case that the increased solubility of zinc acetate is not due to the general salt effect alone, but that specific chemical effects, as suggested above, must be an important factor. Hence the application of the term "amphoteric" to this acetate, and to others which exhibit similar properties, appears to be justified.

Summary

1. The solubilities of cupric acetate in potassium acetate solutions in acetic acid, and of zinc acetate in ammonium acetate solutions, have been determined over a wide range of temperatures and concentrations.

2. In each instance the solubility of heavy metal acetate, at a fixed temperature, has been found to vary with the concentration of alkali acetate in the same general manner as in the cases previously reported.

3. Two new ternary addition compounds, $KC_2H_3O_2 \cdot 2Cu(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ and $Zn(C_2H_3O_2)_2 \cdot 2NH_4C_2H_3O_2 \cdot 6HC_2H_3O_2$, have been isolated and analyzed.

4. Resemblances between the ternary compounds obtained in these studies and analogous compounds of the water system have been pointed out, and their significance, from the point of view of theories of amphoteric behavior, has been discussed.

5. It has been shown that the effects of sodium and ammonium acetates upon the solubility product of zinc acetate are approximately the same, and that the activity coefficient of zinc acetate in the presence of alkali acetates falls off much more rapidly with increasing ionic strength than does that of barium acetate in binary solution.

6. The large increases in solubility observed in these studies have been attributed mainly to specific chemical effects, analogous to those which occur in solutions of amphoteric hydroxides in aqueous alkalies.

LAWRENCE, KANSAS RECEIVED NOVEMBER 1, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Potassium Lead Sulfate, Lead Sulfate, Lead Iodide, Potassium, Sulfate and Iodide Ions at 25°

BY MERLE RANDALL AND DONALD L. SHAW

In this paper we shall give measurements of the equilibrium at 25° of the reaction

$$PbSO_4 \cdot K_2SO_4(s) = PbSO_4(s) + 2K^+ + SO_4^= \qquad (1)$$

in which the double potassium lead sulfate is decomposed into lead sulfate and aqueous potassium sulfate. This equilibrium combined with our measurements of the reaction

$$PbI_2(s) + 2SO_4^= + 2K^+ = PbSO_4 \cdot K_2SO_4(s) + 2I^- \qquad (2)$$

gives a new determination of the reaction

$$PbI_2(s) + SO_4^= = PbSO_4(s) + 2I^- \qquad (3)$$

which was studied by Findlay[1] in the presence of sodium ion.

Equilibrium was obtained by rotating in sealed flasks about 20 g. of each of the pure solid phases with about 250 ml. of solution at 25°, after the procedure of Randall and Vietti.[2] A dilute solution of pure lead nitrate was added slowly with mechanical stirring to a solution of sodium sulfate, all in conductivity water. Lead iodide was similarly prepared.

Potassium lead sulfate was prepared by allowing solutions containing known weights of lead acetate to react with solutions containing the quantities of saturated potassium sulfate solution calculated to form $PbSO_4 \cdot K_2SO_4$. The compound formed was dried by suction and all possible moisture removed by pressure between absorbent papers. It was then dried and weighed. The filtrate always contained only a slight excess of either lead or sulfate ions and the composition of the double salt thus formed corresponded to the formula, $PbSO_4 \cdot K_2SO_4$.

Samples of the filtered equilibrium solutions were weighed for analysis from a weight buret. Iodide ion was determined by slowly adding a standardized solution of silver nitrate from a weight buret while the flask was shaken vigorously. When the precipitation was complete a small excess of silver nitrate was added and the

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(1) (a) Findlay, *Z. physik. Chem.*, **34**, 409 (1900); (b) Stoffella [*Boll. chim. farm.*, **64**, 481 (1925), through *C. A.*, **20**, 346 (1926)] studied this reaction in the presence of zinc ion. The latter measurements are qualitative; (c) see Brönsted, *Z. physik. Chem.*, **77**, 315 (1911).

(2) Randall and Vietti, THIS JOURNAL, **50**, 1528 (1928).

excess back titrated (weight buret, ferric ammonium alum as indicator) with a standardized solution of potassium thiocyanate. Sulfate ion was determined as barium sulfate in the usual manner.

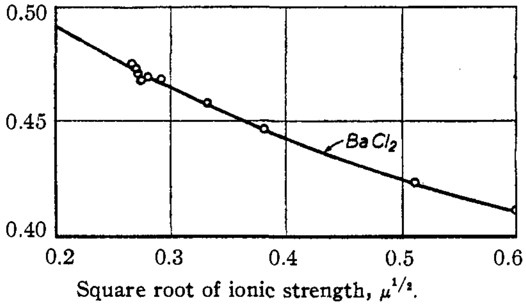

Fig. 1.—$PbI_2(s) + 2SO_4^{--} + 2K^+ = PbSO_4 \cdot K_2SO_4(s) + 2I^-$.

$PbSO_4 \cdot K_2SO_4(s) = PbSO_4(s) + 2K^+ + SO_4^=$.—Samples of the double salt were rotated with conductivity water at 25°. The average of 12 analyses after the composition of the solution became constant showed 0.02245 ± 0.00001 *M* potassium sulfate. Pure lead sulfate was rotated with solutions of potassium sulfate at different molalities. When the concentration of the potassium sulfate was above 0.023 *M* its concentration gradually decreased and analyses of the mixture gave 0.02245 *M* for the equilibrium molality of the aqueous potassium sulfate. Taking log γ equal to -0.200 for this solution,[2] $\mu^{1/2} = 0.06735$, we have

$$PbSO_4 \cdot K_2SO_4(s) = PbSO_4(s) + 2K^+ + SO_4^=;$$
$$\log K = -4.9437; \quad \Delta F^\circ_{298.2} = 6742 \text{ cal.} \qquad (4)$$

TABLE I

$PbI_2(s) + 2SO_4^= + 2K^+ = PbSO_4 \cdot K_2SO_4(s) + 2I^-$

		Ion molalities				
		From analysis				
Init. K molality	Rotation days	Sulfate	Iodide	Potassium	Ionic strength	1/8 log K_m
0.004	6	0.00881	0.04395	0.06157	0.07038	0.4751
.005	6	.00910	.04515	.06235	.07245	.4735
.01	6	.00931	.04594	.06454	.07387	.4709
.015	6	.00953	.04636	.06542	.07495	.4680
.02	6	.00961	.04955	.06660	.07838	.4688
.04	8	.00985	.05516	.07366–	.08476	.4685
.10	8	.011299	.07514	.09774	.10904	.4583
.20	8	.013182	.10635	.13271	.14590	.4470
.40	8	.017325	.21032	.24497	.26179	.4242
.60	8	.019568	.29995	.33909	.35865	.4124

$PbI_2(s) + 2K^+ + SO_4^= = PbSO_4 \cdot K_2SO_4(s) + 2I^-$.—Flasks containing a mixture of the double salt and lead iodide as the solid phases in contact with potassium sulfate of the different molalities, given in Column 1, Table I, were rotated for the number of days given in Column 2. Columns 3, 4 and 5 indicate the molalities of the respective ions in the equilibrium solution, Column 6 the ionic strength, and Column 7 gives one-eighth of the equilibrium molality quotient. The quotient of Column 7 is arrived at in the following manner.[3]

The logarithm of an equilibrium constant may be regarded as the sum of the logarithms of the equilibrium molality quotient, log K_m, and a function of the activity coefficients

$$\log K = \log K_m + \log f(\gamma) \qquad (5)$$

The equilibrium molality quotient has the same form as the equilibrium constant except that molalities are substituted for activities and likewise activity coefficients are substituted for the activities to form the function of the activity coefficients. In very dilute solutions the activity of an individual ion is given by the expression

$$\log \gamma = -0.5\, z^2 \mu^{1/2} \qquad (6)$$

Substituting, then, the value of log γ from Equation 6 in the equilibrium expression corresponding to the reaction of Equation 2, we have

$$\log K = \log K_m + 4\,\mu^{1/2} \qquad (7)$$

and by transposition of terms and division we have

$$-\frac{1}{8}\log f(\gamma) + \frac{1}{8}\log K = \frac{1}{8}\log K_m \qquad (8)$$

because $-{}^1/_8 \log f(\gamma)$ in the limit is $-0.5\mu^{1/2}$, which is just the expression for log γ of a uni-univalent salt.

If the values of $^1/_8$ log K_m are plotted against the square root of the ionic strength upon the same scale as that used in Fig. 2 of Randall and Vietti,[2] then the expression ($^1/_8$ log $f(\gamma)$ + a constant) in the limit approaches parallelism with the 45° broken line shown in that figure, and by

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[3] (a) Randall, *J. Chem. Ed.*, **8**, 1062 (1931); (b) Randall, *Trans. Faraday Soc.*, **23**, 502 (1927); (c) this method was referred to by Bray and Hershey, THIS JOURNAL, **56**, 1889 (1934).

sliding one plot vertically with respect to the other, the points representing $^1/_8 \log K_m$ will superimpose upon one of the characteristic curves of Fig. 2 of Randall and Vietti. The value read from the superimposed curve at zero ionic strength is the value of the constant, or $^1/_8 \log K$.

The values of $^1/_8 \log K_m$ are plotted in Fig. 1 against the square root of the ionic strength. The solid curve, $^1/_2 \log \gamma$ for barium chloride, is plotted on the same scale.[2] The points superimpose on the curve of barium chloride better than that of any other salt. The value of $^1/_8 \log K$ which is the point of intersection of the superimposed curve of $^1/_2 \log \gamma$ for barium chloride at $\mu^{1/2} = 0$ is 0.566. We thus find

$$PbI_2(s) + 2SO_4^{=} + 2K^+ = PbSO_4{\cdot}K_2SO_4(s) + 2I^-;$$
$$\log K_{298.2} = 4.528;\ \Delta F^\circ_{298.2} = -6266 \text{ cal.} \quad (9)$$

Combining Equations 4 and 9 we have

$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-;\ \log K = -0.416;$$
$$\Delta F^\circ_{298.2} = 476 \text{ cal.} \quad (10)$$

The values of $^1/_2 \log K_c$ (Equation 3) as determined by Findlay[1a] are plotted against the square root of the ionic strength in Fig. 2. The solid curve is $^1/_2 \log \gamma$ for sodium sulfate at 25°. The superposition is satisfactory, giving $^1/_2 \log K = -0.163$ and $\log K = -0.326$ (*cf.* Equation 10)

$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-;$$
$$\Delta F^\circ_{298.2} = 445 \text{ (Findlay)} \quad (11)$$

Findlay also measured cells from which the free energy of this reaction can be calculated disregarding liquid potentials. Using late unpublished values for the activity coefficients, we find

$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-;$$
$$\Delta F^\circ_{298.2} = 250 \text{ (Findlay)} \quad (12)$$

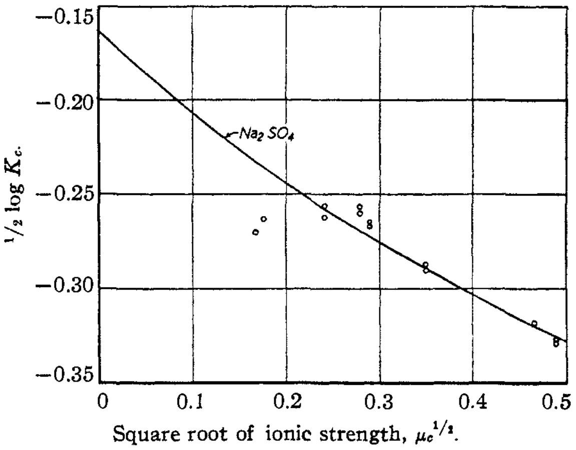

Fig. 2.—$PbI_2(s) + 2SO_4^{--} = PbSO_4(s) + 2I^-$.

Summary

1. From new equilibrium measurements involving solid lead potassium sulfate, lead sulfate and lead iodide and potassium, sulfate and iodide ions, a new determination of the equilibrium between lead iodide, sulfate ion, lead sulfate and iodide ions has been calculated.

2. The mean activity coefficient of the ions in the equilibrium solutions is closely related to that of barium chloride and the equilibrium data as well as analysis of the solid show that one of the solid phases involved in the equilibria was $PbSO_4{\cdot}K_2SO_4$.

BERKELEY, CALIFORNIA
NORTH VANCOUVER HIGH SCHOOL
NORTH VANCOUVER, B. C.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR, AT THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities at Low Temperatures of the Oxides of Strontium and Barium[1]

BY C. TRAVIS ANDERSON[2]

In a previous report from the Pacific Experiment Station of the United States Bureau of Mines, low-temperature thermal data were presented for the carbonates of calcium, strontium and barium.[3] The present paper presents data on the oxides of strontium and barium. Low-temperature specific heat measurements on calcium oxide have been published previously.[4]

The method, apparatus, and accuracy have also been described previously.[5]

Materials

The samples of strontium and barium oxides were Kahlbaum best grade. An analysis of the

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant physical chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, California.

[3] Anderson, THIS JOURNAL, **56**, 340 (1934).

[4] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[5] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).