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Studies on Aging of Precipitates. XXV. The Speed of Solution of Lead Sulfate as an Indication of the Progress of Aging

BY I. M. KOLTHOFF AND WILLIAM VON FISCHER¹

In previous papers it has been shown that lead sulfate, freshly precipitated from not too dilute solutions, perfects itself readily as a result of recrystallization when left in contact with the mother liquor. The perfection process occurs most rapidly during the early stages of aging. Hence, it was to be expected that the speed of solution of fresh imperfect precipitates of lead sulfate would be relatively great, and that the rate of solution would decrease rapidly with increasing perfection of the solid. This is shown to be true in the present study.

Experimental

Lead Sulfate Samples. A.—Precipitates were prepared by the addition of 20 ml. of 0.0665 *M* potassium sulfate solution to 20 ml. of 0.0665 *M* lead nitrate solution. The suspensions were shaken for various periods of time (designated as "age") and filtered through sintered glass crucibles. They were washed quickly with five 10-ml. portions of conductivity water (about three minutes) and five times with 10-ml. portions of ethanol, and were made air-dry by drawing pure air through the crucibles for twenty minutes.

B.—A fresh, air-dried product obtained by precipitation from 0.1 *M* solutions.

C.—A well-aged product prepared by the addition of 2 *N* sulfuric acid moderately slowly to a solution of 200 g. of pure lead nitrate in 8 liters of water. The precipitate was filtered, washed, and digested in 1 *N* nitric acid for one week at 94°.

D.—A well-aged product obtained by addition of an ice-cold 2 *N* sulfuric acid solution in 50% ethanol to a cold 2 *N* lead nitrate solution in the same solvent. The precipitate was filtered, washed, kept in distilled water for four months and made air-dry.

Speed of Solution. 1. Chemical Method.—To 240 ml. of conductivity water in a paraffined bottle was added 0.1 g. of the lead sulfate, and the mixture was shaken on a mechanical shaker at 25° ($\pm 1^\circ$). After a given period of time, the suspension was centrifuged quickly and 200 ml. of the supernatant liquid removed immediately by a siphon arrangement. The lead was determined in this volume by precipitation as lead chromate and titrating the latter iodometrically. In these experiments the lead sulfate was aging during the centrifuging, and the real "age" of the precipitate is therefore greater than given in Table I. The uncertainty in the exact age is eliminated in the

determination of the speed of solution by the conductivity method.

2. Conductivity Method.—A 300-ml. cylindrical Pyrex cell was used. Two large circular platinum disks were sealed in a vertical position near the bottom of the cell. A glass rod, flattened vertically at the end, was used as a stirrer. It was rotated by a stirring motor; the speed of stirring was the same in all the experiments. The stirring was efficient enough to keep all of the lead sulfate in suspension. The cell constant was determined at 25° with 0.001 *M* potassium chloride and found to be 0.01912. In making a run 240 ml. of conductivity water was placed in the cell in a thermostat at 25.00 \pm 0.01°. The stirrer was put in operation and carbon dioxide-free air was bubbled through the liquid until the conductivity became constant. Then 0.1 g. of lead sulfate was added and the resistance of the suspension measured after various time intervals. The specific conductance of the water was smaller than 10^{-6} cm.⁻¹ ohm⁻¹. The conductivity of the water was determined in each experiment, and its specific conductance was subtracted from the measured conductivity of the suspension. The data on the speed of solution by this method are not identical with those obtained by the chemical method, because the age of the precipitate and its time of contact with water were not well defined in the latter case. Moreover, the stirring conditions in both methods were different.

Experimental Results

1. Chemical Method.—The results obtained by the chemical method with the fresh, air-dried product B and the well-aged product C are given in Table I.

TABLE I
SPEED OF SOLUTION OF PRODUCTS B AND C (CHEMICAL METHOD)

Time of shaking, min.	Lead in solution, equiv. $\times 10^4$ p. l. 0.1 g. each of B and C		
	Product B	Product C	
0.5	3.00	0.81	2.76
1	3.16	1.02	3.16
2	3.41	..	3.40
3	3.28
5	3.21	..	3.12
10	3.18	1.48	3.10
30	3.14	2.00	3.09
120	3.10	2.42	..
1 day	3.09	2.70	3.09
3 days	3.09	3.04	..

The difference between the speeds of solution of the two products is quite striking. With the fresh product a supersaturated solution of lead sulfate was obtained after two minutes of shaking,

(1) From a thesis submitted by William von Fischer to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1937.

whereas with the old product the solution was not saturated even after shaking for a whole day. The maximum found with the fresh product after two minutes of shaking cannot be conclusively attributed to the fact that imperfect lead sulfate has a greater solubility than more nearly perfect products. The fresh products A and B contain coprecipitated lead nitrate (1 to 1.5%); on aging, part of this coprecipitated lead nitrate is fairly rapidly eliminated from the crystals. Thus the solutions (product B, Table I) will contain more lead than sulfate. From a few determinations of sulfate in the supernatant liquids, this was shown to be the case. The amount of coprecipitated nitrate in the precipitate, however, is too small to account for the high lead concentration after two minutes of shaking (product B). The results would indicate, at least, that the solubility of highly imperfect lead sulfate is greater than that of more nearly perfect products.

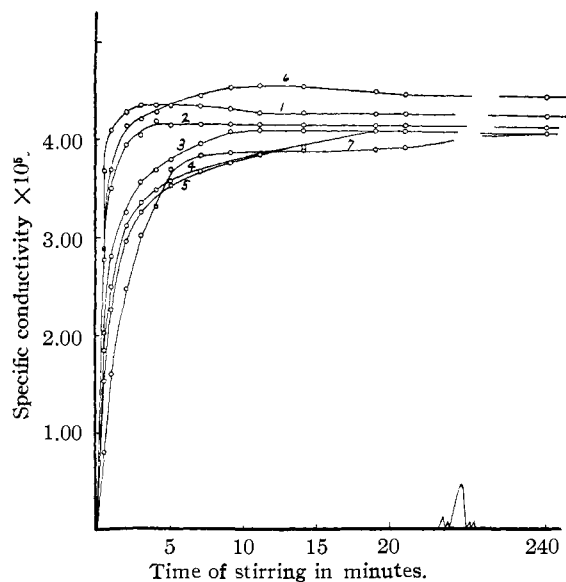


Fig. 1.—Speed of solution of lead sulfate at 25°; 1, age 50 sec.; 2, 20 min.; 3, 1 hour; 4, 3 hours; 5, 24 hours; 6, Product "B;" 7, Product "C."

2. Conductivity Method.—Products A of varying age were used; in addition, experiments by this method were made (1) with fresh product B, and (2) with the well-aged product C. The conductivities (corrected for the conductivity of the water) are recorded in Table II and are shown graphically in Fig. 1.

Discussion

1.—With the fresh products (A, 50 sec.; A, 20 min.) a maximum in the conductivity is found

TABLE II
SPEED OF SOLUTION OF 0.1-G. SAMPLES OF LEAD SULFATE OF VARIOUS AGE (CONDUCTIVITY METHOD)

Time of stirring, min.	Specific conductance of suspensions $\times 10^5$						
	A, 50 sec.	A, 20 min.	A, 1 hr.	A, 3 hrs.	A, 24 hrs.	B (fresh)	C (aged)
0.5	3.68	2.77	2.03	1.84	1.53	2.89	0.80
1	4.09	3.50	2.81	2.57	2.26	3.63	1.68
2	4.28	3.94	3.36	3.13	2.97	4.14	2.47
3	4.35	4.04	3.57	3.36	3.26	4.21	3.02
4	4.35	4.19	3.69	3.49	3.46	4.28	3.32
5	4.35	4.14	3.80	3.58	3.54	4.35	3.70
7	4.34	4.15	3.97	3.68	3.66	4.45	3.85
9	4.32	4.15	4.08	3.77	3.74	4.53	3.87
11	4.28	4.15	4.10	3.86	3.86	4.56	3.88
14	4.28	4.15	4.10	3.94	3.96	4.55	3.90
19	4.28	4.15	4.10	4.11	4.10	4.50	3.92
21	4.28	4.15	4.10	4.11	4.10	4.48	3.93
120	4.28	4.15	4.10	4.11	4.10	4.48	4.02
140	4.03
240	4.28	4.15	4.10	4.11	4.10	4.48	4.09
420	4.11	4.10	4.48	4.09

after about four minutes of stirring. This is attributed to coprecipitated lead nitrate, part of which is eliminated from the crystals during the early stages of recrystallization. The final values of the conductivity with products A (50 sec.), A (20 min.), and B, are greater than with the other samples. This is also due to coprecipitated material. When after attainment of equilibrium another 0.100-g. sample of the same product was added to the suspension, the final value increased from 4.28 to 4.79×10^{-5} (A, 50 sec.); and from 4.15 to 4.20×10^{-5} (A, 20 min.); and from 4.48 to 4.87×10^{-5} (B); whereas in all of the other cases the conductivity remained unchanged.

2.—From the results in Table II it is seen that the speed of solution of products A decreases rapidly with increasing perfection (age) of the crystals. The differences are particularly striking after relatively short periods of stirring. No correlation was found between the specific surface of the products and the speeds of solution. The specific surfaces of the products were found by measuring the amounts of wool violet adsorbed on the saturated surface and by determining the thorium B exchange after covering the surfaces first with wool violet. The values obtained (mg. of lead per gram of lead sulfate) given in the order as the products are listed in Table II, were as follows: 1.5, 0.85, 0.80, 0.70, 0.65, 0.75, 0.70. The well-aged product C had a specific surface slightly greater than product A which had been aged for twenty-four hours, but the speed of solution of the former was markedly less than that of

the latter. The difference in the rate of solution, then, has to be attributed to the difference in the magnitude of active surface of the various products. With the same specific surface the active surface is greater the less perfect the particles are. This conclusion is in agreement with results of Roller,² who found the dissolution factor of anhydrite proportional to the surface exposed with particles of a size greater than 8 microns, but for smaller particles the dissolution factor became greater and was determined mainly by active centers.

3.—From the results in Table II it follows that the specific conductance of a solution saturated with lead sulfate at 25° is equal to 4.10×10^{-5} ohm⁻¹ cm.⁻¹. If the equivalent conductance of lead sulfate at various concentrations were known at 25° the solubility could be calculated from the specific conductivity. Such data, however, are not reported in the literature, but figures are given at 18°. Kohlrausch³ at this temperature found the equivalent conductance of a 1.5×10^{-4} molar lead sulfate solution (approximately corresponding to the concentration of the saturated solution at 25°) equal to 120.2. From this value and the relation⁴

$$\Lambda_t = \Lambda_{18}[1 + A(t - 18) + B(t - 18)^2]$$

in which $A = 0.0235$ and $B = 0.00015$ a value of 140.6 was calculated for the equivalent conductance of the 1.50×10^{-4} molar lead sulfate solution at 25°. Using the relation

$$\Lambda_{\text{PbSO}_4} = \Lambda_{\text{Pb(NO}_3)_2} + \Lambda_{\text{Na}_2\text{SO}_4} - \Lambda_{\text{NaNO}_3}$$

in which Λ is the equivalent conductance at an ionic strength of 0.0006, and interpolating conductance data given in the "International Critical

Tables," an equivalent conductance of 141.9 was calculated. Taking 141 as the average value of the equivalent conductance of saturated lead sulfate solution at 25°, a solubility of 1.46×10^{-4} molar is calculated. This value is considerably greater than the figure 1.34×10^{-4} molar in the "International Critical Tables,"⁶ which is based on Böttger's⁷ work. The latter found a specific conductance of the saturated lead sulfate solution at 25° of $4.04 (\pm 0.02) \times 10^{-5}$ ohm⁻¹ cm.⁻¹, but used an equivalent conductance of 151.2 in the calculation of the solubility. Taking the equivalent conductance equal to 141, a solubility of 1.44×10^{-4} molar is calculated from his results. Our calculated value of 1.46×10^{-4} molar is in good agreement with the value of 1.463×10^{-4} M reported by Crockford and Brawley,⁸ who determined the solubility at 25° by chemical analysis and the average value of 1.48×10^{-4} M found in this Laboratory⁹ by a similar method.

Summary

1. The speed of solution of lead sulfate was found to decrease rapidly with increasing perfection of the crystals, it being mainly determined by the magnitude of the active surface.

2. Highly imperfect lead sulfate crystals show a maximum in the solubility-time curve which may be due to coprecipitated impurities. No conclusive evidence has been found that the imperfect crystals have a greater solubility than the more nearly perfect ones.

3. The solubility of lead sulfate at 25° is equal to 1.48×10^{-4} molar $\pm 2\%$.

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(3) F. Kohlrausch, *Z. physik. Chem.*, **64**, 156 (1908).

(4) F. Kohlrausch and F. Rose, *ibid.*, **12**, 241 (1893).

(5) F. Kohlrausch, *ibid.*, **44**, 231 (1903); **64**, 129 (1908).

(6) "International Critical Tables," Vol. VI, p. 257.

(7) W. Böttger, *Z. physik. Chem.*, **46**, 604 (1903).

(8) H. D. Crockford and D. J. Brawley, *THIS JOURNAL*, **56**, 2600 (1934).

(9) Cf. I. M. Kolthoff and C. Rosenblum, *ibid.*, **55**, 2656 (1933).