2.   From these data and those obtained previously the molal heats of formation at 25° have been calculated.

3.   The heats of formation for a portion of the range have been calculated from the data of Smith on the temperature coefficient of electromotive force for cells containing cadmium amalgams.   These do not agree with the calorimetric data.   Possible reasons are given for the disagreement.

4.   The e. m. f. data of Hulett and DeLury, Richards and Forbes, Smith and Bijl have been combined.

5.   From these data, the molal free energies of formation of cadmium amalgams at 25° have been calculated.

6.   It is shown that the molal free energy of formation appears to approach zero instead of becoming infinite at $N_2 = 0$ and probably also at $N_2 = 1$.

7.   The liquidus curve obtained by Bijl has again been confirmed. A revision of his solidus curve is indicated.

8.   Conclusions made by Bijl, Smith, Cohen and Mehl concerning the system cadmium–mercury, are in the main substantiated.

CAMBRIDGE, MASSACHUSETTS
BERKELEY, CALIFORNIA

THE PREPARATION OF LEAD DISULFIDE BY THE REACTION BETWEEN LEAD MERCAPTIDES AND SULFUR[1]

BY WALLACE E. DUNCAN AND EMIL OTT

There is no evidence given in the literature proving the existence of any sulfides of lead other than normal lead sulfide, with the one exception of lead pentasulfide reported by Bodroux.[2]   Berzelius[3] observed that potassium pentasulfide when added to a solution of a lead salt gave a "beautiful blood red" precipitate which decomposed immediately into a mixture of the ordinary sulfide and sulfur.   However, he did not determine the composition of this red precipitate which, judging from the results of the present investigation, was probably essentially the disulfide.   The existence of the sesquisulfide, Pb_2S_3, as the mineral jonstonite, reported by Playfair and Joule[4] has not been confirmed.   Some authorities[5] believe it

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[1] From the thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy by Wallace E. Duncan.

[2] M. F. Bodroux, *Bull. soc. chim.*, [3] **23**, 501 (1900);   *Compt. rend.*, **130**, 1397 (1900).

[3] J. Berzelius, *Ann. chim. phys.*, [2] **20**, 127 (1822).

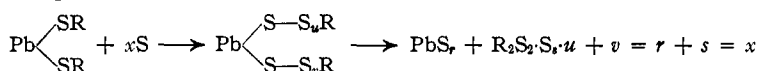[4] L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **3**, 89 (1848).

[5] J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 793 (1927).

to be a mixture of galena and sulfur produced by decomposition of a portion of the mass.
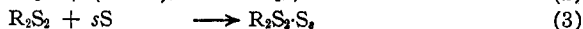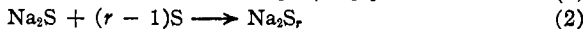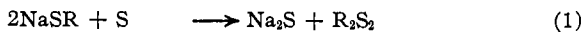
Several unsuccessful attempts have been made to prepare the disulfide, PbS_2, corresponding to the dioxide, PbO_2. Hutchinson and Pollard[6] found no evidence of the formation of the disulfide by the action of hydrogen sulfide on lead tetracetate. Štĕrba-Boehm and Auerspergrová[7] came to the conclusion, after studying the reaction between hydrogen sulfide and lead dioxide, that lead disulfide is either very unstable or else incapable of existing. However, Hofmann and Wölfl[8] consider that the sulfohalides of lead which they have prepared contain the disulfide in combination with the lead halide. Thus the compound $Pb_3S_4I_2$ is written $2PbS_2 \cdot PbI_2$.

Since so little is known about lead polysulfides, it was deemed desirable to undertake an investigation to see if it were possible to prepare other polysulfides of lead in addition to the reported pentasulfide.

Ott and Reid,[9] in their study of the reactions of lead mercaptides and sulfur, had obtained evidence indicating that lead disulfide was a component of the mixture produced in some cases. It was decided to study this reaction further as a possible method for preparing polysulfides of lead. It offered the advantage that it could be carried out entirely in organic solvents, thus precluding the interference of hydrolysis which is usually a disturbing factor in polysulfide formation in aqueous solution. The general reaction postulated by them was

$$Pb{\overset{SR}{\underset{SR}{<}}} + xS \longrightarrow Pb{\overset{S-S_uR}{\underset{S-S_vR}{<}}} \longrightarrow PbS_r + R_2S_2 \cdot S_t \cdot u + v = r + s = x$$

It had previously been shown by Müller,[10] by Böttger[11] and by Holmberg[12] that alkali mercaptides react with sulfur to form alkali and alkyl polysulfides. However, since alkali sulfides add sulfur to form polysulfides it is impossible in this case to determine whether the polysulfides are produced directly by the reaction or in a secondary addition of sulfur. Holmberg[12] implies that the latter is the case. This viewpoint has found quite general acceptance, the underlying equations being

$$2NaSR + S \longrightarrow Na_2S + R_2S_2 \qquad (1)$$
$$Na_2S + (r-1)S \longrightarrow Na_2S_r \qquad (2)$$
$$R_2S_2 + sS \longrightarrow R_2S_2 \cdot S_s \qquad (3)$$

The third equation had to be assumed because small amounts of higher alkyl polysulfides were always accompanying the alkyl disulfide. How-

[6] A. Hutchinson and W. Pollard, *J. Chem. Soc.*, **69**, 220 (1896).

[7] J. Štĕrba-Boehm and M. Auerspergrová, *Rec. trav. chim.*, **44**, 390 (1925).

[8] K. A. Hofmann and V. Wölfl, *Ber.*, **37**, 249 (1904).

[9] Emil Ott and E. E. Reid, *Ind. Eng. Chem.*, **22**, 884 (1930).

[10] M. Müller, *J. prakt. Chem.*, [2] **4**, 40 (1871).

[11] H. Böttger, *Ann.*, **223**, 346 (1884).

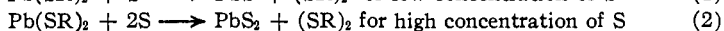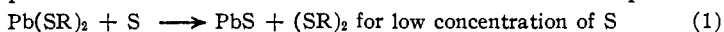[12] Holmberg, *ibid.*, **359**, 82 (1908).

ever, it is well known that alkyl disulfides add sulfur very slowly, if at all, at room temperature,[12] making thus the above mode of reaction very doubtful.

In the case of lead mercaptide the addition of sulfur should give lead sulfide only according to Holmberg's view, since lead sulfide does not add sulfur to form polysulfides; on the other hand, lead polysulfides would be anticipated by our reaction in increasing amount with raising of the S/Pb ratio.

A series of experiments was performed in which benzene solutions of sulfur and *sec.*-butyl lead mercaptide were shaken together with the atomic ratio S/Pb varying from 1 to 50. For a ratio of 8 and higher, lead disulfide was obtained in practically pure form, whereas for the lower ratios lead sulfide was formed also. Thus we have definite proof that the reaction under discussion does not occur in the fashion assumed by Holmberg. The fact that no lead polysulfide higher than the disulfide could be obtained by this reaction indicates the preferential stability of this polysulfide.

The formation of alkyl polysulfides (disulfide and higher sulfides) in the reaction was proved in all cases by their reduction to the mercaptan. The presence of higher alkyl polysulfides was shown in representative cases by their reaction with metallic mercury. It was also shown that these polysulfides could not have been produced by the interaction of sulfur with the disulfide. The amount of the polysulfides increased according to the increased S/Pb ratio used in the reaction.

It is therefore fully established that the interaction between mercaptides and sulfur occurs according to the mode of reaction given by us. However, the higher alkyl polysulfides are formed in relatively small amounts so that we may represent the final reaction in the case of the lead compounds as

$$Pb(SR)_2 + S \longrightarrow PbS + (SR)_2 \text{ for low concentration of S} \quad (1)$$
$$Pb(SR)_2 + 2S \longrightarrow PbS_2 + (SR)_2 \text{ for high concentration of S} \quad (2)$$

It is evident that the procedure given above will be applicable for other heavy metals provided their mercaptides are sufficiently soluble. It is hoped to extend an analogous study of polysulfides to some further metals which otherwise provide difficulties.

The product formed in the cases where the ratio S/Pb was taken at 8 or more in the above series of experiments in benzene solution was found upon analysis to have a composition that agreed well with the formula PbS_2. The fact that the composition of the product was the same even though the ratio S/Pb was varied from 8 to 50 is a positive indication that a true chemical compound is formed and not merely a mixture or solid solution of sulfur in lead sulfide. This is also demonstrated by the fact that a sample dried at $0°$ and then rewashed with a large amount of benzene showed little change in composition while another portion of the same sample dried at $50°$ and rewashed in the same way had a composition indicating that it was now almost entirely lead sulfide. This would seem

to indicate that the lead disulfide is decomposed into lead sulfide and sulfur when heated at 50°, and that this sulfur can then be washed out by benzene. Further evidence against considering this product as a mixture of lead sulfide and sulfur is the fact that a sample which was allowed to remain in the reaction mixture for one day at room temperature before filtering and washing as usual, was mainly lead sulfide in composition although it had been in contact with the excess sulfur in the solution. The conclusive proof that this product is lead disulfide is given by the fact that colorless hydrogen disulfide is formed when the compound is decomposed by a cold, concentrated solution of hydrochloric acid. This also gives definite information as to the structure for if the constitution of hydrogen disulfide is accepted as H—S—S—H then the two sulfur atoms in lead disulfide must also be joined together. The structure is therefore $_S\overline{Pb}_S$ indicating bivalent lead and polysulfide sulfur which would be assumed *a priori* from the method of preparation. Since the polysulfides of the heavy metals are usually considered[13] to differ from the alkali and alkaline earth polysulfides it is interesting to note that in this case a heavy metal polysulfide has a corresponding constitution.

Lead disulfide as obtained from our reaction is of deep reddish-brown color. It is insoluble in water and common organic solvents; it decomposes with mineral acids. It is unstable and decomposes readily into lead sulfide and sulfur. This latter point is also demonstrated by an x-ray study. It was hoped at first to determine the lattice type of the disulfide, which was found impossible under the experimental conditions available.

A freshly prepared sample when photographed immediately after preparation gave a pattern showing only faint lines characteristic for galena. Similar samples showed the same pattern, however, with increasing intensity as the time of standing before exposure was increased. The time of exposure was four hours in all cases. It is therefore obvious that at room temperature appreciable decomposition occurs in the course of a few hours in accordance with our previously mentioned results. The galena resulting from the decomposition is of colloidal particle size as indicated by the broadness of the diffraction lines.

The immediate determination of the density of a freshly prepared sample in alcohol at 25° gave the value of 4.7 g./cc. The value calculated for a corresponding mixture of galena and rhombic sulfur is 6.8.

Due to the decomposition mentioned the density is expected to increase with time. This is actually observed, the density increasing very gradually and reaching an apparent value of 5.5 after nineteen hours.

In the experiments where the ratio S/Pb used was taken at 3.5 and 5 the analyses indicated a mixture of lead sulfide and disulfide, and when the

[13] F. Ephraim, "Anorganische Chemie," 1929, p. 452.

ratio was 2 the product was nearly pure lead sulfide.   In the case where lead and sulfur were present in equivalent amounts a precipitate did not settle out except by allowing the solution to stand for several hours or by flooding with ether.   The product obtained in either case, however, contained considerable organic matter in addition to the lead and sulfur so it is possible that lead mercaptide-sulfur complex, such as the one indicated by Ott and Reid, is included in the precipitate.

Since the reaction between lead mercaptide and sulfur did not give a polysulfide higher than the disulfide it was decided to attempt the preparation of higher lead polysulfides by the action of alkali and alkaline earth polysulfides upon solutions of a lead salt.   In the reported preparation of lead pentasulfide by Bodroux[2] an aqueous calcium polysulfide solution was used.   This work was very carefully repeated using the method of Divers and Shimidzu[14] for the preparation of calcium polysulfide solution.   The various solutions prepared had a S/Ca ratio of 4.74, 4.71, 4.72.   When added to an excess of a 1% lead nitrate solution at 0° a voluminous red precipitate, similar to lead disulfide in appearance, was obtained.   This was further treated according to Bodroux's procedure and analyzed.   The S/Pb ratio of six preparations varied between 2.16 to 2.42 (average 2.28); Pb + S between 98.39 to 99.80 (average 99.25); lead between 72.05 and 74.77 (average 73.38) and sulfur from 25.03 to 27.02 (average 25.87).   When decomposed with concentrated hydrochloric acid, hydrogen sulfide and yellow-orange colored hydrogen polysulfide were formed.   It is thus evident that in this preparation no uniform product is obtained and that lead pentasulfide, if present at all, could only be formed to a minor extent.

If the above reaction is carried out at room temperature, the product obtained has a S/Pb ratio approximating 2.   However, the hydrogen polysulfide obtained from it is of deep color indicating again a mixture.

By using 25% excess of calcium polysulfide solution at 0° the red precipitate obtained at first changes rapidly to black, giving an analyses of Pb 84.36, S 15.14, Pb + S 99.50, S/Pb 1.16, indicating the essential formation of lead sulfide.

The preparation of lead pentasulfide from calcium polysulfide solution appears thus as impossible, the impure disulfide being formed instead.   This is also supported by the fact that Hofmann and Wölfl[8] obtained a derivative of lead disulfide in the interaction of lead iodide and ammonium polysulfide solution (essentially pentasulfide).

In order to have a more reliable pentasulfide, the above experiments were repeated by using pure ammonium pentasulfide prepared according to Mills and Robinson.[15]   The red polysulfide obtained gave the analyses Pb 70.08,

[14] E. Divers and T. Shimidzu, *J. Chem. Soc.*, **45**, 270 (1884).

[15] M. Mills and P. L. Robinson, *ibid.*, 2326 (1928).

S 27.90, Pb + S 97.98, S/Pb 2.57.   Thus it has a somewhat higher S/Pb ratio but is otherwise not essentially different from the previous products.

To eliminate hydrolysis as a possible explanation of the low values obtained experiments were performed with anhydrous methyl alcohol as the solvent.   Pure potassium pentasulfide prepared by the method of Rule and Thomas[16] served as the polysulfide.   By using an otherwise similar procedure as before, the red polysulfide of lead had the composition: Pb 74.05, S 22.30, Pb + S 96.35, S/Pb 1.95.

Thus it appears very unlikely that Bodroux prepared lead pentasulfide.

By using pure sodium disulfide in the interaction with lead nitrate solution, the formation of pure lead disulfide might be expected.   However, we were unable to obtain a pure compound by this procedure.   Sodium disulfide was prepared according to Rule and Thomas.[17]   When the reaction was carried out in absolute methyl alcohol at 0° the red precipitate gave Pb 73.10, S 19.70, Pb + S 92.80, S/Pb 1.76.   When water was used as solvent the analyses gave Pb 75.13, S 20.03, Pb + S 95.16, S/Pb 1.72. It is likely that these products are derivatives of the lead disulfide analogous to those mentioned of Hofmann and Wölfl.

In summarizing it is certain that no pure lead polysulfides are obtained by the usual interaction of polysulfides with lead salts and in all cases the lead disulfide is the main constituent in such reaction products.

Experimental

Materials Used and Methods of Analysis

The sec.-butyl mercaptan was prepared in this Laboratory and was of a high degree of purity.   It was used in c. p. benzene solution approximately 0.184 molar.   This mercaptan was preferred since it may be obtained relatively easily in a pure state, it is not too volatile and its neutral lead salt is readily soluble in benzene.   Qualitative experiments show that results obtained with this mercaptan may be applied to other members of the series.

The sulfur was recrystallized twice from carbon disulfide and dried at 80–90°.   A benzene solution of known concentration was prepared.

The sodium plumbite solution was prepared by saturating a 0.5 N sodium hydroxide solution with lead hydroxide, freshly prepared by precipitation from lead acetate solution with sodium hydroxide and washed free of acetate as shown by the absence of the odor of cacodyl oxide when heated with arsenic trioxide.   Analysis of the solution gave a lead content of 0.0348 mole/liter.

Lead was determined by weighing as the sulfate.   The sample was decomposed with sulfuric acid, heated to expel excess acid and then gently ignited.

Sulfur was determined in most cases by the modified Parr bomb method described by Ott and Reid.[18]   As a check on the accuracy of this method some analyses were made by the sodium peroxide method modification of Fresenius' method for insoluble sulfides given by Treadwell and Hall.[19]

[16] A. Rule and J. S. Thomas, J. Chem. Soc., 105, 2819 (1914).

[17] A. Rule and J. S. Thomas, ibid., 105, 177 (1914).

[18] E. Ott and E. E. Reid, Ind. Eng. Chem., 22, 878 (1930).

[19] Treadwell and Hall, "Analytical Chemistry," 1928, Vol. II, p. 316.

The percentages of sulfur of two samples analyzed by the two methods are given.

Determined by modified Fresenius method, A, 18.86; B, 49.14.
Determined by modified Parr bomb method, A, 18.93; B, 49.09.

The two methods are therefore equally accurate.

The Addition of Sulfur to Lead Mercaptide Solutions at Various Ratios of Sulfur to Lead.—A measured volume of the *sec.*-butyl mercaptan solution was shaken with sodium plumbite solution in such a proportion that there was a slight excess of mercaptan over the two moles required for one of lead, according to the reaction, $Pb(OH)_2 + 2BuSH \longrightarrow Pb(SBu)_2 + 2H_2O$. This ensured the formation of the neutral lead mercaptide essentially as has been shown by Ott and Reid.[19] The benzene layer, containing the lead mercaptide, was carefully separated from the aqueous layer. A volume of the benzene solution of sulfur containing the amount of sulfur desired was diluted with benzene to a volume sufficient to prevent the precipitation of any sulfur when the solution was subsequently cooled down to 5°. The cold sulfur solution was then added to the mercaptide solution, also cooled down to 5° and the mixture shaken vigorously. The clear yellow color of the mercaptide deepened to an orange, then to a red which darkened to a reddish-brown as the solution became opaque due to the formation of a voluminous precipitate. This reddish-brown precipitate was filtered off; washed back into a flask and shaken with a large quantity of benzene, refiltered and washed well with benzene. In some cases it was also washed with carbon disulfide.

The product was then freed of retained solvent by drying in a vacuum desiccator, evacuated by a Cenco Hyvac pump. If it were desired merely to analyze the product it was dried at 50° in a current of carbon dioxide (to avoid oxidation).

The results obtained when the S/Pb ratio was varied from 0.5 to 50 are given in the following tables. Check analyses were run in nearly all cases.

TABLE I

ANALYTICAL RESULTS

Sample	S/Pb added	Pb	S	Pb + S	S/Pb
A	0.5	80.52	10.05	90.57	0.81
B	1.0	82.95	10.85	93.80	0.85
C	1.0	75.83	14.03	89.86	1.20
D	2.0	83.53	14.45	97.98	1.12
E	2.0	83.83	14.15	97.98	1.09
F	2.0	83.33	14.24	97.57	1.10
G	2.0	83.45	13.65	97.10	1.06
H	2.0	82.93	14.27	97.20	1.11
I	2.0	81.02	15.18	96.20	1.21
J	3.5	80.11	19.62	99.73	1.58
K	5.0	76.77	22.63	99.40	1.90

Calculated for PbS: Pb, 86.60; S, 13.40; PbS_2: Pb, 76.37; S, 23.63.

In the first three cases a dark reddish-brown suspension persisted instead of the usual rapidly-forming precipitate as in all other cases.

It is probable that *sec.*-butyl disulfide, one of the products of the reaction, is strongly adsorbed, perhaps chemically combined due to incomplete splitting off from some intermediate compound such as $Pb\!<^{S-SBu}_{S-SBu}$. Samples D to I inclusive have low Pb + S values, indicating the probable presence of such residues. If they are considered to be mixtures of PbS and $(SBu)_2$, their theoretical composition may be calculated from the observed lead content. The calculated sulfur content of such a mixture agrees fairly

well in most cases with the observed value.   The color of the precipitates was black for
A and B, dark brown for C and reddish-brown in all the other cases.

TABLE II
ANALYTICAL DATA

Sample	S/Pb added	Analyses Pb	S	Pb + S	S/Pb	Calcd. composition PbS$_2$	PbS	(SBu)$_2$	Calcd.% S of mixture
A	8	75.62	23.85	99.47	2.04	99.0	0	1.0	23.75
B	10	75.74	23.77	99.51	2.02	99.2	0	0.8	23.73
C	10	75.31	23.89	99.20	2.05	98.6	0	1.4	23.80
D	10	75.75	23.72	99.47	2.02	99.2	0	0.8	23.73
E	10	76.03	23.82	99.85	2.02	99.6	0	0.4	23.68
F	10	75.61	23.73	99.34	2.03	99.0	0	1.0	23.75
G	10	75.37	23.63	99.00	2.03	98.7	0	1.3	23.79
H	10	76.50	23.21	99.71	1.96	94.9	4.6	0.5	...

Calculated for PbS$_2$: Pb, 76.37; S, 23.63.

Samples C, D, G and H were dried in a vacuum desiccator at room temperature.
A and B were dried in an atmosphere of carbon dioxide at 50° while E and F were dried
in the air at 50°.   Since there are no uniform differences in the results when the samples
were dried in the presence or absence of air it is evident that oxidation during the drying
of the sample is negligible.

In preparing sample H the sulfur solution was added at room temperature, while in
all other cases both the mercaptide and sulfur solutions were cooled to 5°.   In this case
the S/Pb ratio is less than two, so evidently some lead sulfide is formed under these con-
ditions.

Sample G was washed with carbon disulfide in addition to benzene and its analysis
is in agreement with the other results, so evidently all free sulfur is washed out by the
benzene used in the other cases.

TABLE III
ANALYTICAL DATA

Sample	S/Pb added	Analyses Pb	S	Pb + S	S/Pb	Calcd. composition PbS$_2$	PbS	(SBu)$_2$
A	30	75.58	23.63	99.20	2.02	99.0	..	1.0
B	30	76.24	23.38	99.62	1.98	96.3	3.1	0.6
C	50	76.88	22.57	99.45	1.90	87.8	12.4	0.8

Samples B and C show some decomposition due to very prolonged washing.

An attempt to introduce a higher concentration of sulfur by using carbon disulfide
as solvent proved unsatisfactory.

The Stability of Lead Disulfide

Effect of Standing in the Reaction Mixture at Room Temperature.—A sample of
lead disulfide[20] was prepared, part of which was washed and analyzed as usual while the
remainder was allowed to stand for a day in the reaction mixture.   It was then washed
and analyzed in exactly the same way as the first portion.   The analyses were

Pb, 75.61   S, 23.73   Pb + S, 99.34   S/Pb, 2.03
Pb, 81.56   S, 17.73   Pb + S, 99.29   S/Pb, 1.40

Thus approximately 60% of the lead disulfide decomposed under these conditions.

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[20] All samples of lead disulfide used in this and the following experiments were pre-
pared using the S/Pb ratio of 10.

Another example was allowed to stand in the reaction mixture for twenty-nine days. This gave an analysis of Pb, 82.03; S, 13.67; Pb + S, 95.70; S/Pb, 1.08. The analysis of the original sample was Pb, 76.28; S, 23.16; Pb + S, 99.44; S/Pb, 1.96. From the S/Pb ratio of the product after standing, it is apparent that the disulfide originally present changed almost entirely to the sulfide. The Pb + S value is considerably less due to some oxidation with prolonged contact of the reaction mixture with air. As would be expected, experiments show that prolonged washing with benzene or carbon disulfide at room temperature will result in decomposition. Lowering of the temperature reduced this decomposition considerably.

Effect of Heating.—A large sample of lead disulfide was prepared and the reaction mixture containing the suspended precipitate was divided into several parts. One portion was treated as usual and analyzed.

Anal. Pb, 76.28; S, 23.16; Pb + S, 99.44; S/Pb, 1.96.

Another portion was heated for one hour at 50° and then washed, dried and analyzed as usual.

Anal. Pb, 82.15; S, 16.41; Pb + S, 98.56; S/Pb, 1.29.

Another portion of the above sample was filtered and washed with benzene, then heated in benzene at 50 and 80°, respectively, for one hour, and gave the analyses

Pb, 82.83 S, 14.71 Pb + S, 97.54 S/Pb, 1.15
Pb, 83.79 S, 14.09 Pb + S, 97.88 S/Pb, 1.09

A dry sample of PbS_2 was heated for four hours at 138°. It was then carefully washed again with benzene to remove sulfur that might have been freed by the heating.

Anal. Pb, 85.13; S, 13.46; Pb + S, 98.59; S/Pb, 1.02.

Preparation of Hydrogen Disulfide from Lead Disulfide.—Lead disulfide was prepared in the usual way but was dried in a vacuum desiccator surrounded by a freezing mixture of ice and salt. A fine brown powder resulted to which some concentrated hydrochloric acid, cooled to −20°, was added. A slight odor of hydrogen sulfide was noticeable and a white suspension of lead chloride was formed. As this settled some clear colorless oily drops appeared on the surface; these were decanted from the main reaction mixture and washed with cold concentrated hydrochloric acid. Upon standing they gradually became yellow in color. It was impossible to collect the drops in sufficient quantity to make a freezing point determination but they remained liquid even though the hydrochloric acid solution on which they were floating was cooled to −50° (melting point of H_2S_2, −88.6 to −89.8°).[21] A method of analyzing hydrogen persulfide given by Walton and Parsons[22] was followed qualitatively. Upon decomposition hydrogen sulfide was given off and sulfur remained after evaporation. Hence the oily liquid obtained when lead disulfide is treated with hydrochloric acid is undoubtedly a hydrogen polysulfide and since it is colorless when formed it must be the disulfide, as all the other hydrogen polysulfides are colored.

Some of the droplets were dissolved in benzene and the resulting solution shaken with solutions of lead acetate and lead nitrate. Red-brown precipitates resulted similar in appearance to the lead disulfide. These rapidly darkened and became brown.

Summary

1. Lead disulfide has been prepared by the action of sulfur on *sec.*-butyl lead mercaptide in benzene solution.

[21] K. H. Butler and O. Maass, THIS JOURNAL, **52**, 2184 (1930).

[22] J. H. Walton and L. B. Parsons, *ibid.*, **43**, 2542 (1921).

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.

BALTIMORE, MARYLAND

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

BY H. V. TARTAR, MAUD R. RICE AND B. J. SWEO

No investigation of the systems $SrO-As_2O_5-H_2O$ and $PbO-As_2O_5-H_2O$ has been reported in the literature.   Fairhall[1] has studied the closely related system $PbO-P_2O_5-H_2O$.   The systems $SrO-P_2O_5-H_2O$ and $BaO-P_2O_5-H_2O$ have been investigated in this Laboratory by Tartar and Lorah.[2] Cameron and his co-workers[3] and Bassett[4] have reported very thorough studies of the system $CaO-P_2O_5-H_2O$.

The system $PbO-As_2O_5-H_2O$ 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).