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THERMODYNAMIC PROPERTIES OF MOLTEN SULPHIDES Cu_2S–PbS

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ABSTRACT

Measurements of vapour pressure above the molten sulphide solution Cu_2S–PbS have been made by the effusive Knudsen method. The measurements were carried out under isothermal conditions, at temperatures of 1042, 1081 and 1103 K in the PbS concentration range 80–20 wt.%. High temperature mass spectrometric measurements proved that the predominant gas phase constituent comprised molecules of PbS(g).

Utilising the formerly determined vapour pressure above pure PbS, its activity in the investigated solution has been calculated. The temperature and concentration dependence of the PbS activity in molten Cu_2S–PbS has been described by the Redlich–Kister equation

$$\ln(a_{PbS}/X_{PbS}) = (1 - X_{PbS})^2\{-5.84 + (2756.26/T) + [3.9 - (5058.7/T)](4X_{PbS} - 1) - [1.315 - (3115.727/T)](1 - 2X_{PbS})(6X_{PbS} - 1)\}$$

The results obtained indicate negative deviation from an ideal solution and are in good agreement with part of the literature data. For the determined points of the liquidus line, good compliance with the phase equilibrium diagram, and agreement of the vapour pressure of PbS in the two-phase area with the vapour pressure above pure PbS, have also been achieved. The activity coefficient of PbS in the state of infinite dilution is described with the following temperature dependence

$$\log \gamma^0_{PbS} = (1913.95/T) - 2.78$$

The obtained dependence of γ^0_{PbS} was determined by extrapolation over a wide range of concentrations, therefore its value is somewhat uncertain. Because of substantial discrepancies in the literature, it is necessary to undertake further studies in this area.

INTRODUCTION

For many copper concentrates, a high concentration of lead (which, along with arsenic, antimony and bismuth, is an undesirable constituent of smelted copper) is characteristic. An analysis of the distribution of impurities during the converting process shows the possibility of elimination of a high proportion of the lead during the evaporation process [1]. The basic problem in considering the lead distribution in residual products of the process is determination of the thermodynamic activity of PbS in molten solution with Cu_2S.

TABLE 1

Results of earlier investigations of activity of PbS in Cu_2S-PbS

No.	Activity as compared with the ideal	Investigation method	Literature
1	Slight positive deviation of a_{PbS} in the whole range of concentration	Calculation based on phase diagram and and Krupkowski equation	Block-Bolten [5]
2	Fulfills the Temkin model relationship $0 < X_{Cu_2S} < 0.75$	Calculation based on phase diagram	Lumsden [6]
3	Positive deviation for low concentrations of PbS; negative deviation for high concentrations of PbS $1423\ K \leqslant T \leqslant 1523\ K$	Dew point temperature measurement	Azuma et al. [7]
4	Negative deviation in whole concentration range $1323\ K \leqslant T \leqslant 1523\ K$	Transport method	Isakova et al. [8,9]
5	Negative deviation at $T = 1473$ K	Dew point temperature measurement	Eric and Timucin [10]
6	Negative deviation	Measurement of coefficient of distribution of Pb between copper and matte	Sinha et al. [11]

The Cu_2S–PbS system is an eutectic, in which the eutectic coordinates are: $T_e = 813$ K and $X_{PbS} = 0.39$ [2], $T_e = 803$ K and $X_{PbS} = 0.37$ [3]; a distinct effect of excess sulphur on the eutectic temperature value is observed [3]: $T_e = 823$ K for $Cu_{1.9}S$–PbS and $T_e = 838$ K for $Cu_{1.8}S$–PbS.

It is generally thought that Cu_2S–PbS, like other pseudobinary sulphide systems of the same type (e.g., FeS–PbS, FeS–Cu_2S, PbS–AgS_2 and Cu_2S–Ni_3S_2), obeys the Raoult law, or only slightly deviates from the ideal [4]. This view was confirmed by calculations (based on phase diagrams) of PbS activity in the Cu_2S–PbS system by Block-Bolten [5] and Lumsden [6]. However, recent experimental data do not confirm these calculated results [7–11]. The data which have been brought together in Table 1 demonstrate both positive and negative deviations from the ideal. Azuma et al. [7] obtained positive deviation of the activity from the ideal in the low PbS concentration range and negative deviation in the high concentration range of PbS in Cu_2S. Other authors [8–11] reported negative deviations over the whole range of concentrations, and the differences between individual values are high.

TABLE 2

Comparison of calculated values of activity coefficient in the state of infinite dilution

Molar ratio		Value of activity coefficient γ^0_{PbS}					
X_{FeS}	X_{Cu_2S}	Sinha et al. [11]		Nesterov et al. [9]	Eric and Timucin [10]	Azuma et al. [7]	
		1405 K	1505 K	1473 K	1473 K	1405 K	1505 K
0	1.00	0.18	0.16	0.13 [a]	0.035	2.9	2.1
0.159	0.841	0.17	0.15	–	–	2.8	2.0
0.276	0.724	0.16	0.15	–	–	2.6	2.0

[a] $X_{PbS} = 0.0429$.

These findings were confirmed by differences between the values of the activity coefficient in the state of infinite dilution of PbS, listed in Table 2. The values of the activity coefficient at a temperature of 1405 K were in a wide range, from 0.18 [11] to 2.9 [7].

Such discrepancy was the reason for undertaking investigations in this area, utilising effusive methods of vapour pressure measurement.

EXPERIMENTAL METHODS AND PROCESSING OF RESULTS

Materials

For the measurements, the chemical compounds Cu_2S and PbS were prepared from the pure constituents: spectral purity lead and sulphur, and copper of 99.999% purity. In a quartz ampoule, prewashed with acetone and heated at 500 K, weighed amounts of the pure constituents were placed and fusion sealed in vacuum. Thus prepared, the sample was put into a resistance furnace and slowly heated during several hours until a temperature of 700 K was reached then heating at a temperature of 900 K was continued for 20 h. To homogenize the samples, the ampoules were heated to the temperature of fusion of the sulphides and kept at the same temperature for 2 h. X-ray radiographic analyses of samples thus prepared did not show the presence of any impurities, but trace amounts of $Cu_{1.9}S$ were detected.

Method of measurement

Samples weighing 0.20–0.38 g were prepared, in which the PbS content was 70–80 wt.% of the whole. Initial determinations of the gas phase composition above the sample were made with a mass spectrometer provided with Knudsen cell, at a temperature of 1030 K.

Measurements of mass loss were carried out using a Mettler TA-1 thermobalance. The sensitivity of mass measurement was 10^{-5} g, and the reading error was 2.5×10^{-6} g. During measurements, a vacuum of ca. 10^{-3} Pa was maintained. Temperature measurements were made with a Pt, Pt–10% Rh thermocouple calibrated for the Al, Cu, Ag and Ni melting points.

For the measurements, alundum crucibles with an effusion orifice of effective area $A_e = 0.0728 \pm 0.0008$ mm^2, silver calibrated, were used. The description of the apparatus and the measurement methods, as well as the calibration technique, were described previously [12]. Measurements of vapour pressure above the Cu_2S–PbS system were performed in isothermal conditions at three temperatures: 1042, 1081 and 1103 K. The initial concentration of PbS was 80, 78.5 and 83.0 wt.%, respectively.

Method of processing of results

The following assumptions have been made

(1) In the applied temperature range of 1042–1103 K the vapour pressure of Cu_2S, when compared with that of PbS (calculated via the equations from Ref. 13) is very small and amounts to 0.03%, therefore the vapour pressure of Cu_2S was omitted, the assumption being made that the vapour contains constituents originating solely from PbS evaporation,

(2) Because the measured total pressure above the sample, p_{tot}, is the sum of

$$p_{tot} = p_{PbS} + p_{Pb} + p_{S_2} + p_{Pb_2S_2} \tag{1}$$

where p_{Pb}, p_{S_2} and $p_{Pb_2S_2}$ are negligibly small [14], therefore the simplification

$$p_{tot} = p_{PbS} \tag{2}$$

was made.

Considering the above-mentioned conditions, the vapour pressure of PbS for the Knudsen effusive method has been calculated from the equation

$$p_{tot} = \frac{\mathrm{d}m}{\mathrm{d}t}\frac{1}{A_e}\left(\frac{2\pi RT}{M}\right)^{1/2} \tag{3}$$

where T is the absolute temperature, M is the molecular mass of the effusing vapour, A_e is the effective area of the effusive orifice and $\mathrm{d}m/\mathrm{d}t$ is the rate of mass loss of PbS.

Values thus determined for the vapour pressure have been used to determine the activity and the activity coefficient of PbS in the system Cu_2S–PbS according to the equation

$$a_{PbS} = \gamma_{PbS} X_{PbS} \tag{4}$$

where a_{PbS} is the activity of PbS, γ_{PbS} is the activity coefficient of PbS and X_{PbS} is the molar ratio of PbS.

The activity of PbS was determined from the equation

$$a_{\mathrm{PbS}} = \frac{p_{\mathrm{PbS}}}{p^0_{\mathrm{PbS}}} \tag{5}$$

where p_{PbS} is the pressure of PbS above the Cu_2S–PbS solution and p^0_{PbS} is the pressure of pure liquid PbS. Considering the previously determined [14] vapour pressure (in Pa) of PbS above solid PbS

$$\log\left[p^0_{\mathrm{PbS(s)}}\right] = -11\,489.974/T + 12.366 \tag{6}$$

and enthalpy of fusion of PbS [9], $\Delta H^{\ominus} = 49\,400$ J mol^{-1}, the equation for the vapour pressure above liquid PbS has been derived in the form

$$\log\left[p^0_{\mathrm{PbS(l)}}\right] = -8908.249/T + 10.503 \tag{7}$$

From eqn. (4), and considering eqns. (3), (5) and (7), the values of the activity coefficient above Cu_2S–PbS have been calculated. Based on the experimental values, the coefficients of the Redlich–Kister equation [15] have been calculated, the equation for the two-constituent system being expressed as

$$RT \ln \gamma_{\mathrm{PbS}} = (1 - X_{\mathrm{PbS}})^2\left[A_0 - A_1(4X_{\mathrm{PbS}} - 1) - A_2(1 - 2X_{\mathrm{PbS}})(6X_{\mathrm{PbS}} - 1)\right] \tag{8}$$

where A_i are equation coefficients, R is the gas constant and T is the temperature in K.

For each series of measurements the linear regression method in the system of coordinates ln γ in dependence on $(1 - X^2_{\mathrm{PbS}})$ [16] has been used. From the obtained equations the values of the activity coefficient in the state of infinite dilution, γ^0_{PbS}, have been determined by means of extrapolation of X_{PbS} to zero.

The values of γ^0_{PbS} thus obtained have been described by means of the equation:

$$\log \gamma^0_{\mathrm{PbS}} = A + \frac{B}{T} \tag{9}$$

RESULTS OF MEASUREMENTS

Analysis of the gas phase constituents above the sample of Cu_2S–PbS has been performed at a temperature of 1030 K. Measurements of total ion currents were made during isothermal evaporation of PbS from the Cu_2S–PbS melt by means of the JEOL IMS-01BK mass spectrometer; the ion currents of S_2^+, Pb^+ and PbS^+ were recorded. On analysing the respective parts of the currents it was found that the total ion current of Pb^+ originated from PbS fragmentation in the region of the ion source, whereas

TABLE 3

Results of measurements of vapour pressure of PbS by the Knudsen method for $T = 1042$ K and $A_e = 0.0728$ mm^2

PbS (wt.%)	X_{PbS}	p_{PbS} (Pa)	a_{PbS}	γ_{PbS}
1	2	3	4	5
79.12	0.716	21.40	0.248	0.346
78.11	0.704	21.68	0.251	0.357
76.64	0.686	21.58	0.250	0.364
75.77	0.675	21.66	0.251	0.371
73.95	0.654	21.70	0.251	0.384
73.17	0.645	21.73	0.252	0.390
71.30	0.623	21.68	0.251	0.403
69.76	0.605	21.63	0.250	0.414
68.50	0.591	21.25	0.246	0.416
67.57	0.581	20.62	0.239	0.411
66.89	0.573	20.11	0.233	0.406
66.40	0.568	19.78	0.229	0.403
66.15	0.565	19.65	0.228	0.403
65.09	0.554	18.87	0.219	0.395
63.40	0.535	17.70	0.205	0.383
62.17	0.522	16.90	0.196	0.375
61.20	0.512	16.28	0.189	0.368
60.18	0.501	15.65	0.181	0.362
58.69	0.486	15.31	0.172	0.355
58.32	0.482	15.71	0.170	0.354
57.55	0.474	14.10	0.163	0.344
57.38	0.472	15.27	0.166	0.351
57.19	0.470	15.08	0.164	0.348
56.77	0.466	14.92	0.162	0.347
56.36	0.462	14.70	0.160	0.345
56.32	0.462	13.39	0.155	0.336
55.75	0.456	14.35	0.156	0.341
55.33	0.452	14.07	0.153	0.338
55.12	0.450	13.98	0.152	0.337
54.98	0.448	12.66	0.147	0.327
54.65	0.445	13.78	0.150	0.336
52.65	0.425	10.92	0.126	0.298
52.09	0.420	12.39	0.136	0.323
51.10	0.410	11.88	0.130	0.317
50.32	0.403	11.57	0.127	0.315
49.49	0.395	11.16	0.122	0.310
48.66	0.387	10.73	0.118	0.304
47.83	0.379	10.41	0.114	0.301
47.07	0.372	9.11	0.106	0.284
46.92	0.370	10.03	0.110	0.297
45.68	0.359	9.46	0.104	0.289
44.73	0.350	9.08	0.100	0.284
42.33	0.328	8.06	0.088	0.267
41.97	0.325	7.96	0.086	0.266

TABLE 3 (continued)

PbS (wt.%)	X_{PbS}	p_{PbS} (Pa)	a_{PbS}	γ_{PbS}
1	2	3	4	5
40.88	0.315	7.60	0.083	0.262
40.75	0.314	6.87	0.080	0.253
39.72	0.305	7.19	0.078	0.256
38.32	0.292	6.08	0.070	0.241
38.10	0.290	6.69	0.073	0.250
36.86	0.280	6.30	0.068	0.245
36.53	0.277	5.54	0.064	0.232
35.94	0.272	6.02	0.065	0.240
35.63	0.269	5.32	0.062	0.229
34.69	0.261	5.10	0.059	0.226
33.22	0.249	5.05	0.055	0.223
32.26	0.241	4.89	0.054	0.223
31.18	0.232	4.83	0.053	0.229
29.12	0.215	4.85	0.053	0.248
26.94	0.197	4.86	0.053	0.270
25.65	0.187	4.80	0.053	0.282

the values for the ion current of S_2^+ are within ca. 1% of that for PbS^+. Thus the assumption of the dominant character of PbS(g) in the gas phase above molten solutions of Cu_2S–PbS has been confirmed.

Tables 3–5 show the results of measurements of the vapour pressure of PbS above the Cu_2S–PbS system, determined by the Knudsen method. Columns 1 and 2 contain, respectively, the percentage and molar ratio of PbS, column 3 gives the values of vapour pressure of PbS calculated from eqn. (3), column 4 gives the values of activity calculated from eqns. (5) and (7), and column 5 gives the values of the activity coefficient of PbS.

In Tables 3 and 5, values of the vapour pressure of PbS in the initial range of X_{PbS} oscillate around a certain constant value of p_{PbS}, which according to the assumptions made should be equal to the vapour pressure of PbS above pure solid PbS. At a temperature of 1042 K for $X_{PbS} \geqslant 0.59$ the value is $p_{PbS} = 21.59$ Pa, and at a temperature of 1103 K for $X_{PbS} \geqslant 0.647$ the value is $p_{PbS} = 87.95$ Pa. Values for the vapour pressure of PbS above pure solid PbS (p^0_{PbS}) determined in a previous work [14] were, respectively: p^0_{PbS} ($T = 1042$ K) = 20.711 Pa and p^0_{PbS} ($T = 1103$ K) = 88.629 Pa.

Therefore, the determined vapour pressures, p_{PbS}, above Cu_2S–PbS in the two-phase system are close to the vapour pressure p^0_{PbS} above pure solid PbS. At a temperature of 1081 K, measurements of the vapour pressure of PbS commenced when the system Cu_2S–PbS already existed as a liquid phase only.

In Table 6, the coordinates of the points of the liquidus line, determined geometrically from the experimental values of the activity coefficient as functions of temperature and constitution, are presented.

TABLE 4

Results of measurements of vapour pressure of PbS by the Knudsen method for $T = 1081$ K and $A_e = 0.0728$ mm^2

PbS (wt.%)	X_{PbS}	p_{PbS} (Pa)	a_{PbS}	γ_{PbS}
1	2	3	4	5
77.20	0.692	49.41	0.270	0.390
74.77	0.663	49.27	0.269	0.406
73.48	0.648	49.17	0.269	0.414
71.01	0.620	47.38	0.259	0.418
68.02	0.586	42.11	0.230	0.393
67.00	0.575	40.65	0.222	0.387
65.88	0.562	39.01	0.213	0.379
64.73	0.550	37.58	0.205	0.374
63.51	0.536	36.02	0.197	0.367
62.62	0.527	34.96	0.191	0.362
59.68	0.496	31.08	0.170	0.342
58.07	0.479	29.49	0.161	0.336
56.25	0.461	27.21	0.149	0.323
53.67	0.435	24.57	0.134	0.308
51.49	0.414	22.35	0.122	0.295
48.24	0.383	19.60	0.107	0.280
43.58	0.339	15.11	0.083	0.243
41.99	0.325	13.97	0.076	0.235
37.88	0.288	11.85	0.065	0.225
35.33	0.266	10.46	0.057	0.215
32.64	0.244	9.08	0.050	0.204
27.98	0.205	8.46	0.046	0.225
24.17	0.175	7.63	0.042	0.239
17.99	0.127	6.48	0.035	0.278
16.38	0.115	5.90	0.032	0.280

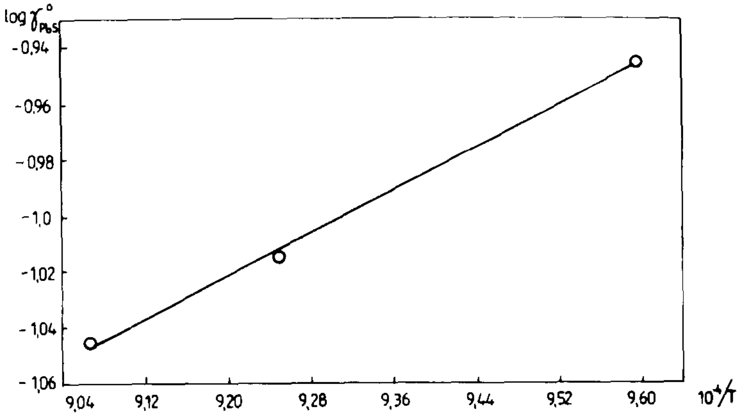

Fig. 1. Dependence of the activity coefficient in the state of infinite dilution (eqn. (11)) on temperature.

TABLE 5

Results of measurement of vapour pressure of PbS by the Knudsen method for $T = 1103$ K and $A_e = 0.0728$ mm^2

PbS (wt.%)	X_{PbS}	p_{PbS} (Pa)	a_{PbS}	γ_{PbS}
1	2	3	4	5
82.99	0.765	87.61	0.329	0.431
82.40	0.757	90.05	0.339	0.447
80.56	0.734	89.56	0.337	0.459
79.31	0.718	89.16	0.335	0.467
78.52	0.709	88.91	0.334	0.472
77.67	0.698	88.48	0.333	0.476
76.75	0.687	88.02	0.331	0.482
75.75	0.675	87.13	0.328	0.485
74.67	0.662	86.17	0.324	0.489
73.38	0.647	84.36	0.317	0.490
71.73	0.628	80.98	0.304	0.485
70.75	0.617	78.38	0.295	0.478
69.17	0.599	73.97	0.278	0.464
67.34	0.579	68.77	0.259	0.447
65.33	0.556	63.59	0.239	0.430
62.84	0.530	57.20	0.215	0.406
61.20	0.512	53.88	0.203	0.395
60.37	0.504	51.96	0.195	0.388
58.94	0.489	48.85	0.184	0.376
56.08	0.460	42.85	0.161	0.351
55.71	0.456	42.78	0.161	0.353
54.65	0.445	40.36	0.152	0.341
53.51	0.434	38.30	0.144	0.332
52.34	0.422	36.69	0.138	0.327
50.69	0.406	34.09	0.128	0.315
49.39	0.394	32.07	0.121	0.306
47.95	0.380	30.04	0.113	0.297
45.91	0.361	27.14	0.102	0.283
44.34	0.347	25.19	0.095	0.273
42.65	0.331	23.19	0.087	0.263
40.18	0.309	20.39	0.077	0.248
38.23	0.292	18.32	0.069	0.236
32.97	0.247	13.25	0.050	0.202
30.63	0.227	12.96	0.049	0.214
27.94	0.205	12.66	0.048	0.232
24.06	0.174	11.79	0.044	0.254
20.87	0.149	11.15	0.042	0.281

Based on the coordinates of the points of the liquidus line (Table 6), the regions of existence of a homogeneous liquid phase, for which the activity of PbS has been determined, have been delineated.

The experimental values of a_{PbS} and γ_{PbS}, the activity coefficient, above liquid Cu_2S–PbS have been used to determine the Redlich–Kister coeffi-

TABLE 6

Coordinates of the points of the liquidus line for the Cu_2S–PbS system determined in the present work

No.	T (K)	PbS (wt.%) (2)	PbS (wt.%) (1)
1	2	3	4
1	1042	–	68.5
2	1081	32	71.5
3	1103	31.5	72.5

cients [15]. The following form of eqn. (8) has been obtained

$$\ln \gamma_{PbS} = (1 - X_{PbS})^2\left[-5.84 + \frac{2756.26}{T} + \left(3.9 - \frac{5058.7}{T}\right)(4X_{PbS} - 1) - \left(1.315 - \frac{3115.727}{T}\right)(1 - 2X_{PbS})(6X_{PbS} - 1)\right] \tag{10}$$

Equation (9) for the activity coefficient γ^0_{PbS} in the state of infinite dilution, as presented in Fig. 1, has taken the form

$$\log \gamma^0_{PbS} = \frac{1913.95}{T} - 2.78 \tag{11}$$

DISCUSSION OF RESULTS

Investigations of the Cu_2S–PbS solution by means of a mass spectrometer have shown that the predominant constituent of the gas phase in the investigated range of temperature is PbS(g). This corroborates the earlier conclusion on the congruent evaporation of lead sulphide [14].

By means of mass effusion, measurements of vapour pressure above the Cu_2S–PbS system at constant temperatures of 1042, 1081 and 1103 K have been carried out. The initial concentration of PbS in the samples was 80, 78 and 83 wt.%, respectively.

During the isothermal evaporation, the amount of PbS in the samples decreased until its final concentration was 25.65, 16.38 and 20.87 wt.%, respectively.

Utilising the results for the vapour pressure of PbS above the Cu_2S–PbS system in the range of existence of a homogeneous liquid phase, together with previously calculated vapour pressures above pure PbS, the activity of PbS in the investigated binary solution of lead and copper sulphides has been calculated.

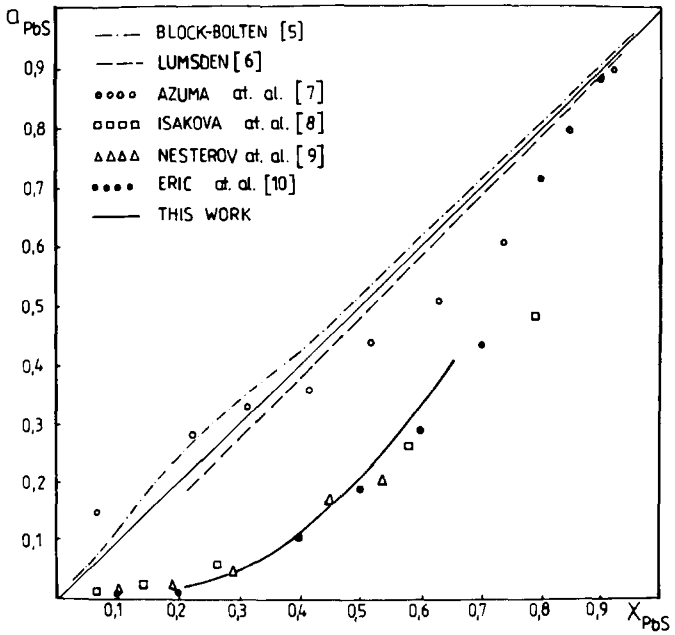

Fig. 2. Dependence of PbS activity in the system Cu_2S–PbS (eqn. (10)) vs. concentration of PbS at 1473 K compared with literature data.

The temperature and concentration dependence of the activity of PbS has been described by the Redlich–Kister equation (eqn. (10))

$$\begin{aligned}\ln(a_{\mathrm{PbS}}/X_{\mathrm{PbS}}) &\\ = (1-X_{\mathrm{PbS}})^2\Big[-5.84+\frac{2756.26}{T}&+\Big(3.9-\frac{5058.7}{T}\Big)(4X_{\mathrm{PbS}}-1)\\ -\Big(1.315-\frac{3115.727}{T}\Big)&(1-2X_{\mathrm{PbS}})(6X_{\mathrm{PbS}}-1)\Big] \qquad (12)\end{aligned}$$

A comparison of the results obtained with literature data is presented in Fig. 2. The obtained results point to the appearance of negative deviation from the ideal in the investigated system. Qualitatively, the results are in good conformity with the results obtained by Isakova [8], Nesterov [9] and Eric [10] and their co-workers.

The dependence of the activity coefficient of PbS in Cu_2S–PbS on the PbS concentration allowed determination of the coordinates of the points of the liquidus line in the phase system PbS–Cu_2S. The results presented in Fig. 3 point to satisfactory compliance with the phase equilibrium diagram [3]. The obtained vapour pressures of PbS in the two-phase range are in exact agreement with the vapour pressures above pure PbS which were determined in earlier work [14]. This validates the measurement methods used.

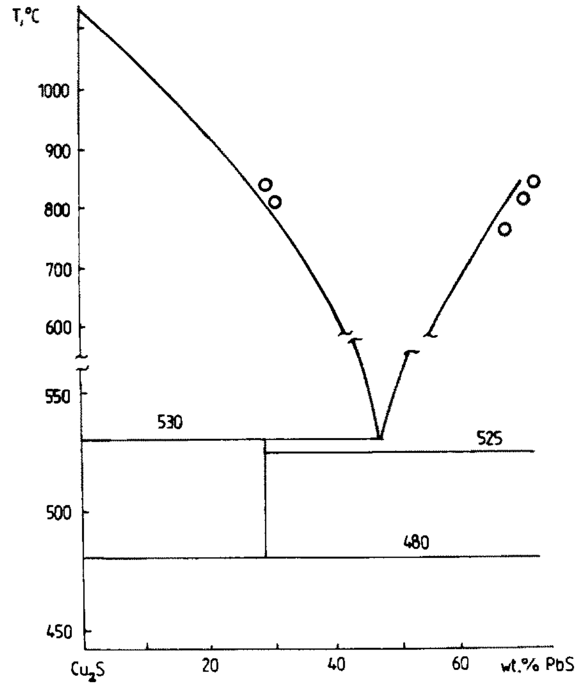

Fig. 3. Position of determined points of the liquidus line on the phase equilibrium diagram of Cu_2S–PbS [3].

The concentration extrapolation of the eqn. (10) allowed calculation of the activity coefficient of PbS in the state of infinite dilution, the temperature dependence of the coefficient being described by eqn. (11):

$$\log \gamma^0_{PbS} = \frac{1913.95}{T} - 2.78$$

In Fig. 4 the obtained results are presented in comparison with the literature data. The currently obtained value of $\gamma^0_{PbS} = 0.033$ at a temperature of 1473 K is in good agreement with the data of Eric and Timucin [10]. It is however, lower, than those of Nesterov et al. [9] and of Sinha et al. [11]. In the work of Sinha et al. [11], the value was determined based on measurements of the distribution coefficient of lead between copper and copper matte, utilising a series of thermodynamic data; some of the data were chosen arbitrarily owing to the lack of experimental data. Thus, the error in their γ^0_{PbS} value [11] includes experimental errors and also errors of estimation of the thermodynamic data.

The value of γ^0_{PbS} obtained in the present work is based on temperature and concentration extrapolation. This fact should be also considered when evaluating the precision of the obtained value. Continuation of work in this area would seem to be necessary.

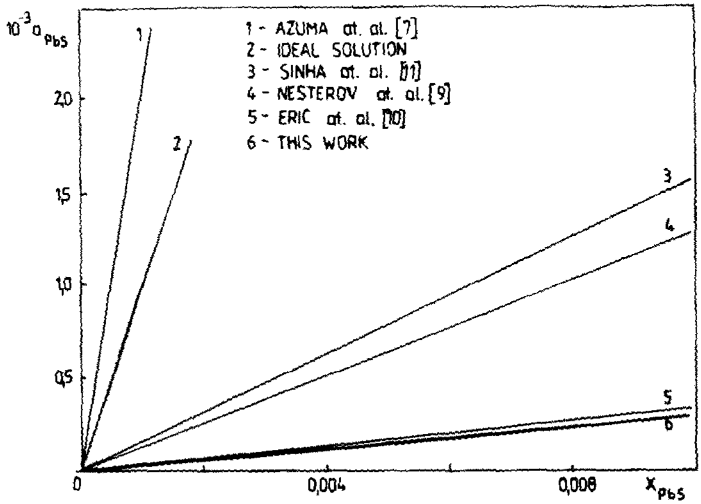

Fig. 4. Comparison of determined activity of PbS in the diluted solution with literature data.

Utilising the method of effusive measurement of vapour pressure, it is possible to determine directly the value of the activity coefficient of PbS in the Cu_2S–PbS solution in the range of low concentrations of lead sulphide.

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