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Decomposition pressure and standard enthalpies of sublimation and of formation of iron monoselenide

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Abstract

The vapour pressure of iron selenide measured by the torsion method shows that in a first step at temperatures below 1149 K the compound sublimes according to the decomposition reaction

$$FeSe(s) \longrightarrow Fe(s) + 0.5Se_2(g)$$

The temperature dependence of the selenium pressure is well represented in the experimental range by the equation

$$\lg p(\mathrm{kPa}) = 6.96 \pm 0.45 - (12\,755 \pm 400)/T$$

with a standard sublimation enthalpy $\Delta_{sub}H°_{298}$ of 1 mol of Se_2 of 278 ± 8 kJ mol^{-1}, as calculated via the second and third laws from the experimental results. On increasing temperature over 1149 K, according to the phase diagram, the peritectoid modification of iron monoselenide in the δ' phase (approximately $FeSe_{0.96}$) occurs with a pressure–temperature equation practically equal to that found above FeSe(s):

$$\lg p(\mathrm{kPa}) = 6.98 \pm 0.48 - (12\,867 \pm 562)/T$$

1. Introduction

The phase diagram of the Fe–Se system [1, 2] shows that at high temperatures (above 800 K) this system presents a phase (δ phase, having a hexagonal NiAs-like structure) with a wide homogeneity range having the stoichiometric iron monoselenide as the iron-rich boundary. As reported by Schuster *et al.* [2] and according to Kullerud [3] at 1149 K the peritectoid decomposition of the δ phase to a high temperature modification of unknown structure (δ' phase, with an approximate formula $FeSe_{0.96}$) occurs (Fig. 1). In the iron-rich side of the phase diagram at 1215 K a eutectic equilibrium between iron and δ' phase is also present.

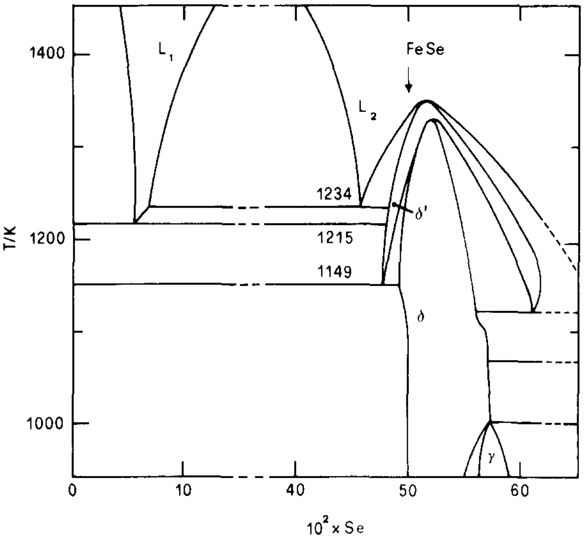

Fig. 1. Phase diagram of Fe–Se as reported in the literature [1–3].

The known thermodynamic parameters associated with the vaporization of FeSe are poor. In particular, as concerns the decomposition pressures of this compound apparently the only data are those reported by Rumyantsev *et al.* [4] obtained by the Knudsen effusion method and those measured by Svendsen [5] above FeSe in equilibrium with pure iron by using the same method. Unfortunately, both the total vapour pressures and the second law vaporization enthalpies evaluated from the slopes of the pressure–temperature equations (154 kJ mol^{-1} and 262 kJ mol^{-1} for Rumyantsev *et al.* [4] and Svendsen [5] respectively) are definitely in disagreement. Concerning standard enthalpy of the formation of iron monoselenide, Wagman *et al.* [6] reported a value of −75.3 kJ mol^{-1} derived from recalculation of solution calorimetry data due to Fabre

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[7] while Azerbaeva and Tseft [8] found $\Delta H^\circ_{298} = -58.2$ kJ mol^{-1} by employing the same technique. Grønvold [9] and Kapustinskii and Golutvin [10] found the values -66.9 kJ mol^{-1} and -75.3 ± 1.3 kJ mol^{-1} respectively by high temperature reaction calorimetry. From vapour pressures measured by Svendsen [5] and Rumyantsev *et al.* [4] the standard enthalpies of formation -74.1 kJ mol^{-1} and -49.0 kJ mol^{-1} respectively were calculated.

In a continuing investigation of iron chalcogenide vaporization [11, 12], we have measured a new vapour pressure set for iron monoselenide by a torsion–effusion method and determined its standard sublimation and formation enthalpies.

2. Experimental details

The vapour pressures of the iron selenide were determined by using the torsion assembly described in a previous work [13]. Commercial FeSe, supplied by Johnson Matthey Alfa Products with a nominal purity of 99.9%, was employed in this study.

A conventional graphite torsion cell having effusion holes about 1 mm in diameter was used. The instrument constant K necessary to calculate the vapour pressure p_i from the experimental torsion angle α_i ($p_i = \alpha_i K$), was determined by vaporizing standards (lead, silver and tin) having well-known vapour pressures [14]. The three K values obtained agree within about 2%. In Fig. 2 the vapour pressure values measured in a typical vaporization run of this compound are drawn. After an outgassing step at about 450 K (about 0.1% of the initial weight) and a first very short vaporization step, in which the amount of sample vaporized is very small (less than 0.05%), the pressure rapidly decreases by about two orders of magnitude, exhibiting reproducible values with both ascending and descending temperatures. In Table 1 are reported the vapour pressures measured in each experiment at temperatures below 1149 K when FeSe, in equilibrium with a very small amount of pure iron formed on the sample surface, is at nearly unit activity. As the sublimation is continued, the iron originating from decomposition produces a small decrease in the activity of this compound so when pressure values measured were not reproducible they were not used for the calculation of the sublimation enthalpy of FeSe. In one experiment (run D), in which a relatively large amount of sample (about 500 mg) was used, various short runs were carried out.

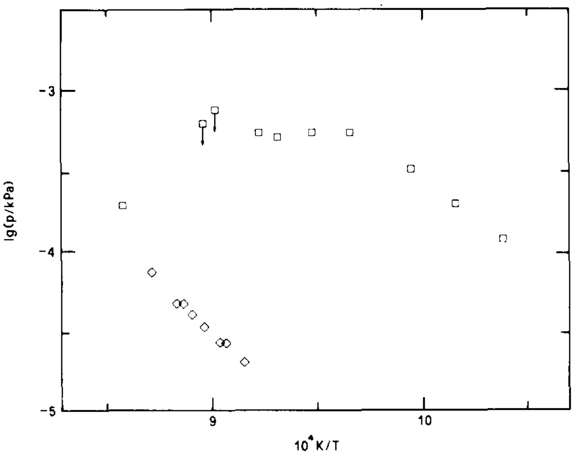

Fig. 2. Behaviour of the first step of vaporization of iron monoselenide.

The least-squares treatment of the results obtained in each run gave the lg p *vs.* $1/T$ equations reported in Table 2. By weighting their slopes and intercepts according to the experimental points, the following equation was selected in the temperature range 1092–1149 K:

$$\lg p(\mathrm{kPa}) = 6.96 \pm 0.45 - (12\,755 \pm 400)/T \qquad (1)$$

The quoted errors are estimated by taking into account the largest uncertainties in the temperature measurements (± 2 K) and in the torsion angles determined at low temperatures ($\pm 0.2^\circ$).

In experiment D, when about 15% of the initial weight of the sample was vaporized, the temperature was increased beyond 1149 K but kept below 1215 K (eutectic point) so that, according to the phase diagram, the peritectoid modification of iron monoselenide in the δ' phase (approximately $FeSe_{0.96}$) occurs and the measured vapour pressures were referred to this phase in equilibrium with pure iron. These values, reported in Fig. 3, are fitted by the equation

$$\lg p(\mathrm{kPa}) = 6.98 \pm 0.48 - (12\,867 \pm 562)/T \qquad (2)$$

(in which the associated errors are standard deviations); this equation is practically identical, within the experimental uncertainties, to eqn. (1) found above FeSe.

3. Discussion

The vapour pressure–temperature equation (1) determined in the present work is compared in Fig. 4 with the experimental data found in the literature. Our results agree well with the Knudsen pressure values reported by Svendsen [5]. In the first step of our vaporizations (see Fig. 2), a very small amount of selenium (perhaps present in the sample as an impurity but sufficient to produce a system inside the δ phase region) results in vapour pressure values definitely higher than those measured over pure FeSe. This behaviour agrees with the pressures measured by Svendsen [5] above $FeSe_{1+x}(0 < x \leq 0.2)$ alloys practically in

TABLE 1. Vapour pressure and third-law standard sublimation enthalpy of FeSe according to the reaction $FeSe(s) \rightarrow Fe(s) + 0.5Se_2(g)$

Run	T (K)	p ($\times 10^{-4}$ kPa)	$-0.5R \ln p(Se_2)$ (J mol^{-1} K^{-1})	$-\Delta_r[(G^\circ_T - H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	$\Delta_r H^\circ_{298}$ (kJ)
A	1092	0.206	64.06	65.48	141.4
	1103	0.275	62.84	65.35	141.4
	1112	0.344	61.92	65.23	141.4
	1122.5	0.447	60.83	65.15	141.4
	1134	0.550	59.96	64.94	141.6
	1144	0.688	59.04	64.77	141.7
B	1092.5	0.206	64.06	65.48	141.5
	1106	0.275	62.84	65.31	141.7
	1107	0.275	62.84	65.31	141.9
	1115.5	0.344	61.92	65.19	141.8
	1123	0.413	61.17	65.10	151.8
	1128	0.482	60.54	65.02	141.6
	1132.5	0.482	60.54	64.94	142.1
	1148	0.757	58.66	64.73	141.6
C	1094	0.206	64.06	65.44	141.7
	1100	0.241	64.43	65.40	141.7
	1106	0.275	62.84	65.31	141.7
	1115	0.344	61.92	65.19	141.7
	1121	0.413	61.17	65.10	141.6
	1127.5	0.482	60.54	65.02	141.6
	1128	0.482	60.54	65.02	141.6
	1134.5	0.550	59.96	64.94	141.7
	1142.5	0.619	59.50	64.81	142.0
D	1106	0.275	62.84	65.31	141.7
	1115	0.310	62.38	65.19	142.2
	1129	0.482	60.54	65.02	141.7
	1140.5	0.585	59.71	64.85	142.0
	1102	0.241	63.43	65.35	141.9
	1114.5	0.344	61.92	65.19	141.7
	1123.5	0.413	61.17	65.06	141.8
	1134	0.550	59.96	64.94	141.6
	1144.5	0.654	59.24	64.77	142.0
	1094.5	0.206	64.06	65.44	141.7
	1107	0.275	62.84	65.31	141.9
	1118	0.310	62.42	65.15	142.6
	1129.5	0.482	60.54	64.98	141.8
	1139.5	0.550	59.96	64.85	142.2
	1149	0.757	58.66	64.68	141.8
	1104.5	0.275	62.84	65.31	141.6
	1114	0.310	62.38	65.19	142.1
	1124	0.413	61.17	65.06	141.9
	1135	0.550	59.96	64.94	141.8
	1143.5	0.654	59.24	64.69	141.9
	1100.5	0.241	63.43	65.36	141.7
	1115.5	0.310	62.38	65.19	142.3
	1125.5	0.413	61.17	65.06	142.1
	1138	0.585	59.71	64.89	141.8
	1147.5	0.688	59.08	64.73	142.0
	1102	0.241	63.43	65.35	141.9
	1117	0.344	61.92	65.15	142.0
	1132	0.482	60.54	64.98	142.1
	1145	0.654	59.24	64.77	142.0
Mean					141.8±0.6

TABLE 2. Temperature dependence of the vapour pressure above FeSe

Run	Number of points	ΔT (K)	$\lg p$ (kPa) $=A-B/T$	
			A	B
A	6	1092–1144	6.73±0.28	12462±318
B	8	1192.5–1148	6.95±0.41	12729±461
C	9	1094–1142.5	7.02±0.32	12802±362
D	29	1094.5–1149.5	7.00±0.27	12809±301

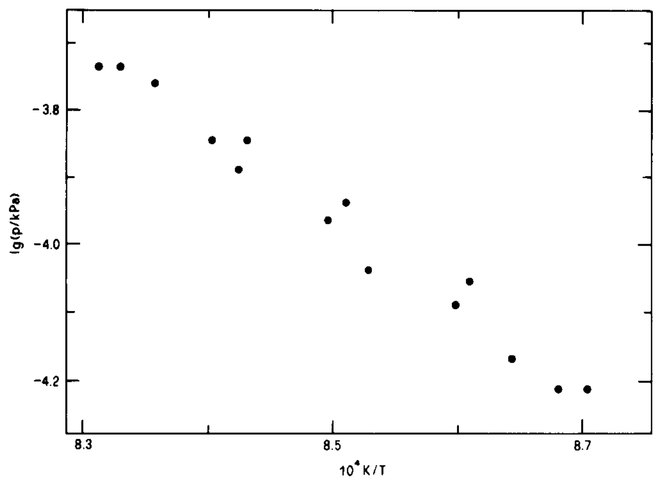

Fig. 3. Vapour pressure of $FeSe_{0.96}$ (δ' phase).

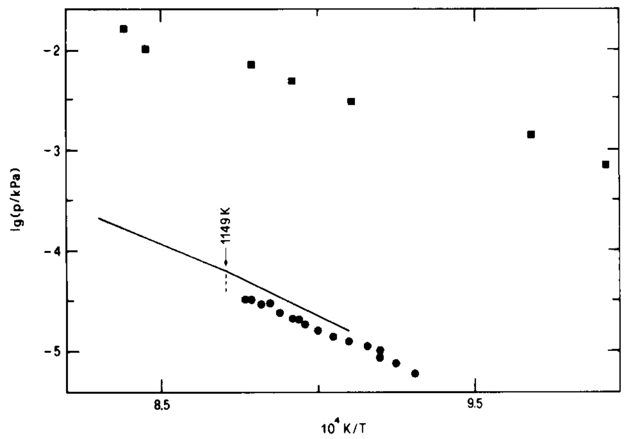

Fig. 4. Comparison of the vapour pressure measured above FeSe with those reported in the literature: ●, Svendsen [5]; ■, Rumyantsev *et al.* [4]; ——, this work.

the δ phase region. Probably Rumyantsev *et al.* [4] in their experiments used samples having a composition inside the δ phase (even if near to the iron-rich boundary) in large amounts so that the vaporization of selenium did not produce an appreciable change in the original composition of the sample and the pressures measured by these researchers are referred to the δ phase having this particular but unknown composition.

On this basis we conclude that iron monoselenide sublimes according to the decomposition reaction

$$FeSe(s) \longrightarrow Fe(s) + 0.5Se_2(g) \qquad (3)$$

and that eqn. (1) represents the temperature dependence of the total vapour pressure above this compound.

Because the sublimation of pure iron and FeSe is negligible compared with that of selenium, the measured vapour pressures are considered equal to the partial pressures of $Se_2(g)$, so that, from the slope of the pressure–temperature equation (1), a second-law enthalpy $\Delta_r H°_{1120}$ associated with reaction (3) of 122±4 kJ was derived. The standard enthalpy of this reaction was calculated by third-law treatment of the results. The necessary free energy function for solid FeSe is interpolated from the data for $FeSe_{0.96}$ and $FeSe_{1.14}$ reported by Mills [15] and extrapolated above 1050 K (limit for the data cited); the functions for Fe(s) and $Se_2(g)$ are those selected by Hultgren *et al.* [14] and Mills [15] respectively. The third-law $\Delta_r H°_{298}$ values calculated at each experimental temperature are reported in Table 1. The average third-law standard enthalpy of reaction (3), $\Delta_r H°_{298} = 141.8 \pm 0.6$ kJ, is slightly higher than that found from the second-law procedure, $\Delta_r H°_{298} = 133 \pm 4$ kJ, obtained reporting at 298 K the $\Delta_r H°_{1120}$ by using the heat contents taken from the same references and procedures as the free energy function data.

On this basis we propose as the standard enthalpy associated with the sublimation of 1 mol of $Se_2(g)$ from FeSe(s) a selected value of 278 kJ mol^{-1} with an estimated error of about 8 kJ mol^{-1}. By combining appropriately this value with the standard sublimation enthalpy of selenium in $Se_2(g)$ (139±2 kJ mol^{-1} [15]), a standard enthalpy of formation of FeSe equal to $\Delta_f H°_{298}$ 69±5 kJ mol^{-1} was derived. This value is reported in Table 3 for comparison with the literature data.

The vapour pressures measured over 1149 K when the condensed phase is constituted by $FeSe_{0.96}$ (δ' phase)

TABLE 3. Standard enthalpy of formation of FeSe(s)

Reference	Method	$-\Delta_f H°_{298}$ (kJ mol^{-1})
[6]	Solution calorimetry	75.3[a]
[9]	Calorimetry (heat of synthesis)	67[b]
[10]	Calorimetry (heat of synthesis)	75.2±1.2
[8]	Solution calorimetry	58
[4]	Vapour pressure (Knudsen)	49
[5]	Vapour pressure (Knudsen)	74±6
This work	Vapour pressure (torsion)	69±5

[a] Recalculated from the solution calorimetric data reported by Fabre [7].

[b] Obtained for $FeSe_{0.96}$.

TABLE 4. Vapour pressure above δ' phase ($FeSe_{0.96}$) measured in run D and third-law sublimation enthalpy associated with the decomposition reaction $FeSe_{0.96} \rightarrow Fe(s) + 0.48Se_2(g)$

T (K)	p (tot) ($\times 10^{-4}$ kPa)	$-0.48R \ln p(Se_2)$ (J mol^{-1} K^{-1})	$-\Delta_r[(G^\circ_T - H^\circ_{298})/T]$ (J mol^{-1} K^{-1})	$\Delta_r H^\circ_{298}$ (kJ)
1152	0.688	56.69	63.60	139.2
1161.5	0.894	55.65	63.60	138.5
1175	1.17	54.56	63.60	138.6
1186	1.44	53.72	63.18	138.7
1196.5	1.75	52.97	63.18	138.8
1149	0.619	57.11	63.60	138.9
1163	0.826	55.94	63.60	139.0
1177	1.10	54.81	63.18	139.1
1190	1.44	53.72	63.18	139.1
1203	1.86	52.72	63.18	139.2
1157	0.688	56.69	63.60	139.2
1172.5	0.929	55.48	63.60	139.4
1187	1.31	54.14	63.18	139.3
1200.5	1.65	53.18	63.18	138.9
Mean				139.0 ± 0.4

in equilibrium with iron are reported in Table 4 and treated by second- and third-law procedures in order to determine the standard enthalpy of the decomposition reaction

$$FeSe_{0.96}(s) \longrightarrow Fe(s) + 0.48Se_2(g) \qquad (4)$$

The free energy functions and the heat contents of $FeSe_{0.96}$ are those selected by Mills [15]. At each temperature the calculated third-law $\Delta_r H^\circ_{298}$ values are also shown in Table 4. The average value $\Delta_r H^\circ_{298} = 139.0$ kJ with a semidispersion of 0.4 kJ is comparable with the second-law value calculated from the slope of eqn. (2) and reported at 298 K, $\Delta H^\circ_{298} = 131 \pm 5$ kJ (the error is the standard deviation). Unfortunately, the short experimental temperature range covered and the not well-defined stoichiometric composition of δ' phase (which influences the third-law ΔH°_{298} calculations) lead us to estimate a large error associated with the final selected value of the standard enthalpy for reaction (4): $\Delta_r H^\circ_{298} = 135 \pm 10$ kJ.

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