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Vaporization behavior and thermodynamic stability of $V_2P(s)$

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Abstract

The vaporization behavior and thermodynamic stability of $V_2P(s)$ were investigated by mass loss effusion and effusion mass spectrometry, the latter by an ion current ratio method. Enthalpies of formation with white phosphorus as the reference state and enthalpies of atomization were calculated. Results from the two types of experiments are in good agreement. Mean values of $V_2P(s)$: $\Delta_f H^\circ_{298.15} = -209.0 \pm 5$ kJ mol^{-1}, $\Delta_{at} H^\circ_{298.15} = 1556.4$ kJ mol^{-1}. Recalculated values for $V_3P(s)$: $\Delta_f H^\circ_{298.15} = -233.13 \pm 5$ kJ mol^{-1}, $\Delta_{at} H^\circ_{298.15} = 2096.0$ kJ mol^{-1}.

1. Introduction

The research described here is part of a larger investigation of transition metals with the p-block elements aluminum, silicon and phosphorus. The current focus in this broader investigation is on 10-electron systems with a stoichiometric ratio of 1:1, namely TiS, VP, CrSi and MnAl (solid solution). The goals of this investigation are to acquire reliable thermodynamic data, to establish trends in stability and to develop an understanding of these trends in terms of chemical bonding and stability with the aim of developing a predictive model for stability. The only published experimental stability data for the V–P system are the mass loss effusion study on $V_3P(s)$ reported earlier from this laboratory [1] and an estimate of the enthalpy of formation of VP(s) based on the results of chemical transport experiments [2]. The present research is subsequent to the study of the vaporization behavior of $V_3P(s)$ reported earlier [1] and continues work toward an evaluation of the thermodynamic stability of VP(s). In as much as the earlier study established that V_3P vaporizes incongruently under equilibrium conditions with preferential loss of phosphorus, the vaporization of V_2P was also expected to be incongruent. The study reported here employed both mass loss effusion and effusion mass spectroscopy.

2. Experimental details

Samples were prepared by direct combination of the elements in evacuated and sealed Vycor glass tubes as described earlier [3]. The crude vanadium phosphide samples were annealed either in a vacuum induction furnace or in the mass loss effusion apparatus. The samples and residues from effusion runs were characterized by X-ray powder diffraction; the experimental diffraction patterns were compared with powder patterns generated by computer [4] from published crystal structure data [5].

Effusion cells were fabricated from high density graphite or from tungsten and were lined with tantalum. All cells used for mass loss experiments, two graphite and one tungsten, had cylindrical channel orifices. Effective orifice areas were obtained by a calibration which employed the known vapor pressure of silver [6]. A black-body hole was drilled into the lateral surface of the base of the cell in order to achieve accurate temperature measurement with the pyrometer. This hole did not penetrate the interior of the cell. The Knudsen cells used in the mass spectrometry experiments were fabricated from graphite. One cell had a graphite lid with a channel orifice, while the others had a graphite outer lid and an inner tantalum foil (0.006 inch) lid pierced with a pinhole orifice which ranged from 0.2 to 0.3 mm in diameter.

The apparatuses for mass loss effusion [1] and effusion mass spectrometry [7] have both been described earlier. In both experiments temperatures were monitored with a W-5%Re/W-26%Re thermocouple with digital readout. In the mass loss experiments the thermocouple

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was mounted just below the effusion cell, whereas in the mass spectrometry experiments it was inserted into the hole in the bottom of the cell which did not penetrate to the interior of the cell. Temperatures were measured with optical pyrometers (Pyrometer Instrument Company) with certificates of calibration traceable to the US National Bureau of Standards. Appropriate corrections were made for light absorption by windows and prisms. The V_2P–V_3P two-phase region was studied by the mass loss technique in the temperature range 1677–1845 K and by mass spectrometry in the range 1770–2100 K. The lower limit in each case was dictated by the respective limit of detection and the upper limit by significant reaction with the container. Measurement times of several hours were required in the mass loss experiments, which restricted the upper limit of the useful temperature range.

Since the achievement of equilibrium has proved to be a problem in effusion studies on transition metal phosphides [1, 3], samples in the mass loss experiments were routinely removed from the effusion cell and ground after collection of data at a given temperature. This was done to minimize the effects of decreased surface area due to sintering. Between runs in the mass spectrometry experiments, samples were routinely ground and a new tantalum liner was installed.

Ion intensities for P_2^+ and V^+ were of primary interest in the mass spectrometry experiments as confirmed by appearance potential determinations. A mass spectrometry experiment consisted of at least two cyclical temperature ramps (down, up, down, up). The duration was generally less than 3 h. An ionizing electron energy of 30 eV was used in all runs and the intensity of the peak was determined using an integration time of 10 s. In most of the experiments data were collected manually and the net ion intensity was obtained by subtraction of the background signal. A few of the runs were done with the mass spectrometer in an automated mode in which the computer collected peak intensities and thermocouple readings every 2 min; the temperature was controlled using a ramp program and thermocouple temperatures were corrected by comparison with pyrometer readings made during the run. No background correction was made in the automatic mode, but any difference in results was well within experimental uncertainty.

3. Treatment of data

3.1. Mass loss experiments

The primary data in the mass loss experiments were temperatures and rates of mass loss and were treated in terms of the reaction

$$6V_2P(s) \rightleftharpoons 4V_3P(s) + P_2(g) \qquad (1)$$

where $P_2(g)$ was presumed to be in equilibrium with $P(g)$; $P_4(g)$ is not important in the experimental temperature–pressure regime. Partial pressures were calculated from the effusion equations. For vanadium,

$$\begin{aligned} P_v &= \frac{m_v}{a}\left(\frac{2\pi RT}{M_v}\right)^{1/2} \\ &= \frac{Cm_v}{a}\left(\frac{T}{M_v}\right)^{1/2} \end{aligned} \qquad (2)$$

where m_v is the partial rate of mass loss for vanadium, a is the effective orifice area, T is the Kelvin temperature and M_v is the atomic weight of vanadium. When the partial mass loss rate is in milligrammes per minute and the orifice area in square centimetres, the partial pressure of vanadium is obtained in bars when the constant C has the value 3.810×10^{-7}. For phosphorus [1, 3],

$$\begin{aligned} P_{P_2} &= \frac{K}{8}\left\{\left[1 + \frac{8m_P}{aK}\left(\frac{\pi RT}{M_P}\right)^{1/2}\right]^{1/2} - 1\right\}^2 \\ &= \frac{K}{8}\left\{\left[1 + \frac{C'm_P}{\mathrm{aK}}\left(\frac{T}{M_P}\right)^{1/2}\right]^{1/2} - 1\right\}^2 \end{aligned} \qquad (3)$$

where K is the equilibrium constant for the dissociation of 1 mol P_2, m_P is the partial rate of mass loss for phosphorus, a is the effective orifice area, T is the Kelvin temperature and M_P is the atomic weight of phosphorus. The partial pressure is obtained in bars when the rate of mass loss is in milligrammes per minute, the orifice area is in square centimetres, and the constant C' has the value 2.155×10^{-6}. The equilibrium constant K was calculated at each experimental temperature from data in ref. 8. Since vanadium atoms, in addition to phosphorus species, proved to be important in the vapor, it was necessary to apportion the total rate of mass loss into partial rates for the two elements. This was done by an iteration procedure in which the total rate was initially assigned to phosphorus and an approximate vanadium partial pressure was calculated from the previously measured [1] free energy of formation of $V_3P(s)$. This vanadium partial pressure was used to calculate a partial mass loss rate for vanadium which was subtracted from the total to obtain a partial rate for phosphorus, which in turn was used to calculate a second approximation to the vanadium partial pressure. Three such cycles were sufficient for convergence.

3.2. Mass spectrometry

The mass spectrometry data were treated by an ion current ratio method which is reported in detail elsewhere [9]. The partial pressure of a parent species is related to the ion current through the relation

$$P_i = C\frac{I_i T}{\sigma_i \gamma_i A_i} \quad (4)$$

where I_i is the ion current intensity of species i, T is the Kelvin temperature, σ_i is the ionization cross-section for species i, γ_i is the multiplier gain for the ion of species i, A_i is the abundance of the isotopic mixture in the observed species i and C is an instrument sensitivity which is independent of the species but depends on the experimental arrangement, including electrical and geometric factors. For the reaction

$$5V_3P(s) + P_2(g) \rightleftharpoons 7V_2P(s) + V(g) \quad (5)$$

the equilibrium constant is

$$K = \frac{P_V}{P_{P_2}} = \frac{I_V}{I_{P_2}}\left(\frac{\sigma_{P_2}\gamma_{P_2}A_{P_2}}{\sigma_V\gamma_V A_V}\right) \quad (6)$$

in which the instrument sensitivity C has cancelled. The experimental results for the respective species were expressed for each run as a least-squares fit

$$\log(I_i^+ T) = \frac{A_i}{T} + B_i \quad (7)$$

The ion current ratio as a function of temperature for a specific run is given by

$$\log\left(\frac{I_V^+}{I_{P_2}^+}\right) = \frac{A_V - A_{P_2}}{T} + B_V - B_{P_2} \quad (8)$$

To determine the equilibrium constants, the cross-section ratio $\sigma_V/\sigma_P = 1.33$ was calculated from the data given by Mann [10], the ratio $\sigma_{P_2}/\sigma_P = 1.5$ was estimated in comparison with other diatomics [11] and the ratio σ_V/σ_{P_2} was then calculated to be 0.89; the multiplier gain was assumed to be inversely proportional to the square root of the ion mass, *i.e.* $\gamma_V/\gamma_{P_2} = 1.10$; the isotopic abundance ratio is $A(^{51}V)/A(^{31}P^{31}P) = 0.9975$.

3.3. *Thermodynamics*

Thermodynamic stability data at standard temperature, 298.15 K, were obtained by a third-law procedure:

$$\Delta_r H^\circ_{298.15} = \Delta_r G^\circ_T - T\Delta_r \Phi'_T$$

where

$$\Phi'_T = -\frac{G^\circ_T - H^\circ_{298.15}}{T}$$

It had been assumed earlier [1] that the necessary thermal functions for $V_3P(s)$ could be approximated adequately by those of $V_3Si(s)$ [12]. However, recent results of scanning calorimetry experiments [13] on V_3P and V_3Si have provided a revised estimate of 23.5 J g-atom^{-1} K^{-1} for the standard molar entropy of $V_3P(s)$, which is significantly lower than the preferred value for $V_3Si(s)$, 25.6 J g-atom^{-1} K^{-1}. Free-energy functions for V_3P were calculated from the revised standard molar entropy combined with the high temperature heat capacity of V_3Si. An estimate of the standard molar entropy of $V_2P(s)$ was obtained by interpolation to the M_2X composition, on an atomic fraction basis, between the values [12] for V_3Si and V_5Si_3 and then multiplying by 23.5/25.6. Estimates of heat capacities were also obtained by interpolation between values for V_3Si and V_5Si_3. Free-energy functions for V(s), V(g) and $P_2(g)$ were taken from ref. 8.

4. Results

The initial work on the system was done to investigate the nature of the vaporization. In samples exhibiting diffraction patterns of both V_2P and V_3P, the intensity of peaks assigned to V_2P decreased following an extensive effusion run; likewise, the intensity of peaks due to V_3P was enhanced. This led to the conclusion that the vaporization of V_2P was incongruent, yielding V_3P and phosphorus gas according to eqn. (1), where P_2 is presumed to be in equilibrium with other phosphorus species, principally P(g). Results with the mass spectrometer confirmed this conclusion, although V(g) was also important in the vapor.

4.1. *Mass loss experiments*

Partial pressures of $P_2(g)$ were obtained by the iterative process described above. These partial pressures are given in Table 1 along with calculated thermodynamic quantities. The results are plotted as the logarithm of the partial pressure (in bars) of V(g) and $P_2(g)$ *vs.* $10000/T$ in Fig. 1. The data obtained with the tantalum-lined graphite cells agreed within experimental uncertainty, whereas the data found with the tantalum-lined tungsten cell were systematically lower. It had been observed earlier [1] that tungsten was not a suitable liner material for a graphite effusion cell containing vanadium phosphide samples, and the present observations suggest that tungsten is unsuitable even when contact is only through the vapor. The experiments in the tungsten cells were presumed not to be at equilibrium and the results were not used in subsequent thermodynamic calculations. Although the effective orifice areas for the two graphite cells differed by a factor of 3, the agreement between these sets of data supports the presumption that equilibrium was achieved in these experiments.

Standard enthalpies of formation and atomization of $V_2P(s)$ were calculated from the standard enthalpy of formation of $P_2(g)$ given in ref. 8 and the standard

TABLE 1. Mass loss effusion data for $6V_2P(s) \rightleftharpoons 4V_3P(s) + P_2(g)$

Temperature (K)	dm/dt $\times 10^4$ (mg min^{-1})	$\mathrm{Log}(P_{P_2}/P^\circ)$	$\mathrm{Log}(P_v/P^\circ)$	ΔG°_T (kJ mol^{-1})	$\Delta\Phi'$ (J mol^{-1} K^{-1})	$\Delta_r H^\circ_{298.15}$ (kJ mol^{-1})	$\Delta_f H^\circ_{298.15}$ (V_2P,s) (kJ mol^{-1})
(a) Graphite channel, area 0.00185 cm^2							
1788	3.06	−6.017	−7.350	206.0	139.8	455.9	−207.8
1800	2.99	−6.037	−7.198	208.4	139.4	459.8	−208.4
1763	2.15	−6.169	−7.578	208.2	140.3	455.6	−207.7
1766	3.19	−5.989	−7.577	202.5	140.2	450.2	−206.8
1817	4.17	−5.888	−7.087	204.8	139.1	457.6	−208.1
1846	3.82	−5.958	−6.800	210.6	138.5	466.3	−209.5
(b) Graphite channel, area 0.000596 cm^2							
1677	3.75	−6.411	−8.466	205.9	142.3	444.4	−205.9
1694	3.44	−6.452	−8.268	209.3	141.9	449.6	−206.7
1706	5.12	−6.275	−8.165	205.0	141.6	446.5	−206.2
1729	5.56	−6.242	−7.921	206.6	141.1	450.6	−206.9
1755	7.22	−6.130	−7.667	206.0	140.5	452.5	−207.2
1777	9.24	−6.025	−7.459	205.0	140.0	453.8	−207.4
1778	11.0	−5.947	−7.462	202.5	140.0	451.3	−207.0
1794	11.0	−5.950	−7.302	204.4	139.6	454.8	−207.6
1782	9.03	−6.038	−7.407	206.0	139.9	455.3	−207.7
1740	8.82	−6.037	−7.839	201.1	140.8	446.2	−206.1
1757	11.5	−5.919	−7.681	199.1	140.4	445.9	−206.1
1701	4.03	−6.382	−8.202	207.9	141.7	448.9	−206.6
1746	6.94	−6.146	−7.758	205.5	140.7	451.1	−207.0
1766	5.90	−6.228	−7.537	210.6	140.2	458.2	−208.2
1805	6.74	−6.195	−7.152	214.1	139.4	465.7	−209.4
1765	4.44	−6.361	−7.525	215.0	140.2	462.5	−208.9
(c) Tungsten channel, area 0.00162 cm^2							
1799	3.82	−6.413	−7.175				
1842	4.58	−6.365	−6.940				
1817	3.89	−6.442	−6.995				
1845	5.07	−6.369	−6.740				
Average (excluding (c) data)				206.6		453.8	−207.4
Standard deviation				3.8		6.0	1.0

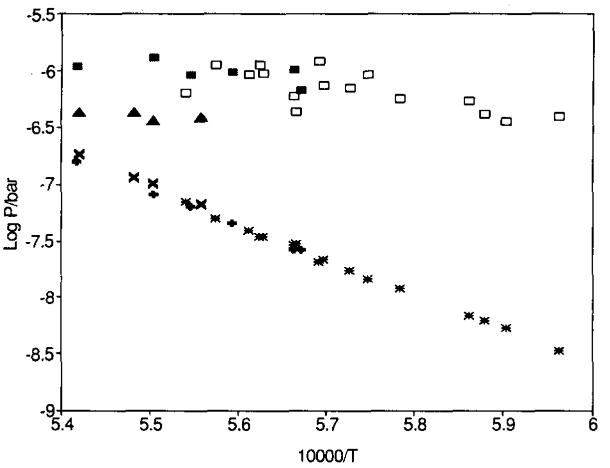

Fig. 1. Mass loss data for $6V_2P(s) \rightleftharpoons 4V_3P(s) + P_2(s)$: ■, P_2, 0.001 85 cm^2 orifice; □, P_2, 0.000 596 cm^2 orifice; ▲, P_2, 0.001 63 cm^2 orifice (tungsten cell); +, V, 0.001 85 cm^2 orifice; *, V, 0.000 596 cm^2 orifice; ×, V, 0.001 63 cm^2 orifice (tungsten cell).

enthalpy of formation of V_3P determined earlier in this laboratory [1] but corrected to accommodate the revised standard molar entropy [13]. In addition, the values were adjusted to the white form of phosphorus as the reference state [8]. The resulting enthalpies are given in Table 2.

4.2. *Mass spectrometry results*

The results from the mass spectrometry experiments for four different effusion cells are given in Table 3;

TABLE 2. Preferred thermodynamic results

	V_2P^a	V_2P^b	V_2P^c	V_3P
$\Delta_f H^\circ_{298.15}$ (kJ mol^{-1})	−207.4	−211.3	−209.4	−233.6
$\Delta_{at} H^\circ_{298.15}$ (kJ mol^{-1})	1554.8	1558.7	1556.8	2096.5

[a] Mass loss.
[b] Mass spectrometry.
[c] Mean value.

TABLE 3. Mass spectrometry effusion data for $5V_3P(s)+P_2(g)\rightleftharpoons 7V_2P(s)+V(g)$

Temperature range (K)	Number of points	A_v $\times 10^{-4}$	B_v	A_{P_2} $\times 10^{-4}$	B_{P_2}	I_v/I_{P_2} 1850 K	$\Delta_rG^\circ_{1850}$ (kJ mol^{-1})	$\Delta_rH^\circ_{298.15}$ (kJ mol^{-1})	$\Delta_fH^\circ_{298.15}$ (V_2P,s) (kJ mol^{-1})
(a) 1×9 mm channel orifice									
1770–1944	39	−2.349	5.594	−3.146	10.427	0.299	18.2	62.0	−211.1
1868–1974	19	−1.964	3.521	−2.310	6.055	0.217	23.1	66.9	−210.4
1899–1989	70	−2.647	7.077	−2.930	9.095	0.325	16.9	60.7	−211.3
1816–1962	27	−2.432	6.063	−3.132	10.403	0.278	19.3	63.1	−211.0
1860–2016	38	−2.718	7.390	−3.259	11.082	0.171	26.8	70.6	−209.9
(b) Pinhole orifice									
1929–2049	15	−2.090	3.401	−3.565	11.707	0.464	11.4	55.2	−212.1
1900–2090	111	−1.570	0.731	−3.435	11.139	0.471	11.2	54.9	−212.1
(c) Pinhole orifice									
1800–1957	34	−1.847	2.415	−3.041	9.246	0.420	13.0	56.7	−211.9
(d) Pinhole orifice									
1856–1972	42	−2.598	6.312	−2.843	7.959	0.476	11.0	54.8	−212.1
Average							16.8	60.5	−211.3
Standard deviation							5.3	5.34	0.8

the data agree within experimental uncertainty. Data obtained with a fifth cell with a knife-edge orifice 0.5 mm in diameter did not agree with the data collected with the other cells, all of which had smaller effective orifice areas; it was presumed that equilibrium was not obtained in this cell and the data were not retained for thermodynamic calculations. The standard free energy of reaction was calculated at 1850 K and the standard enthalpies of formation and atomization of $V_2P(s)$ at 298.15 K were evaluated from the mean enthalpy of reaction and are given in Table 3.

For purposes of comparison with the earlier mass loss results for $V_3P(s)$, a single experiment was performed with the mass spectrometer on a phosphide sample in the V_3P–V two-phase region using another "pinhole" Knudsen cell and the data were treated by the ion current ratio method in terms of the reaction

$$7V(s)+P_2(g) \rightleftharpoons 2V_3P(s)+V(g)$$

As has been noted elsewhere [9], the resulting free energy of formation at 1850 K for $V_3P(s)$, −117.7 kJ mol^{-1}, agrees quite satisfactorily with the value of −111.3 kJ mol^{-1} obtained by an extrapolation of the mass loss results [1].

4. *Thermodynamic data*

The preferred value for the standard enthalpy of formation of $V_2P(s)$ (from white phosphorus) is obtained as the mean of values obtained from the two sets of experiments:

$$\Delta_fH^\circ_{298.15}(V_2P,s) = -209.4\pm 5\ \text{kJ mol}^{-1}$$

The recalculated enthalpy of formation of V_3P (from white phosphorus) is based on the earlier mass loss study [1] as modified by the new standard molar entropy for $V_3P(s)$:

$$\Delta_fH^\circ_{298.15}(V_3P,s) = -233.6\pm 5\ \text{kJ mol}^{-1}$$

The mass spectrometry study in the V_3P–V region was done only for comparison purposes and was not extensive enough to be included. The stated uncertainties include the standard deviations in the experimental results and, for V_2P, the uncertainty for V_3P; uncertainties in the free-energy functions are not included.

5. Discussion

The strength of chemical bonding in V_2P, expressed as the atomization enthalpy to valence state atoms [14], continues a trend of increasing stability in the series Ni_2P, Co_2P, Fe_2P, Mn_2P as shown in Fig. 2. The higher energies calculated for binding in V_2P can be explained in part as being due to a greater extent of π-type overlap between the filled p-orbitals of the phosphorus atom with the empty d-orbitals of vanadium. This interaction becomes less important as the number of d-electrons on the metal increases and as the d-orbitals contract. In comparison (on a gramme-atom basis) with the other vanadium phosphides, V_2P is more stable than V_3P. This is seen from Fig. 3, which shows the free energy of formation at 1850 K as a function of the atomic fraction of phosphorus. Also included in Fig. 3 is the free energy of formation of VP calculated

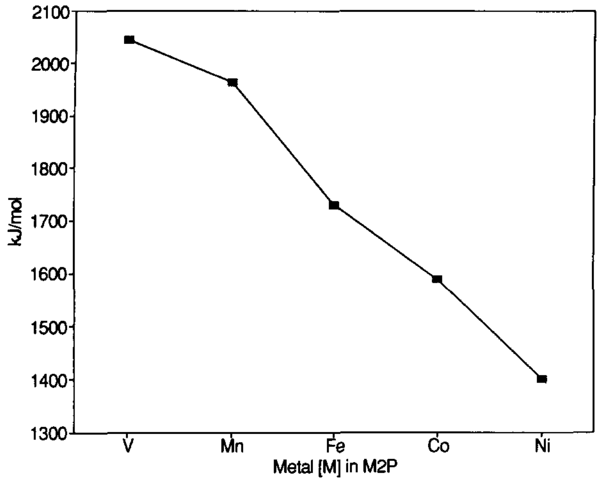

Fig. 2. Enthalpy of atomization of M_2P solids to valence state metal atoms.

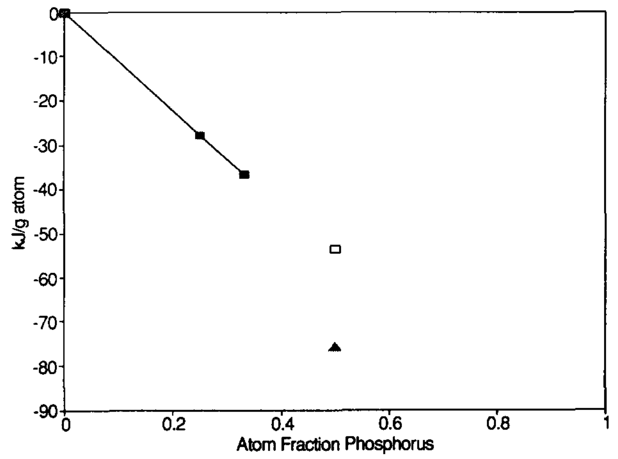

Fig. 3. Free energy of phase formation at 1850 K: ■, this work, $V_3P(s)$ and $V_2P(s)$; ▲, Glaum and Gruehn estimate [2] for VP(s); □, limit of stability for VP(s).

from Glaum and Gruehn's estimate [2] of the standard enthalpy of formation of VP. Their result implies that both V_3P and V_2P are unstable with respect to disproportionation to V and VP. This implication is not supported by the data gathered in this study and the estimate made by Glaum and Gruehn [2] for the standard enthalpy of formation of VP is questionable. As can be seen from Fig. 3, the standard enthalpy of formation of VP can be no more negative than $\Delta_f H^\circ_{298.15}(VP,s) = -211$ kJ mol^{-1}, as extrapolated from the free energies of formation for V_3P and V_2P.

6. Conclusions

The vaporization of V_2P has been shown to be incongruent under equilibrium conditions using both standard mass loss Knudsen effusion and Knudsen effusion mass spectrometry, the latter by an ion current ratio method. Thermodynamic results obtained for experimental runs in the V_3P–V and V_2P–V_3P two-phase regions show V_2P to be more stable (per gramme-atom) than other M_2P compounds and also more stable than V_3P. The standard enthalpy of formation of $V_2P(s)$ was determined to be $\Delta_f H^\circ_{298.15}(V_2P,s) = -209.4 \pm 5$ kJ mol^{-1}. Previous data [1] were recalculated to incorporate a revised [13] standard molar entropy of $V_3P(s)$ to give a revised value for the standard enthalpy of formation of $V_3P(s)$ (from white phosphorus): $\Delta_f H^\circ_{298.15}(V_3P,s) = -233.6 \pm 5$ kJ mol^{-1}.

Acknowledgments

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References

1 C. E. Myers, J. Sloan, R. J. Kematick and J. C. McCreary, *J. Less-Common Met., 160* (1990) 343.
2 R. Glaum and R. Gruehn, *Z. Anorg. Allg. Chem., 568* (1989) 73.
3 C. E. Myers, *High Temp. Sci., 6* (1974) 309.
4 D. T. Cromer, Anisotropic structure factor calculations (ANIFAC), in A. C. Larson and R. B. Roof Jr. (eds.), *Report LA3335* (Los Angeles Scientific Laboratory).
5 P. Villars and L. D. Calvert (eds.), *Pearson's Handbook of Crystallographic Data,* American Society for Metals, Metals Park, OH, 1985, p. 2891.
6 D. R. Stull and G. C. Sinke, *Adv. Chem. Ser., 18* (1956) 186.
7 C. E. Myers and R. J. Kematick, *J. Electrochem. Soc., 133* (1987) 720.
8 M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, *JANAF Thermochemical Tables,* American Chemical Society, Washington, DC and American Institute of Physics, New York, 3rd edn., 1986.
9 M. V. Korobov, J. C. McCreary, R. J. Kematick and C. E. Myers, *J. Chem. Thermodyn.,* in press.
10 J. B. Mann, *J. Chem. Phys., 46* (1967) 1646.
11 J. Drowart and P. Goldfinger, *Angew. Chem. Int. Edn., 6* (1967) 581.
12 J. F. Smith, *Bull. Alloy Phase Diag., 2* (1981) 42.
13 B. E. White Jr., E. J. Cotts, C. E. Myers, J. C. McCreary and R. J. Kematick, *J. Chem. Phys., 96* (1992) 9243.
14 J. S. Griffith, *J. Inorg. Nucl. Chem., 3* (1956) 15.