

Phase equilibria and thermodynamics in the lead-lead sulphide system

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SYNOPSIS

High-temperature phase relations in the Pb-PbS system were established by the quenching of samples equilibrated in evacuated and sealed silica capsules. The liquid-miscibility gap seen in some previously published phase diagrams was not observed. The thermodynamic activities of PbS in liquid solutions of this system were derived at 1473 K from the isopiestic equilibration of samples belonging to this solution series with Cu_2S -PbS melts of known PbS activities. The behaviour of Pb-PbS melts was found to be compatible with a subregular solution model. This model also made it possible to obtain an analytical liquidus for PbS that was in excellent agreement with the experimental determination.

SAMEVATTING

Hoëtemperatuurfaseverhoudings in die Pb-PbS-stelsel is bepaal deur die blus van monsters wat in geëwakuëerde en verseëde silikakapsules in ewewig gebring is. Die vloeistofmengbaarheidsontbreking wat te sien was in sommige fase-diagramme wat voorheen gepubliseer is, is nie waargeneem nie. Die termodinamiese aktiwiteite van PbS in vloeistofoplossings van hierdie stelsel is by 1473 K verkry van die isopiëstiese ewwilibrering van monsters wat aan hierdie oplossingsreeks behoort, met Cu_2S -PbS-smetsels met bekende PbS-aktiwiteite. Daar is gevind dat die gedrag van Pb-PbS-smetsels versoenbaar is met 'n subreëlmatige oplossingmodel. Hierdie model het dit ook moontlik gemaak om 'n analitiese liquidus vir PbS te kry wat uitstekend met die eksperimentele bepaling ooreengestem het.

Introduction

A knowledge of the high-temperature thermodynamic properties and phase equilibria of the Pb-PbS system is essential for a proper understanding of the extraction and refining processes for lead, especially those based on a continuous direct-smelting route. Furthermore, a knowledge of the activities of sulphide components in such melts has considerable theoretical significance in broadening the spectrum of liquid sulphide-system structures.

The system Pb-PbS is part of the main Pb-S binary. Phase diagrams published for this system fall into two general categories: (i) those with a single eutectic reaction at approximately 326 °C adjacent to the lead corner and having a continuous liquidus curve extending from the eutectic point up to the melting point of PbS, and (ii) those with a monotectic reaction at approximately 1040 °C in addition to the low-temperature eutectic isotherm.

Hansen's¹ compilation, based upon the studies of a number of authors²⁻⁴, resulted in the single eutectic type of phase diagram shown in Fig. 1. In an independent study, Miller and Komarek⁵ examined the position of the PbS liquidus by thermal analysis within the range 966 to 1113 °C. The extrapolation of their liquidus, in Fig. 1, to lower temperatures makes a good fit to the solubility data of Blanks and Willis⁶. These and the data from studies of other investigators⁷⁻⁹ on the solubility of PbS in liquid lead were taken into consideration in a relatively recent thermodynamic analysis of the system by Schuh-

mann and his co-workers¹⁰. Schuhmann *et al.*¹⁰ correlated the thermodynamic properties of the Pb-S liquid system in terms of a regular solution model, which fitted to the available data summarized above reasonably well.

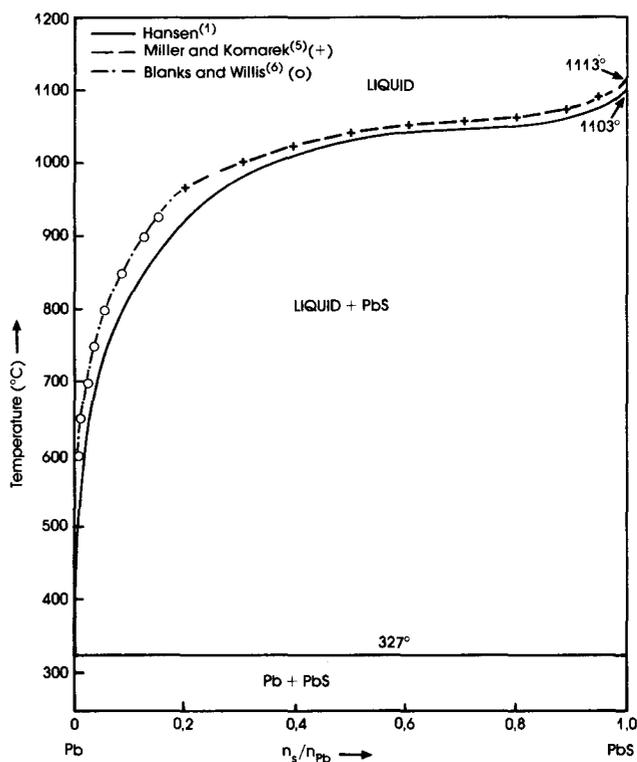


Fig. 1—Phase diagram for the system Pb-PbS (after Hansen¹, and Miller and Komarek⁵)

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Kullerud^{11,12} examined the phase relations in the Pb-S system twice and observed a monotectic, and thus liquid immiscibility, in this binary in both his attempts. His first diagram, represented by dashed curves in Fig. 2, showed the monotectic isotherm at 1043 °C, and the monotectic liquid contained 84 mole per cent PbS. The immiscibility dome was estimated to close at approximately 1075 °C. In the later study, Kullerud¹² refined this diagram mainly by differential thermal analysis (DTA), which resulted in a narrower immiscibility region. In the new diagram, shown by solid lines in Fig. 2, the monotectic isotherm did not change much (1041 °C), but the composition of the monotectic liquid shifted to 65 mole per cent PbS.

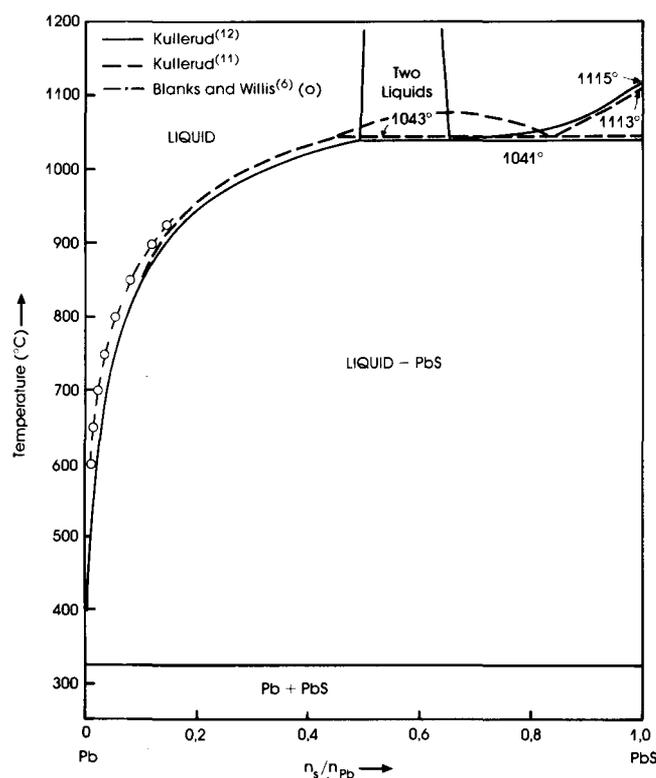


Fig. 2—Phase diagram for the system Pb-PbS (after Kullerud^{11,12})

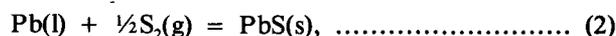
These gross differences between the single eutectic and the monotectic type phase diagrams can be attributed to errors in the interpretation of the phases present in quenched samples of this system.

Both end-members of the Pb-PbS binary, especially PbS, are volatile at high temperatures. Numerous data¹³⁻¹⁵ are available on the standard free energy of vaporization of liquid lead. Thus, for the vaporization equilibrium



a number of linear equations of standard free energy are available. The agreement between the vapour pressures of liquid lead obtained from these equations is satisfactory, and these give almost identical activities for Pb when they are used in measurements of the vapour phase.

A number of investigators¹⁶⁻²⁰ have studied the thermodynamic properties of lead sulphide by chemical-equilibrium, vapour-pressure, and electrochemical techniques, and by DTA calorimetry. For the reaction



the agreement between the reported equations for changes in standard free energy is quite satisfactory. The change in standard free energy attending the fusion of PbS according to the reaction



has been estimated by Schuhmann *et al.*¹⁰ as

$$\Delta G^\circ = 46\,423 - 33,45T \text{ J/mole.} \dots\dots\dots (4)$$

The enthalpy of fusion (46 423 J/mole) in this equation was made higher than the value recommended by Elliott and Gleiser²¹ (36 418 J/mole) in order to keep the regular solution model for Pb-PbS solutions valid over the entire composition range. This arbitrary value compares fairly well with the recent direct measurement of Shamsuddin²⁰, who reported a value of $49\,400 \pm 2100$ J/mole for the enthalpy of fusion of PbS obtained by DTA calorimetry. The standard free energy of fusion calculated by use of this new enthalpy is

$$\Delta G^\circ = 49\,400 - 35,64 T \text{ J/mole.} \dots\dots\dots (5)$$

This equation was used in the present investigation for the necessary calculations.

Colin and Drowart²² studied the vaporization chemistry of PbS by mass-spectrometric measurements, and determined the composition of the lead sulphide vapour phase as a function of temperature in the interval 979 to 1182 K. Their results reveal that the vapour phase consists of the species PbS, Pb₂S₂, Pb, and S₂, where PbS is by far the predominant component. From an extrapolation of the data²² to 1200 °C, it can be estimated that the concentrations of Pb and Pb₂S₂ will be less than 1 per cent each, and that of S₂ will be negligibly small in the gas phase. Hence the isopiestic technique, which will be explained later, can be accepted as giving practically unambiguous results of PbS activities for the system Pb-PbS.

Thermodynamic activities of PbS in Pb-PbS solutions were measured by Yazawa *et al.*¹⁹ using the transpiration-carrier gas technique in the temperature range 1060 to 1200 °C. Their results suggest that temperature variations do not influence the chemical activity of PbS. The observed very strong positive deviation from ideality was more or less independent of temperature. No other direct experimental determination is given in the literature on the activities in this system. However, Schuhmann *et al.*¹⁰ calculated PbS activities assuming regular behaviour of Pb-PbS solutions. The results of their calculations at 1200 °C also show positive but moderate deviations from ideality. Therefore, there is no sound agreement between their calculated PbS activities and the directly measured PbS activities of Yazawa *et al.*¹⁹.

Thus, the present study was initiated (i) to establish the high-temperature phase relations in the Pb-PbS partial system by conventional quenching experiments, and (ii) to measure the PbS activities in binary Pb-PbS liquid solutions at 1473 K by employing the isopiestic equilibration technique. This particular technique makes use of the volatility of components in solution, and thus circumvents the problems encountered in open-system measurements like gas-equilibration and the e.m.f. method for

such systems. The isopiestic technique is known to be one of the most accurate methods for the determination of comparative vapour pressures, and thus activities, of a volatile component in solution^{23,24}. Samples are equilibrated through the vapour state isothermally so that they assume a common vapour pressure of a component. Analyses of these samples then provide the necessary compositional information about the system. The technique is based on the holding of two or more samples (most frequently in evacuated and sealed containers) at the same temperature and the equilibration of one or more volatile components in these samples²³. One of the samples, which does not have to be the pure component, acts as the main vapour source for which accurate vaporization or activity data are available. When equilibrium is attained, all the samples assume a common vapour pressure, and the entire isopiestic assembly is quenched to room temperature. Both the source and the sinks are analysed chemically to determine their final compositions. The activity of the volatile species in the source corresponding to the final source composition is equal to the activity of the same species in the sink at the temperature of equilibration.

Experimental Procedure

The primary starting materials were electrolytic copper (99,99 per cent minimum purity), triply distilled sulphur, and lead metal produced by hydrogen reduction of analytical-grade Merck PbO powder. PbS was prepared by the reacting of a stoichiometric mixture of lead and sulphur in an evacuated (about 10^{-7} atmospheres) and sealed silica tube. The tube was heated first at 500 °C for 48 hours, and the Pb and S became molten and reacted rapidly to form PbS. In a second-stage heating, PbS was melted and homogenized at 1150 °C for 4 hours. Cu₂S was synthesized from its elements by this same procedure, except that the initial heating was at 700 °C and the final melting was at 1200 °C. At the end of the melting stage, the molten sulphides were quenched to room temperature by plunging the silica tubes into water. X-ray-diffraction analyses of the products verified their complete formation. Chemical analyses showed that the compounds had correct stoichiometric compositions within the limits of analytical error.

The classical equilibration–quenching technique was used to establish the high-temperature phase relations of the Pb–PbS melts. Samples of desired compositions were prepared by the mixing of Pb and PbS. These were placed in transparent silica tubes of 10 mm internal diameter, which were evacuated to about 10^{-7} atmospheres. The tubes were gettered with copper gauze at 500 °C for 6 hours and then sealed to a final length of about 3 cm. These capsules were introduced into a vertical tube furnace, wound from 1 mm Kanthal wire, the temperature of which was controlled to $\pm \frac{1}{2}$ °C by Pye Ether Digi controllers coupled to thyristor units. Control and measuring thermocouples were of the Pt vs Pt 13% Rh type, which were frequently calibrated against a reference standard thermocouple of the same composition, and also against the melting points of gold and silver. The overall accuracy in the measured and controlled temperatures was estimated as ± 2 °C.

Time to reach equilibrium was established in initial ex-

periments by chemical and metallographic analyses of quenched samples at intervals of 2 hours for a total of 8 hours. It was found that, after 4 hours of heating, samples gave identical analyses and microstructure within experimental error. At the end of the equilibration, the capsules were quenched to room temperature by being dropped into water. The samples were removed and divided into two; one portion was analysed chemically by standard procedures for sulphur and lead to give the final composition, and the other was used to observe the phases present by metallographic methods, and by electron-probe microanalyser (EPMA) where necessary. The chemical analyses were accurate and reproducible to within $\pm 1,0$ mass per cent for each element. Metallographically, the appearance of large angular PbS grains in a matrix of quenched liquid evidenced the two-phase liquid + PbS(s) region. On the other hand, the samples quenched from above the liquidus showed no solid phases, and the single liquids had a dendritic appearance.

For the isopiestic experiments, two compositionally different Pb–PbS mixtures were equilibrated with a mother Cu₂S–PbS solution of known PbS activity²⁵, which acted as the source. The compositions of the two Pb–PbS samples were selected so that they would lie on opposite sides of the expected activity–composition curve. This procedure permitted equilibrium to be attained from both sides, and it was possible to bracket the superimposed activity value between two very close composition limits of the unknown sample. In this way, one sample would absorb PbS while the other would reject some during the course of equilibration and, ideally, the final composition of the initially different two samples should come out the same.

The Pb–PbS mixtures weighing about 1,5 to 2,0 g each were contained in thin silica crucibles approximately 2 cm in length and 8 mm in diameter. These were inserted into a larger silica tube of 25 mm internal diameter and approximately 3 cm final length, which contained about 10 to 12 g of the selected Cu₂S–PbS mixture. The large silica tube containing all three mixtures was evacuated, gettered, and sealed in exactly the same manner as explained above for the preparation of the capsules for the equilibration–quenching method. The arrangement of the isopiestic probe is shown schematically in Fig. 3. The isopiestic probe was heated in the same furnace as that described above. Preliminary tests indicated that the composition of the Pb–PbS melts converged within 5 hours of heating and remained unaltered thereafter within limits of analytical error. At the end of the equilibration, the probe was quenched to room temperature by being dropped into water, and chemical analyses were conducted to give the final compositions of the Pb–PbS and Cu₂S–PbS melts.

The analyses of the Cu₂S–PbS melts revealed that the final compositions were different from those of the original Cu₂S–PbS mixtures placed in the probe, but the sulphur content of the final Cu₂S–PbS melts always met the stoichiometry of the sulphide composition. This indicated that the exchanged gas species was PbS, and that there was negligible transport of Pb between the source and the sink. Comparatively larger amount of source in comparison with the sinks also ensured the exchange of PbS.

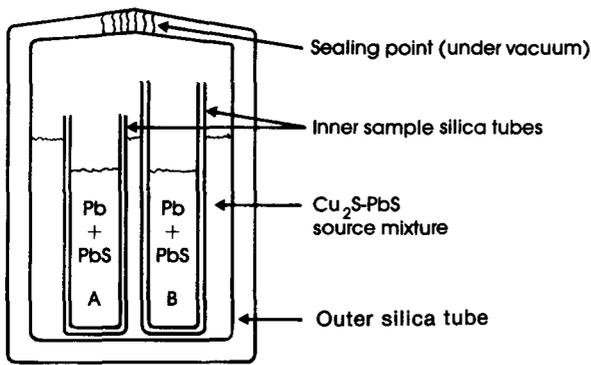


Fig. 3—Schematic illustration of the isopiestic probe

The thermodynamic activities of PbS in $\text{Cu}_2\text{S-PbS}$ melts at 1473 K were obtained from Eric and Timucin²⁵, who had investigated the system in detail by precise dew-point measurements. Their activity-composition plot at 1473 K, which was used in this study, is reproduced in Fig. 4.

Results and Discussion

Phase Equilibria in the Pb-PbS System

The phases present in the various samples of the Pb-PbS system, and their compositions at the equilibration temperatures as identified by the methods discussed earlier, are shown graphically in Fig. 5. These data were obtained mainly with the purpose of delineating the PbS liquidus between 880 and 1110 °C, over which controver-

sy exists. The empty circles in Fig. 5 represent single liquid phase, whereas the full circles belong to the two-phase samples. Also included in the diagram are liquidus lines from Miller and Komarek⁵ (dashed lines) and from Hansen¹ (dash-dot lines) for comparison. The solid line is the analytical liquidus calculated in this work from the subregular solution model, which will be discussed later. However, there is very good agreement between the experimental points and the analytical liquidus line of this work. Therefore, it can safely be concluded that the analytical line represents the best fit to the experimental points. All the two-phase samples are below, and all the single liquid-phase samples are above, the line, thus bracketing the liquidus satisfactorily.

The general shape of the liquidus determined in this investigation is in agreement with the liquidus of Hansen,¹ and that of Miller and Komarek⁵. However, throughout the composition range, Miller and Komarek report higher liquidus temperatures and lower solubility of sulphur in liquid lead. On the other hand, the liquidus temperatures of Hansen¹ are higher than those of the present investigation, up to about $n_s/n_{pb} = 0,55$ (where n_i represents the gram atoms or moles of elemental species). After this composition, Hansen's¹ values are lower.

The Pb-S phase diagrams determined by Kullerud^{11,12} using quenching and DTA techniques involving a liquid miscibility gap are grossly different from the present findings. Since the flatness of liquidus between $n_s/n_{pb} = 0,4$ and $n_s/n_{pb} = 0,8$ may suggest the possibility of mono-

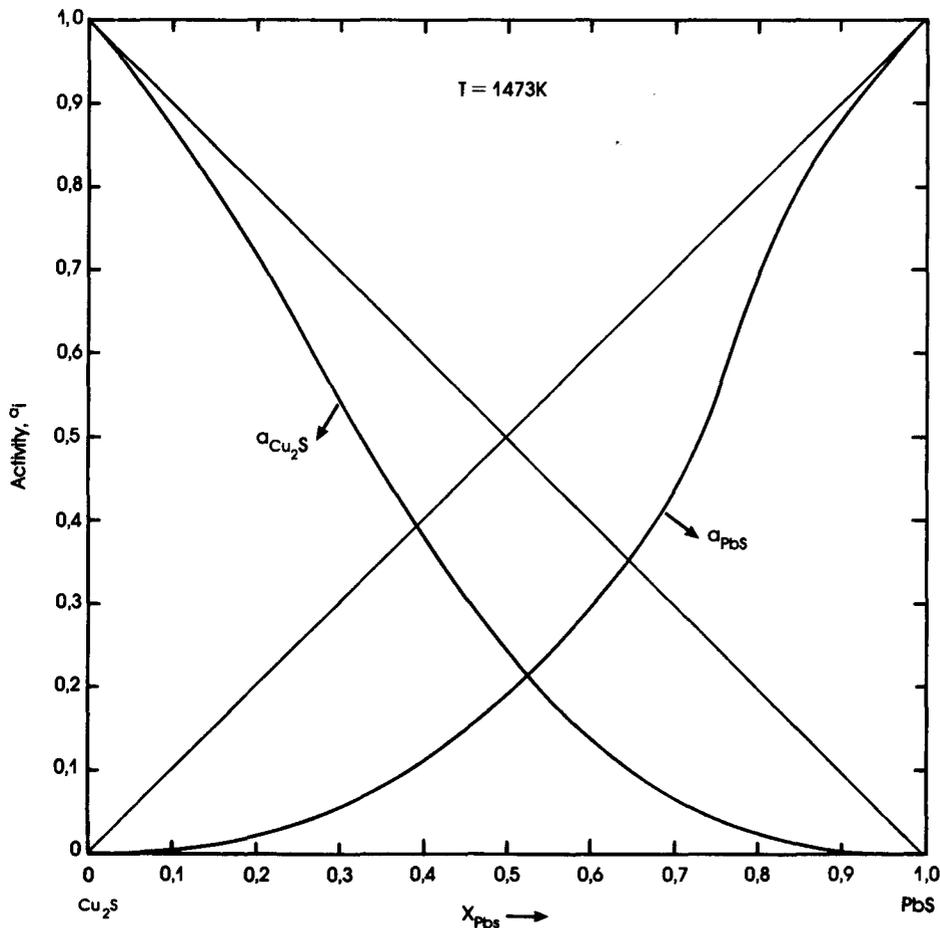


Fig. 4—Activities in binary $\text{Cu}_2\text{S-PbS}$ mattes at 1473 K (after Eric and Timucin²⁵)

tectic conditions, care was taken during the present investigation to reveal it, if it existed between the above composition limits. EPMA scanning of several samples within the quoted composition range equilibrated at 1060 °C showed a smooth Pb and S distribution within the whole mass, indicating the non-existence of any immiscibility. Metallographic examination of the quenched samples belonging to the region of alleged immiscibility showed a dendritic single-liquid texture, which supports this conclusion.

Thermodynamic Activities in the Pb-PbS System

PbS activities of the selected binary Pb-PbS liquid solutions with pure liquid PbS as the standard state at 1473 K that were obtained by the isopiestic equilibration technique are given in Table I. Activities of PbS in the source Cu₂S-PbS solutions were derived from the final compositions given by the chemical analyses using the

data of Eric and Timucin²⁵ that are reproduced in Fig. 4. Within the Pb-PbS system, the mole fractions of PbS and Pb were defined in terms of the number of moles of the true binary species, sulphur and lead, as the following:

$$x_{\text{PbS}} = n_{\text{S}}/n_{\text{Pb}} \dots\dots\dots (6a)$$

and

$$x_{\text{Pb}} = (n_{\text{Pb}} - n_{\text{S}})/n_{\text{Pb}} \dots\dots\dots (6b)$$

where x_i refers to the atom or mole fraction of the species.

This approach is fundamental and necessary because, in the liquid state, Pb-PbS melts are actually Pb-S solutions of varying lead and sulphur contents. However, the composition of the main vaporizing species from these melts corresponds to the stoichiometric PbS formula²², permitting the derivation of lead sulphide activities. Table I, for the sake of clarity, does not contain the mole frac-

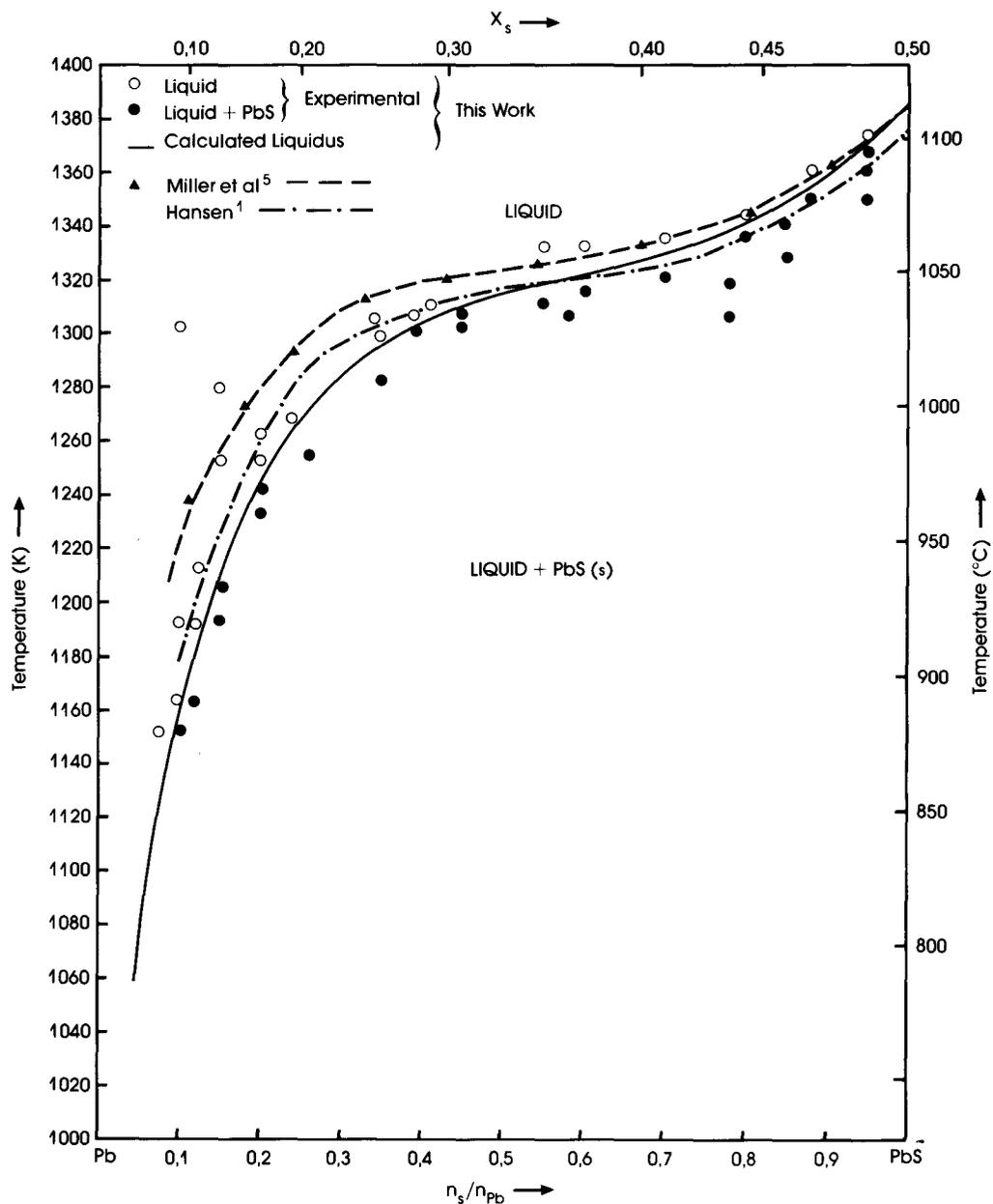


Fig. 5—High-temperature portion of the PbS liquidus in the system Pb-PbS

TABLE I
DATA ON THE COMPOSITIONS AND ACTIVITIES IN ISOPIESTIC EXPERIMENTS FOR THE Pb-PbS SYSTEM AT 1473 K

| Initial composition | | | Final composition* | | | Imposed PbS activity α_{PbS} |
|--------------------------|--------------------------|---------------------|--------------------------|--------------------------|----------------------|-------------------------------------|
| Sample A n_s/n_{Pb} | Sample B n_s/n_{Pb} | Source x_{PbS} | Sample A n_s/n_{Pb} | Sample B n_s/n_{Pb} | Source† x_{PbS} | |
| 0,006 | 0,010 | 0,380 | 0,019 | 0,027 | 0,334 | 0,075 |
| 0,050 | 0,130 | 0,610 | 0,085 | 0,100 | 0,604 | 0,300 |
| 0,170 | 0,250 | 0,730 | 0,190 | 0,200 | 0,733 | 0,500 |
| 0,100 | 0,150 | 0,820 | 0,194 | 0,213 | 0,747 | 0,540 |
| 0,120 | 0,150 | 0,890 | 0,180 | 0,220 | 0,753 | 0,560 |
| 0,300 | 0,450 | 0,800 | 0,345 | 0,390 | 0,801 | 0,700 |
| 0,380 | 0,480 | 0,840 | 0,440 | 0,460 | 0,817 | 0,740 |
| 0,560 | 0,660 | 0,830 | 0,580 | 0,620 | 0,843 | 0,790 |
| 0,740 | 0,750 | 0,900 | 0,760 | 0,765 | 0,871 | 0,840 |
| 0,750 | 0,800 | 0,950 | 0,800 | 0,830 | 0,890 | 0,870 |

* In general, the analysis for the elemental constituents totalled $99,8 \pm 0,5$ mass %; these were slightly corrected to make the total 100%
† The analysis for source always yielded stoichiometric Cu_2S -PbS mixtures within analytical error

tions of Pb in the Pb-PbS system and the mole fractions of Cu_2S in the Cu_2S -PbS system, although these were also analysed chemically. The data of Table I are shown in Fig. 6. The experimental PbS activities are given with their ranges of compositional error arising from the use of two samples.

The α_{PbS} function defined as

$$\alpha_{PbS} = \ln \gamma_{PbS} / (1 - n_s/n_{Pb})^2 \dots \dots \dots (7)$$

was found to vary linearly with the composition, as shown in Fig. 7. The average value of the compositional range (from Samples A and B) was considered for each activity value in this plot. The regression analysis applied to the points yielded the following equation with a correlation factor of 0,91:

$$\alpha_{PbS} = 1,362 + 0,605 (n_s/n_{Pb}) \dots \dots \dots (8)$$

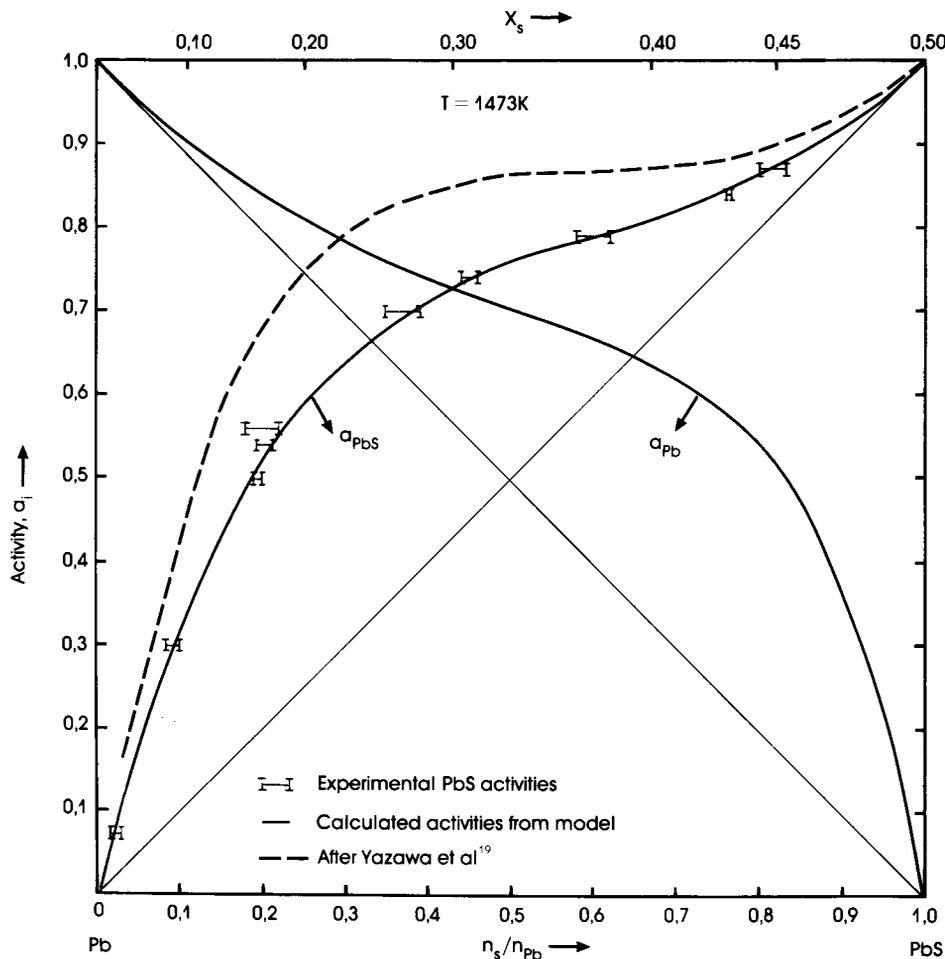


Fig. 6—Activity-composition relations in Pb-PbS melts at 1473 K

The corresponding α function for Pb was obtained by a Gibbs-Duhem integration of equation (8), and the result is

$$\alpha_{Pb} = 1,665 - 0,605 \left(\frac{n_{Pb} - n_S}{n_{Pb}} \right) \dots\dots\dots (9)$$

With the help of equations (8) and (9), the analytical values of the activity coefficients, and thus the activities of PbS and Pb, were derived at 1473 K. These are shown as solid lines in Fig. 6.

The linearity of α functions was compatible with Hardy's subregular solution model²⁶ in which thermodynamic functions can be expressed by two-constant linear equations. From the definition of the α function and from the equality

$$G_i^E = RT \ln \gamma_i, \dots\dots\dots (10)$$

where G_i^E is the partial excess free energy and γ_i is the activity coefficient, the following expressions can be written based on the assumption that partial excess free energies are temperature-independent for Pb-PbS melts:

$$G_{PbS}^E = [16\,680 + 7409(n_S/n_{Pb})] \left(\frac{n_{Pb} - n_S}{n_{Pb}} \right)^2 \text{ J/mole} \dots\dots\dots (11)$$

and

$$G_{Pb}^E = \left[20\,391 - 7409 \left(\frac{n_{Pb} - n_S}{n_{Pb}} \right) \right] \left[\frac{n_S}{n_{Pb}} \right]^2 \text{ J/mole} \dots\dots\dots (12)$$

The assumption of temperature-independent excess free energies is inherent in the regular and subregular solution models.

This subregular model for Pb-PbS solutions permits the development of equations for activity coefficients, and thus activities of PbS and Pb, for any temperature if each of equations (11) and (12) is combined with (10) and the mole fractions are taken into consideration. The following are obtained:

$$\ln \alpha_{PbS} = \ln(n_S/n_{Pb}) + 1/T [2006 + 891(n_S/n_{Pb})]$$

$$\left[\frac{n_{Pb} - n_S}{n_{Pb}} \right]^2 \dots\dots\dots (13)$$

$$\ln \alpha_{Pb} = \ln \left(\frac{n_{Pb} - n_S}{n_{Pb}} \right) + 1/T$$

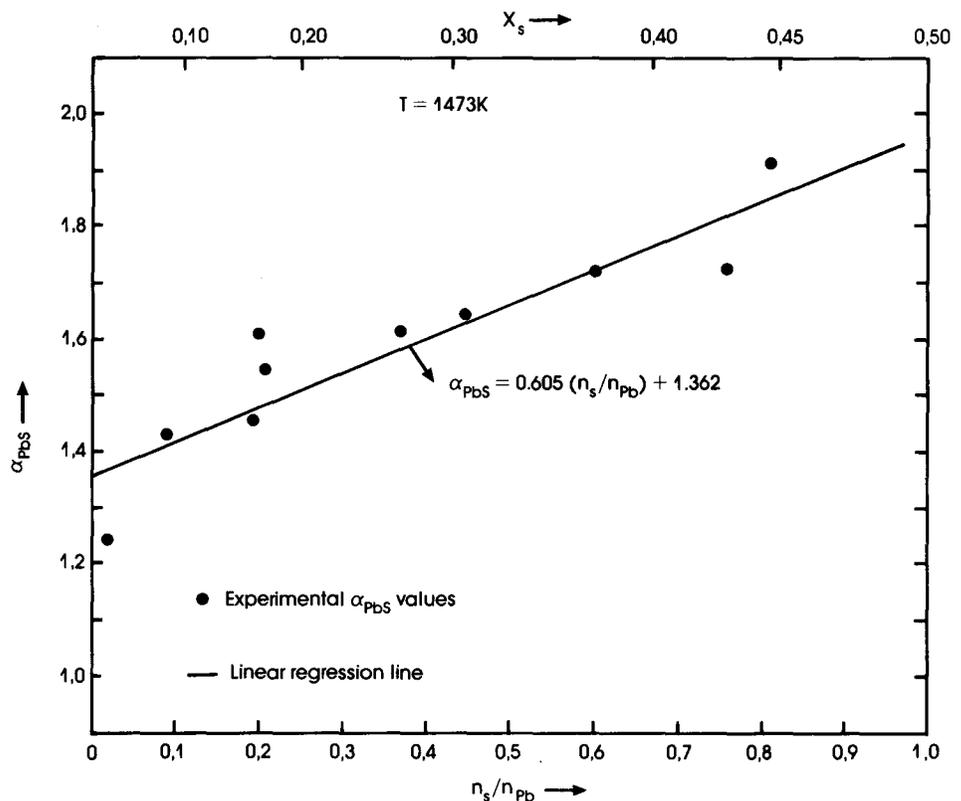
$$\left[2453 - 891 \left(\frac{n_{Pb} - n_S}{n_{Pb}} \right) \right] \left[\frac{n_S}{n_{Pb}} \right]^2 \dots\dots\dots (14)$$

By the help of equation (5), which gives the standard free energy of melting of PbS, it is possible to derive the liquidus temperature of PbS analytically; that is, for PbS liquids in equilibrium with solid PbS, the following is obtained from equation (5):

$$\ln \alpha_{PbS} = 5942/T + 4,287. \dots\dots\dots (15)$$

If equations (13) and (15) are combined and temperature T is solved for, the following relationship, which describes the position of the PbS liquidus, is derived:

Fig. 7— α -function of liquid PbS in Pb-PbS melts at 1473 K

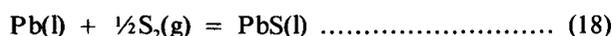


$$T = \frac{\left(\frac{n_{\text{Pb}} - n_{\text{S}}}{n_{\text{Pb}}}\right)^2 [2006 + 891 (n_{\text{S}}/n_{\text{Pb}})] + 5942}{4,287 - \ln (n_{\text{S}}/n_{\text{Pb}})} \quad (16)$$

The curve of this equation is shown in Fig. 5 by the solid line. For equilibrium (2), the change in standard free energy as modified by Schuhmann¹⁰ is

$$\Delta G^\circ = -159\,905 + 84,35 T \text{ J/mole.} \quad (17)$$

By the addition of equilibrium (2) to equilibrium (3) and equation (5) to equation (17), the standard free energy of formation of liquid PbS can be obtained:



and

$$\Delta G^\circ = -110\,505 + 48,71 T \text{ J mole.} \quad (19)$$

By use of equation (19), the sulphur potentials over the Pb–PbS melts can be computed as a function of temperature and composition with the aid of equations (13) and (14). The final equation is

$$\begin{aligned} \ln p_{\text{S}_2}(\text{atm}) = & \ln \left(\frac{n_{\text{S}}}{n_{\text{Pb}} - n_{\text{S}}} \right)^2 + \frac{2}{T} \\ & \{ [2006 + 891 (n_{\text{S}}/n_{\text{Pb}})] \left[\frac{n_{\text{Pb}} - n_{\text{S}}}{n_{\text{Pb}}} \right]^2 - \\ & [2453 - 981 \left(\frac{n_{\text{Pb}} - n_{\text{S}}}{n_{\text{Pb}}} \right)] \left[\frac{n_{\text{S}}}{n_{\text{Pb}}} \right]^2 - \\ & 13\,291 \} + 11,72. \quad (20) \end{aligned}$$

Thus, equations (13), (14), (16), and (20) completely define the high-temperature thermodynamic properties and phase equilibria of the system Pb–PbS.

Activities of both components of the Pb–PbS liquid solutions at 1473 K deviate positively from ideality as stated in previous reports^{10,19}. However, the activities reported by Yazawa *et al.*¹⁹ are considerably higher than the present values. They measured PbS vapour pressure over Pb–PbS solutions by the transpiration–carrier gas method. In such systems, both Pb and PbS are vaporized from Pb–PbS melts, and they apparently measured the sum of p_{Pb} and p_{PbS} , rather than only p_{PbS} , which explains the high activities derived. It is a fact that the transpiration technique is not applicable to systems where more than one species vaporizes, however small the contribution of these species. The regular solution model of Schuhmann *et al.*¹⁰ predicts slightly lower activities than those in the present investigation. Their activities are not direct measurements, but were calculated indirectly. The differences result mainly from their model, which depended on low-temperature solubility data. On the other hand, the subregular solution model developed in this investigation depends on direct activity measurements at high temperature and is more refined. That this is so is supported by the excellent agreement of the analytical liquidus and experimental points, and the excellent agreement of the analytical and experimental activities.

The main sources of error in the activities measured by the isopiestic technique are the uncertainties in chemical analysis and in the data used for the source. The

chemical analyses were accurate and reproducible to within $\pm 1,0$ mass per cent. Furthermore, the use of two separate samples permitted bracketing of the activity value. Thus, for a measured activity, the widest range of error in the composition in terms of the mole fraction of PbS ($n_{\text{S}}/n_{\text{Pb}}$) was $\pm 0,0225$. The smallest range was $\pm 0,0025$. The maximum error in the PbS activities of the Cu₂S–PbS system was reported to be about 4 per cent²⁵. It should be noted that these maximum errors are not necessarily additive, and thus it is estimated that the results of this investigation are correct to within 5 per cent in general.

Conclusions

The high-temperature thermodynamic properties and phase relations in the system Pb–PbS have been established. The system was found to form continuous solutions in the liquid state. The activities of PbS in these melts at 1473 K were derived from the isopiestic equilibration of samples belonging to these solution series with Cu₂S–PbS melts of known activities. The PbS activities showed positive departures from ideality and were compatible with the subregular solution model. This model permitted the development of equations describing the activities of both Pb and PbS, as well as the partial pressures of sulphur, for these solutions. It was also possible to derive an analytical expression describing the position of the PbS liquidus. The model liquidus and activities were in excellent agreement with the actual direct experimental results, which firmly precluded the possibility of a miscibility gap in the system.

The presence or absence of a liquid miscibility gap in the phase diagram of a metal sulphide system has direct implications for the technology of metal extraction from sulphide melts. For example, the system Cu–Cu₂S is characterized by a large miscibility gap in the liquid state. During the production of copper from liquid white metal (Cu₂S) in a conventional side-blown converter, this miscibility gap ensures that a sulphide phase of roughly constant sulphur content is exposed to the air blast during most of the process. As the copper-rich phase is produced, it separates easily, by virtue of immiscibility, from the sulphide phase and sinks to the bottom of the converter owing to its higher density. This separation and sinking behaviour minimizes the oxidation of the metal produced.

In contrast to copper, the absence of a liquid miscibility gap in the system Pb–PbS implies that, when lead sulphide is converted to metal, the bath is a single Pb–PbS solution of decreasing sulphur content. If this bath is not mixed thoroughly, the region of the bath exposed directly to the air blast will be temporarily depleted in sulphur and preferential oxidation reactions will occur, resulting in the formation of liquid PbO. This PbO will increase the viscosity of that part of the bath and will further reduce the rate of mixing, which aggravates the extraction process. The failure in lead production through the use of side-blown converters²⁷ can be attributed largely to the situation described above. The solution to this problem may lie in the employment of a top-blown rotary converter (TBRC), which has been used successfully in the conversion of nickel sulphide. Similarly, the system Ni–NiS has no liquid immiscibility, and the mixing of the

bath, which is more crucial in the extraction of nickel, is achieved readily through the use of a TBRC.

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