Study of the vaporization behaviour of iron monotelluride

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Abstract

The iron–tellurium system presents a single-phase region, β phase, with boundaries at compositions near to the stoichiometric one, FeTe, and to the formula $FeTe_{0.85}$. By the torsion–effusion method the total vapour pressure of the β phase at these two boundary compositions was measured. The pressure–temperature equations $\log p(\text{kPa}) = (8.37 \pm 0.45) - (9353 \pm 376)/T$ and $\log p(\text{kPa}) = (7.76 \pm 0.10) - (10229 \pm 109)/T$, associated respectively with the vaporization processes $33.3 \, FeTe(s) \rightarrow 33.3 \, FeTe_{0.94}(s) + Te_2(g)$ and $2.35 \, FeTe_{0.85}(s) \rightarrow 2.35 \, \alpha\text{-Fe}(s) + Te_2(g)$, were derived. The enthalpies associated with these reactions are $\Delta H^{\circ}_T = 180.3 \pm 10 \text{ kJ mol}^{-1}$ derived from the only second-law treatment of the data for the first reaction, and $\Delta H^{\circ}_{298} = 209.5 \pm 2.0 \text{ kJ mol}^{-1}$ for the second reaction as the average of the second- and third-law development of the partial pressure of Te_2. From the last reaction, the heat of formation of $FeTe_{0.85}$ $\Delta_{\text{form}} H^{\circ}_{298} = 17.5 \pm 2.0 \text{ kJ mol}^{-1}$ was derived.

1. Introduction

In a continuing investigation on the iron chalcogenides [1], we have studied the vaporization of iron telluride.

The phase diagram of the iron–tellurium system, selected by Moffatt [2], is that determined by Ipser *et al.* [3] from thermal, X-ray and isopiestic investigations. The partial diagram of this system of interest in the present work, given in Fig. 1, shows that FeTe is a non-stoichiometric compound, exhibiting phase homogeneity over a large range of compositions, and that the β phase presents boundary lines that are not well characterized. On the iron-rich side, in equilibrium with α-Fe, this phase presents a composition of 47.3 at.% Te or 48.5 at.% Te according to Gronvold *et al.* [4] or Ipser *et al.* [3] respectively. At this boundary of the β phase, a nominal composition of $FeTe_{0.9}$ was assigned and several thermodynamic properties such as enthalpy of formation [5], specific heat [6] and entropy [7] are referred to this formula. The most recent studies by Ipser and Komarek [8] and Saha and coworkers [9, 10] found two new compositions for iron-rich and tellurium-rich boundaries of the β phase to which the nominal formulae $FeTe_{0.81}$ and $FeTe_{0.94}$ correspond respectively.
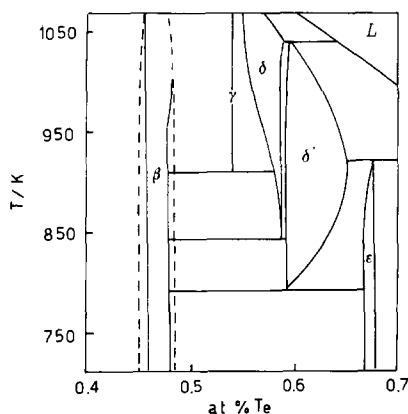
Fig. 1. Fe–Te phase diagram as reported in ref. 3: — — —, the boundary found by Saha *et al.* [9].

On this basis the vaporization process of the Fe–Te system can be referred to two different situations: one occurring from the coexisting phases FeTe$_{0.94}$(s) and δ or δ' or γ depending on the temperature (see Fig. 1), and the other occurring from the coexisting phases α-Fe(s) and FeTe$_{0.81}$(s). As observed mass spectrometrically [10] in both cases the predominant species in the vapour above the condensed phases is constituted by Te$_2$(g).

Apparently the vapour pressure data available in the literature above the mixture FeTe$_{0.94}$ (β phase at the tellurium-rich side) and δ phase are those reported by Rumyantsev *et al.* [11] obtained by the Knudsen method and by Sai Baba *et al.* [10] using the mass-spectrometric method. Above the mixture α-Fe and FeTe$_{0.81}$ (β phase at the iron-rich side), the only vapour pressure measurements are those reported by Saha *et al.* [9]. Two isolated total vapour pressure values can be derived from ref. 8 (8×10^{-2} kPa and 9×10^{-3} kPa at 1106 K and 973 K respectively).

The aim of the present work is to measure new vapour pressure data sets and to determine the tellurium sublimation enthalpies from both the two-phase systems.

2. Experimental details

The iron monotelluride used was supplied by Johnson Matthey–Alfa with a nominal purity of 99.9%.

The vapour pressure of this compound was measured by the torsion–effusion method employing the apparatus described in previous work [12]. The torsion assembly is suspended on an arm of a Chan RH vacuum microbalance in order to measure, by the Knudsen method, the molecular weight of the effusing vapour. The instrument constant necessary for the pressure calculation from the torsion angle measurements was determined by vaporizing pure benzoic acid [13], urea [14] and cadmium [15] as standards.
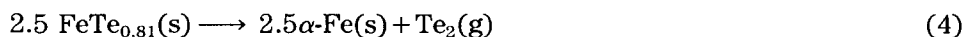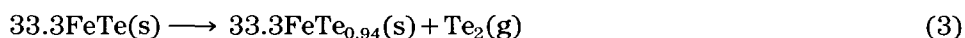
At about 600 K, after an initial vaporization of 0.1–0.2% of the original weight, probably due to tellurium impurities, the sample presents a vaporization behaviour as drawn in Fig. 2. In the first very short step the pressure values are reproducible but when about 0.8–1.0% of the sample is vaporized the pressure, initially at a rapid and progressively at a slower rate, decreases by about a factor of 10. At this step the pressure once again reached a steady state showing reproducible values with varying temperature. The molecular weight of the effusing vapour, determined by the Knudsen method from measurements of the sample weight loss rate, confirms that the gaseous phase is constituted mainly by $Te_2(g)$. Taking into account the phase diagram one may conclude that the first and the last step relate to the vaporization of Te_2 from the β phases at compositions of the tellurium- and iron-rich side and that between these two steps the sample crosses through the region of the single β phase. On this basis the vapour pressures measured in the first and in the last step, reported in Figs. 3 and 4, are practically those above FeTe(s) and $FeTe_{0.81}(s)$ respectively.

The intercepts and the slopes of log p vs. $1/T$ lines obtained by least-squares treatment of the data of each run (see Table 1) allow us to derive the following selected equations:

$$\log p(kPa) = (8.37 \pm 0.45) - (9353 \pm 376)/T \tag{1}$$

$$\log p(kPa) = (7.76 \pm 0.10) - (10229 \pm 109)/T \tag{2}$$

respectively for the vaporization processes

$$33.3 FeTe(s) \longrightarrow 33.3 FeTe_{0.94}(s) + Te_2(g) \tag{3}$$

$$2.5 FeTe_{0.81}(s) \longrightarrow 2.5\alpha\text{-}Fe(s) + Te_2(g) \tag{4}$$

By stopping the vaporization run during the last step, the condensed phase is constituted by α-Fe and $FeTe_{0.81}$ β phase, their amounts depending
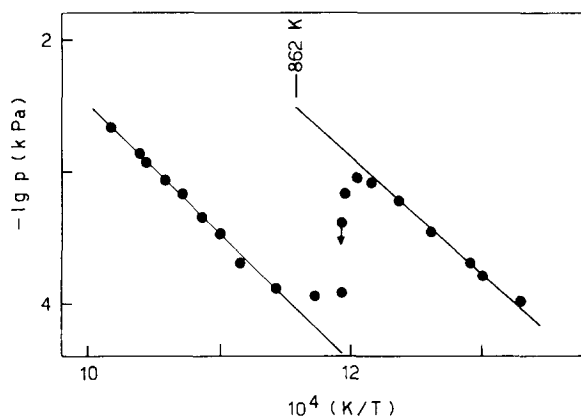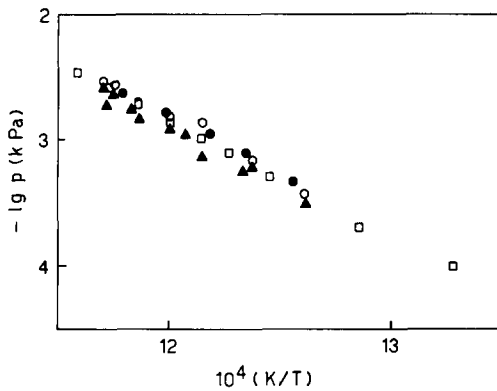

Fig. 2. Vaporization behaviour of FeTe.

Fig. 3. Vapour pressures of the β phase (tellurium-rich side) as a function of temperature: □, run A; ▲, run B; ○, run C; ●, run D.
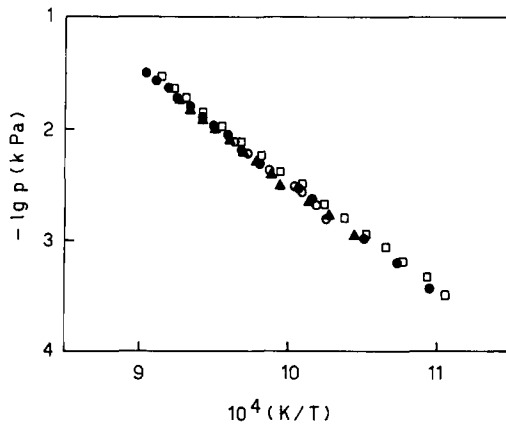
Fig. 4. Vapour pressures of the β phase (iron-rich side) as a function of temperature: □, run A; ▲, run B; ○, run C; ●, run D.

on the tellurium evaporated as was clearly observed by scanning electron microprobe analysis (Fig. 5).

An evaluation of the position of the β-phase boundaries was made during some isothermal experiments carried out by measuring the torsion angle during the vaporization of tellurium, and evaluating, from the weight loss of the sample, the composition of the vaporization residue. The compositions of the boundaries were evaluated by integrating the loss of tellurium between the time t_a and t_b (see Fig. 6). At the end of each experiment, after complete depletion of tellurium, the residue (practically constituted by pure iron) was weighed in order to verify the exact initial composition of the sample.

In the temperature range 870–980 K, it was found that the compositions of the β phase are 46.0 ± 1.5 and 48.7 ± 0.5 at.% Te. Unfortunately, employing the procedure illustrated, the large uncertainties in the evaluation of the times t_b lead to inaccurate formulae being assigned at the iron-rich side

TABLE 1

Experimental total vapour pressure–temperature equation parameters above the iron telluride

Run	Number of points	ΔT (K)	A^a	B^a (K)
A	9	753–863	8.21 ± 0.20	9211 ± 171
	16	905–1092	7.76 ± 0.05	10184 ± 54
B	11	793–854	8.44 ± 0.61	9458 ± 510
	12	957–1079	7.83 ± 0.16	10339 ± 169
C	8	793–854	8.72 ± 0.60	9604 ± 496
	9	973–1037	7.88 ± 0.23	10364 ± 235
D	5	796–848	7.96 ± 0.32	8974 ± 260
	16	913–1106	7.64 ± 0.04	10114 ± 45

[a] $\log p \ (kPa) = A - B/T$; the errors are standard deviations.
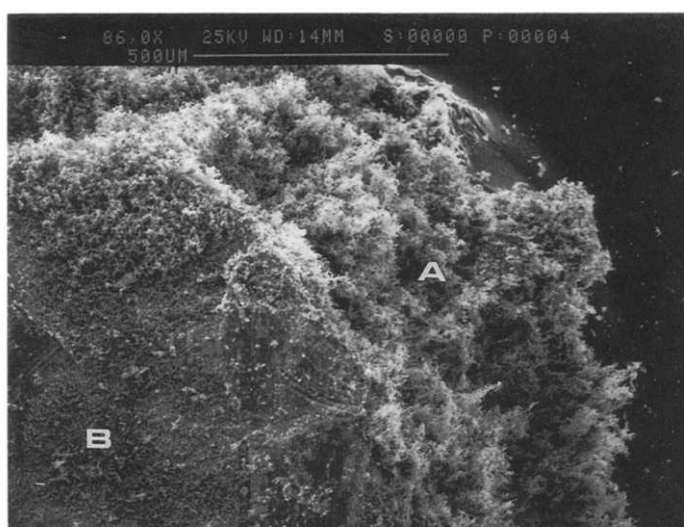
Fig. 5. Section of a residue of one FeTe lump observed by scanning electron microscopy and microanalysis when the vaporization process is stopped in the two-phase α-Fe–β-FeTe$_{0.8}$ region: A, surface of the piece constituted by only pure iron; B, bulk constituted by β-FeTe$_{0.8}$ phase.

boundary of the β phase, these ranging from those reported in the literature (FeTe$_{0.8}$ and FeTe$_{0.9}$). As concerns the tellurium-rich side boundary of the β phase our result (FeTe$_{0.95}$) agrees well enough with that selected by Sai Baba et al. [10].

3. Conclusions

The vapour pressure–temperature eqns. (3) and (4) selected in the present work are given in Fig. 7 and Table 2 for comparison with the data reported in the literature.
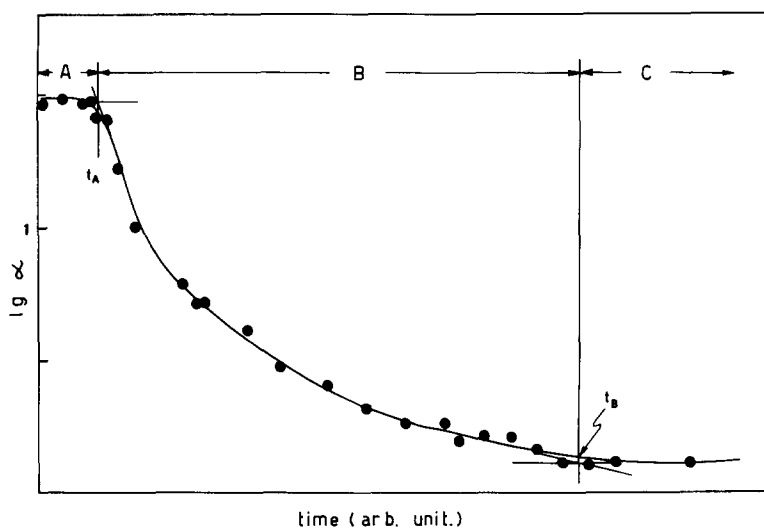
Fig. 6. Isothermal vaporization of iron telluride at 863 K. In the first step (A) the system is constituted by β phase (tellurium-rich side) and δ phase; in the intermediate step (B) by β phase; and in the last step (C) by α-Fe and β phase (iron-rich side).
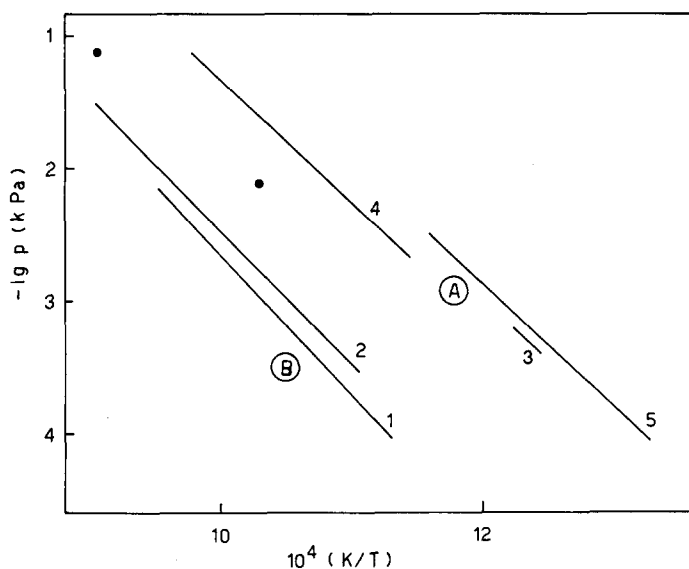
Fig. 7. Total vapour pressures above the β phase on the tellurium-rich side (line 3, ref. 10; line 4, ref. 11; line 5, this work) and above the β phase on the iron-rich side (line 1, ref. 9; ●, ref. 8; line 2, this work).

As concerns the first step owing to the vaporization of tellurium, the system rapidly crosses the tellurium-rich side boundary of the β phase, so that a small temperature range can be covered in each run and not many

TABLE 2

Total vapour pressure–temperature equation parameters above the iron–tellurium system

System	Ref.	ΔT (K)	A^a	B^a (K)
β phase	[10]	803–818	6.640 ± 1.895	8047 ± 1536
(Te-rich side)	[11]	873–1023	7.86 ± 0.38	9208 ± 358[b]
	This work	753–863	8.37–0.45	9353 ± 376
β phase	[9]	885–1048	8.12 ± 0.29	10759 ± 284
(Fe-rich side)	This work	905–1106	7.76 ± 0.10	10229 ± 109

[a]$\log p$ (kPa) $= A - B/T$.
[b]Calculated from the experimental data reported in the original paper; the associated errors are standard deviations.

pressure data have to be taken. From the slope of the pressure–temperature equation an enthalpy of the reaction in eqn. (3) $\Delta H_T = 180$ kJ was calculated with an error estimated to be not less than 10 kJ.

The experimental data were used to calculate the standard enthalpy of the same reaction (3) by the third law of thermodynamics, considering in the first approximation the free energy functions of FeTe(s) to be equal to those of $FeTe_{0.94}(s)$. The $\Delta H^0{}_{298}$ values obtained (about 300 kJ) are decidedly higher than those found by the second law and present evident temperature trends. This large disagreement cannot be due to errors in the pressure or temperature measurements but is probably due to a small difference between the free energy functions of FeTe and $FeTe_{0.94}$, a difference which is enhanced considering the stoichiometric coefficients of these compounds in the reaction (3). For the same reason, no reliable correction at 298 K of the second-law $\Delta H^0{}_T$ could be made.

As concerns the vaporization of $Te_2(g)$ from $FeTe_{0.81}$ (the β phase at the iron-rich side), according to the reaction (4), the second-law enthalpy was calculated at a mid-temperature from the slope of the selected eqn. (2): $\Delta H^0{}_{1000} = 196.3 \pm 4.0$ kJ. The partial Te_2 pressures, obtained by correcting the measured total vapour pressures by a factor 0.95 [12], were used to calculate the standard third-law enthalpy of the same reaction (4). The necessary Gibbs energy function of $FeTe_{0.81}(s)$ was obtained from $S^0{}_{298} = 80$ J K^{-1} mol^{-1} and the heat capacities measured in ref.7 and ref. 6 respectively, even if referred to the formula $FeTe_{0.9}$; the Gibbs energy functions of $Te_2(g)$ and Fe(s) are those selected by Mills [5] and Hultgren et al. [16] respectively. The individual $\Delta H^0{}_{298}$ values of reaction (4) so obtained and reported in Table 3 present a small decreasing trend with increasing temperature and their average value (199.8 kJ) is lower than that obtained from the second law $(\Delta H^0{}_{298} = 209.5 \pm 2.0$ kJ); this value was corrected at 298 K by using heat capacities taken from the same references as in the case of the Gibbs energy functions.

TABLE 3

Third-law ΔH^0_{298} (kJ mol^{-1}) associated with the vaporization reactions (a) $2.5\text{FeTe}_{0.8}(s) \rightarrow 2.5\alpha\text{-Fe}(s) + \text{Te}_2(g)$ and (b) $2.35\text{FeTe}_{0.85}(s) \rightarrow 2.35\alpha\text{-Fe}(s) + \text{Te}_2(g)$

Run	T (K)	$-\log p$ (kPa)	Reaction (a)		Reaction (b)	
			ΔFEF^a (J K^{-1})	ΔH^0_{298} (kJ)	ΔFEF^a (J K^{-1})	ΔH^0_{298} (kJ)
A	905	3.50	116.3	200.6	125.9	209.2
	929	3.20	115.8	200.1	125.5	209.1
	938	3.07	115.7	199.6	125.3	208.6
	950	2.97	115.4	199.9	125.1	209.1
	963	2.80	115.2	199.4	124.9	208.8
	977	2.68	114.9	119.8	124.7	209.3
	991.5	2.51	114.6	199.3	124.4	209.9
	1005	2.38	114.3	199.2	124.2	209.1
	1017	2.24	114.1	198.6	124.0	208.6
	1032	2.11	113.8	198.6	123.7	208.9
	1046.5	1.98	113.5	198.6	123.5	208.9
	1061	1.84	113.0	198.1	123.2	208.8
	1073.5	1.73	113.0	198.0	123.0	208.7
	1083	1.64	112.8	197.6	122.9	208.5
	1092.5	1.54	112.6	197.1	122.7	208.1
B	957	2.96	115.3	201.3	125.0	210.6
	973	2.78	115.0	200.9	124.7	210.4
	986	2.64	114.7	200.7	124.5	210.4
	1005.5	2.51	114.3	201.8	124.2	211.7
	1011	2.39	114.2	200.5	124.1	210.4
	1021.5	2.28	114.0	200.2	123.9	210.3
	1031	2.20	113.8	200.3	123.7	210.5
	1041	2.10	113.6	200.2	123.6	210.4
	1051	1.99	113.4	199.5	123.4	210.0
	1060.5	1.91	113.3	199.5	123.2	210.1
	1070	1.83	113.1	199.5	123.1	210.2
	1079	1.75	112.9	199.3	122.9	210.1
C	973	2.80	115.0	201.3	124.7	210.8
	981	2.68	114.8	200.5	124.6	210.1
	991	2.57	114.6	200.3	124.4	210.0
	995	2.52	114.6	200.1	124.4	209.9
	1009	2.39	114.3	200.1	124.1	210.0
	1012	2.36	114.2	200.1	124.1	210.0
	1021.5	2.27	114.0	200.0	123.9	210.1
	1029	2.21	113.9	200.0	123.8	210.3
	1037	2.12	113.7	199.7	123.6	210.0
D	913	3.43	116.2	201.0	125.8	209.7
	932	3.20	115.8	200.7	125.4	209.7
	951	2.98	115.4	200.4	125.1	209.7
	984	2.63	114.8	200.2	124.6	209.8
	994	2.55	114.6	200.5	124.4	210.2
	1009	2.39	114.3	200.1	124.1	210.0
	10$\bar{1}$9	2.29	114.1	200.0	124.0	210.1

(continued)

TABLE 3 (*continued*)

Run	T (K)	$-\log p$ (kPa)	Reaction (a)		Reaction (b)	
			ΔFEF[a] (J K^{-1})	ΔH^{0}_{298} (kJ)	ΔFEF[a] (J K^{-1})	ΔH^{0}_{298} (kJ)
	1032	2.16	113.8	199.7	123.7	209.9
	1042	2.07	113.6	199.6	123.6	210.0
	1052	1.98	113.4	199.5	123.4	210.0
	1060	1.88	113.3	198.9	123.2	209.5
	1069.5	1.81	113.1	198.9	123.1	209.7
	1079	1.73	112.9	198.9	122.9	209.7
	1088	1.64	112.7	198.5	122.8	209.4
	1096.5	1.57	112.6	198.3	122.6	209.4
	1106	1.50	112.4	198.4	122.5	209.6

[a]Gibbs free energy function (FEF) $= (G^{0}_{T} - H^{0}_{298})/T$.

Of course the calculations of the third-law ΔH^{0}_{298} of reaction (4) and the correction at 298 K of the second-law ΔH^{0}_{T} of the same reaction involve a knowledge of the stoichiometric coefficient in the vaporization process.

Considering FeTe$_{0.9}$(s) to be the formula of the β phase (iron-rich side) and employing the same Te$_2$ partial pressure values the second- and the third-law ΔH^{0}_{298} of the reaction

$$2.22\text{FeTe}_{0.9}(\text{s}) \longrightarrow 2.22\alpha\text{-Fe(s)} + \text{Te}_2(\text{g}) \tag{5}$$
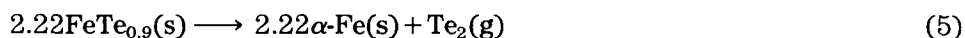
were calculated. Now the ΔH^{0}_{298} values determined from second-law evaluation of the data of each run (see Table 4) are lower than those calculated from the third-law procedure, so that we believe the β phase should have the intermediate composition FeTe$_{0.85}$.

In fact, if the experimental pressure data are used to determine the standard enthalpy of the evaporation of β phase according to the reaction

$$2.35\text{FeTe}_{0.85}(\text{s}) \longrightarrow 2.35\alpha\text{-Fe(s)} + \text{Te}_2(\text{g}) \tag{6}$$
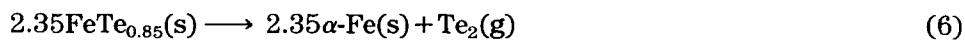
the third-law ΔH^{0}_{298} values do not present an evident temperature trend (see Table 3) and their average value $\Delta H^{0}_{298} = 209.9 \pm 0.4$ kJ is in very good agreement with that derivable from the second-law procedure $\Delta H^{0}_{298} = 209.3 \pm 4.0$ kJ.

On this basis we believe that the β phase at the iron-rich side boundary presents in our experimental temperature range the formula FeTe$_{0.85}$ (46.0 at.% Te) as found, albeit with a large uncertainty, in our isothermal runs and that the ΔH^{0}_{298} associated with the vaporization of 1 mol of Te$_2$(g) from this phase should be equal to 209.5 kJ with an estimated error that does not exceed 2.0 kJ. Combining this value with the standard sublimation enthalpy of tellurium in Te$_2$(g) [16], a heat of formation of FeTe$_{0.85}$

TABLE 4

Second- and third-law $\Delta H^0{}_{298}$ (kJ) for the reactions (a) $2.5FeTe_{0.8}(s) \rightarrow 2.5\alpha\text{-}Fe(s) + Te_2(g)$, (b) $2.22FeTe_{0.9}(s) \rightarrow 2.22\alpha\text{-}Fe(s) + Te_2(g)$, and (c) $2.35FeTe_{0.85}(s) \rightarrow 2.35\alpha\text{-}Fe(s) + Te_2(g)$

Run	ΔT (K)	$\Delta H^0{}_{1000}$ 2nd law	$\Delta H^0{}_{298}$ (reaction (a))		$\Delta H^0{}_{298}$ (reaction (b))		$\Delta H^0{}_{298}$ (reaction (c))	
			2nd law	3rd law	2nd law	3rd law	2nd law	3rd law
A	913–1106	193.6 ± 0.9	206.6 ± 0.9	199.6 ± 0.9	202.3 ± 0.9	218.7 ± 0.3	204.3 ± 0.9	210.0 ± 0.2
B	973–1037	198.4 ± 4.5	211.4 ± 4.5	200.2 ± 0.5	207.1 ± 4.5	218.7 ± 0.3	209.1 ± 4.5	210.1 ± 0.3
C	957–1079	197.9 ± 3.2	210.9 ± 3.2	200.3 ± 0.8	206.6 ± 3.2	219.0 ± 0.4	208.6 ± 3.2	210.4 ± 0.4
D	905–1092	195.1 ± 1.3	208.1 ± 1.3	199.0 ± 0.9	203.8 ± 1.3	217.6 ± 0.3	205.8 ± 1.3	208.9 ± 0.3
Average[a]		196.3 ± 4.0	209.3 ± 4.0	199.8 ± 1.0	204.9 ± 4.0	218.5 ± 0.4	209.3 ± 4.0	209.9 ± 0.4

[a]Estimated errors.

$\Delta H^{\circ}_{298} = -17.5 \pm 2.0$ kJ mol^{-1} was derived, in good agreement with that selected by Mills [5] (23 kJ mol^{-1}).

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