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Thermodynamics of the Zinc Sulphide Transformation, Sphalerite \rightarrow Wurtzite, by Modified Entrainment

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The dissociative sublimation of both α - and β -zinc sulphide, ZnS(c) = Zn(g) + $\frac{1}{2}S_2(g)$, has been studied by modified entrainment in the temperature range 1010–1445 K. The following free-energy equations were derived:

$$\Delta G^{\circ}(\alpha)/J \text{ mol}^{-1} = 376\ 700 - 191.9T/K$$

and

$$\Delta G^{\circ}(\beta)/J \text{ mol}^{-1} = 3/4 \ 200 - 190.4 \ T/K$$

from which the enthalpy and entropy changes of transformation $(\beta \rightarrow \alpha)$ at the transition temperature (1293 K) were -2.5 ± 1.5 kJ mol⁻¹ and -1.5 ± 1.3 J K⁻¹ mol⁻¹. The corresponding $\Delta H^{\circ}(\beta \rightarrow \alpha)$ at 298.15 K obtained by the third-law method was -2.3 ± 0.9 kJ mol⁻¹. This enthalpy change is at variance with the currently accepted value of *ca*. 13 kJ mol⁻¹.

Zinc sulphide exists in two principal forms, sphalerite (β , cubic, or 3C) and wurtzite (α , hexagonal or 2H). The low-temperature form is the β -phase, the transition temperature¹ is 1293 ± 10 K, and the α -form is metastable at room temperature. Numerous intermediate forms (polytypes or superstructures), with crystal structures closely related to the principal forms, have been characterized.² Most compilations of thermodynamic data³⁻⁵ quote standard enthalpies of formation that imply $\Delta H(\beta \rightarrow \alpha) 298 \approx 13$ kJ mol⁻¹. This is based on an early solution calorimetric study⁶ at 293 K. More recent heat-capacity studies^{7,8} suggest that the transition is nearly athermal.

There is commercial interest in the use of molten zinc chloride as a hydrocracking solvent.^{9,10} Sulphur in the feedstock causes a steady accumulation of zinc sulphide in the melt. A proposed regeneration procedure involves conversion of the zinc sulphide *via*

$$ZnS(c) + 2HCl(g) = ZnCl_2(l) + H_2S(g)$$

followed by separation of the zinc chloride in a fluidized-bed combustor. The efficiency of the above conversion depends, *inter alia*, on the equilibrium constant and its temperature dependence. To estimate the latter, reliable thermodynamic data for the heats of formation of zinc sulphide in its common forms are necessary.

The modified entrainment method has been used to study the reductive transport [eqn (1)] of $ZnS(\beta)$ in the range 1012–1271 K and $ZnS(\alpha)$ in the range 1300–1443 K:

$$ZnS(\alpha,\beta) + H_2(g) = Zn(g) + H_2S(g).$$
(1)

Heats of formation of $ZnS(\alpha, \beta)$ were obtained from the temperature dependence of K_1 in combination with well established ancillary thermodynamic data.

Apparatus

Experimental

The modified entrainment method (MEM) has previously been described in detail.^{11, 12} In summary, ZnS (*ca.* 300 mg) is contained in a spherical silica capsule, the orifice of which comprises a vertical capillary (*ca.* 2 cm long, 1 mm i.d.). The capsule is suspended from one arm of a recording microbalance and the transporting gas (hydrogen) flows

downwards (*ca.* 80 cm³ min⁻¹) over the capsule and flushes away the gaseous products of equilibrium (1). The capsule is positioned in the region of a temperature plateau generated by a vertically mounted tube furnace. The experimental parameter is the rate of mass loss ($\dot{\omega}/\text{kg s}^{-1}$) of ZnS at a preset temperature, *T*. Sample temperatures were measured with a calibrated Pt–Pt/13% Rh thermocouple to a precision of ± 2 K. The design of the previously used capsules were improved in this work by insetting the capillary by *ca.* 2 mm into the capsule body rather than joining it *via* a short flared section; this enabled the diffusive resistance of the capillary ($l/\pi r^2$: l = length and r =radius) to be determined with greater precision. Three different capsules were used with capillary resistances from 1.912×10^4 to 2.132×10^4 m⁻¹. For ZnS(β), 92 data points were recorded with $\dot{\omega}$ ranging between 7.4×10^{-12} kg s⁻¹ (at 1012 K) and 2.8×10^{-10} kg s⁻¹ (at 1271 K). For ZnS(α), 199 data points were noted from 1300 K ($\dot{\omega} \approx 3.6 \times 10^{-10}$ kg s⁻¹) to 1433 K ($\dot{\omega} \approx 1.6 \times 10^{-9}$ kg s⁻¹).

Differential Scanning Calorimetry

A Stanton Redcroft Model 1500 was used with a scan speed of 5 K min⁻¹ from 1073 to 1423 K with the sample (43 mg) in a flowing nitrogen atmosphere.

Materials

Zinc sulphide (Aldrich Gold Label, 99.99%, batch no. 0301 JK) was used without further purification. Surprisingly, it was common to lose several mass per cent of volatile material during initial heating. The sample was characterized by emission spectroscopy, X-ray diffraction (X.r.d.), thermogravimetric analysis (t.g.a.), mass spectrometry (m.s.) and elemental analysis. Trace metallic impurities were determined by emission spectroscopy and were present at the following concentrations: Cd, 10 ppm; Na, 10 ppm; Pb, 2 ppm; Mo, 1 ppm; Ca, < 1 ppm; Mg, < 1 ppm. X.r.d. showed the sample to be 95 + % sphalerite. It has been reported¹³ that ZnS is slowly oxidised to ZnSO₄ in moist air and that the freshly precipitated material adsorbs water, thus giving a continuous dehydration loss on drying. Sulphate was shown to be absent from both the stock material and heated samples. T.g.a. (Perkin-Elmer TGS-2) in flowing nitrogen from 300 to 973 K at 20 K min⁻¹ showed a near-linear mass loss of 2.95 mass %, terminating between 920 and 970 K. The dissociation pressure above ZnS at 1000 K is ca. 10^{-2} Pa so no contribution was expected from this source. M.s. (AEI MS 30) with a solid injection probe was used to identify the volatile species. The sample was heated from ca. 350 to 623 K while continuously monitoring the mass spectrum in the m/erange 14–220. Water was noted at all temperatures, the maximum evolution being at ca. 450 K and decreasing thereafter. H₂S was observed from 480 K, rising to a maximum at 540 K and decreasing thereafter. SO₂, in smaller quantities, was also observed at temperatures in excess of 480 K. No other volatile material that originated from the sample was detected. Clearly the stock material was significantly contaminated with moisture which is evolved continuously. The H₂S probably arises from the reaction

$3S + 2H_2O = 2H_2S + SO_2$

which is known to proceed slowly on boiling S in H_2O (the sample was slightly sulphurrich, see below). Elemental analysis showed the stock material to have a Zn:S ratio of 0.993 ± 0.002 . It has been suggested¹⁴ that the stability of sphalerite depends on it being slightly S-rich but the non-stoichiometry range is small, 0.998 ± 0.001 . In summary, the stock material was contaminated with both moisture and S and has a composition $ZnS_{1.007\pm0.002} \cdot 0.168 H_2O$. These impurities have no influence on the MEM results as the minimum temperature for the MEM study was 1010 K, by which temperature the impurities were lost by volatilization. This was confirmed by elemental analyses on heated samples (see table 1).

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| | | | - |
|---|----------|---------------|-------------------|
| treatment | β | α | Zn:S ratio |
| ambient (stock sample) | dominant | < 5% | 0.993 ± 0.002 |
| 700 °C/24 h/H _a | dominant | < 5 % | 0.998 ± 0.002 |
| 800 °C/24 h/H ₂ | dominant | < 5 % | |
| 900 °C/24 h/H ₂ | dominant | $\approx 5\%$ | 0.999 ± 0.002 |
| $900 \text{ °C}/32 \text{ days}/\text{Ar}^a +$ | dominant | 5-10 % | |
| 900 °C/10 min/H, | | | |
| 1100 °C/14 days/Ar | minor | dominant | 0.999 ± 0.002 |
| to 1130 °C/10 K min ⁻¹ /N ₂ + | trace | dominant | |
| to 900 °C/10 K min ⁻¹ /N ₂ | | | |
| to 1230 °C/20 K min ⁻¹ / N_2 | trace | dominant | Million August |
| · - | | | |

Table 1. The treatment of $ZnS(\beta)$ and its subsequent analysis by X.r.d.

^a Hydrogen cannot be used for long periods at high temperatures because of transport by reductive sublimation [eqn (1)].

Hydrogen was purified by passage through a palladium diffuser (model H28/1, Johnson Matthey). Argon was purified using a commerical rare-gas purifier (model RGP-4, B.O.C.).

Results and Discussion

Differential Scanning Calorimetry

An attempt was made to measure the enthalpy of transition directly using d.s.c. The results were ambiguous; there was a slow endotherm with an onset at 1173 K that merged into a more rapid exotherm, which was complete at 1333 K. It was not possible to deconvolute these two features. These results suggest the data points from modified entrainment above 1173 K with the β -phase should be treated with caution. An X-ray diffraction study of the $\beta \rightarrow \alpha$ phase transition has been reported by Baars and Brandt¹⁵ who steadily heated a 'weakly disordered cubic' phase from 293 K while monitoring the diffraction pattern. At *ca.* 1173 K, the residual disorder decreased until at 1273 K it had been eliminated. Above 1273 K there was a rapid, quantitative conversion to the hexagonal phase, with complete conversion at 1400 K. The implication of this study on our reported enthalphy and entropy of transition is considered below.

Modified Entrainment

The dissociative sublimation [eqn (2)] of zinc sulphide is known to be congruent,¹⁶ and the concentration of molecular ZnS(g) in the equilibrium vapour over our temperature range is negligible:¹⁷

$$ZnS(c) = Zn(g) + \frac{1}{2}S_2(g).$$
 (2)

Also there is insignificant contribution from $S_n(g)$ (n > 2 or n = 1) in this temperature range.¹⁸ Initial experiments performed with Ar as carrier gas in the temperature range where the β -phase is stable (< 1293 K) gave extremely low rates of mass loss. All subsequent experiments were performed in hydrogen, where the participation of the equilibrium

$$H_{2}(g) + \frac{1}{2}S_{2}(g) = H_{2}S(g)$$
(3)

enhanced the rate of mass loss by ca. three orders of magnitude.

The conversion of the β -phase to the α -phase has been extensively investigated and the effects of impurity levels,^{2,19} particle size,²⁰ mechanical stress²¹ etc. on both the rate and temperature of conversion are well documented. The conversion is facile and it was clearly necessary to establish the identity of the material used in modified entrainment, especially in the region ca. 100 K below the transition temperature, where a slow

conversion to the α -phase could invalidate the experiments. Accordingly, batches of stock ZnS were heated in flowing H₂, N₂ or Ar for at least 24 h to simulate their behaviour in the modified entrainment rig, quenched rapidly and examined by X.r.d. Samples sizes and irradiation times were such that the level of discrimination between the phases was *ca.* 5%. Table 1 summarises the sample treatment, the X.r.d. results and elemental analyses on the heated samples.

Two separate modified entrainment experiments on the β -phase were completed with different initial samples and different temperature sequences. In one set the temperature was increased steadily from 1120 K to within 50 K of the transition temperature and decreased to 950 K, recording 55 data points $[\dot{\omega}(T)]$ at regular intervals. For the second set, the temperature was decreased from 1150 K to 910 K, then increased to 1250 K, noting 37 values of $\dot{\omega}(T)$. An analysis of covariance on the regression lines ($\Delta G_2^{\circ}/J \mod^{-1} vs. T/K$) showed no significant difference. For experiments with the α -phase, zinc sulphide was maintained at 1440 K in H₂ for 2 h to ensure complete conversion.

Only two of eqn (1)–(3) are independent and it is convenient to write the flux equations in terms of eqn (2) and (3) and so extract an expression for the equilibrium constant for dissociative sublimation (K_2) ,

$$K_2 = \left(\frac{\dot{\omega} R T l}{M_5 A}\right)^2 / (D_4 D_2 K_3 p^{\circ} P)$$
(4)

where $\dot{\omega}$ is the rate of mass loss of ZnS, l/A is the length over the cross-sectional area (the diffusive resistance) of the capillary, M_5 is the molecular mass of ZnS, D_i are quaternary diffusion coefficients, K_i are equilibrium constants, p^{\ominus} is the standard-state pressure (101325 Pa) and P is the working pressure in the MEM rig. The following notation is used throughout: $1 \equiv H_2$, $2 \equiv H_2S$, $3 \equiv S_2$, $4 \equiv Zn$ and $5 \equiv ZnS$. The diffusion coefficients (D_i) include a power-law dependence on temperature and are formulated in terms of the corresponding binary diffusion coefficients (\mathcal{D}_{i1}) into the majority component (H_2) and a multicomponent diffusion correction term (γ_i).

$$D_{i} = \mathcal{D}_{i1} / \gamma_{i} = \mathcal{D}_{i1}^{\circ} (T/273.15)^{1+s} / \gamma_{i}.$$
(5)

The derivation of eqn (4) and the form of γ_i are outlined in the Appendix. Use of eqn (4) implies a knowledge of K_3 and its temperature dependence. The thermodynamic parameters for the components in eqn (3) have been assessed by the compilers of the JANAF tables,¹⁸ and values of ΔG_3° were calculated at 100 K intervals from 900 to 1500 K from

$$\Delta G_3^\circ = \Delta H_{298}^\circ - T\Delta(\text{fef}) \tag{6}$$

$$(\text{fef}) = -(G_{\rm T}^{\circ} - H_{298}^{\circ})/T$$
(7)

using JANAF data for ΔH_{298}° and Δ (fef). Regression of these results with T yielded

$$\Delta G_3^{\circ} / \text{J mol}^{-1} = (-90\,333 \pm 110) + (49.3 \pm 0.1) T; \quad (900 - 1500 \text{ K}). \tag{8}$$

The uncertainty intervals are standard deviations of the regression coefficients. A recommended expression²² for equilibrium (3) over a much wider temperature range (298–1750 K) agrees with eqn (8) to within 0.2% at 900 K and to within 3.3% at 1444 K, the upper temperature limit in this work.

The results from two independent experiments with $ZnS(\beta)$ using capsules with different channel dimensions were pooled, K_2 extracted from eqn (4), and ΔG_2° regressed with T to yield an equation in the form of eqn (8). A statistical routine was used which identified outliers (data pairs for which the standardized residual > |2|), which were then rejected, the rejection sequence terminating when $r^2 = 0.998$ (n = 79). The initial r^2 was 0.995 for all data points (n = 92), where r = correlation coefficient.

$$\Delta G_{2}^{\circ}(\beta) / \mathrm{J} \,\mathrm{mol}^{-1} = (374200 \pm 1200) - (190.4 \pm 1.1) \,T; \quad 1010 - 1270 \,\mathrm{K} \tag{9}$$

where

A similar procedure was adopted for the experiments with the α -phase when the results from three separate experiments with the same capsule were pooled ($n = 199, r^2 = 0.997$), the final regression equation being based on n = 192.

$$\Delta G_2^{\circ}(\alpha) / \text{J mol}^{-1} = (376700 \pm 900) - (191.9 \pm 0.6) T; \quad 1300 - 1440 \text{ K}. \tag{10}$$

In both cases the rejected data points were randomly distributed throughout the temperature range; the uncertainty intervals in eqn (9) and (10) are standard deviations of the regression coefficients. Assuming that these equations may be extrapolated to the transition temperature (1293 K) which is equivalent to the approximation,

$$\Delta C_p^{\beta}(1010 - 1293 \text{ K}) = \Delta C_p^{\alpha}(1293 - 1440 \text{ K}) \approx 0$$

$$\Delta H^{\circ}(\beta \to \alpha) \ 1293 = -2.5 \pm 1.5 \text{ kJ mol}^{-1}$$

we derive

$$\Delta H^{\circ}(\beta \to \alpha) \ 1293 = -2.5 \pm 1.5 \text{ kJ mol}^{-1} \left\{ \Delta S^{\circ}(\beta \to \alpha) \ 1293 = -1.5 \pm 1.3 \text{ J K}^{-1} \text{ mol}^{-1} \right\}$$
(11)

The heat capacities for $ZnS(\alpha)$ and $ZnS(\beta)$ at both high⁸ and low⁷ temperatures have been reported by the Bureau of Mines (U.S.A.) group (BM). The high-temperature work revealed no enthalpy of transition and the results in combination suggest

$$\Delta S^{\circ}(\beta \to \alpha) \ 1300 \approx 0.4 \text{ J } \text{K}^{-1} \text{ mol}^{-1} \left\{ \Delta (H^{\circ}_{1300} - H^{\circ}_{298})(\beta \to \alpha) \approx 0 \text{ kJ mol}^{-1} \right\}$$
(12)

Our results are in satisfactory agreement with the BM study.

A recent study²³ of a high-temperature solid electrolyte cell yielded Gibbs free energies for the reversible cell reaction,

$$ZnS(\beta) + 3Cu_2O(c) = ZnO(c) + 6Cu(c) + SO_2(g)$$

which, in combination with ancillary thermodynamic data, gave

$$\Delta G_{2}^{\circ}(\beta) / J \text{ mol}^{-1} = 387000 - 199T; \quad 1180 - 1210 \text{ K}.$$
(13)

Over the common temperature range our results for ΔG_2° are ca. 2% low compared with those from eqn (13), but the constants are quite different, suggesting internal compensation. A comparison of ΔG_2° from several sources is given in table 2.

The constants A and B in eqn (9) and (10) correspond, in a second-law analysis, to ΔH_2° and ΔS_2° , respectively, at the mid-points of the experimental temperature ranges. They may be converted to apply to the standard formation reaction (298 K),

$$Zn(c) + S(rhomb) = ZnS(\alpha, \beta)$$
(14)

using ancillary thermodynamic data for zinc,²⁶ sulphur¹⁸ and zinc sulphide.⁸ These second-law conversions yield

$$\Delta H_{14}^{\circ}(\beta) = \Delta H_{\rm f}^{\circ}[{\rm ZnS},\beta]298 = -190.2 \pm 4.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{14}^{\circ}(\alpha) = \Delta H_{\rm f}^{\circ}[{\rm ZnS}, \alpha]298 = -196.4 \pm 4.0 \text{ kJ mol}^{-1}$$

where the uncertainty intervals are ± 2 standard deviations, the usual practice for $\Delta H_{\rm f}^{\circ}$.

The results were also processed by the third-law method. Here, the complete data set of $\dot{\omega}(T)$ was used (92 points for the β -phase and 199 points for the α -phase), each data pair yielding a value for K_2 from eqn (4). Eqn (15) was then used to derive a set of values for ΔH_{298}° :

$$\Delta H_2^{\circ}(\alpha, \beta, 298) = T\Delta[-(G_T^{\circ} - H_{298}^{\circ})/T] - RT \ln K_2.$$
(15)

Gibbs free energy functions for ZnS were calculated from the heat capacities and derived functions reported in the BM study.^{7,8} Corresponding functions for Zn(g) were taken from ref. (26) and for $S_2(g)$ from the JANAF compilation.¹⁸ Finally, combining with $\Delta H_{\rm f}^{\circ}[S_2, g]298 = 128.49 \pm 0.29^{18} \text{ kJ mol}^{-1} \text{ and } \Delta H_{\rm f}^{\circ}[Zn, g]298 = 137.74 \pm 0.42^{26} \text{ kJ mol}^{-1},$

| phase | temperature range/K | A ∕J mol⁻¹ | <i>B</i> /J K ⁻¹ mol ⁻¹ | ref. |
|-------|------------------------|---------------|--|-----------|
| β | 1180-1210 | 387 000 | 199 | 23 |
| β | 1180-1210 | 391 200 | 201 | 24 |
| β | < 1293 | 374 300 | 193 | 25 |
| β | 1010-1270 | 374 200 | 190 | this work |
| α | 1323-1473 | 360 900 | 183 | 25 |
| α | 1300-1440 | 376 700 | 192 | this work |

Table 2. A comparison of literature data for the equilibrium $ZnS(\alpha, \beta) = Zn(g) + \frac{1}{2}S_2(g), \Delta G_2^{\circ}/J \text{ mol}^{-1} = A - BT$

Table 3. Comparison of second-law and third-law enthalpies of formation at 298 K

| | $ZnS(\beta)$ | $ZnS(\alpha)$ | |
|--|--|---|--|
| $\Delta H_{\rm f}^{\circ}/{\rm kJ} {\rm mol}^{-1}$, 2nd law $\Delta H_{\rm f}^{\circ}/{\rm kJ} {\rm mol}^{-1}$, 3rd law $\Delta H^{\circ}(\beta \to \alpha)/{\rm kJ} {\rm mol}^{-1}$, 2nd law $\Delta H^{\circ}(\beta \to \alpha)/{\rm kJ} {\rm mol}^{-1}$, 3rd law | $ \begin{array}{r} -190.2 \pm 4.6 \\ -194. \pm 0.5^{a} \\ -6.3 \\ -2.3 \end{array} $ | $-196.4 \pm 4.0 -196.3 \pm 0.5^{a} \pm 6.1 \pm 0.7$ | |

^a The uncertainty intervals quoted for the third-law results are ± 2 standard deviations.

standard enthalpies of formation corresponding to eqn (14) were derived. These are compared with the second law values in table 3.

Notwithstanding the identification of our low-temperature phase as $95 + \% \beta$ by X.r.d. (see table 1), Samelson and Brophy¹⁹ maintain that chemically pure ZnS(β) always contains stacking faults, mostly arising from twinning. Aminoff and Broomé²⁷ have shown that α -ZnS exists in the vicinity of the interfacial planes of this cubic twin. The experiments of Baars and Brandt,¹⁵ referred to earlier in the discussion of our d.s.c. results, suggest that the concentration of the α -phase in a weakly disordered cubic phase could be *ca*. 20%. Our d.s.c. results show a feature that occurs in the same temperature interval (900–1020 °C) in which Baars *et al.* note annealing of the residual disorder in their weakly disordered cubic phase. Together, this evidence suggests that our transition data could refer to the process $(0.8\beta+0.2\alpha) \rightarrow \alpha$ rather than $\beta \rightarrow \alpha$. This introduces an additional uncertainty into the transition data and all results specific to the β -phase. The error limits quoted reflect this additional uncertainty. The second and third law values for the α -phase are in good agreement, but for the β -phase the agreement is less good. The transition enthalpies agree within the quoted uncertainty intervals.

The principal conclusion from this work is that the transition $ZnS(\beta) \rightarrow ZnS(\alpha)$ is nearly athermal, both at the transition temperature and at 298 K. This is in agreement with the BM results,^{7,8} but at variance with Kapustinskii and Chentzova's solution calorimetric study.⁶ Briefly, this Russian work consisted of measuring the enthalpies of reaction of the α - and β -phases in concentrated HCl using an adiabatic calorimeter. With the same final thermodynamic state in each case, the difference in the heats of reaction is equal to the heat of transition. The solution of the β -phase was complete within 10 min, but the solution of the α -phase was so sluggish that the experiments were truncated when disolution was *ca*. 90% complete, the extent of reaction being determined by analysis. The uncertainty attendant on solution calorimetry with slow reactions is well established,²⁸ and the truncation procedure must be regarded as of

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doubtful validity. Also, when this work was repeated by the BM group,²⁹ it was the β -phase that proved difficult to dissolve,²³ and no results were reported for it. Their result by reaction calorimetry for $\Delta H_{\rm f}^{\circ}[{\rm ZnS}, \alpha]298 = 191.9 \pm 0.8$ kJ mol⁻¹ differs by 4.4 kJ mol⁻¹ from our third-law result.

Appendix

Under conditions of modified entrainment (see Experimental section) the partial pressure, p_i , of a single substance, *i*, contained in the capsule and using a single carrier gas is given¹¹ by

$$p_i = P(1 - \exp(-\xi_i)] \tag{A1}$$

$$\xi_i = \dot{\omega} \mathbf{R} T l / (A M_i P \mathcal{D}_i). \tag{A 2}$$

The term $[1 - \exp(-\xi_i)]$ in eqn (A 1) may be approximated to ξ_i to an accuracy of 5% when $\xi_i < 0.1$. Mass transport in the capillary is by diffusive and convective flow, and Cussler³⁰ has shown that this exponential approximation is equivalent to the assumption that transport is entirely diffusive (the dilute-gas approximation).

Extension³¹ of the treatment to multicomponent systems is straightforward, and equilibrium constants may be formulated in terms of the partial pressures of each gasphase component, the exponential approximation being invoked for algebraic tractability. For zinc sulphide entrainment only two of the eqn (1)–(3) are independent and it is convenient to write the mass balance and flux equations in terms of eqn (2) and (3). A coupling parameter, δ , is defined as the flux ratio in the capillary of Zn(g) to S₂(g) (for transport in argon, $\delta = 2$ as the sublimation is congruent). Hence

$$K_2 = \left(\frac{\dot{\omega} \mathbf{R} T l}{M_5 A p^{\odot}}\right)^{1.5} / (D_4 [D_3 \delta]^{0.5}) \tag{A 3}$$

$$K_3 = \frac{\delta - 2}{PD_2} \left(\frac{\dot{\omega} \mathbf{R} T l D_3 p^{\ominus}}{M_5 A \delta} \right)^{0.5}.$$
 (A 4)

The term $\dot{\omega}$ is readily eliminated from these equations, leaving a cubic in δ . Using eqn (8) to obtain K_3 , and literature data²³ for K_2 , the cubic which has only one real positive root was solved exactly giving $\delta \approx 1.4 \times 10^8$ at 1000 K to $\delta \approx 10^3$ at 1425 K. Consequently $\delta - 2$ was approximated to δ in eqn (A 4) and then δ is elimated from eqn (A 3) and (A 4) to give

$$K_2 = \left(\frac{\dot{\omega} R T l}{M_5 A}\right)^2 / (D_4 D_2 K_3 p^{\Theta} P)$$
 (A 5)

which is identical to eqn (4). The physical significance of the large values of δ is that because equilibrium (3) lies to the right in our temperature range, the S₂ is transported mainly as H₂S.

In a system of more than two components the effects of multicomponent diffusion³² must be included. A second-order treatment of this effect³³ permits the multicomponent diffusion coefficient (D_i) to be written in terms of the corresponding binary diffusion coefficient (\mathcal{D}_{ij}) with respect to the majority component (hydrogen)

$$D_2 = D(H_2S-H_2, S_2, Zn) = \mathscr{D}(H_2S-H_2)/\gamma_2$$
(A 6)

$$D_3 = D(S_2 - H_2, H_2S, Zn) = \mathscr{D}(S_2 - H_2)/\gamma_3$$
(A 7)

$$D_4 = D(Zn-H_2, H_2S, S_2) = \mathcal{D}(Zn-H_2)/\gamma_4$$
(A 8)

$$\begin{split} \gamma_2 &= 1 + \left[\left(\frac{\delta D(1,4) D(2,4)}{(\delta+1)} + \frac{D(1,3) D(2,3)}{(\delta+1)} \right) - 1 \right] \frac{\xi_2}{2} \\ \gamma_3 &= 1 + \left[\left(\frac{\delta D(1,4) D(3,4)}{(\delta+1)} + \frac{D(1,2) D(3,2) (\delta-2)}{(\delta+1)} \right) - 1 \right] \frac{\xi_3}{2} \\ \gamma_4 &= 1 + \left[\left(\frac{D(1,3) D(4,3)}{(\delta+1)} + \frac{D(1,2) D(4,2) (\delta-2)}{(\delta+1)} \right) - 1 \right] \frac{\xi_4}{2} \\ D(k,l) &= (M_l / M_k)^{\frac{1}{2}} - 1 \end{split}$$

and

The expressions for γ_i contain both δ and ξ_i , which themselves are functions of D_i . As D_i are evaluated from a knowledge of γ_i , a reiterative procedure is used in which γ_i is set initially to unity, then refined until successive estimates differ by < 1 in 10⁴. Some typical values of γ_i are shown in table A1.

 $\xi_i = \frac{\dot{\omega} R T l(\delta + 1)}{D_i A M_5 P \delta}.$

| Table | A 1 | . Correct | ion | fact | ors | for | multic | om- |
|-------|------|-----------|------|------|-----|-------|----------|-----|
| por | nent | diffusion | [see | eqn | (A | 6) ai | nd (A 8) |)] |

| T/K | γ_2 | γ_4 |
|------|------------|------------|
| 1010 | 1.0001 | 0.9998 |
| 1129 | 1.0006 | 0.9988 |
| 1225 | 1.0019 | 0.9962 |
| 1320 | 1.0048 | 0.9901 |
| 1428 | 1.0130 | 0.9735 |

Binary diffusion coefficients (\mathcal{D}_{ij}) may be calculated with good precision from a knowledge of Lennard-Jones potential parameters and kinetic theory.³⁴ Lennard-Jones constants are available³⁴ from experimental viscosity results for H₂S and H₂. The usual combining rules were used. For $\mathcal{D}(Zn-H_2)$, independent experimental data exist³⁵ in the range 690–1120 K, and these were assumed to apply in the overlapping experimental temperature range of this work, 1010–1445 K. Estimates of $\mathcal{D}(S_2-H_2)$, required for preliminary calculations, were obtained from Svehela's estimated³⁶ Lennard-Jones potential parameters for S₂. The following equations were derived as described above and refer to atmospheric pressure and 1000–1450 K.

$$\begin{aligned} \mathscr{D}(\text{Zn-H}_2)/\text{m}^2 \text{ s}^{-1} &= 8.109 \times 10^{-5} (T/273.15)^{1.539} \\ \mathscr{D}(\text{H}_2\text{S}-\text{H}_2)/\text{m}^2 \text{ s}^{-1} &= 6.004 \times 10^{-5} (T/273.15)^{1.671} \\ \mathscr{D}(\text{S}_2-\text{H}_2)/\text{m}^2 \text{ s}^{-1} &= 3.961 \times 10^{-5} (T/273.15)^{1.702} \end{aligned}$$

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