concentrations considerably over 0.0002 *M*. The catalyzed photolysis of Eder's reaction is not affected by the simultaneous presence of cobaltous salts at low concentrations.

4. The inhibiting effect of oxygen is greatest with the catalyzed photolysis of Eder's reaction, less with the uncatalyzed photolysis of Eder's reaction, and least with the photolysis of the cobaltioxalate alone.

5. At 100° in oxalic acid solution the induction factors decrease in the order: cobaltioxalate ion, potassium permanganate, and manganioxalate ion. The longer lived complex gives the largest yield of calomel. The induction factor is decreased by rise of temperature and by increase in acidity, both of which changes shorten the life of the inductor. The presence of the ferric and cobaltic oxalate complexes also accelerates the oxidation of oxalic acid by very dilute potassium permanganate.

These facts indicate that the presence of the cobaltioxalate or manganioxalate ion is significant for the enhanced oxidizing activity of the mercuric chloride. The discussion of the details of the mechanism of the reaction will be postponed until the experiments have been carried somewhat further.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DAVIS AND ELKINS COLLEGE]

The Solubilities of Sparingly Soluble Salts Using Large Volumes of Solvents. I. The Solubility of Lead Sulfate[1]

BY R. B. PURDUM AND H. A. RUTHERFORD, JR.

A series of investigations has been begun in this Laboratory in an effort to obtain accurate data for the solubilities of sparingly soluble salts by the direct measurement of solution equilibrium using large volumes of solvents and samples prepared by different methods. This paper presents data on the solubility of lead sulfate in water and dilute sulfuric acid solutions at 20°. A number of recent investigations of the solubility of this salt have been reported.[2] These will be considered in connection with our own data.

Materials.—Four samples of lead sulfate were used. These were prepared as follows.

1. A slight excess of 5% sodium sulfate in 0.1 *N* sulfuric acid was slowly added with rapid stirring over a period of three hours to a 5% solution of lead nitrate. The precipitated lead sulfate was then washed repeatedly in two-week periods with 5-gallon portions of water for one year.

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(1) Presented before the division of Physical and Inorganic Chemistry at the Washington meeting of the American Chemical Society, March, 1933.

(2) (a) Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 1919, pp. 363–365, and Supplement to same, 1928, pp. 1266–1267; (b) Huybrechts and Ramelot, *Bull. soc. chim. Belg.*, **36**, 239 (1927); (c) Huybrechts and de Langeron, *ibid.*, **39**, 43 (1930).

2. This sample was prepared in a manner similar to 1 except that the initial precipitation was effected by adding a slight excess of 5% sulfuric acid to 5% lead acetate.

3. For this sample an excess of 1% sodium sulfate was added over a period of seventy-two hours to a 0.7% solution of lead nitrate in 0.1 *N* nitric acid. It was subsequently treated the same as 1.

4. This sample is identical with 3.

All precision ware used had been certified by the Bureau of Standards. All weighings were made at 20° and at approximately the same humidities.

Apparatus and Method.—Saturation was effected in a large thermostat maintained at constant temperature within ±0.1°. In this bath there were suspended four 5-gallon Pyrex bottles fitted with special gas-tight internal stirrers. The bottles were kept at atmospheric pressure under protection of a soda lime tower.

Approximately 50-g. samples of the salts were placed in the bottles and the latter filled with freshly distilled water which had been boiled and cooled under protection of soda lime. On the basis of preliminary experiments the solutions were stirred for two days at about 21°, the temperature then slowly lowered to 20° and stirring continued for an additional three days. The suspended solid was then allowed to settle for from three to nine days. All data have been obtained with a single set of samples.

Two 6000-ml. samples were removed from each bottle by slowly siphoning out the saturated solution. Each sample was evaporated, in the presence of ammonium acetate, to a volume of 400 ml., the solution made slightly acid with acetic acid and the lead precipitated as lead chromate by slow addition of potassium dichromate. The mixture was digested for twelve hours, filtered through an R. B. porcelain crucible and the lead chromate dried in an oven at 115°. Blank determinations were run with samples of pure lead sulfate, the results of these tests indicating an accuracy within 0.1%.

Experimental Results

Our data for the solubilities of the several samples of lead sulfate in water are presented in Table I. Six to eight determinations were made on each of the four samples. The maximum deviation from the mean for any one sample was 0.2 mg. and the mean deviation for any one sample ±0.1 mg.

TABLE I

SOLUBILITY OF LEAD SULFATE IN WATER AT 20°

Milligrams of Lead Sulfate per 1000 ml. of Water

Sample number	1	2	3	4
Solubility	43.3	43.3	43.7	43.7

The average value from previously reported data is about 41 mg. per liter at 20°.

In Table II results are given for the solubility of lead sulfate in dilute sulfuric acid solutions. Each value is the mean of at least two determinations on each of the four samples, no measurable differences between the individuals being observed. The values have been read from a large-scale plot.

TABLE II

SOLUBILITY OF LEAD SULFATE IN SULFURIC ACID AT 20°

Sulfuric acid, eq. per liter	0.0	0.001	0.002	0.005	0.01	0.02	0.05
Lead sulfate, mg. per liter	43.5	15.5	10.4	6.6	5.3	4.6	4.3

Discussion

The values in Table I are slightly higher than the average of previously reported data. Our data also show a small, but persistent, difference in the solubilities of the samples. The larger solubility of samples 3 and 4 is most likely due to the more perfect development of these crystals resulting from the slower rate of precipitation used in their preparation.

Considering the temperature difference the data of Table II are in good agreement with those of Huybrechts and Ramelot[2b] and Pleissner.[3]

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Summary

1. Using large volumes of solvent and four different samples the solubility of lead sulfate in water at 20° has been found to be 43.5 ± 0.1 mg. per liter.

2. Data have been obtained for the solubility of lead sulfate in dilute sulfuric acid solutions at 20°.

[3] Pleissner, *Arb. Kais. Gesundheitsamt*, **26**, 384 (1907).

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Thermal Data on Organic Compounds. XII. The Heats of Combustion of Nine Hydrocarbons

BY HILDEGARD BANSE AND GEORGE S. PARKS[1]

In the calculation of the free energy of formation of an organic compound by means of the third law of thermodynamics and the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$, the heat of combustion of the compound in question enters as a very important quantity. In fact, at the present time it is frequently the most serious source of error in the resulting free energy value, as most of the available combustion data for organic compounds were determined prior to 1900 at a time when calorimetric methods and the purification of such substances had not reached so high a standard as at present. For this reason there is now a very urgent need for new combustion determinations on organic compounds.

In this paper we shall present combustion values which we have recently obtained for the following nine hydrocarbons: diisobutylene, *n*-octane, *n*-dodecane, durene, isodurene, prehnitene, pentamethylbenzene, hexamethylbenzene and dibenzyl.

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[1] Fellow on the John Simon Guggenheim Memorial Foundation during 1931–1932.