[Contribution from the Chemistry Departments of the University of Malaya and of Canterbury University College]

# The Constitution of the Lead Halides in Aqueous Solution

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By spectrophotometric methods the dissociation constants of the $PbCl^+$, $PbBr^+$ and $PbI^+$ ions have been found to be 0.027, 0.017 and 0.012, respectively, at 25°. Recent work on the incomplete dissociation of lead nitrate, with formation of the $PbNO_3^+$ ion, has been confirmed. The osmotic and activity coefficients of magnesium nitrate, lead nitrate and lead perchlorate have been measured over a wide concentration range.

Although lead chloride is supposed to form $PbCl^+$ ions in aqueous solution, the published dissociation constants for the reaction: $PbCl^+ \rightleftarrows Pb^{++} + Cl^-$ range from 0.023[1] to 0.10.[2] Recent improvements in spectrophotometric methods afford additional techniques which we have applied to this equilibrium and the analogous bromide and iodide equilibria, using the Uvispek instrument, but, before describing this work, some measurements of a different nature of solutions of magnesium nitrate, lead perchlorate and lead nitrate may be mentioned.

**Magnesium Nitrate.**—In the course of this work we had to prepare some pure magnesium nitrate and the opportunity was taken to extend earlier measurements[3] of the osmotic and activity coefficients, up to higher concentrations, 1.5 to 5 *M* using the isopiestic vapor pressure[4] method at 25° (the temperature at which all measurements recorded in this paper were made). Table I gives the results of the isopiestic measurements while Table II contains the calculated osmotic and activity coefficients.

Table I

Molalities of Isopiestic Solutions of Calcium Chloride and Magnesium Nitrate

| $CaCl_2$ | $Mg(NO_3)_2$ | $CaCl_2$ | $Mg(NO_3)_2$ | $CaCl_2$ | $Mg(NO_3)_2$ |
|---|---|---|---|---|---|
| 1.517 | 1.502 | 2.520 | 2.556 | 3.798 | 3.935 |
| 1.827 | 1.823 | 2.997 | 3.072 | 4.302 | 4.493 |
| 1.930 | 1.931 | 3.365 | 3.463 | 4.888 | 5.123 |
| 2.047 | 2.053 | 3.707 | 3.837 | | |

Table II

Osmotic and Activity Coefficients of Magnesium Nitrate

| $m$ | $\varphi$ | $\gamma$ | $m$ | $\varphi$ | $\gamma$ |
|---|---|---|---|---|---|
| 1.6 | 1.251 | 0.692 | 3.5 | 1.878 | 1.940 |
| 1.8 | 1.311 | 0.760 | 4.0 | 2.043 | 2.60 |
| 2.0 | 1.372 | 0.837 | 4.5 | 2.209 | 3.51 |
| 2.5 | 1.535 | 1.090 | 5.0 | 2.376 | 4.75 |
| 3.0 | 1.710 | 1.452 | | | |

**Lead Perchlorate.**—In the derivation of the dissociation constant of the $PbCl^+$ ion we shall have to assume that lead perchlorate is a fully dissociated electrolyte; there is little proof of this apart from argument by analogy with other bivalent metal perchlorates, such as those of zinc and magnesium,[5] and we have therefore used the isopiestic method to determine the osmotic and activity coefficients of lead perchlorate in aqueous solution at 25°. The solution was prepared by adding an excess of purified lead carbonate to perchloric acid and filtering, the concentration of this stock solution being determined by gravimetric analysis of the lead content. The *p*H of an aliquot diluted to 0.1 molar was 4.3. From the results given in Tables III and IV, it will be seen that in dilute solution the osmotic coefficients of lead perchlorate are close to those of cobalt chloride and on this analogy the activity coefficient at 0.1 *M* was taken as 0.524; the activity coefficients of lead perchlorate are then much lower than those of zinc and magnesium perchlorate; thus at 1 *M* we find figures of 0.522, 0.929 and 0.946, respectively; that for lead perchlorate at 1 *M* is comparable with 0.531 for cobalt chloride, a figure which has been interpreted[6]

Table III

Molalities of Isopiestic Solutions of Lead Perchlorate and Calcium Chloride or Sulfuric Acid

| $CaCl_2$ | $Pb(ClO_4)_2$ | $CaCl_2$ | $Pb(ClO_4)_2$ | $CaCl_2$ | $Pb(ClO_4)_2$ |
|---|---|---|---|---|---|
| 0.09573 | 0.09529 | 1.715 | 1.712 | 4.917 | 5.315 |
| .2019 | .2001 | 1.985 | 1.999 | 5.598 | 6.109 |
| .4060 | .4008 | 2.927 | 3.015 | 6.251 | 6.827 |
| .7722 | .7632 | 3.738 | 3.928 | 6.819 | 7.397 |
| .8119 | .8030 | 4.085 | 4.327 | 7.002 | 7.592 |
| .8783 | .8685 | 4.379 | 4.675 | 7.805 | 8.294 |
| 1.035 | 1.025 | 4.536 | 4.861 | 9.096 | 9.304 |
| 1.338 | 1.330 | | | | |
| $H_2SO_4$ | $Pb(ClO_4)_2$ | $H_2SO_4$ | $Pb(ClO_4)_2$ | $H_2SO_4$ | $Pb(ClO_4)_2$ |
| 13.667 | 9.324 | 16.264 | 11.014 | 16.993 | 11.520 |
| 14.813 | 10.074 | 16.377 | 11.094 | 18.501 | 12.579 |
| 15.289 | 10.397 | | | | |

Table IV

Osmotic and Activity Coefficients of Lead Perchlorate

| $m$ | $\varphi$ | $\gamma$ | $m$ | $\varphi$ | $\gamma$ |
|---|---|---|---|---|---|
| 0.1 | 0.858 | 0.524 | 2.5 | 1.521 | 1.043 |
| .2 | .870 | .482 | 3.0 | 1.693 | 1.383 |
| .3 | .886 | .466 | 3.5 | 1.853 | 1.827 |
| .4 | .907 | .461 | 4.0 | 1.999 | 2.39 |
| .5 | .930 | .464 | 4.5 | 2.137 | 3.21 |
| .6 | .954 | .470 | 5.0 | 2.271 | 4.04 |
| .7 | .976 | .478 | 5.5 | 2.399 | 5.22 |
| .8 | 1.002 | .490 | 6.0 | 2.516 | 6.66 |
| .9 | 1.031 | .505 | 7.0 | 2.737 | 10.67 |
| 1.0 | 1.060 | .522 | 8.0 | 2.915 | 16.28 |
| 1.2 | 1.118 | .562 | 9.0 | 3.057 | 23.7 |
| 1.4 | 1.179 | .612 | 10.0 | 3.194 | 34.0 |
| 1.6 | 1.240 | .668 | 11.0 | 3.297 | 46.7 |
| 1.8 | 1.301 | .733 | 12.0 | 3.365 | 61.3 |
| 2.0 | 1.363 | .807 | | | |

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(1) J. C. James, This Journal, **71**, 3243 (1949).

(2) R. M. Garrels and F. T. Gucker, *Chem. Revs.*, **44**, 117 (1949).

(3) R. A. Robinson, J. M. Wilson and H. S. Ayling, This Journal, **64**, 1469 (1942).

(4) R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

(5) R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946).

(6) R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

by assuming that 13 water molecules are "attached" to the cobalt ion. Moreover, the activity coefficient of lead perchlorate at 1 $M$ is much greater than that of sodium sulfate (0.201) at this concentration, the latter salt being one in which we have good reason[7,8] to believe intermediate ions are formed. Thus, whilst the possibility of a small amount of intermediate ion formation with lead perchlorate cannot be ruled out, it should be negligibly small at the low concentrations used in our work on the lead halide intermediate ions. Moreover, we have examined the absorption spectrum at a concentration of 0.0005 mole per liter over the range 2000–4000 Å. and found no evidence for any absorption except around 2085 Å. where we found the characteristic absorption due to the $Pb^{++}$ ion, the extinction coefficient being $\epsilon = 8500$. Measurement in 10, 20, 30, 60 and even 80 mole % dioxane failed to reveal any other absorption peak, nor did the addition of 4.6 moles of perchloric acid per liter change the character of the absorption; in particular, there was no indication of the peak at 2270 Å. which is found in lead chloride solutions. This evidence, negative although it is, favors almost complete dissociation of lead perchlorate.

**Lead Nitrate.**—Lead nitrate behaves very differently as may be seen from its osmotic and activity coefficients, the data being given in Tables V and VI. Randall and Vanselow[9] found $\gamma = 0.369$ at 0.1 $M$ from freezing point measurements and, in the absence of data at 25°, we calculated our results relative to this value at 0.1 $M$.

TABLE V

MOLALITIES OF ISOPIESTIC SOLUTIONS OF LEAD NITRATE AND CALCIUM CHLORIDE

| $CaCl_2$ | $Pb(NO_3)_2$ | $CaCl_2$ | $Pb(NO_3)_2$ | $CaCl_2$ | $Pb(NO_3)_2$ |
|---|---|---|---|---|---|
| 0.07763 | 0.08801 | 0.3038 | 0.4295 | 0.6305 | 1.165 |
| .1207 | .1437 | .3533 | .5222 | .6715 | 1.279 |
| .1924 | .2464 | .4321 | .6792 | .7456 | 1.487 |
| .2306 | .3057 | .5075 | .8511 | .7918 | 1.627 |
| .2425 | .3250 | .5390 | .9245 | .8597 | 1.825 |
| .2552 | .3459 | .5932 | 1.055 | .9082 | 1.988 |

TABLE VI

OSMOTIC AND ACTIVITY COEFFICIENTS OF LEAD NITRATE

| $m$ | $\varphi$ | $\gamma$ | $m$ | $\varphi$ | $\gamma$ |
|---|---|---|---|---|---|
| 0.1 | 0.746 | 0.369 | 0.9 | 0.545 | 0.140 |
| .2 | .692 | .290 | 1.0 | .533 | .132 |
| .3 | .656 | .244 | 1.2 | .511 | .119 |
| .4 | .628 | .213 | 1.4 | .494 | .107 |
| .5 | .606 | .192 | 1.6 | .481 | .099 |
| .6 | .588 | .174 | 1.8 | .472 | .092 |
| .7 | .572 | .161 | 2.0 | .465 | .087 |
| .8 | .558 | .149 | | | |

The activity coefficient at 1 $M$ (0.132) is, with the exception of the cadmium halides, lower than any we have observed for any salt of this valence type, the nearest being that of sodium sulfate (0.201).

There is no direct confirmation of these values for lead nitrate but Landolt–Börnstein[10] quote the following activity coefficients derived from freezing point measurements: 0.373 (0.369), 0.275 (0.290), 0.168 (0.192) and 0.112 (0.132) at 0.1, 0.2, 0.5 and 1 $M$, respectively, the figures in parentheses being the ones derived in the present work; better agreement could not be expected since there is a considerable difference of temperature between the two sets. Ratner[11] has made vapor pressure measurements at 70° from which he calculated the following activity coefficients: 0.369 (0.369), 0.306 (0.290), 0.256 (0.244), 0.205 (0.192), 0.163 (0.132) and 0.125 (0.087) at 0.1, 0.2, 0.3, 0.5, 1.0 and 2 $M$, respectively, the figures in parentheses again being the results of the present work; again the agreement is all that could be expected in view of the temperature difference. Finally Dingemans[12] has given a formula for the water activity of the saturated solution over a temperature range, from which we calculate an osmotic coefficient at 25° of 0.496 assuming that the concentration of the saturated solution is 1.80 $M$.[13] Stokes[14] has shown that the presence of the $ZnCl_4^{=}$ ion in solutions of zinc chloride can be revealed by making vapor pressure measurements of solutions of magnesium and zinc chloride of constant total molality but varying Mg:Zn ratio $(1 - x):x$; a plot of the vapor pressure against $x$ should show a discontinuity at $x = 0.5$ if $ZnCl_4^{=}$ ions are formed and at $x = 0.33$ if $ZnCl_3^-$ ions are formed. Neither of the species $ZnCl^+$ or $ZnCl_2$ should give a discontinuity. Stokes observed a discontinuity at $x = 0.5$. Table VII contains the results of some similar measurements of magnesium nitrate–lead nitrate mixtures; a plot of the vapor pressure against the fraction ($x$) of lead nitrate in the mixture shows no discontinuity like that observed by Stokes for the zinc halides and this rules out the formation of significant amounts of $Pb(NO_3)_3^-$ or $Pb(NO_3)_4^{=}$ ions. In passing, we may remark that a plot of $(1/x)\log a_w$ against $x$ gives a good straight line indicating that Harned's Rule applies and, from the slope and intercept of this straight line, it can be calculated that the activity coefficient of lead nitrate in this mixture is given by

$$-\log \gamma = 0.720 + 0.267x$$

TABLE VII

VAPOR PRESSURE OF AQUEOUS LEAD NITRATE–MAGNESIUM NITRATE MIXTURES AT A CONSTANT TOTAL MOLALITY OF 1.5

| $x^a$ | $R^b$ | $-\log a_w$ |
|---|---|---|
| 0 | 1.0100 | 0.04304 |
| 0.2011 | .8897 | .03609 |
| .2809 | .8450 | .03364 |
| .3879 | .7863 | .03052 |
| .5433 | .7056 | .02646 |
| .6419 | .6583 | .02416 |
| .7623 | .5954 | .02128 |
| .9075 | .5405 | .01887 |
| 1.0 | .5000 | .01717 |

[a] $x$ = fraction of $Pb(NO_3)_2$ in $Pb(NO_3)_2$–$Mg(NO_3)_2$ mixture. [b] $R$ = isopiestic ratio = ratio of molality of $CaCl_2$ solution to the total molality of the $Pb(NO_3)_2$–$Mg(NO_3)_2$ solution of the same vapor pressure.

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[7] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[8] I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2695 (1950).

[9] M. Randall and A. P. Vanselow, *ibid.*, **46**, 2418 (1924).

[10] Landolt-Börnstein "Tabellen," fifth edition, zweiter Ergänzungsband, 1931, p. 1128.

[11] A. P. Ratner, *J. phys. Chem. U.S.S.R.*, **9**, 257 (1937).

[12] P. Dingemans, *Rev. trav. chim.*, **64**, 194 (1945).

[13] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 220.

[14] R. H. Stokes, *Trans. Faraday Soc.*, **44**, 137 (1948).

A reasonable explanation of the very low osmotic coefficients of lead nitrate can be sought in the possible formation of the $PbNO_3^+$ ion or the $Pb(NO_3)_2$ molecule. The former was postulated many years ago by Righellato and Davies[7] and has recently received confirmation by Hershenson, Smith and Hume.[15] They first used Job's[16] method of "continuous variations" to determine the formula of the complex as $PbNO_3^+$. Solutions of lead perchlorate and sodium nitrate were made with the salts in various ratios but at a constant total molarity of 0.1. The solution containing sodium nitrate only absorbs at 300 mμ. This is caused by the nitrate ion but on the addition of the lead salt there is increased absorption which, it is assumed, is due to a lead complex also absorbing at this wave length. The optical density, $D$, is measured at this wave length for each solution including the one containing only sodium nitrate ($x = 1$, $x$ being the fraction of sodium nitrate in the salt mixture), this latter measurement giving the extinction coefficient of the nitrate ion, $D' = c\epsilon_{NO_3^-}$ (assuming, for simplicity, that 1 cm. cells are used). It can be demonstrated that, if ions of formula $Pb(NO_3)_n$ with $(n - 2)$ negative charges are formed, a graph of $(D - xD')$ against $x$ will have a maximum at

$$x_{max} = n/(n + 1)$$

and Hershenson, *et al.*, found $x_{max} = 0.5$ and, therefore, $n = 1$. We have repeated these measurements and confirmed the presence of a distinct maximum in the curve at $x = 0.5$, although our curve did not exhibit that skew in the direction of the higher nitrate fractions observed by Hershenson *et al.*, and interpreted by them as a small contribution by a higher complex, such as the un-ionized lead nitrate molecule.

Having determined the formula of the complex, they used the method of McConnell and Davidson,[17] to estimate the extent to which it is formed. For this purpose they made a series of solutions each 0.05 $N$ in sodium nitrate but varying in lead perchlorate concentration between 0.1 and 0.6 molar, the total ionic strength being maintained at $I = 2$ by addition of the requisite amount of sodium perchlorate and measured the optical density at 300 mμ for each solution. It is easy to show that

$$ab/(D - D') = k/\Delta\epsilon + (a + b)/\Delta\epsilon$$

(Hershenson, *et al.*, seem to omit the $b$ term from the third term but we think this is the correct form of the equation, because, let

$a$ = the stoichiometric concn. of lead perchlorate
$b$ = the stoichiometric concn. of sodium nitrate
$x$ = concn. of $PbNO_3^+$
$D$ = obsd. optical density
$D' = a\epsilon_{Pb^{++}} + b\epsilon_{NO_3^-}$
$\epsilon_{Pb^{++}}, \epsilon_{NO_3^-}, \epsilon_{PbNO_3^+}$ = extinction coefficients of $Pb^{++}$ nitrate and $PbNO_3^+$, respectively,
$\Delta\epsilon = \epsilon_{PbNO_3^+} - \epsilon_{NO_3^-} - \epsilon_{Pb^{++}}$
$k = [Pb^{++}][NO_3^-]/[PbNO_3^+]$
Then $[Pb^{++}] = a - x$, $[NO_3^-] = b - x$
and $x(k + a + b) = ab + x^2$ in which equation $x^2$ is negligible if the $PbNO_3^+$ ion is formed in small amount.
Then $D = (b - x)\epsilon_{NO_3^-} + x\epsilon_{PbNO_3^+} + (a - x)\epsilon_{Pb^{++}}$ or $D - D' = x\Delta\epsilon$

whence the above equation follows). We have repeated these experiments at $I = 0.5$, 1 and 2 (Table VIII), using perchloric acid instead of sodium perchlorate, and found good straight line plots of $ab/(D - D')$ against $(a + b)$, whence we found $k = 0.56$, 0.49 and 0.44, respectively.

TABLE VIII

DISSOCIATION CONSTANT OF THE $PbNO_3^+$ ION

$a$ = molarity of lead perchlorate, $b$ = molarity of sodium nitrate, measurements made at 300 mμ.

$D' = 0.155a + 6.86b$

| $a$ | $b = 0.025$ $I = 0.5$ $D$ | $b = 0.05$ $I = 1.0$ $D$ | $b = 0.05$ $I = 2.0$ $D$ |
|---|---|---|---|
| 0.050 | 0.211 | ... | ... |
| .075 | .233 | ... | ... |
| .100 | .249 | 0.464 | ... |
| .125 | .263 | ... | ... |
| .150 | .280 | .509 | ... |
| .2 | ... | .553 | 0.566 |
| .25 | ... | .593 | ... |
| .3 | ... | .628 | .634 |
| .4 | ... | ... | .704 |
| .5 | ... | ... | .744 |
| .6 | ... | ... | .803 |
| $k$ = | 0.56 | 0.49 | 0.44 |

(The results at $I = 0.5$ are of poor accuracy because $D'$ is large compared with $D$.) Hershenson, *et al.*, found $k = 0.6$ at $I = 2$ (although their data also seem to be consistent with a somewhat lower value, about $k = 0.5$) and they quote $k = 0.3$ at $I = 6$. These dissociation constants should be "classical," because no activity coefficients have been introduced; we can therefore calculate degrees of dissociation of the $PbNO_3^+$ ion in lead nitrate solution directly as $\alpha = 0.67$, 0.50, 0.33 and 0.12 at lead nitrate molarities of 0.167, 0.333, 0.667 and 2.0, respectively. Righellato and Davies[7] found $\alpha = 0.67$ at a molarity of 0.05.

The degree of dissociation of the $PbNO_3^+$ ion can however be calculated in another way. The activity coefficients, $\gamma$, given in Table VI, are stoichiometric coefficients calculated on the assumption of complete dissociation. The other activity coefficient, $\gamma'$, calculated from the true lead and nitrate ion concentrations, is related[18] to $\gamma$ by the equation

$$4\gamma^3 = \alpha(1 + \alpha)^2\gamma'^3$$

If we assume that $\gamma'$ for lead nitrate is equal to that for barium chloride, we can calculate $\alpha = 0.72$, 0.46, 0.33 and 0.20 at 0.05, 0.167, 0.333 and 0.667 molar, values which differ from those derived from spectrophotometric measurements. (At 0.05 molar, $\gamma$ was taken from the freezing point data of Randall and Vanselow.[9]) We could use another salt than barium chloride to represent the lead and nitrate ions but a salt with a higher activity coefficient would give results in even worse agreement while a salt with an even lower activity coefficient is probably associated itself and cannot be taken as typical of a completely dissociated electrolyte. Part of the discrepancy may be explained by some formation of

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(15) H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

(16) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(17) H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

(18) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, England, 1955, p. 37.

the $Pb(NO_3)_2$ molecule although this is not likely to be appreciable at the lower concentrations. A more likely explanation is to be found in an assumption in the McConnell–Davidson method valid in some circumstances but perhaps dubious in this case. It is assumed that the dissociation constant, $k$, is a true constant for a set of solutions of constant total ionic strength. This is equivalent to assuming that the activity coefficients of the various ionic species are constant at constant total ionic strength. This may well be true if the sodium nitrate and lead perchlorate concentrations are small compared with the total concentration; unfortunately, the extinction coefficients of this system are small and, in order to obtain optical densities measurable with any accuracy, it is necessary to have moderately concentrated solutions. Thus in the third set of measurements recorded in Table VIII the composition of the solutions varied from 0.2 molar lead perchlorate +0.05 $N$ sodium nitrate +1.35 $N$ perchloric acid to 0.6 molar lead perchlorate +0.05 $N$ sodium nitrate +0.15 $N$ perchloric acid. With such extreme variations in the nature of the solution, the assumption of a constant activity coefficient becomes very dubious. Under such circumstances, only an approximation to the dissociation constant can be expected.

**The Halides of Lead.**—Figure 1 shows some Job plots for mixtures of lead perchlorate and potassium chloride, bromide or iodide which demonstrate clearly that the maximum occurs at $x = 0.5$ and that the formula of the halide complex must be $PbX^+$. The McConnell–Davidson method is simpler in its application to these systems partly because there is no contribution to the optical density from the potassium halide and partly because the component salts contribute little to the total ionic strength in the solution. Tables IX–XI give the results of our measurements; for $PbCl^+$ two sets of measurements were made using two different potassium chloride concentrations.

TABLE IX

DISSOCIATION CONSTANT OF THE $PbCl^+$ ION

$a$ = molarity of lead perchlorate, $b$ = molarity of potassium chloride.

Series A, $b$ = 0.002; measurements made at 240 mμ.

| $a$ | $I$ = 0.02<br>$D$ | 0.04<br>$D$ | 0.06<br>$D$ | 0.08<br>$D$ | 0.10<br>$D$ |
|---|---|---|---|---|---|
| | | $D' = 12.0a$. | | | |
| 0.002 | 0.246 | ... | ... | ... | ... |
| .003 | .359 | ... | ... | ... | ... |
| .004 | .472 | 0.416 | 0.382 | 0.359 | 0.341 |
| .005 | .581 | ... | ... | ... | ... |
| .006 | .692 | .602 | .555 | .524 | .506 |
| .008 | ... | .783 | .723 | .682 | .653 |
| .010 | ... | .962 | .893 | .837 | .802 |
| .012 | ... | 1.119 | 1.043 | .980 | .951 |
| $K$ | 0.030 | 0.028 | 0.029 | 0.025 | 0.028 |

Series B, $b$ = 0.003; measurements made at 245 mμ.

| $a$ | $I$ = 0.04<br>$D$ | 0.06<br>$D$ | 0.08<br>$D$ | 0.10<br>$D$ | 0.12<br>$D$ |
|---|---|---|---|---|---|
| | | $D' = 2.56a$. | | | |
| 0.003 | 0.214 | ... | ... | ... | ... |
| .006 | .406 | 0.372 | 0.349 | 0.328 | 0.317 |
| .009 | .587 | .536 | .512 | .478 | .466 |
| .012 | .755 | .688 | .649 | .615 | .594 |
| .015 | ... | .828 | .779 | .744 | .714 |
| .018 | ... | .966 | .915 | .867 | .844 |
| $K$ | 0.029 | 0.027 | 0.025 | 0.027 | 0.025 |

Av. $K$ = 0.027

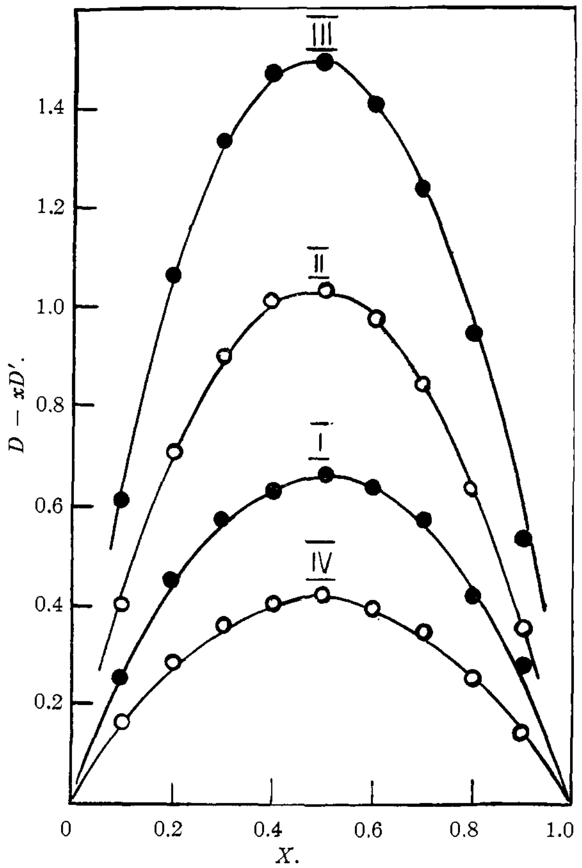

Fig. 1.—Job plots for lead halides: I, lead perchlorate–potassium chloride mixtures at a total concentration of 0.005 molar and at a wave length of 234 mμ; II, lead perchlorate–potassium bromide mixtures at a total concentration of 0.005 molar and at a wave length of 245 mμ; III, as II but at a wave length of 234 mμ; IV, lead perchlorate–potassium iodide mixtures at a total concentration of 0.00286 molar and at a wave length of 280 mμ.

TABLE X

DISSOCIATION CONSTANT OF THE $PbBr^+$ ION

$a$ = molarity of lead perchlorate, $b$ = molarity of potassium bromide, $b$ = 0.002; measurements made at 250 mμ. $D' = 0.7a$

| $a$ | $I$ = 0.04<br>$D$ | 0.06<br>$D$ | 0.08<br>$D$ | 0.10<br>$D$ |
|---|---|---|---|---|
| 0.004 | 0.733 | 0.681 | 0.622 | 0.608 |
| .006 | 1.052 | .979 | .899 | .879 |
| .008 | 1.347 | 1.258 | 1.160 | 1.132 |
| .010 | 1.609 | 1.498 | 1.400 | 1.374 |
| .012 | 1.846 | 1.737 | 1.616 | 1.556 |
| $K$ = | 0.017 | 0.017 | 0.018 | 0.016 |

Av. $K$ = 0.017

From the results $k$ was evaluated by the method described above for lead nitrate. The thermodynamic dissociation constant is then given by

$$K = k\gamma_{Pb}\gamma_{X}/\gamma_{PbX}$$

TABLE XI

DISSOCIATION CONSTANT OF THE $PbI^+$ ION

$a$ = molarity of lead perchlorate, $b$ = molarity of potassium iodide, $b$ = 0.002; measurements made at 290 mμ. $D' = 0$

| | $I$ = 0.04 | 0.06 | 0.08 | 0.10 |
|---|---|---|---|---|
| $a$ | $D$ | $D$ | $D$ | $D$ |
| 0.004 | 0.537 | 0.490 | 0.470 | 0.444 |
| .006 | .764 | .703 | .666 | .628 |
| .008 | .962 | .890 | .849 | .794 |
| .010 | 1.137 | 1.060 | 1.008 | .954 |
| .012 | 1.303 | 1.209 | 1.156 | 1.089 |
| $K$ = | 0.013 | 0.013 | 0.012 | 0.011 |
| | | Av. $K$ = 0.012 | | |

and to evaluate the activity coefficient term we used Davies' equation[19]

$$-\log \gamma = 0.5092\, z^2\sqrt{I}/(1 + \sqrt{I}) - 0.1zI$$

that is to say, we put $z = 2$ for the lead ion and cancelled out the other two activity coefficients. Satisfactorily constant values of $K$ were obtained over a range of total ionic strengths, the mean values being

$PbCl^+$, $K = 0.027$
$PbBr^+$, $K = 0.017$
$PbI^+$, $K = 0.012$

The result for $PbCl^+$ therefore favors the lower set tabulated by Garrels and Gucker[2] (their Table VII): it is in good agreement with the value of 0.026 calculated by James[1] from conductance data although somewhat higher than that of 0.023 which he obtained from e.m.f. data.

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[CONTRIBUTION OF CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

# The Condensed System Bromine Trifluoride–Antimony Pentafluoride

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Investigation of the system bromine trifluoride–antimony pentafluoride has shown the presence of two incongruently melting compounds, $3BrF_3{\cdot}SbF_5$ and $3BrF_3{\cdot}2SbF_5$, and two congruently melting compounds, $BrF_3{\cdot}SbF_5$ and $BrF_3{\cdot}3SbF_5$. The compound $BrF_3{\cdot}3SbF_5$ undergoes a solid phase transition at −22.6°.

## Introduction

This system was investigated to determine the solubility of antimony pentafluoride in bromine trifluoride and to determine the solid phases formed in the system. This study was made by obtaining time–temperature cooling and thaw curves of synthetic complexes. Bromine trifluoride–antimony pentafluoride mixtures have been used as fluorinating agents.[1] The compound $BrF_3{\cdot}SbF_5$, which was reported to have a melting point at about 200°,[2] has been used by Sheft, Martin and Katz[3] as a fluorinating reagent for the quantitative determination of oxygen in inorganic oxides.

## Experimental

**Materials.**—Bromine trifluoride obtained from the Harshaw Chemical Company was purified by distillation in a forty-inch nickel fractionation column, one-half inch in diameter and packed with one-eighth inch nickel helices. The melting point of the bromine trifluoride, as indicated in Table I, agreed with the literature value[4] within experimental error.

Antimony pentafluoride, also obtained from the Harshaw Chemical Company, was used without further purification. Spectrographic analysis for other metals, and nephelometric analysis for chloride and bromide showed negligible impurities. Melting points were taken of the antimony pentafluoride using a sample from the original container and a sample of a distilled portion. Both gave the same result. This value, as indicated in Table I, agreed closely with the literature value.[5]

**Apparatus and Procedure.**—The apparatus used for the thermal analysis was similar to one previously described.[6,7] The components were introduced under an atmosphere of helium through a one-fourth inch flared nickel fitting into nickel or Monel tubes three-fourths inch in diameter and six inches long. The temperatures were measured with copper-constantan thermocouples in conjunction with a multi-point Brown Recording Potentiometer. The thermocouples and recorder were calibrated against a standardized platinum resistance thermometer employing a Leeds-Northrup G-2 Mueller bridge.

## Results and Discussion

The data, in terms of mole per cent. bromine trifluoride, are listed in Table I and are plotted in the usual fashion in Fig. 1. The values in Table I are the average of several determinations for any one mixture and are assumed to be accurate to within ±0.5°.

Supercooling phenomena were observed for all mixtures below 40°. Many samples would supercool as much as 40° and as a result it was impossible to obtain accurate, reproducible data from cooling curves where this occurred. Therefore, thaw curves were used below 40° and these proved to be quite reproducible. Above 40° good agreement was obtained when both freezing and thaw curves were obtained for a given complex.

The duration of the thermal effects was employed in a qualitative manner to aid in establishing the solid compositions. The compound $3BrF_3{\cdot}SbF_5$ is designated as such on the basis of the thermal halts obtained. The data, however, do not negate the possibility that this compound may be lower in bromine trifluoride content (*e.g.*, $2BrF_3{\cdot}SbF_5$).

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