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Study on sulfur vaporization from covellite (CuS) and anilite ($Cu_{1.75}S$)

B. Brunetti, V. Piacente* and P. Scardala
Dipartimento di Chimica, Università "La Sapienza", Rome (Italy)

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Abstract

Covellite decomposes according to the reaction: $4.667CuS \rightarrow 2.667Cu_{1.75}S(s) + S_2(g)$. The sulfur vapour pressures measured in the temperature range 551.5–627 K by the torsion–effusion method are represented by the equation: $\log p$ (kPa) = $(11.30 \pm 0.30) - (8290 \pm 100)/T$. At high temperature, the anilite vaporizes incongruently according to the equation: $16Cu_{1.75}S(s) \rightarrow 14Cu_2S(s) + S_2(g)$, and the sulfur pressures are well represented in the temperature range 770.5–877 K by the equation: $\log p$ (kPa) = $(10.49 \pm 0.40) - (11\,470 \pm 300)/T$. The enthalpies associated with these reactions are, $\Delta H°_{298} = 178 \pm 4$ kJ mol^{-1} and 268 ± 7 kJ mol^{-1} for reactions 1 and 2 respectively, obtained from second- and third-law treatment of the data. From these reactions, the heat of formation of $Cu_{1.75}S$, $\Delta_{form}H°_{298} = -74$ kJ mol^{-1}, was derived.

1. Introduction

The copper–sulfur system [1] presents two stoichiometric compounds Cu_2S (chalcocite) and CuS (covellite), the last decomposing at 780 K into sulfur vapour and an intermediate solid solution. This solution, according to Ramanarayanan and Jose [2], Wagner [3] and Rau [4], is originated from deviations from the stoichiometry of Cu_2S due to [4] "removing copper from the crystal while the sulfur sublattice seems not to be influenced". In this way, the solid solution presents a high concentration of cation defects in the crystal lattice due to neutral copper vacancy (generated by replacing two Cu^+ ions by one Cu^{++} ion), to a negatively charged copper vacancy (represented by one Cu^+ ion missing) and to an association of these two imperfections. Therefore, this solution can be considered Cu_2S containing different amounts of bivalent copper. The boundaries of this solution below 780 K are Cu_2S on the copper-rich side and a copper sulfide of non-stoichiometric composition, $Cu_{1.75}(s)$ (anilite), on the sulfur-rich side; in particular, this composition depends on the temperature, ranging from about $Cu_{1.77}S$ at 370 K to $Cu_{1.73}S$ at 780 K as reported by Rilling *et al.* [5].

In the region of this solution, other crystallographically characterized species, $Cu_{1.80}S$ (digenite) and $Cu_{1.95}S$ (djurleite), are also present [6].

The sulfur pressure derived from the decomposition of covellite according to the reaction:

$$4.667CuS(s) \longrightarrow 2.667Cu_{1.75}S(s) + S_2(g) \qquad (1)$$

were measured by several authors [7–11] at high temperature by employing static methods while, apparently, no vapour pressure data for covellite at low temperature are reported in literature.

The dissociation pressure of anilite was measured by Nesmeyanov *et al.* [12]. During the vaporization of this compound the authors observed a decrease in the vapour pressure. This fact is probably due to a continuous change of the surface composition of the sample considering that this vaporizes according to the reaction:

$$16Cu_{1.75}S(s) \longrightarrow 14Cu_2S(s) + S_2(g) \qquad (2)$$

and that chalcocite is stable in the experimental temperature range, decomposing at higher temperature as mass-spectrometrically observed by Glazov and Korenchuk [13].

A pressure value of about 0.22 mm Hg was measured at 823 K by Kushida [14] for copper sulfide with composition $Cu_{1.8}S$ (digenite).

As part of a continuing study on the vaporization of chalcogenides [15–21], we have studied the vaporization of covellite and anilite, and have derived the enthalpies associated with decomposition reactions (1) and (2) from the temperature dependence of their vapour pressures measured by the torsion–effusion method.

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*Author to whom correspondence should be addressed.

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2. Experimental details

Commercial covellite (99.5% pure), as supplied by Strem Chemicals Inc., was employed in this study. The torsion assembly used was that described in previous work [22]. Two cells with effusion holes of different sizes were used. Following a standard procedure, the torsion constant necessary to convert the experimental torsion angles into pressure data was determined by vaporizing pure elements (lead and cadmium) for which very reliable vapour pressure data are available [23].

Figure 1 shows the result of a preliminary vaporization of CuS which provides evidence that the vaporization behaviour of this compound can be roughly subdivided into three steps. The first step, in which a very small amount of compound vaporizes (about 0.3% of the original sample weight), was interpreted as due to the vaporization of sulfur solubilized as impurity in CuS; therefore, this step was neglected in subsequent runs. During the second step of vaporization less than about 7% of the original weight was characterized by a reproducible temperature dependence of the vapour pressure that fits well on a log*p* *vs.* 1/*T* line. Considering the sample to vaporize according to decomposition reaction (1), the measured vapour pressures are those of $S_2(g)$. With continued vaporization, the surface of the condensed phase becomes rich in $Cu_{1.75}S$ and the pressure values also decrease, depending on the diffusion of sulfur from inside the sample. When the vapour pressure above the system fell below the sensitivity of our instrument, the weight loss of the sample indicates that all the residue present was of approximate composition $Cu_{1.75}S$. On increasing the temperature at this stage, the third vaporization step starts. During this process, which corresponds to dissociation reaction (2), the sulfur pressures are again reproducible and fit a second log *p* *vs.* 1/*T* line having slope lower than that found for covellite.

After this preliminary run, three vaporization runs were carried out and the obtained vapour pressures above covellite are reported in Fig. 2. The least-squares treatment of the data measured in each run gives the log *p* *vs.* 1/*T* equations reported in Table 1. By using the same procedure, the temperature dependence of the vapour pressure above $Cu_{1.75}S$ has been determined and is also reported in Table 1. The experimental data above $Cu_{1.75}S$ are drawn in Fig. 3.

Comparison with literature data show that our $S_2(g)$ pressures measured above CuS at low temperature (Fig. 4) exhibit a temperature trend different from that found at higher temperatures. Those measured above $Cu_{1.75}S$ (Fig. 5) are decisively lower by about two orders of magnitude than those found by Nesmeyanov *et al.* [12]. We are not at present able to explain the discrepancy of the results obtained on $Cu_{1.75}S$, but a possible explanation can be due to the preparation of the sample obtained by Nesmeyanov *et al.* from the reaction of elemental sulfur and copper in the appropriate proportions heated for 80 h at 873 °C. Probably following

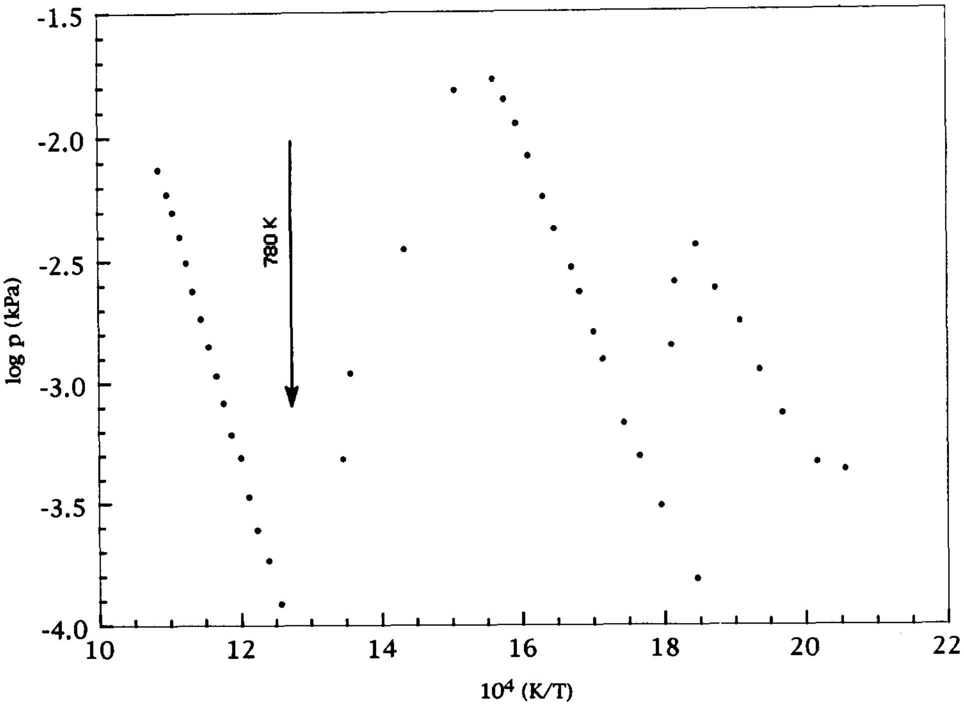

Fig. 1. Vaporization behaviour of CuS.

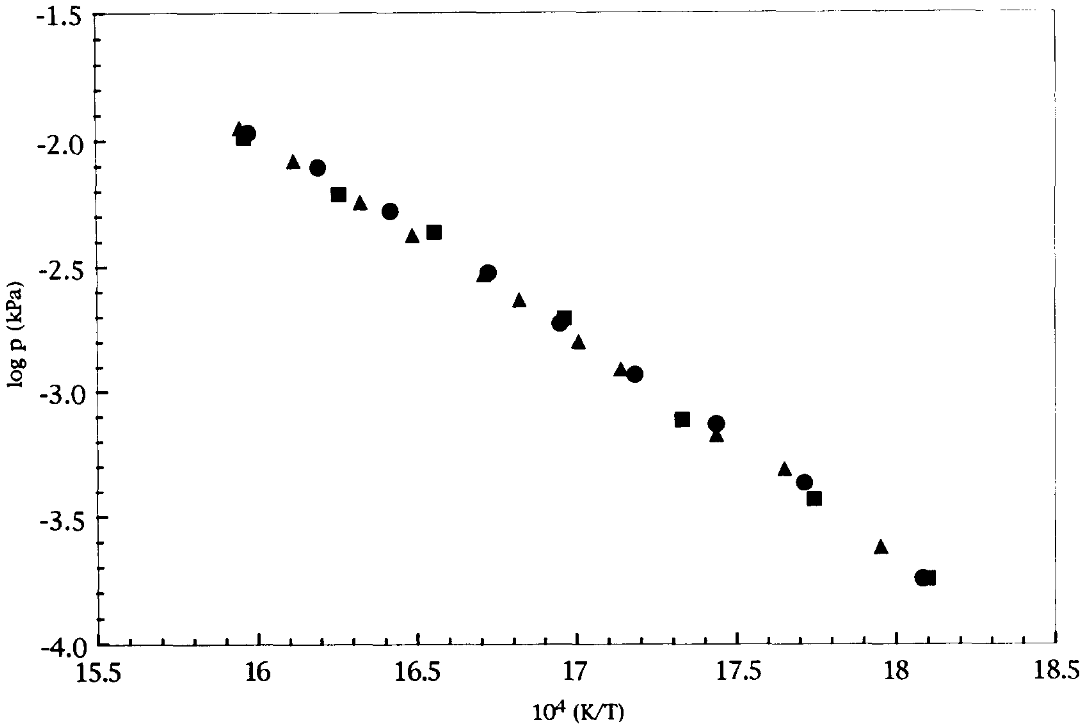

Fig. 2. Vapour pressure above CuS (■ run A; ▲ run B; ● run C).

TABLE 1. Temperature dependence of $S_2(g)$ pressure above covellite and anilite according to reactions (1) and (2) respectively:

$$4.667CuS(s) \longrightarrow 2.667Cu_{1.75}S(s) + S_2(g) \quad (1)$$

$$16Cu_{1.75}S(s) \longrightarrow 14Cu_2S(s) + S_2(g) \quad (2)$$

Reaction	Run	ΔT (K)	Number of points	$\log p$ (kPa) $= A - B/T$	
				A^a	B^a
1	A	551.5–626.5	7	11.24 ± 0.46	8259 ± 270
	B	557–627	11	11.20 ± 0.15	8231 ± 91
	C	553–626	9	11.48 ± 0.24	8392 ± 144
2	A	788.5–877	10	10.84 ± 0.37	11829 ± 306
	B	808–871.5	9	10.24 ± 0.23	11303 ± 193
	C	770.5–821.5	8	10.34 ± 0.41	11205 ± 324

[a] The quoted errors are standard deviations.

this procedure, in addition to $Cu_{1.75}S$, some CuS can be also synthesized.

3. Discussion

By proportion weighing the number of points of the slopes and the intercepts of the $\log p$ *vs.* $1/T$ equations reported in Table 1, the following equations, representative of the temperature dependence of the sulfur pressure above CuS and $Cu_{1.75}S$, are selected:

reaction (1):

$$\log p \text{ (kPa)} = (11.30 \pm 0.30) - (8290 \pm 100)/T \quad (3)$$

reaction (2):

$$\log p \text{ (kPa)} = (10.49 \pm 0.40) - (11\,470 \pm 300)/T \quad (4)$$

The associated errors are estimated by considering only uncertainties in temperature and torsion angle measurements. From the slopes of these equations, the second enthalpy law associated with the decomposition reactions (1) and (2) were calculated at the mid-point experimental temperature, $\Delta H^\circ_{589} = 159 \pm 2$ kJ mol^{-1} and $\Delta H^\circ_{823} = 219 \pm 2$ kJ mol^{-1} respectively. From the heat contents, $\Delta H = H^\circ_T - H^\circ_{298}$, of CuS(s), Cu_2S(s) and S_2(g) reported by Mills [24] and those of $Cu_{1.75}S$ estimated to be equal to $\Delta H(Cu_{1.75}S) = \Delta H(CuS) + 0.75[\Delta H Cu_2S) - \Delta H(CuS)]$, the ΔH°_T of these reactions were reported at 298 K: ΔH°_{298} (1) $= 173 \pm 2$ kJ mol^{-1} and $\Delta H^\circ(298)$ (2) $= 237 \pm 2$ kJ mol^{-1}.

By employing the free energy functions, $(G^\circ_T - H^\circ_{298})/T$, obtained from the same source or procedure used for the heat contents, the third law ΔH°_{298} values for both reactions were calculated at each experimental temperature. The results are given in Tables 2 and 3. These values show temperature trends and are higher than those obtained by the second-law procedure. We have not found a clear explanation for this discrepancy, but we advance two possible causes: an erroneous estimate of the free energy functions for $Cu_{1.75}S$ or a

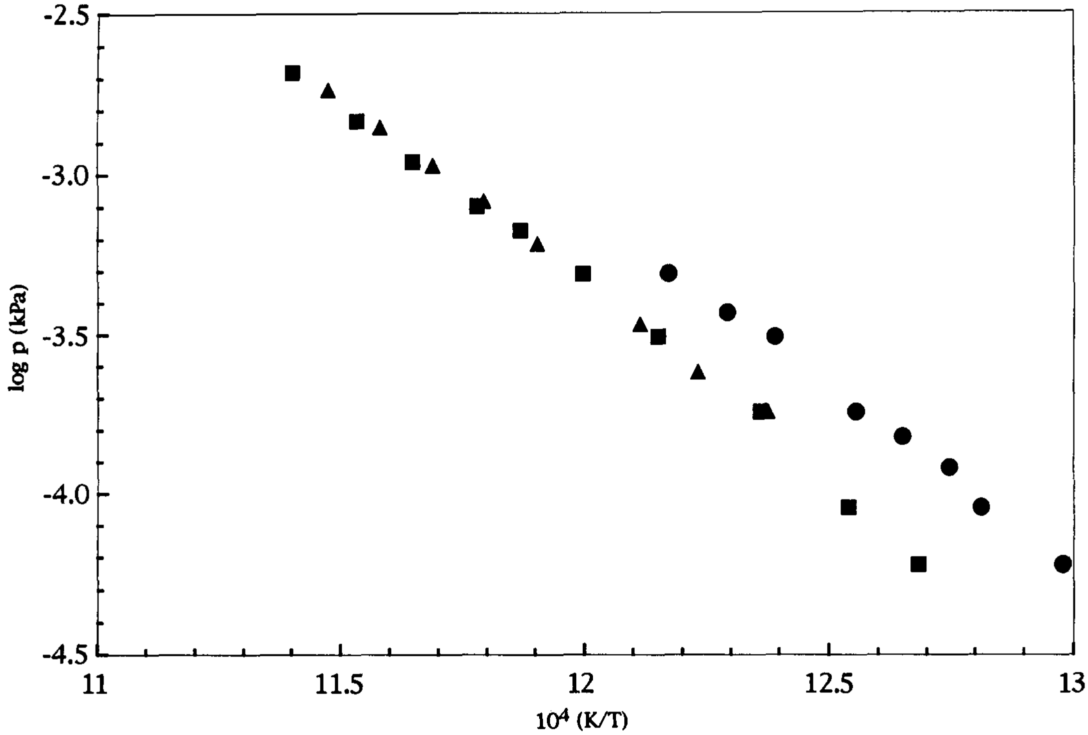

Fig. 3. Vapour pressure above $Cu_{1.75}S$ (■ run A; ▲ run B; ● run C).

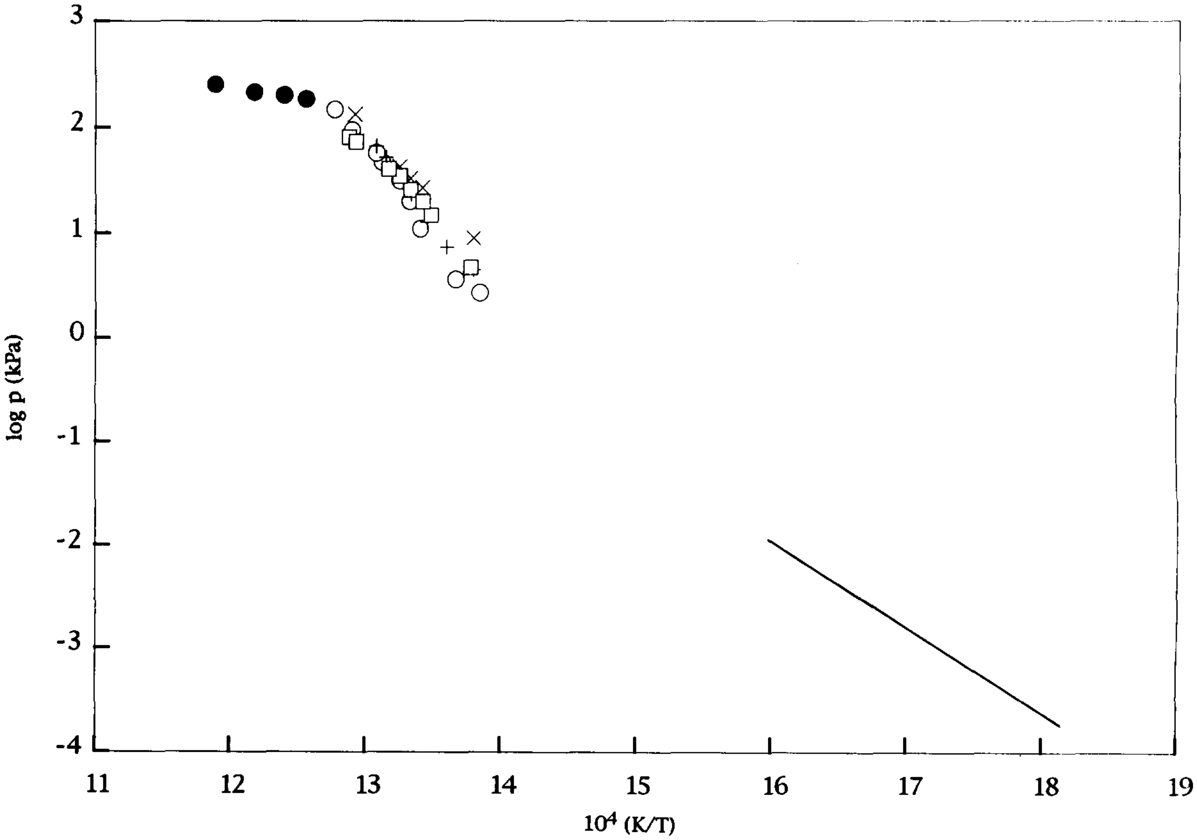

Fig. 4. Comparison of vapour pressure data above CuS (○ ref. 7; + ref. 8; × ref. 9; □ ref. 10; ● ref. 11; —— our data).

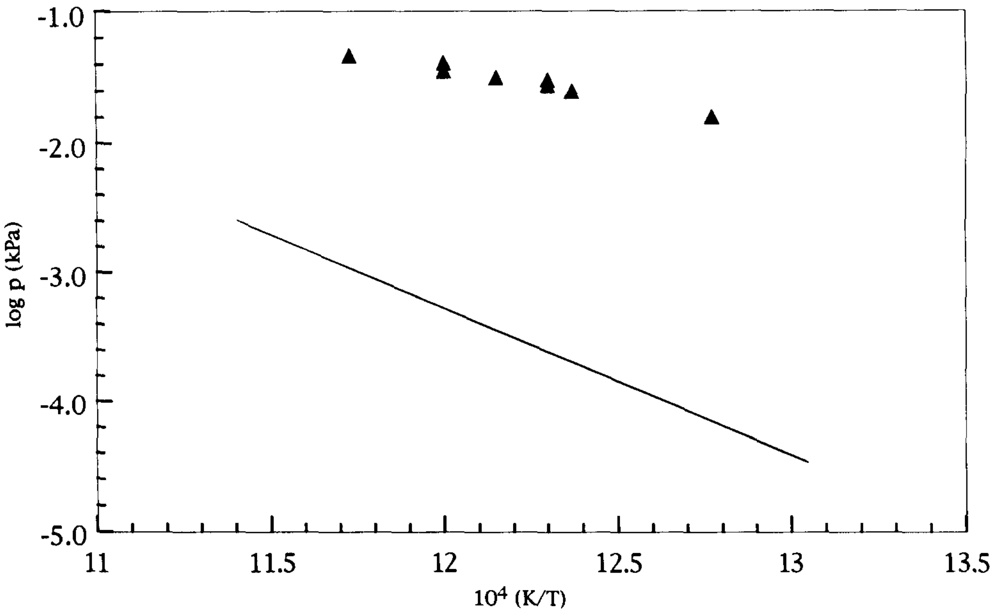

Fig. 5. Comparison of vapour pressure data above $Cu_{1.75}S$ (▲ ref. 12; —— our data).

TABLE 2. Third-law $\Delta H°_{298}$ associated with reaction:

$4.667CuS(s) \longrightarrow 2.667Cu_{1.75}S(s)+S_2(g)$

Run	T (K)	p (10 Pa)	$-R \ln p$ (J mol^{-1} K^{-1})	$-\Delta[(G°_T-H°_{298})/T]$ (J K^{-1})	$\Delta H°_{298}$ (kJ mol^{-1})
A	551.5	1.8	109.9	212.0	177.5
	563.5	3.7	104.1	212.5	178.5
	577	7.7	98.0	213.1	179.5
	589.5	19.6	90.2	213.7	179.2
	604	43.5	83.6	214.3	179.9
	615	61.3	80.7	214.8	181.8
	626.5	102.9	76.4	215.3	182.8
B	557	2.4	107.5	212.2	178.1
	566.5	4.9	101.8	212.7	178.1
	573.5	6.7	99.1	213.0	179.0
	583.5	12.3	94.1	213.4	179.5
	588	15.9	91.9	213.6	179.7
	594.5	23.3	88.8	213.9	180.0
	598.5	29.4	86.9	214.1	180.1
	606.5	42.3	83.8	214.5	181.1
	612.5	57.0	81.4	214.7	181.5
	620.5	83.3	78.2	215.1	182.1
	627	112.2	75.7	215.4	182.7
C	553	1.8	109.9	212.0	178.0
	564.5	4.3	102.9	212.6	178.1
	573.5	7.4	98.4	213.0	178.6
	582	11.7	94.6	213.3	179.2
	590	18.7	90.6	213.7	179.6
	598	30.0	86.7	214.1	179.8
	609	52.7	82.0	214.5	180.6
	617.5	78.5	78.7	214.9	181.3
	626	107.3	76.1	215.3	182.4

TABLE 3. Third-law ΔH°_{298} associated with reaction:

$16Cu_{1.75}S(s) \longrightarrow 14Cu_2S(s) + S_2(g)$

Run	T (K)	p (10 Pa)	$-R \ln p$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J K^{-1})	ΔH°_{298} (kJ mol^{-1})
A	788.5	0.6	119.0	221.5	268.5
	797.5	0.9	115.7	221.7	269.1
	809	1.8	109.9	222.0	268.6
	823	3.1	105.7	222.4	270.0
	833.5	4.9	101.8	222.6	270.4
	842.5	6.7	99.1	222.8	271.2
	849	8.0	97.7	222.9	272.2
	858.5	11.0	95.0	223.1	273.1
	867	14.7	92.6	223.2	273.8
	877	20.8	89.7	223.4	274.6
B	808	1.8	109.9	222.0	268.2
	817.5	2.4	107.5	222.3	269.6
	825.5	3.4	104.9	222.4	270.2
	833.5	4.9	101.8	222.6	270.4
	840	6.1	99.9	222.8	271.1
	848	8.3	97.4	222.9	271.6
	855.5	10.7	95.2	223.1	272.4
	863.5	14.1	93.0	223.2	273.0
	871.5	18.4	90.8	223.3	273.6
C	770.5	0.6	119.0	220.9	262.0
	780.5	0.9	115.7	221.3	263.0
	784.5	1.2	113.3	221.4	262.5
	790.5	1.5	111.4	221.5	263.2
	796.5	1.8	109.9	221.7	264.1
	807	3.1	105.7	222.0	264.4
	813.5	3.7	104.1	222.2	265.4
	821.5	4.9	101.8	222.4	266.3

soft but continuous decrease of the pressure values due to a continuous variation of the sample surface composition during sulfur vaporization in both reactions (1) and (2).

Apart from the need to minimize the discrepancy between the second- and third-law ΔH°_{298}, too large a correction of $Cu_{1.75}S$ free energy functions, a result of this, while reducing the temperature trend of the third-law ΔH°_{298} of one reaction (for example, reaction (1)), enlarges the trend of the other reaction ((2) in our example). The most probable explanation for the discrepancy in our results is the second cause. With continued vaporization, the eventual slow vapour pressure decrease gives, of course, a second-law ΔH°_T value lower than the true one. Moreover, the third-law ΔH°_{298} values calculated at high temperature at the end of the experiment, by employing incorrect pressures, are higher than those calculated from the $S_2(g)$ pressures measured in the first step of the experiments when the sample surface is not contaminated by the product of vaporization.

On this basis, we are persuaded that the more reliable ΔH°_{298} values associated with both reactions are those obtained from third-law treatment of the pressures measured in the first step of the experiments, and we are led to propose as standard enthalpies associated with reactions (1) and (2), values 178 ± 4 kJ mol^{-1} and 268 ± 7 kJ mol^{-1} respectively. The errors are estimated by considering a small uncertainty in the free energy function of $Cu_{1.75}S(s)$.

By employing the heats of formation of CuS (-52 ± 4 kJ mol^{-1}) and Cu_2S (-79 ± 1 kJ mol^{-1}) as selected by Mills [24], and the selected partial standard sublimation enthalpy of sulfur in $S_2(g)$ (121 kJ mol^{-1} [23]), two values for the heat of formation of $Cu_{1.75}S$, $\Delta_{form}H^\circ_{m,298} = -70 \pm 8$ kJ mol^{-1} and -78 ± 2 kJ mol^{-1}, were obtained utilizing the enthalpies of reactions (1) and (2), respectively.

From these values, we propose an average value of -74 kJ mol^{-1} for the heat of formation of the anilite with an uncertainty of about 5 kJ. This value is comparable with that of Cu_2S [24] and may be taken as confirmation that the structure of $Cu_{1.75}S$ is equal to that of Cu_2S with copper vacancies as proposed by Rau [4].

References

1 T.B. Massalski, *Binary Alloy Phase Diagrams,* American Society for Metals, Metals Park, OH, 1986.
2 T.A. Ramanarayanan and P. Jose, *J. Electrochem. Soc., 125* (10) (1978) 1684.
3 C. Wagner, *J. Electrochem. Soc., 99* (1952) 346.
4 H. Rau, *J. Phys. Chem. Solids, 28* (1967) 903.
5 J. Rilling, D. Balesdent and R. Peronne, *Bull. Soc. Chim. Fr., n.5* (1972) 1728.
6 F. Grønvold and E.F. Westrum Jr., *J. Chem. Thermodyn. 19* (1987) 1183.
7 F.W. Dickson, L.D. Shields and G.C. Kennedy, *Econ. Geol., 57* (1962) 1021.
8 E.T. Allen and R.H. Lombard, *Am. J. Sci., 43* (1917) 175.
9 G. Preuner and I.Z. Brockmoller, *Z. Phys. Chem., 81* (1912) 129.
10 K. Wasjuchnova, *Dissertation,* Berlin, 1909.
11 E.F. Westrum Jr., S. Stølen and F. Grønvold, *J. Chem. Thermodyn., 19* (1987) 1199.
12 A.N. Nesmeyanov, G.I. Samal and M.M. Pavlyuchenko, *Rus. J. Inorg. Chem., 12* (1967) 1713.
13 V.M. Glazov and N.M. Korenchuk, *Zh. Fiz. Khim., 45* (10) (1971) 2678.
14 T. Kushida, *J. Sci. Hiroshima Univ., Ser. A, 16* (1952) 75.
15 D. Ferro, V. Piacente and P. Scardala, *J. Chem. Thermodyn., 21* (1989) 483.
16 V. Piacente, P. Scardala and D. Ferro, *J. Mater. Sci. Lett., 9* (1990) 365.
17 P. Scardala, V. Piacente and D. Ferro, *J. Less-Common Met., 162* (1990) 11.
18 G. Bardi, V. Piacente and G. Trionfetti, *J. Mater. Sci. Lett., 9* (1990) 970.
19 V. Piacente, S. Foglia and P. Scardala, *J. Alloys Comp., 177* (1991) 17.
20 V. Piacente, P. Scardala and D. Ferro, *J. Alloys Comp., 178* (1992) 101.
21 V. Piacente, P. Scardala and D. Fontana, *J. Alloys Comp., 189* (1992) 263.
22 V. Piacente, T. Pompili, P. Scardala and D. Ferro, *J. Chem. Thermodyn., 23* (1991) 379.
23 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements,* American Society for Metals, Metals Park, OH, 1973.
24 K.C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides,* Butterworths, London, 1974.