[CONTRIBUTED FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C., AND THE DIVISION OF CHEMISTRY OF THE U. S. NAVAL RESEARCH LABORATORY, WASHINGTON, D. C.]

The Solubility of Lead Sulfate in Water and Aqueous Solutions of Sulfuric Acid[1]

BY H. D. CROCKFORD AND D. J. BRAWLEY

A number of investigators[2] have determined the solubility of lead sulfate over the range 0 to 9.2% sulfuric acid and at acid concentrations above 70% at various temperatures. In this paper are given the data for the solubility of lead sulfate in acid concentrations from 0 to 80% acid at 0, 25, 35 and 50°. The purpose of this work was to furnish the solubility data necessary for the proper development of the theory of the lead–sulfuric acid storage cell. It should be noted that the solubility of lead dioxide is so small that it does not become a component in the storage cell electrolyte.

Experimental Procedure

The usual procedure employed for solubility studies was followed in this work. Solutions were prepared from lead sulfate either by adding an excess of the salt or by adding acid to a saturated solution. The equilibrium conditions are established fairly rapidly, being reached in the acid solutions in about four days with proper stirring. In pure water a somewhat longer time is necessary. Best results were obtained with pure water when the equilibrium was approached from above, that is, when a solution saturated at a higher temperature was allowed to cool to a lower temperature. The maximum temperature variation for the 50° isotherm was ±0.03°. For the 0° isotherm the temperature was never over 0.1°. For the other isotherms the maximum variation was ±0.01°.

The composition of the solid phases was established by analyzing the wet residues and determining the point of intersection of the tie lines.

The water employed was carefully purified by distillation. The sulfuric acid used was the regular reagent grade. The lead sulfate employed was prepared as follows. The reagent grade of lead sulfate was dissolved in concentrated ammonium acetate solution. This solution was made slightly acid with nitric acid and the lead sulfate precipitated with dilute sulfuric acid. After washing the precipitate was allowed to stand overnight in a sulfuric acid solution to ensure complete conversion to the sulfate. It was then washed thoroughly by decantation on a Buchner funnel. After being dried at 150° it was ignited for a few minutes at low red heat. The product was very white and showed the theoretical analysis. All analytical reagents, where necessary, were properly purified and tested.

For the determination of lead sulfate in pure water the lead was precipitated as the chromate and then titrated with standard iodine solution according to the method of Kolthoff and Rosenblum.[2] They claim an accuracy of 2%, which we confirm.

The analysis of the wet residues was effected by first removing the excess solution by suction on a sintered glass filter. The residue was then thoroughly washed and the acid concentration determined by titration of the washings. The remaining solid was found to be always lead sulfate. Its weight was determined after drying at 150°.

For the determination of lead sulfate in the more highly acid solutions in which the concentration is very small a colorimetric method was employed. The lead was precipitated as the chromate in Nessler tubes of 100-ml. capacity the quantity of the sample being so regulated that the tubes would contain between 0.01 and 0.15 mg. of the sulfate. These were compared with a set of standard tubes prepared as nearly like the unknown samples as possible. The method is quite accurate for small quantities of lead when the turbidity produced is not too great. A difference of 0.02 mg. of lead between samples can be detected easily.

The sulfuric acid content of all solutions was determined by titration.

Data and Conclusions

The data as determined were plotted on large coördinate paper and the best curve drawn through the points. Concentrations were then determined from the curve for certain acid concentrations as shown in Table I. In pure water solutions, the most dilute acid concentrations,

TABLE I

Acid concn. wt., %	Lead sulfate, p. p. m. 0°	25°	35°	50°
0.00	33.0	44.5	49.7	57.7
.005	8.0	10.0	11.0	24.0
.01	7.0	8.0	10.0	21.0
.02	6.4	7.0	8.0	18.0
.05	5.2	6.0	6.6	15.0
.10	4.6	5.2	5.6	13.0
.20	3.4	3.8	4.5	12.0
.50	2.0	2.5	4.3	11.5
1.00	1.8	2.2	4.2	11.3
5.00	1.6	2.0	4.0	10.3
10.00	1.2	1.6	3.8	9.6
20.00	0.5	1.2	2.8	8.0
30.00	.4	1.2	2.0	4.6
40.00	.4	1.2	1.8	2.8
50.00	.4	1.2	1.8	2.8
60.00	.4	1.2	2.0	2.8
70.00	1.2	1.8	2.4	3.0
75.00	2.8	3.0	3.8	6.6
80.00	6.5	11.5	24.0	42.0

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[2] Purdum and Rutherford, THIS JOURNAL, **55**, 3221 (1933); Pleissner, "Arbeiten aus dem Reichsgesundheitsamte," **26**, 384 (1907); Sehnal, *Compt. rend.*, **148**, 1394 (1909); Huybrechts and Ramelot, *Bull. soc. chim. Belg.*, **36**, 239 (1927); Donk, *Chemische Weekblad*, **13**, 92 (1916); Ditz and Kanhauser, *Z. anorg. Chem.*, **198**, 128 (1916); Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1927, Vol. VII, pp. 803–828; Kolthoff and Rosenblum, THIS JOURNAL, **55**, 2656 (1933).

and certain of the larger values in the more highly acid solutions the lead sulfate value is considered accurate to at least 2%. For intermediate acid values the accuracy is 0.2 part per million.

It is not thought worth while to give the data on the solid phases. These data, when plotted on large triangular coördinate paper, show beyond doubt that in the solutions studied the solid phase is always the normal lead sulfate.

Our values for the solubility in pure water fall on the accepted straight line as far as the three lower concentrations are concerned. However, our value at 50° is less than that given by Mellor.[2] It is to be noted that Mellor secured this value by extrapolation. It is quite probable that hydrolysis affects the solubility at the higher temperatures. In general our data appear to fit in well with those of other investigators.

Summary

1. The solubility of lead sulfate has been determined in pure water and in sulfuric acid solutions up to 80% acid at 0, 25, 35 and 50°.

2. The solubility falls off rapidly with the addition of minute amounts of sulfuric acid. It increases again when the acid reaches a value around 70%.

3. The solid phase in equilibrium with all solutions studied was the normal lead sulfate

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, NEW YORK CITY, AND THE PALMER PHYSICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

An Investigation of the Relative Abundance of the Oxygen Isotopes O^{16}:O^{18} in Stone Meteorites

BY SAMUEL H. MANIAN, HAROLD C. UREY AND WALKER BLEAKNEY

Introduction

Although terrestrial and meteoric matter have been examined quite extensively for any variations in the abundance of isotopic elements, no work on the oxygen isotopes from meteoric sources has been published. Bradley and Urey[1] give a comprehensive list of references to the literature on this general problem to the end of 1931, while Briscoe and co-workers[2] give a critical survey of the field to 1925. Of the researches published since 1930, the following on terrestrial oxygen are of immediate interest in this investigation: Naudé,[3] Babcock and Birge,[4] Mecke and Childs,[5] Smythe and Mattausch,[6] Aston,[7] Kallmann and Lasareff,[8] and Smythe,[9] also the papers on carbon isotopes by Tate, Smith and Vaughan[10] and Jenkins and Ornstein.[11] The general conclusion from the literature to date is that there is no variation in the relative abundance of the isotopes of an element in terrestrial or meteoric matter.

It is the purpose of this investigation to examine the abundance of oxygen isotopes in those stony meteorites which are said to arise in interstellar space, as deduced from their high heliocentric velocity. The source of information about the origin of meteorites at present is catalog 611, "Orbits of Great Meteors," by G. von Niessl and C. Hoffmeister.[12] Among these great meteors are the following meteorite fireballs, with the date of fall and their heliocentric velocities in km./sec.: 41, Pultusk, 1868, 56; 45, Mocs, 1882, ?; 55, Homestead, 1875, 40; 93, Burbely, 1899, ?; 147, Forest City, 1890, ?; 148, Krähenburg, 1869, 57; 155, Orgueil, 1864, 52; 166, Heschina, 1751, ?; 189, Knyahinya, 1866, ?; 506, Rochester, 1876, 44; 531, Treysa, 1916, 38; 554, Hunsrück, 1920, ?; 556, St. Michel, 1910, 60. The question marks refer to uncertain velocities which, however, are probably high.

The limiting circumsolar velocity, or parabolic velocity, is 42 km./sec. Numbers 41, 148, 155, 506 and 556 are credited with velocities greater

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(3) S. Meiring Naudé, *Phys. Rev.*, **36**, 333 (1930).

(4) H. D. Babcock and R. T. Birge, *ibid.*, **36**, 233 (1930).

(5) R. Mecke and W. H. J. Childs, *Z. Physik*, **68**, 362 (1931).

(6) W. R. Smythe and J. Mattausch, *Phys. Rev.*, **40**, 429 (1932).

(7) F. W. Aston, *Nature*, **130**, 21 (1932).

(8) H. Kallmann and W. Lasareff, *Z. Physik*, **80**, 237 (1933).

(9) W. R. Smythe, *Phys. Rev.*, **45**, 299 (1934).

(10) Tate, Smith and Vaughan, *ibid.*, **43**, 1054 (1933).

(11) F. A. Jenkins and L. S. Ornstein, *Kon. Acad. Wetensch. Pro.*, **35**, 1212 (1933).

(12) G. von Niessl and C. Hoffmeister, *Wiener Denkschriften*, Vol. 100 (1925).