 1943, 11, 18) were used to obtain $f_{(1-1)}$ and in the absence of data for 2 : 1 electrolytes, $[\Lambda_{(\text{Pb}^{2+})} + \Lambda_{(\text{Br}^{-})}]$ values were evaluated from Onsager's equation

$$[\Lambda_{(\text{Pb}^{2+})} + \Lambda_{(\text{Br}^{-})}] = \Lambda^0 - 188.1I^{\frac{1}{2}}$$

Limiting conductivities were obtained by extrapolating the data by Onsager's method (*Physikal. Z.*, 1927, 28, 277): at 35°, $\Lambda^0_{\text{PbBr}_2} = 181.1$. The mobility of the bromide ion being taken as 94.05 (Gunning and Gordon, *loc. cit.*), that of the lead ion is 87.05. At 25°, $\Lambda^0_{\text{Pb}^{2+}} = 69.46$, which compares well with the value, 69.4, obtained by James (*J. Amer. Chem. Soc.*, 1949, 71, 3243) by re-extrapolating Norman and Garrett's conductivity figures for lead chloride (*ibid.*,

1947, 69, 110). The mobilities of intermediate ions PbX^+ , 45 at 25° and 52 at 35° , were estimated from the value used by Righellato and Davies at 18° (*loc. cit.*).

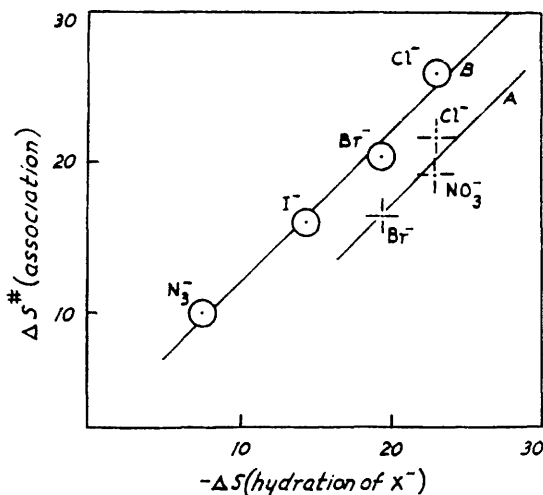
If α is the degree of dissociation and m the molar concentration, the thermodynamic association constant is given by,

$$\log K = \log (1 - \alpha) / \alpha m (1 + \alpha) + 2[I^\ddagger / (1 + I^\ddagger) - 0.2I]$$

and was obtained by successive approximations of I . Values of K are given in Table 1, the mean values being: at 25° , $K_{PbCl^+} = 39.2$, $K_{PbBr^+} = 29.7$, $K_{PbNO_3^+} = 15.1$, and at 35° , $K_{PbBr^+} = 34.8$. The figure for lead chloride agrees closely with the value, 38.5, calculated by James (*loc. cit.*).

DISCUSSION

In Table 2 are given ΔH , ΔG , and ΔS values calculated from the K values at 25° and 35° and using the data at 18° , *viz.*, $K_{PbCl^+} = 32.9$, $K_{KbNO_3^+} = 15.45$ (Righellato and Davies, *loc. cit.*). The Figure suggests that the linear relationship between ΔS (association) and ΔS (hydration) of the anion which was found for other systems (Evans and Nancollas, *Trans. Faraday Soc.*, 1953, 49, 363) is again obeyed.



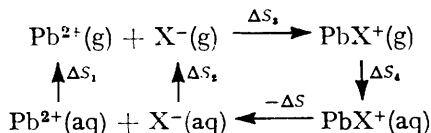
Relation between the entropy of association and the entropy of hydration of the anion.

A, PbX^+ (+).
B, $Co(NH_3)_6X^{2+}$ (O).

TABLE 2. Thermodynamic properties.

| Reaction | ΔG at 25° (kcal./mole) | ΔH (kcal./mole) | ΔS (expt.) (cal./deg. mole) | ΔS (calc.) (cal./deg. mole) |
|---|--|----------------------------|--|--|
| $Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$ | -2.18 | 4.38 | 22.0 | 19 |
| $Pb^{2+} + Br^- \rightleftharpoons PbBr^+$ | -2.02 | 2.88 | 16.4 | 15 |
| $Pb^{2+} + NO_3^- \rightleftharpoons PbNO_3^+$ | -1.62 | -0.57 | 3.5 | 5 |
| $Co(NH_3)_6^{3+} + Cl^- \rightleftharpoons Co(NH_3)_6Cl^{2+}$ | -3.54 | 4.32 | 26 | 19 |
| $Co(NH_3)_6^{3+} + Br^- \rightleftharpoons Co(NH_3)_6Br^{2+}$ | -3.25 | 2.83 | 20 | 14 |
| $Co(NH_3)_6^{3+} + I^- \rightleftharpoons Co(NH_3)_6I^{2+}$ | -2.66 | 2.13 | 16 | 10 |
| $Co(NH_3)_6^{3+} + N_3^- \rightleftharpoons Co(NH_3)_6N_3^{2+}$ | -2.74 | -3.01 | -1.0 | -6 |

The entropy of association in aqueous solution, ΔS , may be evaluated from the entropy cycle :



where $\Delta S_1 = -\Delta S$ (hydration) of gaseous Pb^{2+} ions, $\Delta S_2 = -\Delta S$ (hydration) of gaseous X^- ions, $\Delta S_3 = \Delta S$ (association) in the gas phase, and $\Delta S_4 = \Delta S$ hydration of the ion-pair.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \quad \dots \quad (I)$$

ΔS_1 and ΔS_2 were obtained from the known standard and gas-phase entropies (Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1952). ΔS_4 values were estimated by using the empirical equations suggested by Cobble correlating the partial molar entropies of aqueous complex ions as a function of the ratio of their charge to interatomic distance (*J. Chem. Phys.*, 1953, 21, 1446). They are: $\Delta S_4(\text{PbCl}^+) = -21.5$, $\Delta S_4(\text{PbBr}^+) = -20.5$, and $\Delta S_4(\text{PbNO}_3^+) = -41$ cal./deg. mole.

In calculating ΔS_3 , both translational and rotational terms must be taken into consideration,

$$\Delta S_3 = S_{\text{trans}}(\text{PbX}^+) - S_{\text{trans}}(\text{Pb}^{2+}) - S_{\text{trans}}(\text{X}^-) - S_{\text{rot}}(\text{X}^-) + S_{\text{rot}}(\text{PbX}^+)$$

The first three terms were obtained from the Sackur-Tetrode equation which for 25° may be written $S_{\text{trans}} = 1.5R \ln M + 26.03$, where M = molecular weight. $S_{\text{rot}}(\text{X}^-)$, of consequence only in the case where X^- represents the nitrate ion, was calculated from the equation (Herzberg, "Infra-red and Raman Spectra," Van Nostrand, New York, 1945, Chap. 5) $S_{\text{rot}} = 2.2868 (3 \log T + 3 \log I_A) + 264.65$, where I_A is the moment of inertia about an N-O bond: $S_{\text{rot}}(\text{NO}_3^-) = 19.4$ cal./deg. mole.

PbCl^+ and PbBr^+ being treated as simple "dumbell" molecules, their rotational entropies, $S_{\text{rot}} = 4.606 \log IT + 177.7$, where I is the moment of inertia. Additional terms to account for free internal rotation were introduced for PbNO_3^+ and it was assumed that its centre of mass lies on the Pb-N axis. This is not likely to introduce serious error since it will in any case lie close to this axis. The sum of the translational and rotational contributions,

$$S_{\text{trans}}(\text{PbNO}_3^+) + S_{\text{rot}}(\text{PbNO}_3^+) = 2.2868 (8 \log T + 3 \log M + \log I_A I_B I_C) - 7.697$$

The product, $I_A I_B I_C$, of the moments of inertia was evaluated (Wilson, *Chem. Rev.*, 1940, 27, 17; Hirschfelder, *J. Chem. Phys.*, 1940, 8, 431) by means of

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix}$$

where I_{xx} , I_{xy} . . . are the moments and products of inertia with respect to a co-ordinate system having the centre of mass as origin and the Pb-N axis as x axis: $S_{\text{trans}}(\text{PbNO}_3^+) + S_{\text{rot}}(\text{PbNO}_3^+) = 69.93$ cal./deg. mole. The contribution due to free internal rotation,

$$S_{\text{f.i.r.}} = 2.2868 (\log T + \log I_r - 0.602) + 89.93$$

where I_r , the "reduced" moment of inertia, is given (Herzberg, *op. cit.*) by

$$I_r = I_r^0 [1 - I_r^0 (\lambda_{rA}^2 / I_A + \lambda_{rB}^2 / I_B)]$$

In this formula, I_r^0 is the moment of inertia of the "NO₃ top," and λ_{rA} and λ_{rB} are direction cosines: $S_{\text{f.i.r.}}(\text{PbNO}_3^+) = 5.9$ cal./deg. mole.

Substitution in equation (1) of these calculated entropies enables $\Delta S(\text{association})$ to be determined. Table 2 shows the good agreement with the experimental values. In the figure, the value of $\Delta S(\text{association})$ (PbNO_3^+) is corrected for that part of the rotational entropy of the NO_3^- ion which is destroyed in the course of the reaction.

Many of the reported values for the heats and entropies of complex formation are subject to large errors inherent in the conditions for their study (*i.e.*, high ionic strength). Too little is known of the variation of activity coefficients at constant ionic strength to permit reliable estimates of the uncertainties from this source. Stability constants so obtained, although internally consistent, are inconsistent with data at other values of I . For this reason, the results of previous work on the association of hexamminocobalt with halide and azide ions (Evans and Nancollas, *loc. cit.*) have been corrected by multiplying the association constants by $f_{\text{Co}(\text{NH}_3)_6^{2+}} (f_{\text{X}^-})^{-1}$, the activity coefficients being calculated from the Debye-Hückel equation, $-\log f_i = Az_i^2 I^{1/2}$. Thermodynamic properties are included in Table 2 and plotted in the figure. Despite the difference

in absolute values, it is seen that the same linear relation is obeyed both with uncorrected and with corrected constants. The difference between the parallel straight lines may be expressed as

$$[\Delta S_1(\text{Co}(\text{NH}_3)_6^{3+}) - \Delta S_4(\text{Co}(\text{NH}_3)_6\text{X}^{2+})] - [\Delta S_1(\text{Pb}^{2+}) - \Delta S_4(\text{PbX}^+)]$$

This is about 2.5 cal./deg. mole, which may be compared with the observed difference, 4 cal./deg. mole. The discrepancy between $\Delta S(\text{expt.})$ and $\Delta S(\text{calc.})$ for the hexamminocobalt system is probably due to the difficulty in obtaining a reliable estimate for the hydration entropy of a trivalent cation.

It has been suggested (Bernal and Fowler, *J. Chem. Phys.*, 1933, 1, 515) that ions in aqueous solution order the water molecules around them. The removal of ions from solution accompanying complex formation will lead to a breakdown of this order resulting in an entropy change favouring complex formation. The results of the present work are in support of this, the entropy of association being closely related to the entropy of hydration of the anion. A similar comparison should be possible for the formation of complexes of different cations with the same anion, and in this case, the hydration entropy of the cation should be the controlling factor.

To explain the heat changes upon complex formation, three factors must be taken into consideration: electrostatic and covalent interactions, and additional stabilization due to the different available bonding orbitals of the cation (Williams, *J. Phys. Chem.*, 1954, 58, 121). For bivalent ions of very similar radius, ΔH would be dependent upon the ionization potential of the cation, and if the entropy of association is assumed to be constant, this leads to the linear relationship between $\log K$ and ionization potential which is obeyed approximately for closely related cations (*e.g.*, Calvin and Melchior, *J. Amer. Chem. Soc.*, 1948, 70, 3270; Evans and Monk, *J.*, 1954, 550). More extensive correlations might well be fortuitous until more accurate entropy data are available.

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[Received, November 16th, 1954.]