

THE LEAD-SULFUR SYSTEM

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ABSTRACT. The phase relations in the lead-sulfur system were determined at temperatures ranging from 1200° to 100°C by means of quenching and DTA experiments, using silica tubes as sample containers. Galena (PbS), which is the only compound in the system, melts congruently at 1115°C. It is a true compound, and its composition lies within the limits of the range indicated by the $\text{PbS}_{1.000 \pm 0.003}$ formula.

In the Pb-PbS portion, a field of immiscible liquids exists above 1041°C and between 4.8 and 6.95 wt percent S. In the PbS-S portion, liquid immiscibility occurs above 800°C over a wide composition range, extending from 27.2 to more than 93.2 wt percent S.

Monotectic conditions exist at 1041°C and 6.95 wt percent S and at 800°C and 27.2 wt percent S. Pure Pb melts at $327.2^\circ \pm 0.2^\circ\text{C}$. Eutectic conditions exist on the Pb-PbS join at $326.5^\circ \pm 0.3^\circ\text{C}$ and a composition very near pure Pb. A second eutectic is situated near sulfur composition at a temperature slightly lower than the melting point of pure S (114.0°C).

The occurrence of primary galena in rocks and ore deposits is accounted for by considering the stability curves of this mineral in a P-T diagram. When the sum (P_{total}) of the partial pressures of lead and sulfur is less than about 0.1 atm, small changes in this value greatly affect the stability of galena. At higher P_{total} values the stability of galena is only slightly affected by changes in P_{total} . In ores where galena coexists with minerals such as pyrite, pyrrhotite, and chalcopyrite, $P_{\text{S}_2} \gg P_{\text{Pb}}$, and P_{S_2} can be regarded as essentially equal to P_{total} .

A mechanism for galena transport in the gas or vapor phase exists which may play a very important role in the formation of ores.

INTRODUCTION

Galena (PbS) is the only known compound in the lead-sulfur system. It is the most important source of lead and the fourth most common sulfide mineral. Galena occurs under a very wide range of geological conditions. It is known to form in many sediments and in all grades of metamorphic rocks and occurs as a primary phase in many intrusive and extrusive igneous rocks. It occurs as a major or minor constituent in many different types of ore deposits, ranging from sedimentary through metamorphic, and hydrothermal to magmatic. The lead in the form of galena in many large ore bodies commonly has been regarded as originating from a uniform, deep-seated, possibly upper-mantle source region. However, recent isotope studies indicate a variety of possible sources, and the origin of lead in ores has become a very controversial subject.

Sulfur occurs in the elemental state and is commonly of high purity in a great number of localities. The other end member, lead, occurs in nature as a pure metal but has been reported only from a few localities, such as Långban, Sweden; Ural and Altai districts, U.S.S.R.; Jalapa, Mexico; and Franklin, N. J. Levedev (1967) describes deposition of native lead from a drillhole flow of hot brine at Cheleken in U.S.S.R.

In spite of the common occurrence and importance of galena as a source of lead and of the desirability of developing low-cost commercial processes for metallurgical extraction of the metal from the ores, the lead-sulfur system has not been studied systematically. The purpose of this investigation was to meet this need by determining the phase rela-

tions in the synthetic system Pb-S. This knowledge, in addition to its usefulness in interpreting the geological environments of galena, furnishes fundamental data for investigations of ternary systems such as Fe-Pb-S and quaternary systems such as Cu-Fe-Pb-S.

A preliminary note on the study described in this paper appeared in Carnegie Institution of Washington Year Book 64 (1965, p. 195-197).

NATURAL PbS

Natural material of composition PbS, or close to PbS, is reported to occur in one crystalline modification—galena. Galena was known as a mineral even in the days of Pliny, who mentioned it in his *Historia naturalis* published A.D. 77. It has since been described from thousands of localities.

Galena has a face-centered cubic structure, space group O_h^5 , $Fm\bar{3}m$, with $z = 4$, according to Davey (1921). Lehman (1924), Zeipel (1935), and Wasserstein (1951) determined unit-cell dimensions of natural PbS. Their values when converted to ångström from kX units are 5.966, 5.935, and 5.936 Å, respectively. The a value of Wasserstein (1951) was obtained from a very pure galena sample and agrees closely with the value of $a = 5.9362$ Å (at 26°) determined by Swanson and Fuyat (1953) on pure synthetic PbS. Galena is commonly found as cubes or cube-octahedra, less often as octahedra, and rarely in skeletal, reticulated crystals (Palache, Berman, and Frondel, 1944, p. 201).

A compilation by Seebach (1926) of chemical analyses of galena made in the period 1843 to 1915 indicated that the lead-to-sulfur ratio lies well within the limits of $1:1.0 \pm 0.1$.

Wasserstein (1951) and Fleischer (1955) reviewed the existing data on the contents of trace elements such as As, Sb, Bi, Cd, Cu, Fe, Mn, Ni, Ag, Tl, and Sn in galenas. It appears that these elements often occur in separate minerals intimately admixed with galena (Fleischer, 1955). Galena forms significant solid solutions with Bi_2S_3 (Salanci, 1965) and with PbTe (Darrow, White, and Roy, 1966), complete solid solution with $AgBiS_2$ (matildite) above $215^\circ \pm 15^\circ\text{C}$ (Craig, 1967) and with PbSe above 300°C (Wright, Barnard, and Halbig, 1965).

PREVIOUS EXPERIMENTAL STUDIES ON THE Pb-S SYSTEM

Roessler (1895) heated mixtures of lead and sulfur under borax and showed by chemical analyses that a compound of PbS composition coexists in equilibrium with Pb. Friedrich and Leroux (1905) studied the Pb-PbS portion of the system. They reported that PbS is the only compound and that Pb and PbS are completely miscible in the liquid state. Their liquidus data fell nearly on a horizontal line between about 20 and 40 atomic percent S, and Guertler (1912) therefore suggested that a liquid immiscibility gap might exist in this region. Kohlmeyer (1932) reported a miscibility gap extending from 2.6 to 12.0 wt percent S above 1040°C . However, Guertler (1912), Guertler and Landau (1934), and Leitgeb and Miksch (1934), who also obtained a nearly horizontal

liquidus in differential thermal analysis (DTA) experiments, supported the interpretation of complete miscibility reported by Friedrich and Leroux (1905). Friedrich (1908) reported solidification at 1130°C of a composition containing 51.5 atomic percent S (14.1 wt percent). Data obtained by silica-tube techniques for the melting point of PbS were given by Friedrich and Leroux (1905) as 1103°C, Friedrich (1907a, b) as 1114°C, Biltz (1908) as $1112^{\circ} \pm 2^{\circ}\text{C}$, Truthe (1912) as 1106°C, Heike (1912) as 1106°C, Kohlmeyer (1932) as 1135°C, Bloem and Kröger (1956) as 1127°C, and Van Hook (1960) as $1115^{\circ} \pm 5^{\circ}\text{C}$. Bloem and Kröger (1956) reported that PbS when melting at 1127°C contains 0.03 atomic percent Pb more than stoichiometric PbS and that the maximum homogeneity range of PbS is only 0.08 atomic percent at 900°C.

Pure Pb melts at 327°C, and the temperature of its melting point is not measurably influenced by PbS (Friedrich and Leroux, 1905). The solubility of S in solid Pb was reported as less than 0.0006 atomic percent (0.0001 wt percent) at 300°C by Greenwood and Worner (1939). The solubility of S in liquid Pb was determined at various temperatures by Friedrich and Leroux (1905), who gave the following (atomic percent): about 4 at 800°C, 10 at 925°C, 20 at 1010°C, 30 at 1040°C, and 40 at 1050°C. Blanks and Willis (1961) determined the solubility of S in liquid Pb as follows (atomic percent): 0.03 at 450°C, 0.08 at 500°C, 0.16 at 550°C, 0.33 at 600°C, 0.59 at 650°C, 1.10 at 700°C, 1.85 at 750°C, 2.90 at 800°C, 4.25 at 850°C, 6.25 at 900°C, and 7.6 at 925°C. The data by Blanks and Willis are in agreement with those given by Cheng and Alcock (1961). Blanks and Willis (1961) calculated from their solubility data that the Pb-PbS eutectic at 327°C lies at 0.0017 atomic percent S.

The PbS-S portion of the Pb-S system has not been investigated previously beyond the composition of 51.5 atomic percent S (14.1 wt percent).

METHODS OF INVESTIGATION

Starting materials.—Lead was obtained from the American Smelting and Refining Company and contained 99.999+ wt percent Pb. The producer's analysis of this material (ASARCO-A58) shows Bi = <0.0001, Cu = 0.0001, and Fe = 0.0002 (all in wt percent). No other elements were detected by chemical and spectrographic methods, according to the supplier's certificate of analysis. This material was received in bars, and lead for each experiment was obtained by filing, after the oxide film on the surface of the bar was first removed by filing.

The sulfur was obtained from Dr. W. N. Tuller, Superintendent of Laboratory, Freeport Sulphur Company, Port Sulphur, La., and has only 0.007 percent impurities, all of which is carbonaceous material.

Techniques.—The two methods employed in this study were quenching and differential thermal analysis. Rigid silica-glass tubes with minimum vapor space (Kullerud and Yoder, 1959) were used as sample containers in both methods.

The quenching experiments were prepared by loading weighed amounts of the elements or of previously synthesized PbS into silica-glass

tubes. Loss of material to the vapor phase was effectively reduced by placing closely fitting silica-glass rods over the charge before evacuating and sealing. Tubes thus prepared were heated in horizontal furnaces for various periods of time at fixed temperatures, controlled to within $\pm 1^\circ\text{C}$. The phases formed at elevated temperatures were readily quenched when the tubes were withdrawn from the furnaces with tongs and plunged into water. Cooling to room temperature was effected in 3 to 5 sec by this procedure.

The DTA experiments were prepared by loading weighed amounts of synthetic PbS, synthetic PbS and Pb, or synthetic PbS and S into silica-glass thermocouple-well tubes of the type described by Kullerud and Yund (1962). A few milligrams of finely ground Lake Toxaway quartz were added in these experiments, and the heat effect of the $\alpha\beta$ inversion at 573°C was used as an internal temperature standard. The pressure in the DTA tubes at the temperature of the $\alpha\beta$ inversion varied, depending on bulk composition, from a minimum of about 10^{-4} mm Hg over pure Pb to a maximum of 5 atm over pure S. In this pressure range the influence of pressure on the quartz inversion temperature is negligible.

The DTA tubes have a thermocouple well coaxial with the tube wall and extending about 6 mm into the tube. One of two identical Pt versus Pt90-Rh10 thermocouples was inserted into the well and was thus separated from the charge only by the silica-tube wall (about 1 mm thick). The other thermocouple was placed at a distance of about 1 cm from the sample container. The assemblage of thermocouples and thermocouple-well silica tube was placed in a centered position in an externally heated Stellite bomb equipped with pressure closures and with head arrangements permitting introduction of thermocouple wires and a pressure lead. In some DTA experiments, performed with excess sulfur, the pressure inside the thermocouple-well tubes exceeded 100 bars at elevated temperatures. In such cases a supporting pressure was employed by introduction of helium or argon gas of the desired pressure through the pressure lead. This apparatus is similar to the one described by Kracek (1946); however, a horizontal furnace arrangement, which was found practically to eliminate temperature gradients over the sample, was used rather than the vertical arrangement of Kracek. The best thermal effects were obtained when the heating and cooling rates were 3°C per minute.

Identification of phases.—The products of the experiments were identified at room temperature by their macroscopic physical properties, optical properties in reflected light, and powder X-ray diffraction patterns.

Lead is recognized macroscopically by its dull gray color. In reflected light it appears grayish white on a freshly polished surface, but it tarnishes to gray within an hour. It is isotropic, takes a poor polish, and because of its low hardness, is never free of scratches. The crystal structure of lead (Fm $\bar{3}$ m) was determined by Vegard (1916); the powder

X-ray diffraction pattern and cell edge of $a = 4.9505$ Å at 25°C were given by Swanson and Tatge (1953).

Galena is recognized macroscopically by its metallic luster and well developed crystals. In reflected light it appears bright white. It is isotropic and takes a very good polish. The powder X-ray diffraction data for galena were first given by Lehmann (1924). The unit-cell dimension of galenas produced in quenching experiments was determined by the oscillation technique on a Norelco X-ray diffractometer with Ni-filtered Cu radiation ($\lambda\text{CuK}\alpha = 1.5418$ Å). Each determination was based on eight oscillations run at half a degree per min. The (220) reflection of galena was measured relative to the (220) reflection of CaF_2 ($a = 5.4622$ Å).

Sulfur is readily recognized by its creamy white or yellow color, or pale green color when it contains small amounts of lead. It takes a poor polish but is easily identified in polished sections by its grayish green color, its internal reflections, and its low reflectivity. Powder X-ray diffraction patterns made at room temperatures were always those of orthorhombic sulfur as given by Swanson and others (1960).

EXPERIMENTAL RESULTS

A number of experiments were performed at various temperatures to establish whether compounds in addition to PbS occur. The compositional and thermal stability field of galena was investigated, and the solidus and liquidus relations were determined for the entire system.

The results of experiments designed to establish the phase relations in the system are compiled in tables 1 to 4. Since the interpretation of the results is dependent on the nature of the individual experiments, a few comments on some of the runs are required.

Quenching experiments.—In tables 1 and 3 it is seen that PbS is the only binary solid phase in the Pb-S system, at least in the region between 100° and 830°C. Runs of bulk compositions lying between Pb and PbS, quenched from 100°C through 900°C, produced only mixtures of Pb and PbS (table 1), as demonstrated by powder X-ray diffraction patterns and polished sections. The first experiment listed in table 1 shows that reaction rates are slow at 100°C. Considerable amounts of unreacted sulfur remained, even after 90 days at this temperature. Liquid Pb was observed in polished sections made on material quenched from 400°C and higher temperatures. Exsolution of Pb from PbS was not observed, and the unit-cell dimension of PbS always remained within the limit of error of the value $a = 5.936 \pm 0.001$ Å, which is identical with the value $a = 5.9362$ given for pure PbS by Swanson and Fuyat (1953). This indicates that the solubility of Pb in PbS is very limited, if any exists at all. Textures indicating exsolution of PbS from Pb were not observed in polished sections in spite of the relatively high solubilities reported in the literature. Since Pb liquid remains during the quenching of the tubes to about 327°C, it was at first assumed that the PbS which was in solution in liquid Pb at elevated temperatures crystal-

lized out of the liquid during the cooling period and was separated from it before Pb solidified. However, later experiments, described below, revealed that exsolution does take place, but that the textures are sub-microscopic. Powder X-ray diffraction patterns at room temperature showed a mixture of Pb and PbS.

TABLE 1
Lead and sulfur mixtures in the Pb-PbS (13.40 wt percent S)
composition region (starting material: Pb + S)

Wt % S	Temp, °C	Time, hours	Products at Temp
7.1	100	2160	Pb + PbS + S*
7.1	200	720	Pb + PbS
6.8	300	72	Pb + PbS
6.4	400	24	Pb _l + PbS
6.9	500	10	Pb _l + PbS
7.0	600	10	Pb _l + PbS
7.4	700	8	Pb _l + PbS
7.6	800	8	Pb _l + PbS
6.9	900	4	Pb _l + PbS

*Phase equilibrium not achieved.

TABLE 2
Silica-tube experiments on Pb + PbS mixtures at 1065°C

Composition, wt %		Time of heating, hours	Products at Temp
Pb	S		
96	4	3	Homogeneous liquid
94.5	5.5	4	Two liquids
93	7	9	Homogeneous liquid

Because of the inconsistencies in the literature, discussed above, concerning the high-temperature phase relations in the Pb-PbS portion of the system, additional quenching experiments were performed. In these experiments, listed in table 2, mixtures of Pb and S were first heated together in silica tubes at 500°C for 10 to 12 hours to produce Pb + PbS assemblages, and then the tubes were heated for several hours at 1065°C and quenched.

The textures, as observed in polished sections made on the quenched products, demonstrate that at this temperature liquid Pb dissolves more than 4 wt percent S, whereas a mixture containing 94.5 wt percent Pb and 5.5 wt percent S forms two immiscible liquids. The textures interpreted as due to immiscible liquids are shown in the photomicrograph of plate 1. It is noted in table 2 that a mixture containing 93 wt percent Pb and 7 wt percent S produces homogeneous liquid at 1065°C. On quenching, the homogeneous liquids produced in the first and third experiments listed in table 2 appear completely homogeneous in polished sections, even under the highest magnification. Their reflectivities, which

lie between those of Pb and PbS, are higher than that of Pb and slightly lower than that of PbS. Microprobe analyses performed on a number of grains from the experiment with 7 wt percent S indicate intimate intergrowth of PbS and Pb on the micron scale. Small areas, less than $2\ \mu$ wide, have PbS composition in a matrix that contains essentially Pb. Powder X-ray diffraction patterns made at room temperature on the products of each of the experiments listed in table 2 display the typical peaks of Pb and PbS. These experiments demonstrate that a two-liquid immiscibility region exists at 1065°C in the Pb-PbS portion of the system. This immiscibility field is confined to a narrow composition region situated somewhere between 4 and 7 wt percent S.

TABLE 3
Lead and sulfur mixtures in the PbS-S composition
region (starting materials: PbS + S)

Wt % PbS	Temp, $^{\circ}\text{C}$	Time, hours	Products at Temp
50.0	100	2160	PbS + S
51.2	200	720	PbS + S_L
50.8	300	72	PbS + S_L
55.6	400	24	PbS + S_L
57.2	500	10	PbS + S_L
58.9	600	10	PbS + S_L
53.4	700	8	PbS + S_L
52.7	800	8	PbS + S_L^*
50.0	830	1/2	Two liquids**
85.0	850	1/2	One liquid

*By coincidence this temperature is that of the monotectic at 27.3 wt percent S and $800^{\circ} + 2^{\circ}\text{C}$. The textures produced indicate that either a small temperature gradient existed or the temperature varied slightly during the experiment (see text).

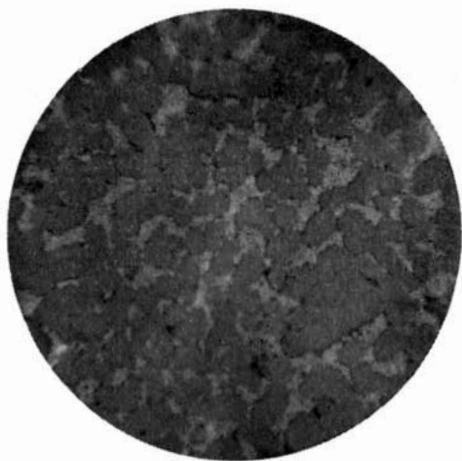
**One liquid is PbS-rich and the other consists essentially of sulfur (S_L).

Runs of bulk compositions lying between PbS and S, quenched from 100° through 830°C , produced only mixtures of PbS and S (table 3). Liquid S occurred in all runs except in the one at 100°C .

Upon quenching, the sulfur that had been heated with PbS at 400°C and higher temperatures appeared pale green in comparison to the yellow color of unreacted sulfur. This greenish tinge was more noticeable in the products of the experiments performed at high temperatures than in those at low temperatures. This discoloration was taken as an indication of solubility of PbS in liquid sulfur.

All PbS synthesized below 800°C appeared homogeneous and dense and frequently occurred as euhedral crystals. In the run at 800°C most PbS grains were homogeneous and dense, but some appeared vesicular and occurred in drop-shaped aggregates. All PbS from the 830°C run had vesicular texture and appeared to have been molten at the temperature of the experiment.

PLATE 1

10 μ

Photomicrograph showing textures of liquid immiscibility. A Pb + PbS mixture, containing 5.5 wt percent S, was heated in a silica tube at 1065°C for 30 min and then quenched. The dark gray material was a Pb-rich liquid, and the light gray material was a PbS-rich liquid at the temperature of the experiment. Upon quenching, both consist of submicroscopic intergrowths of Pb and PbS.

Repetition of the 830°C experiment demonstrated by direct observation that a light, sulfur-rich liquid and a heavy, PbS-rich liquid coexist at this temperature. Apparently, the vesicular texture originates at about 800°C, where through a monotectic reaction, the PbS-rich liquid on cooling reacts to produce PbS and a liquid consisting essentially of sulfur. It was also noted in one additional experiment (table 3) that when a mixture containing 85 wt percent PbS and 15 wt percent S was heated at 850°C, one homogeneous liquid existed. On cooling, liquid sulfur was observed to separate, as if "boiling," from the previously homogeneous liquid. This separation creates the vesicular textures observed in polished sections.

Determinations of the unit-cell dimensions of galenas produced in all experiments listed in table 3 all gave $a = 5.936 \pm 0.001$ Å. Thus, the a value remains unchanged, within the limits of error of the measurements, whether galena coexists with Pb or with S and is identical to the value of $a = 5.9362$ Å (at 26°C) given by Swanson and Fuyat (1953). These results indicate that the solubility of sulfur in PbS is small. To test further this solubility, a tube-in-tube experiment was performed, as described by Kullerud and Yund (1962). In this run 560 mg of previously synthesized stoichiometric PbS was placed in the inner tube and heated at 500°C for 10 days with sufficient sulfur in the outer tube to produce saturated sulfur vapor. Reweighing at the termination of the experiment showed no detectable increase in weight. Even when it is assumed that weighing errors involved in the original PbS synthesis, as well as

those involved in the tube-in-tube experiment, were accumulative (each not exceeding 0.05 mg), the solubility of sulfur in PbS cannot exceed 0.04 wt percent at 500°C. The results of experiments on bulk compositions lying on the Pb side of PbS composition, as well as on the S side, indicate that galena is essentially a stoichiometric compound whose composition lies well within the limits indicated by the $\text{PbS}_{1.000 \pm 0.003}$ formula.

Differential thermal analysis.—The results of all DTA experiments are given in table 4. Interpretation of some of these runs is difficult and requires discussion.

The first experiment listed in table 4a shows that pure Pb melts at 327.0°C. At this temperature a very strong peak begins to develop on the DTA chart. On cooling liquid Pb, beginning of crystallization was recorded at 323°C, again followed by development of a strong peak. In order to determine whether the 4°C discrepancy between the heating and cooling peaks is caused by superheating or supercooling or both, filings of pure Pb were heated in a silica tube adjacent to a standardized thermocouple in a horizontal furnace for 30 min, first at 326.5°C, then at 327.0°C, and finally at 327.4°C. The tube was removed from the furnace, and the filings were observed after each heating period. Melting occurred at 327.4°C but not at 327.0° and 326.5°C. The melting point of pure Pb is taken as $327.2^\circ \pm 0.2^\circ\text{C}$. The difference in temperature between the heating and cooling effect is evidently caused by supercooling of liquid Pb. A series of eight heating and eight cooling curves were made on pure Pb. The heating curves all show very sharply defined melting beginning at 327.0°C; the cooling curves all demonstrate supercooling effects of varying degree when Pb crystallizes.

The second experiment listed in table 4a contained a mixture of Pb and PbS, which had previously been synthesized from Pb and S (2.03 wt percent S) in a silica tube heated at 500°C for 24 hours. Melting of Pb when coexisting with PbS occurs at 326.6°C. Heating to 1150°C produced no additional well-defined heat effects. On cooling, however, a well-defined peak was recorded beginning at 953°C. This effect is interpreted to occur when PbS crystallizes from the cooling liquid through the reaction $\text{L} + \text{V} \rightarrow \text{PbS}^1$. Because of possible supercooling, it can only be concluded from the appearance of this peak on the DTA cooling chart that the solubility of sulfur in liquid Pb is less than 2.03 wt percent at 953°C.

¹ Strong and distinct DTA effects are commonly observed at elevated temperatures when, on heating or cooling of sulfide samples (especially those involving a liquid) in closed tubes, a boundary limiting a divariant field is exceeded, resulting in the development of univariancy through addition of a new phase. An example of this is in the case above, where on cooling $\text{L} + \text{V}$ (divariancy) produces $\text{L} + \text{V} + \text{PbS}$ (univariancy), and numerous additional examples occur in table 4. When crossing the boundary line from divariancy to univariancy, that is on cooling, a well-defined peak appears; but on heating, from univariancy to divariancy, only an ill-defined, dissipated effect is recorded. The appearance of a sharp peak during cooling cannot be explained entirely by crystallization of PbS, because the solubility curve is steep and only very small amounts of PbS are produced. It must be due mainly to condensation from the vapor phase.

TABLE 4
Differential thermal analyses

Composition			Thermal effects on heating		Thermal effects on cooling	
Wt % S	Atomic % S	Phases	Temp, °C	Interpretation	Temp, °C	Interpretation
a. Pure Pb and Pb + PbS mixtures*						
0		Pb	327	Melting	323	Crystallization (supercooled)
2.03	11.81	Pb + PbS	326.6	Eutectic	324	Crystallization (supercooled)
3.50	18.99	Pb + PbS	944		933-4	PbS crystallizes from liquid
			326.6	Eutectic	324	Crystallization (supercooled)
			1020	PbS dissolved in liquid	1015	PbS crystallizes from liquid
4.26	22.34	Pb + PbS	326.2	Eutectic	325	Crystallization (supercooled)
4.30	22.50	Pb + PbS	1035	PbS dissolved in liquid	1021	PbS crystallizes from liquid
			326.6	Eutectic	322	Crystallization (supercooled)
			1040	PbS dissolved in liquid	1024	PbS crystallizes from liquid
4.7	24.17	Pb + PbS	327.4	Eutectic	322	Crystallization (supercooled)
5.65	27.90	Pb + PbS	1041	PbS dissolved in liquid	1031	PbS crystallizes from liquid
			326.6	Eutectic	321	Crystallization (supercooled)
			1041	Monotectic	1041	Monotectic
6.90	32.38	Pb + PbS			1039	See text
			326.2	Eutectic	1025	See text
			1041	Monotectic	321	Crystallization (supercooled)
8.50	37.51	Pb + PbS			1044	Monotectic
			326	Eutectic	1035	See text
			1041	Monotectic	1028	See text
10.05	41.93	Pb + PbS			1042	Monotectic
			1050	Liquidus	1054	Liquidus
			326	Eutectic	322	Crystallization (supercooled)
10.75	43.77	Pb + PbS	1042	Monotectic	1042	Monotectic
			1056	Liquidus	1057	Liquidus
			326	Eutectic	324	Crystallization (supercooled)
			1040.5	Monotectic	1041	Monotectic
			1061	Liquidus	1064	Liquidus

TABLE 4 (continued)

Composition		Thermal effects on heating		Thermal effects on cooling	
Wt % S	Atomic % S	Phases	Temp, °C	Temp, °C	Interpretation
12.06	46.98	Pb + PbS	326.5 1043 1090	322 1042 1085	Crystallization (supercooled) Monotectic Liquidus
13.40	50	PbS	1109 1115 1120	1115	PbS crystallization
17.65	58.07	PbS + S	800	504	Monotectic
22.97	65.84	PbS + S	1000	990	Liquidus
26.48	69.95	PbS + S	800	804	Monotectic
27.50	71.08	PbS + S	883	867	Liquidus
			800	805	Monotectic
			814	813	Liquidus
			800	804	Monotectic
56.95	89.52	Pb + S	799	791	See text
65.30	92.40	PbS + S	799	782	See text
93.12	98.87	PbS + S	799	765	See text
100.00		S	102 114	803	Monotectic; additional peaks at 778 & 771°C (see text)
				802	Monotectic; additional peaks at 767, 756, 762°C, etc. (see text)
				802	Monotectic; peaks at 786, 768, 754, 742°C (see text)
				101	Inversion
				114	Crystallization

*The starting materials for the DTA experiments on Pb + PbS mixtures were synthesized from Pb + S mixtures which were heated for 24 hours at 500°C in silica tubes with minimum vapor space.

**This PbS was presynthesized from Pb + S in the 1:1 atomic ratio by heating for 7 days at 500°C in a silica tube with minimum vapor space.

***PbS + S mixtures were prepared by weighing synthetic PbS (see footnote above) and pure S directly into DTA tubes.

The remaining experiments listed in table 4a all contain mixtures of Pb and PbS synthesized in the manner described above. In all of these experiments, except one containing 4.7 wt percent S, Pb in coexistence with PbS begins to melt between 326.0° and 326.6°C .

Special efforts were made to obtain accurate measurements of the melting points of pure Pb and of Pb + PbS mixtures by frequent calibrations. The temperatures recorded in this way are probably accurate to $\pm 0.3^{\circ}\text{C}$, and accordingly the DTA experiments indicate melting of pure Pb at $327.0^{\circ} \pm 0.3^{\circ}\text{C}$ and of Pb, when coexisting with PbS, at $326.3^{\circ} \pm 0.3^{\circ}\text{C}$. Because of the uncertainty in the DTA temperature determinations, no conclusion can be drawn as to whether these temperatures are identical or whether the presence of PbS actually produces a real decrease in the melting temperature.

In order to determine whether a measureable difference exists, two silica-tube experiments were performed. One tube contained pure Pb filings and the other filings of a finely intergrown Pb + PbS mixture presynthesized from Pb + 1 wt percent S, homogenized at 960°C , and quenched. These tubes were heated adjacent to a standardized thermocouple in a horizontal furnace for 30 min, first at 326°C , then at 326.5°C , next at 327.0°C , and finally at 327.5°C . The tubes were removed from the furnace, and the filings were observed after each heating cycle. Melting was not observed in either tube at 326°C . At 326.5°C the Pb + PbS filings show at least partial melting, whereas pure Pb is unchanged. At 327.0°C the Pb + PbS filings show extensive melting, and Pb remains solid. At 327.5°C melting is very evident in both tubes. Study of a polished section prepared on the Pb + PbS mixture after the final heating reveals that PbS recrystallized during the heating period and that this phase coexisted with the liquid. These experiments show that PbS lowers the melting temperature from $327.2^{\circ} \pm 0.2^{\circ}\text{C}$ (for pure Pb) to $326.3^{\circ} \pm 0.3^{\circ}\text{C}$ for Pb + PbS mixtures. The eutectic in the Pb-PbS portion of the system lies at least 0.4°C below the melting point of pure Pb and maybe as much as 1.0°C . The eutectic liquid contains considerably less than 1 wt percent S, as evidenced by the amount of PbS coexisting with this liquid. In the inset of figure 1, therefore, the melting point of pure Pb is shown as 327°C , and the eutectic temperature as 326°C . The experiment containing 3.5 wt percent S showed a very weak, irregular effect at 1020°C on heating and a well-defined, sharp peak at 1015°C on cooling. Similar irregularities were registered: at 1035°C on heating when 4.26 wt percent S was present, on cooling a sharp peak was recorded at 1021°C ; at 1040°C on heating when 4.30 wt percent S was present, on cooling a defined peak occurred at 1024°C ; and at 1041°C when 4.7 wt percent S was present, on cooling a very sharp peak was recorded also at 1031°C . These experiments indicate that the solubility of sulfur in liquid Pb is as follows (wt percent): <2.03 at 953°C , 3.5 at $1018^{\circ} \pm 3^{\circ}\text{C}$, 4.26 at $1028^{\circ} \pm 7^{\circ}\text{C}$, 4.30 at $1032^{\circ} \pm 8^{\circ}\text{C}$, and 4.7 at 1041°C .

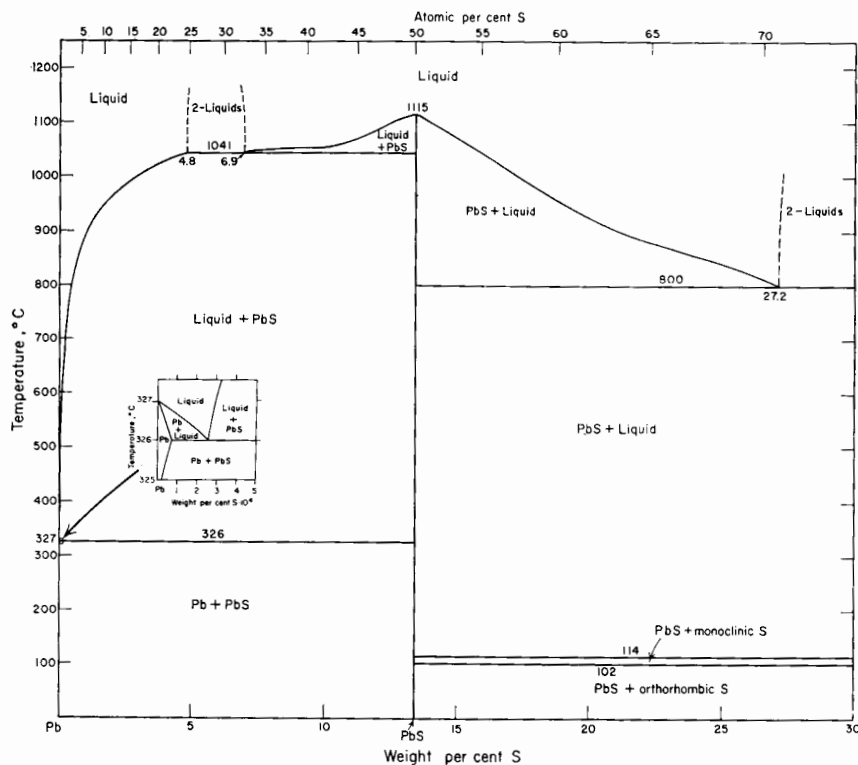


Fig. 1. Phase relations in the portion of the Pb-S system containing 0 to 30 wt percent S. All phases and phase assemblages coexist with vapor.

The experiment containing 5.65 wt percent S (table 4a) produced a well-defined peak at 1041°C on heating as well as on cooling. The cooling chart showed additional sharp peaks at 1039° and 1025°C. These peaks are reminiscent of those produced in many sulfide systems (for instance, in the Ni-S system as discussed by Kullerud and Yund, 1962) when immiscible liquids on cooling participate in a monotectic reaction.

Very similar heating and cooling behaviors were recorded in experiments with 6.90 wt percent S in which effects occurred at 1041°C on heating and at 1044°C on cooling. A number of additional peaks were recorded below 1044°C on cooling, and these are again indicative of liquid immiscibility.

The remaining four experiments listed in table 4a contained 8.5, 10.05, 10.75, and 12.05 wt percent S. Three DTA heating and cooling curves were made on each of these compositions, and in all these experiments well-defined peaks were recorded at 1041°C on heating. On cooling, however, peaks were obtained at 1054°C in the experiment with 8.5 wt percent S, 1057°C with 10.05 wt percent S, 1064°C with 10.74 wt percent S, and 1085°C with 12.05 wt percent S. In addition, small heat effects were recorded at 1041°C in these cooling experiments.

It is noted in table 4b that pure synthetic PbS melts at 1115°C. Direct observation of the charge at about 1120°C reveals that PbS melts congruently. The heating curve begins to show an effect at 1109°C, and a maximum deviation from background is reached at 1115°C. On cooling, a very sharp peak begins at 1115°C. Bloem and Kröger (1956) found that the melting point of lead sulfide varies considerably with change in composition. They reported a maximum melting point at 1127°C when the PbS phase contains an excess of Pb of 3×10^{-4} atoms per molecule PbS (0.03 atomic percent), and that stoichiometric PbS melts as low as 1077°C. In other words the melting temperature is increased by 50°C by addition of only 0.03 atomic percent Pb. This abrupt increase demands a nearly vertical slope of the liquidus curve, which is not very plausible, at least not in the immediate vicinity of PbS composition. They show the total solid solution range in the PbS phase to be only 8×10^{-4} atoms per molecule (0.08 atomic percent) even at 900°C.

DTA experiments on PbS-S mixtures and on S are listed in table 4c. Heat effects due to the orthorhombic-monoclinic inversion and melting of pure sulfur and of sulfur saturated with PbS are not included among those listed in table 4c, except for pure sulfur, in order to save space.

In all DTA experiments on PbS + S mixtures, heat effects were recorded at about 800°C on heating (see table 4c). The first experiment listed gave only a very slight indication of the intersection of the liquidus at about 1000°C. However, very well defined heat effects were recorded at 990° and 804°C on cooling. In the next experiment, which contained 22.97 wt percent S, the liquidus curve was intersected at 867°C. In addition, a sharp peak at 804°C occurred. The third experiment shows the liquidus intersection at about 813°C, and the peak at 804°C also appears in this run. Experiments containing 27.5 wt percent S or more give heat effects only at about 800°C on heating even up to temperatures as high as 1200°C. Cooling of such experiments gives one or more heat effects below 800°C, as also noted in table 4c. From figure 1 it is seen that when the data are plotted as a phase diagram, the DTA experiments demonstrate the existence of monotectic conditions at $800^\circ \pm 2^\circ\text{C}$ and 27.2 ± 0.3 wt percent S. A liquid immiscibility field exists above the monotectic temperature and spans the region from 27.2 ± 0.3 to more than 93.1 wt percent S. The magnitude of the monotectic heat effect decreases gradually with increasing sulfur content in the experiments shown in table 4c. This effect is recorded even in the experiment containing 93.1 wt percent S but is very weak, indicating that the bulk composition of the experiment is within a few wt percent of the sulfur-rich boundary of the two-liquid field.

The PbS + S mixtures containing more than 27.2 wt percent S at $800^\circ \pm 2^\circ\text{C}$ melt to two liquids. These liquids segregate rapidly because of the large difference in their densities; the sulfide-rich liquid, being the heavier, settles to the low end of the DTA tube. During cooling of experiments having bulk compositions of 27.2 to 93.1 wt percent S, the lower limit of the two-liquid field could not be recorded accurately

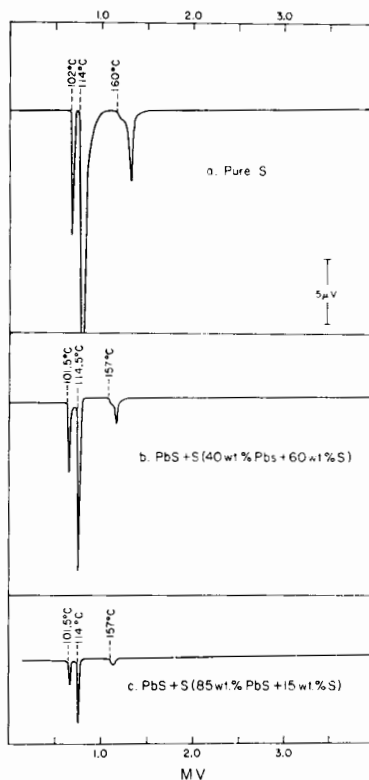


Fig. 2. DTA heating curves on pure sulfur (a) and on PbS + S mixtures (b and c).

because liquid segregation took place even during the heating period. Heat effects consequently were recorded well below 800°C in cooling runs as seen in table 4c. In these experiments, a series of heat effects due to segregation were commonly recorded in the temperature range from 786° to 630°C.

The temperature of the orthorhombic-monoclinic inversion and of melting of sulfur is not measurably influenced by PbS. Table 4c shows that on heating pure sulfur inverts at 102°C and melts at 114°C. Figure 2a shows DTA heating tracings made on pure sulfur, and figure 2b and c shows DTA heating curves made on two PbS + S mixtures with 65.30 and 26.50 wt percent S, respectively.

Eutectic conditions undoubtedly exist between PbS and S, and the eutectic point must lie so near pure S, both in temperature and composition, that it cannot be distinguished from the pure end member by the present experimental methods.

Polymerization of liquid pure sulfur produces a strong, well-defined heat effect at about 160°C (see fig. 2a). The heat effect due to polymerization of sulfur in PbS + S mixtures containing 65.30 wt percent S is

weakened as noted in figure 2b and very weak in the experiment containing 26.5 wt percent S (see fig. 2c). These experiments indicate that under otherwise identical experimental conditions the temperature at which polymerization starts is only slightly influenced by the presence of PbS.

THE Pb-S SYSTEM ABOVE 100°C

The combined data obtained by quenching and DTA experiments were used to draw the phase diagrams of figures 1 and 3. To facilitate presentation only the part of the Pb-S system containing from 0 to 30 wt percent S is shown in figure 1. The complete system above 100°C is given in figure 3. The large difference in atomic weights between Pb (207.31) and S (32.064) results in compression of the Pb-PbS region and corresponding expansion of the PbS-S region of the wt percent diagram. For this reason atomic percent representation was chosen for the diagram of figure 3.

All the experiments required to establish the diagrams of figures 1 and 3 were conducted in rigid silica tubes. Vapor, therefore, is an inherent phase. Blanks and Willis (1961) found that below 923.4°C the solubility of sulfur in liquid Pb obeys Henry's law; its activity can be taken as equal to its atomic percentage, whereas that of lead is equal to its atomic fraction.

Extrapolation to low temperatures (Elliott, 1965, p. 720-721) of the data given in the 923.4° to 427.2°C temperature range for the solubility of S in liquid Pb indicates the Pb-PbS eutectic composition to be 0.0017 atomic percent S. Details of the phase relations near this eutectic are given in the inset of figure 1.

The present experiments indicate that the solubility of sulfur does not follow Henry's law above 925°C but reaches 4.8 wt percent (24.58 atomic percent) at 1042°C. Extrapolation of the data of Blanks and Willis (1961) to 1041°C gives 2.80 wt percent S (15.7 atomic percent). A liquid immiscibility field spans the region between 4.7 and 6.95 wt percent S above 1041°C. The upper boundary of this field was not detected by DTA experiments conducted to temperatures as high as 1180°C. Monotectic conditions exist at 1041°C and 6.95 wt percent S. At the monotectic point the four phases liquid Pb containing 4.7 wt percent S, solid PbS, liquid containing 6.95 wt percent S, and vapor coexist. The liquidus extends smoothly from the monotectic to the melting point of PbS at 1115°C. It is noted from figure 1 that the liquidus is intersected at 1079°C for a composition with about 11.5 wt percent S. Bloem and Kröger (1956) reported that melting of PbS of stoichiometric composition occurs at 1077°C and gave a maximum melting temperature of 1127°C when the PbS phase contains 0.03 atomic percent excess lead. The present experiments, as noted in figure 1 and table 4a, b, c, do not verify the nearly vertical liquidus slope reported by Bloem and Kröger (1956) to occur in the immediate vicinity of PbS composition.

In the PbS-S region, monotectic conditions exist at 27.2 wt percent S (77.7 atomic percent) and $800^{\circ} \pm 2^{\circ}\text{C}$. The four phases PbS, liquid

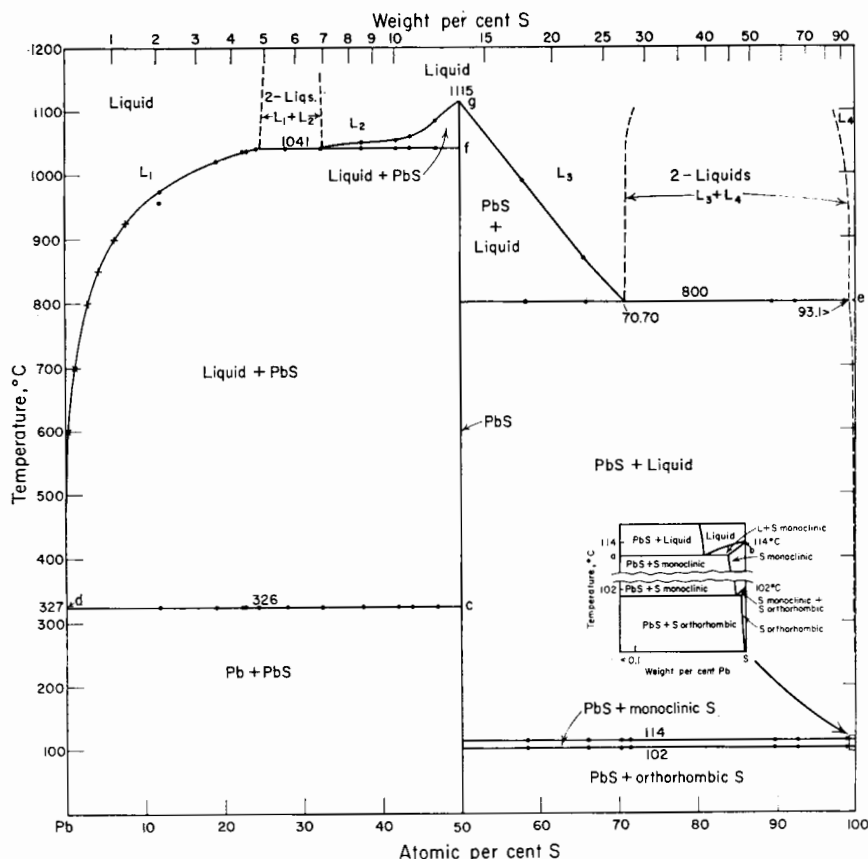


Fig. 3. Phase relations in the Pb-S system. All phases and phase assemblages co-exist with vapor. The curve of sulfur solubility in liquid lead below 925°C is based on the data (crosses) from Blanks and Willis (1961). The results of the present study are indicated by solid circles.

containing 27.2 wt percent S, liquid consisting essentially of sulfur, and vapor are all stable at the monotectic point. The liquid immiscibility field which exists above $800^{\circ} \pm 2^{\circ}\text{C}$ spans the region from 27.2 wt percent S to more than 93.1 wt percent S. The upper boundary of this field was not detected in DTA experiments conducted to 1050°C . The solubility of PbS in liquid S was not determined accurately. DTA experiments show that a mixture of PbS and S containing a total of 93.1 wt percent S produces two liquids above $800^{\circ} \pm 2^{\circ}\text{C}$ (see table 4c). Thus, the solubility of Pb in liquid S is less than 6.9 wt percent at the monotectic temperature. The color of the sulfur, when observed at room temperature at the termination of the DTA repeated heatings and coolings, was affected by PbS as discussed above. Most of the PbS occurred at the bottom of the tubes because of liquid segregation. However, a few cross-shaped PbS crystal aggregates, displaying skeletal growth, were observed

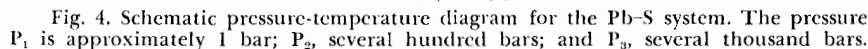
throughout the sulfur. If it is assumed that these crystals exsolved from the sulfur on cooling, it can be concluded that the solubility of Pb in liquid S is clearly much less than 0.5 wt percent at the monotectic temperature. The solubility indicated in figure 3 is probably considerably exaggerated.

The pressure-temperature diagram, figure 4, for the lead-sulfur system may be deduced from published data and the new data presented above by using the phase rule (see Ricci, 1951). Because of the large pressure range, only a schematic diagram can be presented. The temperature scale is maintained where possible.

In order to facilitate the labeling of P-T curves and to avoid confusion concerning the compositions of liquids, the following distinctions are made (see fig. 3): L_1 refers to the field of solubility of sulfur in liquid lead; L_2 refers to the homogeneous liquid existing above 1041°C on the Pb side of PbS composition. Liquids L_1 and L_2 coexist in the lead-rich field of immiscibility. At increasing temperatures above 1041°C, L_1 and L_2 gradually approach each other in composition, and $L_1 = L_2$ at the temperature of closure of the immiscibility gap. The sulfide liquid field existing above 800°C on the sulfur side of PbS composition is referred to by L_3 , and L_4 refers to the field of solubility of lead in liquid sulfur. Liquids L_3 and L_4 coexist in the sulfur-rich field of liquid immiscibility. At increasing temperatures above 800°C, these two liquids gradually approach each other in composition, and $L_3 = L_4$ at the temperature of closure of the immiscibility gap. The liquids produced when pure Pb or S or PbS melts are referred to simply as L or Liquid. For clarity of presentation, the orthorhombic-monoclinic phase change in sulfur has been neglected. Pure monoclinic sulfur melts, L, at a temperature only slightly above that of the PbS + monoclinic sulfur + Liquid + Vapor eutectic, a. In order to show the P-T relations around these invariant points, it was necessary to distort the temperature scale considerably in the 100° to 125°C region. Similar distortion was necessary in the 300° to 330°C region to illustrate the sequence of univariant curves around the melting point of pure Pb, d, and around the eutectic point where PbS + Pb + Liquid + Vapor coexist, c.

Point a is the eutectic, "the minimum temperature of liquefaction" (Guthrie, 1884), of the primitive system Pb-S. One of the four univariant curves labeled S + L + V, originating from a, terminates at the triple point, b, of monoclinic sulfur. Portions of the curves S + V and S + L have been investigated, and the curve L + V, terminating at the critical point of pure sulfur, has been determined. The existing data on sulfur were reviewed by Tuller (1954), by Kullerud and Yoder (1959), and more recently by Meyer (1965).

The univariant curve PbS + L_4 + V terminates at point e, which in the present study was found to lie at 800°C. The three remaining univariant curves arising from point e are L_4 + L_3 + PbS, L_4 + L_3 + V, and PbS + L_3 + V. The first two curves terminate in critical points at undetermined pressures and temperatures. These critical points are



connected by a critical curve along which L_4 and L_3 are identical. The third curve $PbS + L_3 + V$ is a solubility curve ($L_3 \rightleftharpoons PbS + V$) and has been determined in the vicinity of g (Bloem and Kröger, 1956; Isakova, Nesterov, and Shendyapin, 1963). Bloem and Kröger (1956) gave 900°C and about 15 atm as an additional point on the $PbS + L_3 + V$ curve. The continuation of this curve, $PbS + L_2 + V$, is a decomposition curve where $PbS \rightleftharpoons L_2 + V$; it terminates at f. The PbS and vapor phases remain essentially unchanged; however, L_3 contains more sulfur than the crystalline phase, and L_2 contains more lead than PbS . The temperature of point g was determined in the present study as 1115°C. It marks the congruent melting of the binary compound galena under its own vapor pressure. The vapor pressure at point g is about 95.5 mm Hg (0.125 atm) as calculated by using the formula $\log P_{PbS}$ (mm Hg) = $-11,242.5/T^\circ K + 10.08$ (Isakova, Nesterov, and Shendyapin, 1963). Bloem and Kröger (1956) reported that galena is a true compound, that is, it melts directly to liquid that has exactly the same composition as that of the solid and of the vapor. If this is correct, the P-T diagram of figure 4 must contain $PbS + V$, $PbS + L$, and $L + V$ univariant curves which originate in point g. These curves are incorporated in the diagram. PbS and L on these curves have the composition that is fixed at any pressure and temperature by the requirement that $P_{Pb} = 2P_{S_2}$, assuming that the sulfur in the vapor phase is exclusively represented by the S_2 species. Of these curves the one involving $PbS + V$ must lie below that containing $PbS + L_3 + V$ as well as those containing $PbS + L_1 + V$ and $PbS + L_2 + V$. The $L + V$ curve terminates at the critical

point which lies at an unknown pressure and temperature. Critical curves connect the PbS critical point with that of sulfur as well as that of Pb. In other words, if galena is a true compound, the Pb-S system is composed of two true systems: Pb-PbS and PbS-S. At point g, L_2 is identical with L_3 . The curve PbS + L originates at g and is tangent to the egf curve. On the PbS + L curve $L_3 = L_2$, and the liquid, therefore, is referred to as L. No data have been obtained on the PbS + L curve.

The temperature of the invariant point f was determined at 1041°C in the present study. The four phases PbS + L_2 + L_1 + V coexist at f, and three univariant curves in addition to the PbS + L_2 + V curve, discussed above, arise at this point: PbS + L_1 + L_2 , L_1 + L_2 + V, and PbS + L_1 + V. The L_1 + L_2 + PbS and the L_1 + L_2 + V curves terminate at critical points at elevated but undetermined pressures and temperatures. These critical points are connected by a critical curve along which L_1 and L_2 are identical. The fourth curve, PbS + L_1 + V, terminates in point c, which is the eutectic point where Pb + PbS + L_1 + V coexist. Bloem and Kröger (1956) give 900°C and about 0.004 atm as a point on the PbS + L_1 + V curve. The present study indicates that the temperature of the eutectic is 0.4 to 1.0°C below the melting point of pure Pb. Blanks and Willis (1961) calculated the eutectic composition as 0.0017 atomic percent S. The remaining three univariant curves arising from point c are Pb + PbS + V, Pb + PbS + L, and Pb + L_1 + V. No data are available on the P-T relations of the Pb + PbS + V curve, and the Pb + PbS + L_1 curve has not been determined. The Pb + L_1 + V curve terminates at point d, which is the triple point of pure Pb. The available P-T data on the Pb + V and L_1 + V curves over the temperature range from 278°C to the boiling point at about 1751°C have been summarized and evaluated by Nesmeyanov (1963). The vapor pressure over pure Pb at its melting point is of the order of $10^{-8.5}$ mm Hg. The critical point, therefore, must lie at a temperature greater than 1751°C and at a pressure in excess of 1 atm. The critical point of lead, not shown in figure 4, is joined by the critical curve to the critical point of PbS. Johnston and Adams (1911) determined the melting temperature of lead at various pressures up to 2026 bars and found that the Pb + L curve has a positive slope of about 8°C/kb.

GEOLOGICAL IMPLICATIONS

The limits of stability of galena are fixed by the curves in figure 4, PbS + V and PbS + L. Galena may form under pressures and temperatures to the left of these curves. Natural galenas may contain small amounts of Ag which decrease the range of stability of galena to a small extent (Friedrich, 1907a). Galena also forms significant solid solution with Bi_2S_3 , AgBiS_2 , PbSe, and PbTe, as discussed above, which all markedly decrease the range of stability of galena. Neglecting the effects of solid solutions, the circumstances under which galena will exist in an ore or a rock of requisite composition can be deduced from the T-X and P-T projections of figures 3 and 4, respectively. In discussing the

occurrence of the common sulfide pyrite, Kullerud and Yoder (1959) examined two cases wherein (1) the pressure is due to the overlying rock load and the vapor or gas pressure is equal to the rock load, and (2) the pressure on the solid phases is equal to the rock load and the gas pressure consists of the sum of the partial pressures of a sulfur-rich vapor and at least one other gas. They considered these cases in a broad sense similar to the circumstances in an anhydrous sulfide magma and a hydrous vein, respectively.

When considering the P-T projection of the iron-sulfur system, the pressure axis can be taken as expressing sulfur pressure for all mineralogical conditions because the vapor or gas phase even over $\text{Fe} + \text{FeS}$ assemblages consists essentially of sulfur. The contribution of Fe to the vapor phase is negligible, and cases (1) and (2) of Kullerud and Yoder (1959), therefore, can be expressed as $P_s = P_{\text{total}}$ and $P_s < P_{\text{total}}$, respectively.

In the Pb-S system the contribution of Pb to the vapor phase is not always negligible. Bloem and Kröger (1956) showed that in the $\text{Pb} + \text{PbS} + \text{V}$ region of the system the partial pressure of lead is considerably larger than that of sulfur. They found that at temperatures exceeding 500°C the vapor over PbS consists mainly of Pb atoms and S_2 molecules, and they expressed the total pressure over PbS as $P_{\text{total}} = P_{\text{Pb}} + P_{\text{S}_2}$, under the assumption that the partial pressure of PbS molecules can be neglected. It can be shown by differentiation that this P_{total} has a minimum value of about $10^{-3.7}$ atm when $P_{\text{Pb}} = 2P_{\text{S}_2}$, that is, when the vapor has the PbS composition. Bloem and Kröger (1956) found at 900°C that this happens when the solid PbS phase contains an excess of Pb of 3×10^{-4} atm per molecule of PbS. In contrast, the P_{total} over strictly stoichiometric PbS at 900°C is about $10^{-1.5}$ atm, of which the P_{Pb} amounts to only about $10^{-5.5}$ atm. When PbS at the same temperature coexists with sulfide liquid, which the present study has shown to contain 21.2 wt percent S, P_{total} is about 11 to 12 atm, of which the P_{Pb} contribution is only of the order of $10^{-6.5}$ atm (Bloem and Kröger, 1956). Studies of the systems Fe-Pb-S (Brett and Kullerud, 1967) and Cu-Fe-Pb-S (Craig and Kullerud, 1967) show that galena in assemblages involving minerals such as pyrrhotite, pyrite, and chalcopyrite cannot contain an excess of Pb. Since galena in nature almost invariably is associated with one or more of these minerals, the vapor phase over natural galena contains much more sulfur than lead. Thus $P_{\text{S}_2} \gg P_{\text{Pb}}$, and P_{S_2} for all practical purposes is equal to P_{total} in the $P_{\text{total}} = P_{\text{S}_2} + P_{\text{Pb}}$ equation.

A situation in which this P_{total} equals the rock pressure (P_{rock}) can be visualized in an anhydrous environment. Many rocks and ores in which galena forms lie at considerable depths, and the applicable phase diagram represents a section through P-T-X space at constant pressure, for instance $P = P_2$ (see fig. 4). In the construction of such a diagram the influence of pressure on the temperatures of the appearance of the

various liquids is indicated by the slightly positive (that is, nearly vertical) slopes of the vapor-absent curves of figure 4. The effects of pressure on the compositions of the liquids are probably small. Such a diagram, which appears very similar to that of figure 3, shows that galena, being the only compound in the binary system, forms as a primary phase on the liquidus as long as the Pb + S bulk composition lies between the two eutectics. Since one lies very near pure Pb and the other very near pure S, galena forms as a primary phase almost over the entire range of Pb/S ratios.

Because of the shallow slopes of the univariant curves along which vapor is a phase, the stability of PbS is noted in figure 4 to be greatly influenced by small variations in pressure (P_{total} along ordinate of fig. 4) when the pressure does not exceed about 95.5 mm Hg (0.125 atm). This is the P_{total} at point g in figure 4. When P_{total} exceeds the pressure at point g, the upper stability of PbS is limited by the vapor-absent curve PbS + L. This curve has a very steep slope, assumed in figure 4 to amount to about 3° to 5°C/kb . For this reason, an increase beyond the pressure at point g in P_{total} , even of several thousand bars, affects PbS stability less than a pressure change of only a few millimeters Hg when P_{total} is less than that of point g.

Galena forms less than measurable solid solution with pyrite and pyrrhotite. The partial pressure of sulfur is fixed at any temperature by the pyrite-pyrrhotite mineral pair and is 0.1 bar at about 640°C , 0.2 bar at 660°C , and 1.0 bar at 690°C , according to Allen and Lombard (1917). As discussed above, these pressures are much smaller than those over the PbS + L₄ + V assemblage (see fig. 4) at the same temperatures but are considerably larger than that over stoichiometric PbS even at 900°C . This means that in PbS, Fe_{1-x}S, FeS₂ assemblages, galena contains a very slight excess (<0.03 atomic percent) of sulfur.

In the presence of additional volatile components, the sum of the partial pressures of lead (P_{Pb}) and sulfur (P_{S_2}) is smaller than the rock pressure (P_{rock}). It is believed that most natural galena was deposited under conditions where $P_{\text{Pb}} + P_{\text{S}_2} + P_{\text{volatiles}} = P_{\text{rock}}$ and that the major additional volatiles were H₂O and CO₂. The solubilities of lead and sulfur in these volatile components may be considerable; they may affect the phase relations and should be experimentally determined. If the solubilities are small, the assemblages can be represented at least in principle by the projection of figure 3. Galena is again noted to form as a primary phase over practically the entire range of possible bulk compositions.

It is of interest to consider the behavior of galena under conditions where $P_{\text{Pb}} + P_{\text{S}_2} + P_{\text{volatiles}} = P_{\text{rock}}$ and where $P_{\text{Pb}} + P_{\text{S}_2}$ is very small in comparison to $P_{\text{volatiles}}$. Two situations can be visualized, where (1) $P_{\text{S}_2} \gg P_{\text{Pb}}$, as apparently is common in ores, and (2) $2P_{\text{S}_2} < P_{\text{Pb}}$, which may not occur in nature. In case (1) the solid PbS phase will lose more sulfur than lead to the vapor phase, and in case (2) mostly lead

will be lost. In both instances, the condensed PbS phase will change in composition to that which is the most stable, that is, to the composition corresponding to the minimum value of the sum of $P_{\text{Pb}} + P_{\text{S}_2}$ at any given temperature and pressure. Additional vapor or gas produced by the galena phase will coincide in composition with that of the galena and may act as a galena transport agent. In the presence of additional volatiles, such as H_2O or CO_2 , such transport may be greatly facilitated, if galena is at all soluble in the vapor or gas phase. Recent experiments by Kullerud and Yoder (1968) on granite + galena and on granite + galena + H_2O mixtures at temperatures from 650° to 750°C and confining pressures to 5 kb demonstrate extensive galena transport in the experiments containing H_2O by means of the gas phase. Thus a mechanism for galena transport exists which may play a very important role in the formation of galena ores.

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