nium, 10.37% of thorium and 9.26% of lead. If one assumes (1) that our material is essentially free from ordinary lead, (2) that the relation of $Pb^{206}$ to $Pb^{207}$ found by Aston in bröggerite material, 86.8 to 9.6, is the relation in which these isotopes are produced from uranium and (3) that the uranium equivalent of thorium in lead-producing power is 0.38, the average atomic weight of the lead in this specimen of uraninite may be calculated to be 206.23. The difference between this value and our experimental value is far larger than the experimental uncertainty.

With Wells' percentages and the thorium–uranium constant, 0.38, together with the experimental value of the atomic weight of the lead in this uraninite, the average atomic weight of uranium lead is found to be 206.06, while Aston's ratio of $Pb^{206}$ to $Pb^{207}$ gives 206.10. On this basis the ratio of $Pb^{207}$ to $Pb^{206}$ would be a little over half as large as that found by Aston.

The assumption of Aston's ratio of $Pb^{207}$ to $Pb^{206}$ in uranium lead together with Wells' percentages of uranium and thorium and the atomic weight of our specimen of uraninite lead makes it possible to calculate the Th/U constant to be 0.27, a value believed by some to be within the bounds of possibility.

The uncertainty of the assumptions makes the last three calculations of doubtful value.

Cambridge, Massachusetts

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[Contribution from the Chemistry Department of Coe College]

# THE ACTIVITY COEFFICIENT OF COPPER IODATE IN AQUEOUS SALT SOLUTIONS

By Ben H. Peterson and Earl L. Meyers

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Bronsted and La Mer[1] have reduced the Debye and Hückel equation[2] to $-\log f = 0.505\, z_1 z_2 \sqrt{\mu}$ as a limiting law which is valid when the ions are separated to such distances that the actual volume occupied by the ions is of no effect. Considerable research has been done testing the validity of this equation by measuring the activity coefficients of slightly soluble compounds in aqueous salt solutions. La Mer and Goldman[3] have determined the activity coefficients of thallous and lanthanum iodates, and Lewis and Randall[4] have calculated them for barium iodate using the data of Harkins and Winninghoff.[5] The slight solubility of

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[1] Brönsted and La Mer, This Journal, **46**, 560–61 (1924).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185–342 (1923).

[3] La Mer and Goldman, This Journal, **51**, 2632–2645 (1929).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 375.

[5] Harkins and Winninghoff, This Journal, **33**, 1827 (1911).

these salts in pure water ($Ba(IO_3)_2$, 0.000790; $La(IO_3)_3$, 0.00089006; and $TlIO_3$, 0.001844 mole per liter), and the accuracy with which the concentration can be measured render them especially suitable for testing the limiting law. In such dilute solutions the activity coefficient of the solute may be defined by the relation[6]

$$-\log f = \log S/S_0 - \log f_0$$

in which $S$ is the solubility of the saturating salt in the salt solution of varying concentrations, $S_0$ the solubility in pure water, and $f_0$ the activity coefficient in pure water. In such dilute solutions the value of $f_0$ as calculated from the limiting law may be assumed for the purpose of testing the equation. In case of most of the solvent salts used by La Mer and Goldman[3] the curve of the observed values of $-\log S/S_0$ fused into the ideal curve but a characteristic "hump" was observed in the case of potassium sulfate as the solvent salt. The theoretical significance of this positive deviation has been discussed by Gronwall, La Mer and Sandved,[7] and by La Mer and Mason.[8] In as much as the data of La Mer and Goldman[3] are for a mono- and trivalent iodate it seemed advisable to compare these deviations with those of a bivalent iodate in order to determine whether the "hump" observed by them would be in evidence and the relative magnitude of such a positive deviation.

## Experimental

The salt chosen for this purpose was copper iodate. This was prepared by metathesis using purified copper sulfate and potassium iodate. Equivalent amounts of these salts were placed in solution and added dropwise to six liters of doubly distilled water kept at 60° and constantly stirred. The addition required about four hours. The precipitate was then washed several times by decantation and placed in six liters of doubly distilled water. This was kept at 60° and stirred by an electrical stirring device for several days. The salt so prepared was "sedimented" in a tall cylinder and all particles that did not settle readily were siphoned off. By several repetitions of this process it was possible to obtain a crop of crystals which appeared to be uncontaminated with small particles and should consequently be of uniform solubility. This technique is appreciably the same as used by La Mer and Goldman with lanthanum iodate. The salt when filtered and dried over calcium chloride analyzed for $Cu(IO_3)_2 \cdot H_2O$. The solvent salts were recrystallized from a high grade analyzed product, dried and analyzed for moisture and water of crystallization.

The experiments were carried out in a large especially constructed thermostat maintained at 25 ± 0.02°. Ten pyrex Erlenmeyer flasks fitted with especially constructed stoppers through which a stirring rod extended were placed in the thermostat and 5 g. of the iodate added with 250 cc. of the solvent solution. The contents of the flasks were gently agitated for five days, then allowed to stand for twelve hours. These solutions were analyzed for dissolved copper iodate by dissolving 2 g. of potassium iodide in 250 cc. of water in a 500-cc. iodine flask, 5 cc. of 6 *M* sulfuric acid was added, then 25 cc. of

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[6] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358–93 (1928).

[8] La Mer and Mason, THIS JOURNAL, **49**, 410–26 (1927).

the iodate solution. The contents of the flask were immediately titrated with $N/20$ sodium thiosulfate. The thiosulfate was restandardized before and after each run by exactly the same technique using 25 cc. of $N/20$ potassium iodate as the standard. Some trouble was experienced with a slow reaction between the iodide and cupric ions but the technique finally adopted allowed sufficient time to elapse between the completion of the iodate and the beginning of the cupric reaction. This was repeatedly checked using solutions of potassium iodate to which small quantities of copper sulfate had been added. In Table I is given a set of representative data illustrating the reliability of the method.

TABLE I

REPRESENTATIVE DATA

| Sample | $H_2O$, cc. | KI, g. | $H_2SO_4$, cc. | $CuSO_4$, cc. | $KIO_3$, cc. | Thio, cc. |
|---|---|---|---|---|---|---|
| I | 200 | 2 | 5 | 0 | 25 | 28.40 |
| II | 200 | 2 | 5 | 5 | 25 | 28.37 |
| III | 200 | 2 | 5 | 10 | 25 | 28.37 |
| IV | 200 | 2 | 5 | 20 | 25 | 28.37 |
| V | 200 | 2 | 5 | 40 | 25 | 28.39 |
| VI | 200 | 2 | 5 | 100 | 25 | 28.38 |

## Experimental Results

The solubility of copper iodate in solutions of potassium chloride, potassium sulfate, magnesium chloride and magnesium sulfate is given in Table II. The column headings are self-explanatory. The limiting law takes the form

$$-\log f = 1.01\sqrt{\mu}$$

from which the values in Column 6 are calculated. $-\log f_0$ equals 0.1063, obtained from the above equation when $\mu$ represents the ionic strength of the copper iodate in the pure water solution.

TABLE II

SOLUBILITY RELATIONS OF COPPER IODATE IN VARIOUS SOLVENTS

Solvent, Salt, KCl

| Solubility, mole/liter | $\mu$ | $\sqrt{\mu}$ | Log $S/S_0$ | $-\text{Log} f$ (obs.) | $-\text{Log} f$ (calcd.) | $\Delta$ log |
|---|---|---|---|---|---|---|
| 0.003693 | 0.01108 | 0.10526 | ..... | 0.1063 | 0.1063 | 0.0000 |
| .003724 | .01167 | .10803 | 0.00363 | .1099 | .1091 | .0008 |
| .003725 | .01217 | .11032 | .00375 | .1100 | .1114 | −.0014 |
| .003825 | .01647 | .12833 | .01525 | .1215 | .1296 | −.0071 |
| .003992 | .02198 | .14843 | .03381 | .1401 | .1499 | −.0098 |
| .004667 | .06400 | .25300 | .10166 | .2020 | .2555 | −.0535 |
| .005238 | .11571 | .34020 | .15179 | .2581 | .3434 | −.0853 |
| .007689 | .52306 | .72320 | .31849 | .4248 | .7302 | −.3054 |
| .009615 | 1.02884 | 1.01430 | .41557 | .5219 | 1.0241 | −.5022 |
| .013072 | 2.03922 | 1.42800 | .54897 | .6553 | 1.4423 | −.7870 |
| .015820 | 3.04746 | 1.74570 | .63183 | .7381 | 1.7635 | −1.0254 |
| Solvent Salt, $K_2SO_4$ | | | | | | |
| 0.003693 | 0.01108 | 0.10526 | ..... | 0.1063 | 0.1063 | 0.0000 |
| .003785 | .01285 | .11340 | 0.01069 | .1170 | .1145 | .0025 |
| .003882 | .01465 | .12104 | .02168 | .1280 | .1222 | .0058 |
| .004359 | .02808 | .16758 | .07201 | .1783 | .1682 | .0101 |

TABLE II (*Concluded*)

| Solubility, mole/liter | $\mu$ | $\sqrt{\mu}$ | Log $S/S_0$ | $-$Log $f$ (obs.) | $-$Log $f$ (calcd.) | $\Delta$ log $f$ |
|---|---|---|---|---|---|---|
| 0.004856 | 0.04457 | 0.21112 | 0.11890 | 0.2252 | 0.2131 | 0.0121 |
| .006840 | .17052 | .41389 | .26468 | .3710 | .4180 | − .0470 |
| .008279 | .30248 | .55000 | .35060 | .4069 | .5555 | − .1486 |
| .015010 | 1.54503 | 1.24301 | .60900 | .7153 | 1.2524 | − .5371 |
| | | | Solvent Salt, $MgCl_2$ | | | |
| 0.003693 | 0.01108 | 0.10526 | ..... | 0.1063 | 0.1063 | 0.0000 |
| .003775 | .01283 | .11328 | 0.00954 | .1158 | .1144 | .0014 |
| .003821 | .01446 | .12025 | .01480 | .1211 | .1214 | − .0003 |
| .004151 | .02775 | .16659 | .05077 | .1570 | .1683 | − .0113 |
| .004415 | .04355 | .20868 | .07755 | .1838 | .2088 | − .0250 |
| .005742 | .16933 | .41150 | .19168 | .2980 | .4191 | − .1211 |
| .006446 | .32354 | .56880 | .24191 | .3482 | .5745 | − .2263 |
| .009892 | 1.46577 | 1.21070 | .42790 | .5342 | 1.2222 | − .6880 |
| .011658 | 3.11027 | 1.84660 | .49927 | .6056 | 1.8645 | −1.2589 |
| .013946 | 4.38494 | 2.09401 | .57709 | .6834 | 2.1149 | −1.4315 |
| | | | Solvent Salt, $MgSO_4$ | | | |
| 0.003693 | 0.01108 | 0.10526 | ..... | 0.1063 | 0.1063 | 0.0000 |
| .003794 | .01338 | .11568 | 0.01172 | .1180 | .1168 | .0012 |
| .003845 | .01554 | .12463 | .01752 | .1238 | .1258 | − .0020 |
| .004194 | .03288 | .18133 | .05525 | .1616 | .1831 | − .0215 |
| .004526 | .05358 | .23147 | .08833 | .1946 | .2338 | − .0492 |
| .005921 | .21776 | .46665 | .20502 | .3113 | .4713 | − .1600 |
| .006225 | .41867 | .64705 | .22676 | .3331 | .6535 | − .3204 |
| .011294 | 2.03388 | 1.42600 | .48547 | .5918 | 1.4403 | − .8485 |

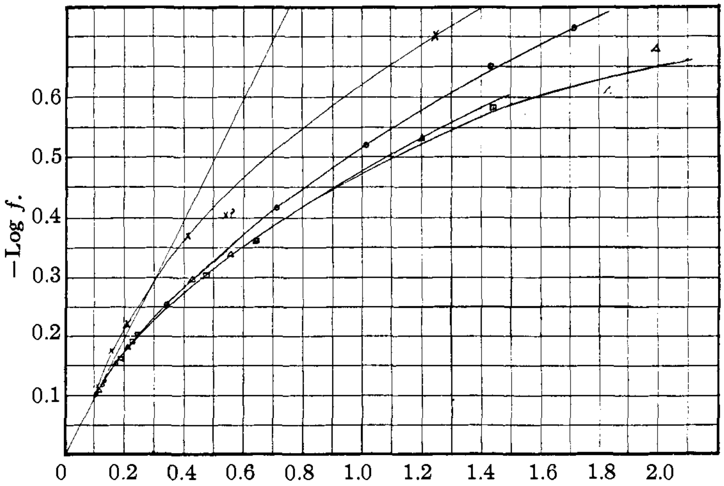

Fig. 1.—The relation of the activity coefficient, $f$, and the ionic strength, $M$, for copper iodate. The straight line is the theoretical equation, $-\log f = 1.01\sqrt{\mu}$; ×, $K_2SO_4$; O, KCl; Δ, $MgCl_2$; □, $MgSO_4$.

A plot of the data is shown in Fig. 1. The line marked "limiting tangent" is the Debye and Hückel limiting law. The potassium chloride, magnesium chloride and magnesium sulfate curves fuse fairly well into the limiting tangent but the potassium sulfate curve shows the characteristic "hump" obtained by La Mer and Goldman for lanthanum and thallous iodates. This salt also increases the solubility of the iodate more than the others. The general deviation from the theoretical lies somewhere between the deviations of the uni- and trivalent iodates mentioned.

## Summary

The activity coefficients of copper iodate have been measured by the solubility method in aqueous solutions of the chlorides and sulfates of potassium and magnesium. The solubility of copper iodate is 0.003693 mole per liter at 25°.

CEDAR RAPIDS, IOWA

# NOTES

**The Detection of Cobalt as Cesium Cobaltinitrites.**—The oxidation of cobaltous ion in acid solution by a concentrated solution of potassium nitrite and its precipitation as the yellow cobaltinitrite are well known in the conventional scheme of analysis. The potassium salt, however, has an appreciable solubility and for low concentrations of cobaltous ion has the undesirable property of precipitating slowly. The corresponding cesium salt, on the other hand, is more insoluble and precipitates and settles much more rapidly. At 17° one cubic centimeter of saturated solution contains approximately 0.05 mg. of the cesium salt.[1] In terms of cobaltous ion the concentration is considerably less and hence serves as a very delicate test for this ion.

**Procedure.**—The mixture of cobalt and nickel sulfides, from the usual procedure, is dissolved in aqua regia and evaporated just to dryness. The residue is dissolved in one or two cc. of 6 *M* acetic acid. To this solution 2 cc. of 6 *M* sodium nitrite and 0.5 cc. of 0.5 *M* cesium nitrate (or 0.25 *M* cesium sulfate suggested as a reagent for aluminum)[2] are added and the yellow $Cs_2NaCo(NO_2)_6$ precipitates.

The following table illustrates the delicacy and rapidity of the test

| | | | |
|---|---|---|---|
| Concn. of cobaltous ion, mg. per cc. | 0.5 and greater | 0.2–0.5 | 0.05 |
| Time for precipitation, min. | Instantaneous | 0.5 | 2 |

The sensitivity of the test may be increased by substituting potassium nitrite for the corresponding sodium salt in the previously described pro-

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[1] Rosenbladt, *Ber.*, **19**, 2531 (1886).

[2] Yagoda and Partridge, THIS JOURNAL, **52**, 3579 (1930).