

2. This compound has been shown to be a polysulfide of bivalent lead since it gives hydrogen disulfide when decomposed with hydrochloric acid.

3. It has been shown that in the reaction between lead mercaptides and sulfur, the sulfur is added at first to form a polysulfide type of compounds. These decompose rapidly into lead sulfide, lead disulfide, alkyl disulfide and alkyl polysulfides.

4. It has been impossible to repeat the reported preparation of lead pentasulfide by the action of calcium polysulfide upon lead nitrate in aqueous solution since a product was obtained in each case which had a composition approaching that of the disulfide and which contained only small amounts of higher polysulfides.

5. When a definite pentasulfide in anhydrous or aqueous solution was used, the composition of the resulting product also approached that of the disulfide, showing that lead pentasulfide, if formed, is very unstable, decomposing rapidly even at 0°.

6. It was also impossible to obtain a pure lead disulfide by the interaction of pure sodium disulfide with lead salts, leaving the procedure given under (1) as the only means available at present for the preparation of this interesting compound.

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THE SYSTEMS, STRONTIUM OXIDE-ARSENIC PENTOXIDE-WATER AND LEAD OXIDE-ARSENIC PENTOXIDE-WATER AT 25° (ACID REGION) AND A BASIC STRONTIUM ARSENATE

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No investigation of the systems $\text{SrO-As}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{PbO-As}_2\text{O}_5\text{-H}_2\text{O}$ has been reported in the literature. Fairhall¹ has studied the closely related system $\text{PbO-P}_2\text{O}_5\text{-H}_2\text{O}$. The systems $\text{SrO-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{BaO-P}_2\text{O}_5\text{-H}_2\text{O}$ have been investigated in this Laboratory by Tartar and Lorah,² Cameron and his co-workers³ and Bassett⁴ have reported very thorough studies of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$.

The system $\text{PbO-As}_2\text{O}_5\text{-H}_2\text{O}$ is of considerable significance because of the wide use of the commercial lead arsenate as an insecticide.

These are three component systems. At constant temperature such a system is univariant when the existence of a single solid phase is indicated

¹ Fairhall, *THIS JOURNAL*, **46**, 1593 (1924).

² Tartar and Lorah, *ibid.*, **51**, 1091 (1929).

³ (a) Cameron and Seidell, *ibid.*, **27**, 1503 (1905); (b) Cameron and Bell, *ibid.*, **27**, 1512 (1905).

⁴ (a) Bassett, *Z. anorg. Chem.*, **59**, 1 (1908); (b) *J. Chem. Soc.*, **111**, 620 (1917).

by a variation in the composition of the solution. The formation of a second solid phase produces an invariant system, the composition of the solution being constant. Analyses of the solid and liquid phases of a series of empirical mixtures at equilibrium afford the data necessary for defining the conditions under which the different compounds exist in solid form.

Isotherms at 25° were determined in this investigation for the conditions under which at least three phases—gas, solid and solution—exist at equilibrium. The composition of the solid phases was found by extrapolation, using Schreinemakers'⁵ residue method. Analyses were made of the saturated solution and of the solid residue together with the adhering mother liquor. The values from the two analyses when plotted on a coordinate system lie on a straight line, which when projected passes through a point representing the composition of the solid phase. Similar lines located by the analyses of different mixtures at equilibrium pass through a common point which represents the composition of the solid phase.

The phase rule study reported herein was confined to the acid region. On the alkaline side there are factors which render the work extremely difficult if not impossible. One of the compounds in the basic region was isolated, a basic strontium arsenate.

1. **Preparation of Materials.**—All the materials used in the preparation and analysis of the various salts were high-grade "C. P. Analyzed" chemicals. The distilled water was "conductivity water" except for the presence of carbon dioxide from air.

The arsenic acid used gave negative tests for nitrate, sulfate and chloride ions. A solution of the acid made by dissolving 75 g. of dry arsenic oxide in 400 cc. of water showed less than 0.1% of reducing substance calculated as arsenious oxide (As_2O_3).

The carbonate-free strontium hydroxide was prepared in the following manner. Solid strontium hydroxide, $Sr(OH)_2 \cdot 8H_2O$, was dissolved in boiling water, filtered hot and allowed to cool and crystallize under carbon dioxide-free conditions. The supernatant liquid was removed by suction and the crystals were washed with carbon dioxide-free water. During this procedure the crystals were kept in a flask and protected by soda-lime tubes through which the air was drawn. Finally the wet crystals were dried on a hot-plate, evaporation taking place through soda-lime tubes.

Monostrontium arsenate, $Sr(H_2AsO_4)_2$, was prepared by adding 24 g. of strontium hydroxide to 90 cc. of a solution containing 60 g. of dissolved arsenic pentoxide. The hydroxide was dissolved by heating and the solution was boiled until considerable monostrontium arsenate crystallized out. The mixture was then cooled and filtered using a Büchner funnel and a hardened filter. More crystals were obtained by a further evaporation of the filtrate. The total precipitate was washed with 95% alcohol and dried. Analysis gave a ratio, As_2O_5/SrO , of 2.233 to 2.301. This result showed a small amount of arsenic acid over the theoretical ratio 2.219; this excess was not objectionable for our purpose.

Distrontium arsenate, $SrHAsO_4$, was prepared by starting with a solution containing approximately 75 g. of arsenic pentoxide dissolved in one and one-half liters of water.

⁵ Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

Solid strontium hydroxide was added slowly with constant stirring until there was a slight permanent turbidity due to undissolved solid. A nearly carbonate-free sodium hydroxide solution, prepared by diluting a saturated solution which had stood for several months to allow precipitation of carbonate, was used to bring the arsenate solution to a P_H of about 5.4. The sodium hydroxide was added a few cc. at a time, the arsenate solution being well stirred so that the precipitate formed when the two solutions came in contact, was rapidly dissolved. After the proper P_H had been reached, the faintly milky solution was heated in small quantities of about 100 to 200 cc. and stirred until the distrontium arsenate precipitated in the form of fine crystals. The supernatant liquid was poured off and again treated with sodium hydroxide and heated, giving a further yield. The entire precipitate was then filtered, washed several times with 95% alcohol and dried in the air. The ratio, As_2O_5/SrO , obtained by analysis was 1.152; theoretical, 1.109.

Monolead arsenate, $Pb(H_2AsO_4)_2$, was prepared in the following manner. To a hot, concentrated solution of arsenic acid, boiling point 129° and arsenic pentoxide concentration about 68%, solid dilead arsenate, $PbHAsO_4$, was added in small quantities with constant stirring. As much dilead arsenate was added as would give a clear solution with the arsenic acid as the boiling point rose to 150° . If the solution became turbid at this density more concentrated arsenic acid was added to dissolve the precipitate. Water was then slowly and cautiously added until the boiling point of the arsenic acid fell to 130° . The monolead arsenate began to crystallize out and as the mixture cooled considerable precipitate formed.

The high density of the solution made filtration difficult. Since the salt was to be added later to arsenic acid solutions in setting up the lead arsenate series (see a later portion of this paper), it was freed as far as possible from the mother liquor by centrifuging and the resulting damp solid used. To be sure that the salt was the monolead arsenate, some of the precipitate was filtered on a hardened filter which rested on a layer of asbestos in a Gooch crucible. It was washed several times with alcohol and dried. Analysis gave a ratio, As_2O_5/PbO , of 1.120 which showed that it was the monolead arsenate with a small excess of arsenic acid, theoretical ratio, 1.030.

For preparing dilead arsenate, $PbHAsO_4$, the method of Tartar and Robinson⁶ was used. Analysis gave 64.73% PbO and 33.43% As_2O_5 , giving the ratio, As_2O_5/PbO , 0.516, the theoretical value.

2. Methods of Analysis. Apparatus.—All volumetric flasks and burets had either been recently calibrated by, or checked against apparatus calibrated by, the U. S. Bureau of Standards.

A Sprengel type pycnometer was used in the density determinations.

Arscopic.—The determination of arsenic was made essentially in accordance with the "official" method⁷ for total arsenic in lead arsenate. The arsenate is first reduced and then titrated with a standard iodine solution in the presence of sodium bicarbonate.

In these phase rule studies, the arsenic was determined in the sample used for the determination of the metal. The filtrates from the precipitation of lead and strontium as sulfates were evaporated to approximately the volume of the sulfuric acid used as precipitant, in order to remove alcohol. Those samples which contained nitric acid were heated until dense fumes of sulfur trioxide were produced. Fifty cc. of water was then added and the mixture again evaporated until dense fumes were given off. The residue was then cooled, made up to 250 cc. volume, and an aliquot portion taken for analysis. The arsenic was estimated as As_2O_5 .

⁶ Tartar and Robinson, *THIS JOURNAL*, **36**, 1843 (1914).

⁷ "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," p. 59 (1920).

Strontium.—The size of sample was about 0.5 g. in the case of the moist solid; it varied in the liquid phase from a fraction of a cc. to 50 cc. depending on the concentration. The wet solid was first dissolved in an Erlenmeyer flask in a small amount of nitric acid in 10 cc. of water. Each sample, except the very large liquid samples, was then diluted to approximately 44 cc. volume. One cc. of concentrated sulfuric acid was added; then an equal volume (about 45 cc.) of 95% alcohol was added, drop by drop, with continuous shaking. The material was now kept at 0° for thirty-six to forty-eight hours or until the supernatant liquid was clear. The precipitate was then removed on an ashless filter, washed with 50% alcohol, dried and ignited in an open platinum crucible. Care was taken to avoid any reduction of the salt during the ignition. The sulfate was weighed and the strontium calculated as SrO.

Lead.—The lead determinations were made by the use of a double precipitation method. The sample was dissolved in nitric acid. Five cc. of sulfuric acid was then added and the nitric acid removed by evaporating and heating. The lead was then precipitated as sulfate in the presence of alcohol. The lead sulfate was next dissolved in 10 cc. of a 30% solution of ammonium acetate. This solution was diluted to about 70 to 100 cc. volume. The lead was then precipitated as the chromate in the usual way.⁸ The lead was calculated as PbO.

All the analytical determinations reported in this paper were made in duplicate except in the case of sample No. 31 in the lead arsenate series.

3. The $\text{SrO-As}_2\text{O}_5\text{-H}_2\text{O}$ Series.—Monostrontium arsenate was dissolved in a series of arsenic acid solutions of varying concentration until the solutions were saturated. An excess of the arsenate was added to produce a fine suspension which on standing overnight partly settled, producing a layer of solid at the bottom of the bottle. Each solution was then "seeded" with distrontium arsenate. The bottles were closed by means of ground-glass stoppers which were bound with fine cord and sealed with paraffin. The bottles were then placed in a thermostat held at $25 \pm 0.03^\circ$ and shaken to hasten equilibrium between the solid and liquid phases.

The shaking device was similar to that used by Smith and Ball.⁹ The bottles were laid on the side and fastened with cord to the rocking brass platform. The driving wheel rotated at a rate of 58 r. p. m. With each revolution, the bottles moved twice through an angle of about 45° , thus giving the contents an end to end motion. In some cases the shaking was continued for several weeks.

It was found difficult to reach an equilibrium condition in the low acid range near the invariant point. Equilibrium was reached much more readily by using a limited series of solutions of proper arsenic acid concentration and solid strontium hydroxide. This series was shaken in the same manner and under the same conditions as the other series. Samples 12 and 14 were obtained by this means.

At equilibrium the solid phases were granular or crystalline.

The sampling for analysis was carried out in a manner similar to that employed by Tartar and Lorah.²

The results of the analyses are given in Table I and presented graphically in Fig. 1. The results show the conditions for the existence of the two solid phases, distrontium arsenate, SrHAsO_4 , and monostrontium arsenate, $\text{Sr}(\text{H}_2\text{AsO}_4)_2$. The region in which the former is stable is bounded by ABC and the latter by CDE. The region below the line ACE is one in which the system is not saturated and where no solid phase can exist in equi-

⁸ Ref. 7, p. 58.

⁹ Smith and Ball, *THIS JOURNAL*, 39, 187 (1917).

TABLE I
ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM $\text{SrO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$

Density of liquid phase	Liquid phase		Wet residue	
	As_2O_5 , %	SrO , %	As_2O_5 , %	SrO , %
1.001	0.18	0.14	30.43	27.74
1.010	1.01	.48	40.22	36.06
1.042	3.33	1.56	36.36	32.29
1.080	5.41	2.43	35.55	31.30
1.126	8.33	3.84	34.23	29.37
1.199	12.29	5.72	36.13	30.22
1.273	17.31	7.30	45.16	20.19
1.339	23.38	6.81	41.58	16.49
1.362	26.06	6.24	44.58	17.57
1.489	33.59	5.98	48.43	17.54
1.542	37.59	5.60	54.86	21.69
1.555	39.71	5.01	55.58	21.48
1.605	42.94	4.44	50.25	13.19
1.805	55.20	2.23	60.02	20.20
1.851	57.97	1.32	60.08	13.99
1.999	64.75	0.43	63.24	15.29
2.236	71.71	0.09	68.90	8.27

librium. The region above the line ABCDE represents a state of supersaturation. At the point C the two solid phases are in equilibrium with a

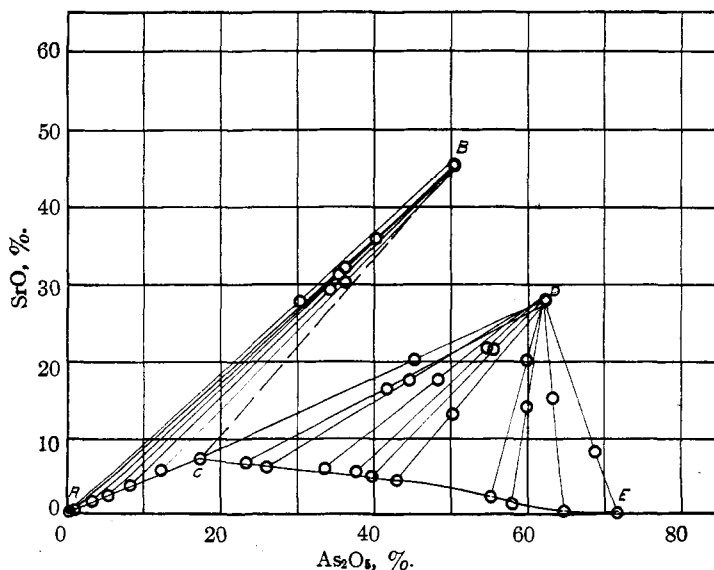


Fig. 1.—The system $\text{SrO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$.

solution which is shown by graphical methods to have a composition 16.9% As_2O_5 and 7.35% SrO . The lines AC and CE are the solubility curves of

di- and monostrontium arsenate, respectively, in solutions of varying concentration of arsenic acid.

4. The PbO-As₂O₅-H₂O Series.—The first series was prepared by adding monolead arsenate to solutions of acid of different concentrations, "seeding" with dilead arsenate and shaking until equilibrium was reached at 25°. This required several weeks in some cases.

The second series comprising samples 27, 24, 31, 33, 32 and 29 was set up by adding lead oxide, PbO, to solutions of arsenic acid of varying concentrations. Equilibrium was obtained in less than two weeks.

The analytical data are reported in Table II and presented graphically in Fig. 2. There are two solid phases, di- and monolead arsenates represented by the points B and I. At the invariant point where the two solid phases are in equilibrium, the liquid has a concentration between 61 and 61.35% of As₂O₅. Point E (71.4% As₂O₅) represents a saturated solution of arsenic acid¹⁰ and is the equilibrium point between monolead arsenate and solid arsenic acid.

TABLE II
ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM PbO-As₂O₅-H₂O

Density of liquid phase	Liquid phase As ₂ O ₅ , %	PbO, %	Wet residue As ₂ O ₅ , %
1.031	2.10	41.1	22.0
1.035	5.08	35.41	20.29
1.113	13.40	26.37	21.23
1.166	18.51	26.12	24.36
1.219	23.50	30.60	28.20
1.311	32.87	17.28	32.92
1.476	42.61	23.03	39.12
1.554	46.36	28.48	40.58
1.732 ^a	54.56	22.84	47.12
1.796	57.14	12.02	52.66
1.812	58.23	19.25	50.66
1.866	60.19	11.94	55.04
1.885	61.05	12.66	55.56
1.894	61.35	26.06	53.02
1.908	61.60	22.90	54.11
2.032	65.90	10.90	61.50
2.098	67.54	17.44	59.98
	68.17	17.33	60.18
2.201	70.70	24.00	58.30

^a Density of liquid phase in Sample 17 was obtained by interpolation.

The graph shows that both the lead arsenates are very insoluble. The liquid phases were submitted to the qualitative tests for the precipitation of lead as sulfate, chromate and sulfide with negative results. In fact, the data indicate that lead can be determined quantitatively by precipitation at a given acidity as dilead arsenate. The data, no doubt, will afford a

¹⁰ Menzies and Potter, THIS JOURNAL, 34, 1452 (1912).

basis for the rapid quantitative determination of lead in commercial lead arsenate.

5. **Preparation of a Basic Strontium Arsenate.**—The phase rule study in the alkaline region was not undertaken. There are complicating factors, such as adsorption or the possible formation of solid solutions, that make the results uncertain. An attempt was made, however, to prepare a basic strontium arsenate, $[\text{Sr}_3(\text{AsO}_4)_2]_3 \cdot \text{Sr}(\text{OH})_2$, analogous in composition to basic calcium arsenate reported by Tartar, Wood and Hiner¹¹ and the basic calcium phosphate also prepared in this Laboratory.¹²

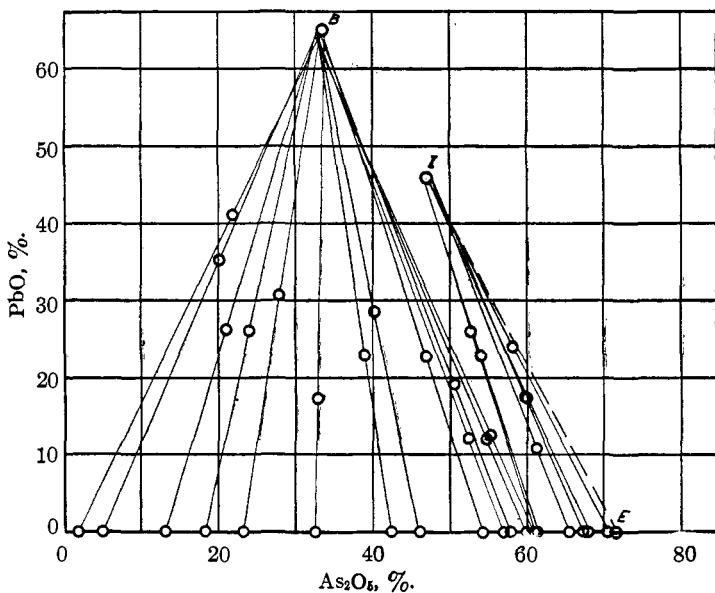


Fig. 2.—The system $\text{PbO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$.

A solution of 24 g. of disodium arsenate in two liters of water was acidified with hydrochloric acid and boiled to expel carbon dioxide. Approximately 100 cc. of a saturated solution of sodium hydroxide was treated with a small quantity of strontium hydroxide solution to precipitate the carbonate ion. After settling, the supernatant sodium hydroxide solution was added to that of the disodium arsenate. To this mixture was slowly added with continuous stirring a solution of 30 g. of strontium hydroxide in a liter of water. Carbon dioxide-free conditions were maintained. A fine, flaky precipitate was produced which was washed nine times with carbon dioxide-free distilled water (2 liters each washing), two days being required for the washings. The precipitate was then refluxed on a water-bath

¹¹ Tartar, Wood and Hiner, *THIS JOURNAL*, **46**, 809 (1924).

¹² Tartar and Lorah, *ibid.*, **51**, 1097 (1929).

about eight hours per day for one week, the water (2 liters) being changed each morning. The purpose of the refluxing was the removal of adsorbed and occluded material. The final insoluble product obtained was dried at 110°. Analysis gave 58.07% SrO and 38.78% As₂O₅, and the ratio SrO/As₂O₅, 1.497. This ratio is within the limits of experimental error of the theoretical ratio, 1.502, for the compound [Sr₃(AsO₄)₂]₃·Sr(OH)₂.

Conclusions

1. A phase rule study of the system SrO-As₂O₅-H₂O in the acid range has been made, defining the limits for the existence at 25° of the two acid strontium arsenates.
2. A similar study of the system PbO-As₂O₅-H₂O has determined the conditions for the two acid lead arsenates.
3. A basic strontium arsenate has been prepared giving the ratio, SrO/As₂O₅, corresponding to the formula [Sr₃(AsO₄)₂]₃·Sr(OH)₂.

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STUDIES ON HYDRAZINE. THE MOBILITY OF THE HYDRAZINIUM ION AT 25°

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Introduction

The conductivity of very few hydrazine salts has been measured, and the mobility of the hydrazinium ion has never been determined accurately. Bredig¹ gives 52 as an approximate value from the conductivity of the chloride. This is shown by the present work to be considerably in error. Two difficulties are met in this problem. In the first place, all hydrazine salts decompose in the presence of platinum black so that polished electrodes must be used. The second and greater difficulty has been the fact that until recently it has been necessary to prepare the salts containing hydrazine and one equivalent of acid by indirect means, generally from those containing two equivalents, and question arises as to the purity of the product. The salts containing two equivalents of acid dissociate almost if not quite completely into the monovalent salt and the free acid, hence are useless from a conductivity standpoint. Perchloric acid and picric acid, however, have been shown to combine directly with hydrazine to form the monovalent salt.² Unpublished work by Mr. Eugene Huffman in this Laboratory shows that with these may be included trinitro-*m*-cresol. This fact and the recent accurate determination of the mobility of the

¹ Bredig, *Z. physik. Chem.*, **13**, 212 (1894).

² Gilbert, *J. Phys. Chem.*, **33**, 1235 (1929).