Thermochimica Acta, 137 (1989) 269–279
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

VAPOUR PRESSURE AND THERMODYNAMICS OF PbS(s)

JAN BOTOR, GRAŻYNA MIŁKOWSKA and JAN KONIECZNY
Institute of Non-Ferrous Metals, 44-101, Gliwice (Poland)

(Received 17 February 1988)

ABSTRACT

Vapour pressure measurements over solid PbS were carried out using two methods: the Knudsen (K) method and the Knudsen cell–mass spectrometry (K–MS) method. The K method was applied over the temperature range 878–1026 K and the K–MS method was employed over the temperature range 796–1096 K.

It was confirmed that PbS(g) evaporates congruently according to the reaction $PbS(s) \rightleftharpoons PbS(g)$. The temperature dependence of PbS vapour, according to the results of the K method is expressed by the equation

$$\log p = -11498.974\left(\frac{1}{T} - \frac{1}{979}\right) + 0.6268$$

where p is given in Pa and T in K. The value of the standard PbS sublimation enthalpy from the results of the K method is 232.4 ± 0.1 kJ mol^{-1}. It agrees with some literature data. The value of $\Delta H^{\ominus}$(298 K) of the dimer dissociation reaction $Pb_2S_2(g) \rightleftharpoons 2PbS(g)$ is 184.3 ± 0.5 kJ mol^{-1} and agrees with literature data.

The standard enthalpy of the dissociation reaction $PbS(g) \rightleftharpoons Pb(g) + 0.5S_2(g)$, determined by the K–MS method, is 156.2 ± 0.7 kJ mol^{-1} and this differs significantly from the value of 120.7 ± 11 kJ mol^{-1} given by Colin and Droward. The authors of this work are of the opinion that both of these values are unreliable and the precise determination of the standard enthalpy still remains a problem. It is hoped that the true value of the standard enthalpy of the PbS dissociation reaction will be found within the region of 140 ± 20 kJ mol^{-1}.

INTRODUCTION

The determination of the thermodynamic properties of metal sulphide phases is a relevant basis for the analysis of many metallurgical processes. For copper or lead metallurgy the systems Cu_2S–FeS–PbS or PbS–FeS are of interest. This work attempts to determine the thermodynamic properties of PbS as a first step in the study of the above systems.

The vapour pressure of solid PbS has been determined many times using various methods: Knudsen [1,2], transport [5,6], torsion effusion [7], Langmuir [8], boiling point [9] and the Knudsen cell–mass spectrometry method [10,11]. The results obtained using the above methods are collected in Table 1 (columns 1 and 2). On the basis of the temperature dependence of the PbS

0040-6031/89/$03.50

TABLE 1

Literature data on the PbS sublimation reaction enthalpy

Literature data $\Delta H^{\ominus}(298\ \mathrm{K})$ (kJ mol^{-1})		Temperature range (K)	Re-calculated data $\Delta H^{\ominus}(298\ \mathrm{K})$ (kJ mol^{-1})		Reference
Second law	Third law		Second law	Third law	
230.1	–	879–1069	192.3 ± 8.2	229.5 ± 3.8	1, 12
196.6	225.9	1093–1268	222.0 ± 10.8	226.8 ± 8.7	9
238.0	234.3	1050–1197	238.2 ± 2.8	235.9 ± 0.3	2
233.5	228.4	877–1020	233.9 ± 0.5	228.9 ± 0.4	7
224.7	229.3	1100–1300	236.1 ± 3.8	230.2 ± 0.6	3
228.1	228.9	1073–1123	231.4 ± 4.3	229.8 ± 0.2	4
231.0	229.7	1113–1373	227.6 ± 6.1	230.5 ± 0.4	5
232.1	230.5	985–1080	232.0 ± 6.2	233.7 ± 0.1	10
226.2	–	773– 923	226.0 ± 6.0	241.2 ± 2.0	8
232.5	–	700–1388	232.2 ± 1.0	230.0 ± 0.6	13
255.6	232.6	995–1313	252.6 ± 2.3	235.2 ± 2.1	6
–	–	950–1100	232.2 ± 1.6	231.2 ± 0.2	14

vapour pressure and using the methods of calculation resulting from the second and third laws of thermodynamics, values of the standard PbS sublimation enthalpy $\Delta H^{\ominus}(298\ \mathrm{K})$ were calculated. The determined Gibbs energy functions were applied in the calculations, utilizing the thermodynamic data included in ref. 12. The calculated values of $\Delta H^{\ominus}(298\ \mathrm{K})$ of the PbS sublimation reaction are given in Table 1. Significant differences in the $\Delta H^{\ominus}(298\ \mathrm{K})$ values are indicated. The values of the standard enthalpy of the PbS sublimation, determined using the second law, range between 192 ± 8 and 252 ± 1 kJ mol^{-1}, whereas the values calculated using the third law range between 227 ± 9 and 241 ± 12 kJ mol^{-1}. Tests carried out [10,11,14] have indicated that PbS evaporates congruently according to the reaction

$$\mathrm{PbS(s)} \rightleftarrows \mathrm{PbS(g)} \tag{1}$$

In the gaseous phase PbS dissociation products are present. The dissociation proceeds according to the reaction [10,11]

$$\mathrm{PbS(g)} \rightleftarrows \mathrm{Pb(g)} + 0.5\mathrm{S_2(g)} \tag{2}$$

and the reaction [10]

$$\mathrm{Pb_2S_2(g)} \rightleftarrows 2\mathrm{PbS(g)} \tag{3}$$

The available data concerning the standard enthalpies of reactions (2) and (3) are also not in agreement. Utilizing the spectrometric data included in ref. 10, the value $\Delta H^{\ominus}(298)$ of reaction (2), calculated using the third law method, is 120.3 ± 3.9 kJ mol^{-1} and that calculated using the second law is 90.8 ± 7.5 kJ mol^{-1}. The value $\Delta H^{\ominus}(298\ \mathrm{K})$ of this reaction, calculated using thermodynamic data [12], is 127.7 kJ mol^{-1}. The standard enthalpy of reaction (3) given by Mills [12] is 187.4 kJ mol^{-1}. The significant discrepancies in the specific values of the standard PbS sublimation enthalpies, as well as the discrepancies in the enthalpies of the dissociation reaction, provide good reason for studying this system.

The aim of this work is to determine the temperature dependence of the vapour pressure over solid PbS using two independent methods: the Knudsen effusion method and the Knudsen cell–mass spectrometry method. In addition the chemical equilibrium constants are calculated and thus the thermodynamic data of the system are investigated.

EXPERIMENTAL

Samples

Spectrally pure PbS was used. Phase analysis indicated the presence of $PbSO_4$ in lead(II) sulphide. Sample purification was carried out by reduction with carbon monoxide at 773 K. Subsequently, the lead(II) sulphide was twice sublimated in vacuo at 950 K. The X-ray phase analysis of the PbS thus obtained did not indicate the presence of any other components.

Experimental procedure

The vapour pressure over solid PbS was determined using two methods. The Knudsen effusion method was used to measure the rate of mass loss $(\mathrm{d}g/\mathrm{d}t)$. In this case

$$p = (\mathrm{d}g/\mathrm{d}t)\cdot(2\pi RT/M)^{1/2}/W\cdot A \tag{4}$$

where p is the vapour pressure of the substance tested, T is the absolute temperature, M is the assigned molecular weight of the effusing vapour, W is the transmission probability of the orifice and A is the area of the effusion orifice.

Knudsen cell–mass spectrometry was the second method applied. The intensities of the ion currents of the individual components were utilized for determining their partial pressures.

A TA1 Mettler thermobalance was used to measure the rate of mass loss via the Knudsen method. The sensitivity of the mass measurement was 10^{-5} g and the recording error was 2.5×10^{-6} g. During the measurements the 10^{-3} Pa vacuum was maintained. The temperature was measured using a Pt,Pt–Rh-10% thermocouple. Before starting the actual measurements, the temperature measuring system was calibrated for the melting points of lead, aluminium, silver and copper. Graphite Knudsen cells were used, whose effective orifice areas were determined experimentally. The Knudsen cell with an effective effusion orifice area of 0.0390 ± 0.0006 mm^2 was denoted as C_1 and the cell with an orifice area of 0.1977 ± 0.0044 mm^2 was denoted as C_2. These cells were heated in vacuo at 1200 K for 8 h to degas them. The measurements were made at 20 different temperatures, chosen at random, in the range 850–1013 K.

The Knudsen cell–mass spectrometry measurements were taken using a Jeol IMS-01BK mass spectrometer. The graphite cells, as described above, were used. Temperature was measured using a W–Re5, W–Re26 thermoelement. The temperature measuring system was calibrated for the melting points of copper and Sb, Ag eutectics. The measurements were taken with the following parameters: ionization voltage, 12 V; ionization current, 300 μA; resolution power, $m/\Delta m = 600$. After identifying the ions S_2^+, Pb^+, PbS^+ and $Pb_2S_2^+$ in the gaseous phase, those of the highest isotope fraction were measured in subsequent experiments, i.e. $^{64}S_2^+$, $^{208}Pb^+$, $^{240}PbS^+$ and $^{478}Pb_2S_2^+$.

The intensities of these ions were recorded several times at several temperatures, after the ion currents had stabilized. Temperature was changed randomly within the region where there was a possibility of recording the PbS ion intensity. Detailed descriptions of the Knudsen method and the Knudsen cell–mass spectrometry method have been given in previous reports [15,16].

Data treatment

The system investigated is in equilibrium as described in reactions (1) and (2). The equilibrium of reaction (2) is determined by the PbS dissociation constant

$$K_Z = \frac{x_{\mathrm{Pb}} \cdot x_{\mathrm{S_2}}^{1/2}}{x_{\mathrm{PbS}}} \cdot p_{\mathrm{tot}}^{1/2} \tag{5}$$

Taking into account the effusion gas flow through the orifice the condition

$$\frac{\mathrm{d}n_{\mathrm{Pb}}}{\mathrm{d}t} = 2\frac{\mathrm{d}n_{\mathrm{S_2}}}{\mathrm{d}t} \tag{6}$$

is fulfilled. Thus by applying the Knudsen equation (eqn. (4)), the relation

$$\frac{p_{\mathrm{Pb}}}{\sqrt{M}_{\mathrm{Pb}}} = 2\frac{p_{\mathrm{S_2}}}{\sqrt{M}_{\mathrm{S_2}}} \rightarrow \frac{x_{\mathrm{Pb}}}{\sqrt{M}_{\mathrm{Pb}}} = 2\frac{x_{\mathrm{S_2}}}{\sqrt{M}_{\mathrm{S_2}}} \tag{7}$$

results. By substituting in eqn. (5), the equation for the total pressure over the PbS sample is obtained

$$p_{\mathrm{tot}} = \frac{K_Z^2\left[1 - \left(1 + 2\sqrt{M}_{\mathrm{Pb}}/M_{\mathrm{S_2}}\right)/x_{\mathrm{S_2}}\right]^2}{4\left(M_{\mathrm{Pb}}/M_{\mathrm{S_2}}\right) \cdot x_{\mathrm{S_2}}^3} \tag{8}$$

where p_{tot} is the total pressure over the PbS sample, x_i and p_i are the molar fractions and partial pressures, respectively, of the individual components, n_i is the number of moles of a given component, K_{Z} is the PbS dissociation constant and M is the molar mass of a component.

The value of the constant K_{Z} was calculated for each measurement temperature using the data given in ref. 12. The total pressure was also determined by the Knudsen equation

$$p_{\mathrm{tot}} = \frac{\mathrm{d}g}{\mathrm{d}t}\frac{\sqrt{2\pi RT}}{\overline{M}} \Big/ A \cdot W \tag{9}$$

where $\overline{M}$ is the mean molecular gas mass, calculated from the equation

$$\overline{M} = \left[x_{\mathrm{Pb}} M_{\mathrm{Pb}}^{-1/2} + x_{\mathrm{PbS}} M_{\mathrm{PbS}}^{-1/2} + x_{\mathrm{S_2}} M_{\mathrm{S_2}}^{-1/2}\right]^{-2} \tag{10}$$

By comparing eqns. (8) and (9), an equation was obtained which allowed the determination of the molar fractions of the individual components in the gaseous phase.

The pressures of the individual components in the Knudsen cell–mass spectrometry method were calculated from the ion current intensity measurements. The ion current I_i^+ of the i component in the ion source, recorded in the detection system, is related to the pressure p_i of the component in the Knudsen cell and the temperature T by

$$p_i = \frac{I_i^+ T}{U_i \sigma_i \gamma_i S} \tag{11}$$

where σ_i is the active cross-section of particle ionization, γ_i is the coefficient of the electron multiplier amplification used for amplifying the measured ion current I_i^+, S is the mass spectrometer sensitivity constant and U_i is the isotope fraction. The value of the constant spectrometer sensitivity, determined from eqns. (9) and (11), allows the calculation of the partial pressures of the individual components.

The temperature dependence of the PbS vapour pressure was determined to be of the form

$$\log p = -A\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) + B \tag{12}$$

where A and B are constant coefficients and T_{m} is the mean temperature.

The calculations of the standard enthalpies of the reaction $\Delta H^{\ominus}(298\ \mathrm{K})$ were carried out using the second and third laws of thermodynamics.

The third law has the form [17]

$$\Delta H^{\ominus}(298\ \mathrm{K}) = -RT\ \ln\left(K_{\mathrm{p}}/\mathrm{Pa}^{m}\right) + T\Delta\phi^{\ominus}(\tau) + 11.526mRT \tag{13}$$

for the reaction described by the equilibrium constant K_{p}. In this equation,

TABLE 2

The Gibbs free energy functions $[G_T^{\ominus} - H^{\ominus}(298)]/T$(J mol^{-1} K^{-1})

T (K)	S_2(g)	Pb(g)	PbS(s)	PbS(g)	Pb_2S_2(g)
298	228.07	174.01	91.21	254.35	350.20
400	229.37	175.20	93.17	254.72	353.40
500	231.87	176.90	96.89	256.91	359.45
600	234.71	178.70	101.09	259.65	366.25
700	237.59	180.47	105.34	262.52	373.08
800	240.39	182.16	109.48	265.34	379.68
900	243.07	183.76	113.46	268.07	385.97
1000	245.62	185.28	117.25	270.66	391.92
1100	248.04	186.71	120.86	273.13	397.54

K_p is the equilibrium constant of the reaction with the unit Pa^m, $\Delta\phi^{\ominus}$ is the Gibbs free enthalpy function at temperature T, related to 298 K, while

$$\phi^{\ominus}(T) = -\frac{\Delta H^{\ominus}(T)}{T} + \Delta S^{\ominus}(T) + S^{\ominus}(298) \qquad (14)$$

where $\Delta H^{\ominus}(T)$ and $\Delta S^{\ominus}(T)$ are the enthalpy and entropy increases on heating the substance from 298 K to T. R is the gas constant. The last part of eqn. (13) results from the fact that the standard pressure is 101 325 Pa.

The Gibbs free energy functions used in this work are listed in Table 2. In the calculations, eqn. (14) was employed using the thermochemical data from ref. 12.

The value of the standard reaction enthalpy was calculated using standard data processing by the sigma method, applying [18]

$$\Sigma(T) = -R\ \ln(K_p/\text{Pa}^m) + \Delta\phi^{\ominus} + 11.526R \qquad (15)$$

RESULTS

Tables 3 and 4 present the results of the PbS vapour pressure measurements taken using the Knudsen effusion method. They are listed in sequence of measurement. Column 1 gives the temperature, column 2 gives the mass loss rate, column 3 lists the total pressure over the PbS surface and column 4 gives the partial PbS pressure. The fifth column presents the third-law values of the standard PbS sublimation enthalpy. Second-law values of the standard sublimation enthalpy are given as footnotes to Tables 3 and 4.

From the PbS vapour pressure data given in Tables 3 and 4, the temperature dependence of the PbS vapour pressure was obtained according to eqn. (12)

$$\log p = -11\,489.974\left(\frac{1}{T} - \frac{1}{T_m}\right) + 0.6268 \qquad (16)$$

where p is given in Pa, T is in K and $T_m = 979$ K.

TABLE 3

The mass loss rates, vapour pressures and standard PbS sublimation enthalpy obtained by the Knudsen method (C_1 cell)

Temperature (K)	$dg/dt \times 10^{10}$ (kg s^{-1})	p_{tot} (Pa)	p_{PbS} (Pa)	$\Delta H^{\ominus}$(298 K) (kJ mol^{-1})
945	1.497	1.79	1.734	231.9
1027	12.151	15.20	14.655	232.7
986	4.113	5.035	4.863	233.0
1014	8.482	10.539	10.165	233.0
1045	19.112	24.128	23.247	232.6
965	2.592	3.134	3.034	232.1
1073	39.276	50.275	48.408	232.0
979	3.546	4.323	4.179	232.6
1015	9.103	11.312	10.915	232.6
1008	7.566	9.365	9.040	232.6
993	5.238	6.435	6.215	232.6
936	1.166	1.386	1.344	232.6
926	0.511	0.607	0.586	231.8
951	1.549	1.859	1.799	232.8
1037	15.481	19.469	18.760	232.8
959	2.137	2.575	2.493	232.2
1060	28.517	36.254	34.928	232.1
996	5.896	7.248	7.005	232.1
1011	8.009	10.046	9.694	232.7

Mean value, 232.5 ± 0.1 kJ mol^{-1}; second-law value, 230.0 ± 2.4 kJ mol^{-1}.

TABLE 4

The mass loss rates, vapour pressures and standard PbS sublimation enthalpy obtained by the Knudsen method (C_2 cell)

Temperature (K)	$dg/dt \times 10^{10}$ (kg s^{-1})	p_{tot} (Pa)	p_{PbS} (Pa)	$\Delta H^{\ominus}$(298 K) (kJ mol^{-1})
878	0.904	0.205	0.199	231.9
918	3.101	0.719	0.698	232.5
898	1.729	0.396	0.385	232.0
996	29.369	7.116	6.879	232.4
947	7.313	1.724	1.670	232.5
1017	49.800	12.200	11.774	232.4
985	2.252	5.419	5.242	232.0
921	3.514	0.816	0.792	232.3
1007	36.232	8.832	8.523	232.9
945	5.788	1.365	1.320	233.9
955	9.332	2.211	2.140	232.6
912	2.475	0.572	0.555	232.6
1026	63.348	15.593	15.044	232.3
964	12.542	2.985	2.890	232.2
1036	81.522	20.167	19.450	232.2
937	5.582	1.309	1.268	232.4
1013	43.810	10.713	10.338	232.6
974	16.279	3.896	3.769	232.3
968	13.671	3.261	3.155	232.3

Mean value, 232.4 ± 0.1 kJ mol^{-1}; second-law value, 231.6 ± 2.2 kJ mol^{-1}.

TABLE 5

Partial vapour pressures and standard enthalpies of reactions (1), (2) and (3) obtained by the Knudsen cell–mass spectrometry method (series I)

T (K)	Partial pressures (Pa)				$\Delta H^{\ominus}$(298 K) (kJ mol^{-1})		
	S_2	Pb	PbS	Pb_2S_2	(1)	(2)	(3)
1008	0.04954	4.01917	8.88768	0.02612	232.8	153.5	179.9
931	–	0.56770	0.87990	–	234.0	–	–
984	0.01638	2.45254	4.64784	0.01427	233.0	153.2	181.6
814	–	0.02125	0.01750	–	232.1	–	–
873	–	0.13208	0.16730	–	232.0	–	–
1073	0.27742	14.59881	34.55802	0.07659	235.1	156.6	176.6
966	0.00731	1.49237	2.85060	0.00862	232.8	153.6	182.2
892	–	0.21937	0.31115	–	232.2	–	–
996	0.02036	3.18801	6.65783	0.02000	232.8	155.1	180.6
947	0.00340	0.96126	1.78381	0.00458	232.1	153.4	181.1
1096	0.38697	19.56040	47.99702	0.14849	236.8	158.8	180.2
1045	0.08500	7.80593	18.17116	0.06176	234.8	157.5	181.4

Mean values, 233.4 ± 0.5, 155.2 ± 0.8 and 180.5 ± 0.6 kJ mol^{-1}; second law, 223.8 ± 2.8, 145.2 ± 18.0 and 189.2 ± 6.4 kJ mol^{-1}.

The mean value of the standard PbS sublimation enthalpy from the values calculated using the second and third laws is 232.4 ± 0.1 kJ mol^{-1}.

The Knudsen cell–mass spectrometry measurements were carried out in two series: series I, Knudsen cell C_1 (temperature range, 814–1096 K); series II, Knudsen cell C_2 (temperature range, 798–985 K). Tables 5 and 6 present

TABLE 6

Partial vapour pressures and standard enthalpies of reactions (1), (2) and (3) obtained by the Knudsen cell–mass spectrometry method (series II)

T (K)	Partial pressures (Pa)				$\Delta H^{\ominus}$(298 K) (kJ mol^{-1})		
	S_2	Pb	PbS	Pb_2S_2	(1)	(2)	(3)
900	0.00018	0.14418	0.23270	0.00078	236.5	155.7	189.8
847	–	0.03125	0.04167	–	235.3	–	–
796	–	0.00537	0.00537	–	235.2	–	–
880	0.00013	0.10591	0.16585	0.00046	233.9	153.1	186.9
962	0.00381	1.15174	2.24513	0.01023	233.9	155.8	186.7
927	0.00009	0.44688	0.76546	0.00300	234.0	163.5	187.3
994	0.01185	2.34057	5.21212	0.02256	234.4	157.5	185.3
942	0.00135	0.61299	1.16313	0.00492	234.3	156.4	187.5
985	0.00748	1.86508	4.10367	0.01782	234.3	157.9	185.7
971	0.00385	1.20226	2.64962	0.01062	234.6	158.3	186.0
820	–	0.01473	0.01885	–	233.5	–	–

Mean values, 234.5 ± 0.3, 157.4 ± 0.9 and 186.9 ± 0.5 kJ mol^{-1}; second law, 236.0 ± 2.6, 148.3 ± 19.4 and 199.5 ± 6.0 kJ mol^{-1}.

the results of the partial pressure measurements for the individual components, as well as the standard enthalpies of reactions (1), (2) and (3), in the sequence of measurement. Column 1 lists the temperatures and columns 2–5 list the partial pressures of S_2, Pb, PbS and Pb_2S_2, respectively. Column 6 presents the third-law values of the standard PbS sublimation enthalpy. Columns 7 and 8 include the third-law values of the standard enthalpies of reactions (2) and (3). In addition, the mean values of the standard enthalpies calculated using the third-law method and the standard enthalpy values of the reactions calculated using the second law are given as footnotes to Tables 5 and 6. The mean value of the standard PbS sublimation enthalpy, based on the third law, is 233.9 ± 0.3 kJ mol^{-1}.

For the results obtained by the Knudsen cell–mass spectrometry method the temperature dependence of the PbS vapour pressure was determined according to eqn. (12)

$$\log p = -11\,521.227\left(\frac{1}{T} - \frac{1}{T_\text{m}}\right) - 0.0089 \qquad (17)$$

where p is in Pa, T is in K and $T_\text{m} = 935.1$ K.

DISCUSSION OF RESULTS

The tests carried out using the mass spectrometry method indicate that PbS(g) is the dominant component in the gaseous phase. The fraction of $Pb_2S_2(g)$ dimer particles is very small in this phase. The dimer ion current intensity is approximately 500 times lower than that of the monomer. This composition of the gaseous phase corresponds with previous investigations on congruent PbS evaporation [10,11].

The PbS vapour pressure measurements were carried out in the ranges 878–1026 K for the Knudsen method and 796–1096 K for the Knudsen cell–mass spectrometry method. The results of all measurements are given in the form of eqns. (16) and (17) for the first and second methods, respectively. The lack of dependence of the PbS vapour pressure on the effective effusion orifice area could suggest that the pressure measured is an equilibrium pressure. The results of the PbS vapour pressures obtained by the methods described are of the same order. For example, the PbS vapour pressure at 800 K is 0.010 Pa as measured by the Knudsen method and is 0.008 Pa as measured by the Knudsen cell–mass spectrometry method. The corresponding values at 850 K are 0.70 Pa and 0.060 Pa, the value at 900 K is 0.397 Pa and the values at 1000 K are 7.507 and 6.170 Pa. The standard sublimation enthalpy values for PbS, $\Delta H^\ominus(298\text{ K})$, given in Tables 3 and 4, show perfect agreement, independent of the calculation method applied. The mean value of $\Delta H^\ominus(298\text{ K})$ is 232.4 ± 0.1 kJ mol^{-1}. From the spectrometric measurements, the standard PbS sublimation enthalpy value, selected on the basis of the third law, is 234.2 ± 0.4 kJ mol^{-1}. This value is different from that obtained using the second law method by 4.05 ± 3.86 kJ mol^{-1}. Taking into account that the Knudsen method for vapour pressure measurement usually gives more precise results and that in this case the $\Delta H^{\ominus}$(298 K) values obtained using the second and third laws are in agreement, it can be stated that eqn. (16) for the temperature dependence of the PbS vapour pressure is determined with higher precision, and the $\Delta H^{\ominus}$(298 K) value of 232.4 ± 0.1 kJ mol^{-1} is more reliable. By comparing the results obtained with the data in the literature it can be seen that our results are similar to the $\Delta H^{\ominus}$(298 K) values given by Novoselova and Pasinkin [14] (232.2 ± 1.6 kJ mol^{-1}) and Colin and Droward [10] (232.0 ± 6.2 kJ mol^{-1}). As indicated by the data given in Table 1, the standard PbS sublimation enthalpy values calculated using the second and third laws [10,14] also show good agreement.

Tables 5 and 6 give the calculated values of the standard enthalpies of reactions (2) and (3) obtained from spectrometric tests. The comparison of the $\Delta H^{\ominus}$(298 K) values obtained for reactions (2) and (3) with the literature data uses the values calculated with the third law. For reaction (2) the $\Delta H^{\ominus}$(298 K) value obtained in this work is 156.2 ± 0.7 kJ mol^{-1}. It is significantly different from that obtained by Colin and Droward [10], who quote a value of 120.7 ± 11 kJ mol^{-1}. Both the value obtained in this work and that given by Colin and Droward seem to be rather unreliable owing to the large differences in the standard enthalpy values obtained using the second and third laws. These differences may result from errors in the ion current measurement, especially as regards S_2. These currents are very low in comparison with the PbS ion current: for example, at 900 K the S_2 to PbS ion current ratio is 1 : 500; at 995 K, it is 1 : 300. It should also be taken into account that the measured Pb ion current may be a sum of currents generated by PbS dissociation and its fragmentation. This would explain the lower PbS vapour pressures compared with those obtained by the Knudsen method. The error in the determination of the PbS(g) dissociation constant is affected by the error in the ion current intensity measurement as well as by the errors resulting from disregarding the probable PbS fragmentation.

The value of the standard enthalpy of reaction (3) obtained in this work is 184.3 ± 0.5 kJ mol^{-1} and is a mean value from the results obtained in the two series of measurements. The given value of $\Delta H^{\ominus}$(298 K) for reaction (3) is in agreement with the literature data. According to Mills [12] it is 187.7 ± 2.1 kJ mol^{-1} and according to Lin et al. [13] it is 187.5 kJ mol^{-1}.

REFERENCES

1 B.K. Veselovsky, Zh. Prikl. Khim., 15 (1942) 398.
2 K. Sudo, Sci. Rep. Res. Inst., Tohuku Univ., Ser. A, 2 (1950) 325; 12 (1960) 54.

3 O.G. Miller and M. Abdeev, Tr. Altai. Gorno-Metall. Nauchno-Issled. Inst., Akad. Nauk Kaz. SSR, 7 (1958) 182.
4 E.J. Boev and N.V. Minaeva, Zh. Fiz. Khim., 6 (1967) 1365.
5 R.A. Isakova and N.V. Nesterova, Zh. Neorg. Khim., 8 (1963) 50.
6 D.T. Ullrich, Naturwiss,-Phil. FFH, Dis. Braunschweig, 1954.
7 E.E. Hansen and R.A. Munir, High Temp. Sci., 2 (1970) 169.
8 C.M. Hsiao and M.W. Schlechten, J. Met., 4 (1952) 65.
9 R. Schenck and A. Albers, Z. Anorg. Chem., 105 (1918) 145.
10 R. Colin and J. Droward, J. Chem. Phys., 37 (1962) 1120.
11 W.A. Spicyn and P.A. Isakova, Izv. Akad. Nauk SSSR, 3 (1977) 56.
12 R.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974.
13 J.C. Lin, R.C. Sharma and Y.A. Chang, Bull. Alloy Phase Diagrams, 7 (1986) 374.
14 A.W. Novoselova and A.S. Pasinkin, Davlenie Para Letvcich Chalkogenidov Metallov, Nauka, Moscow, 1978.
15 J. Botor and A. Zajączkowski, Bull. Pol. Acad. Sci., 35 (1987) 453.
16 J. Golonka, J. Botor and M. Dulat, Rudy Met. Niezelaz., 21 (1976) 330.
17 D. Cubicciotti, J. Phys. Chem., 70 (1966) 2410.
18 G.N. Lewis, M. Randall, K.S. Pitzer and L. Brewer, Thermodynamics, McGraw-Hill, New York, 1961.