

# The vaporization behavior and thermodynamic stability of $V_{12}P_7(s)$ and $V_4P_3(s)$

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## Abstract

The vaporization behavior and thermodynamic stability of  $V_{12}P_7$  and  $V_4P_3$  have been investigated in the temperature ranges 1563–1762 K and 1450–1650 K respectively using a mass loss Knudsen effusion technique. X-ray powder diffraction investigation showed that both compounds vaporize incongruently in this temperature range with phosphorus being lost preferentially. The enthalpies of formation (from metal and white phosphorus) were determined:

$$\Delta_f H_{298.15}^\circ(V_{12}P_7) = -1390 \pm 5 \text{ kJ mol}^{-1} (-73 \text{ kJ (g-atom)}^{-1})$$

$$\Delta_f H_{298.15}^\circ(V_4P_3) = -534 \pm 6 \text{ kJ mol}^{-1} (-76 \text{ kJ (g-atom)}^{-1})$$

**Keywords:** Vanadium phosphides; Knudsen effusion; Enthalpy of formation

## 1. Introduction

Recent research in this laboratory has focused on compounds of transition metals with the p-block elements aluminum, silicon and phosphorus. Goals of this research include acquisition of reliable thermodynamic data, documentation of trends in stability, and development of an understanding of these trends in terms of chemical bonding and stability with the aim of developing a predictive model for stability. Within this broader investigation the emphasis has been on ten-electron systems having a stoichiometric ratio of 1:1, namely TiS, VP, CrSi and MnAl (solid solution) [1]. The only published experimental stability data for the V–P system are the mass loss effusion studies on  $V_3P(s)$  and  $V_2P(s)$  reported earlier [2,3] and an estimate of the enthalpy of formation of VP(s) based on the results of chemical transport experiments [4]. The present research follows the study of the vaporization behavior of  $V_3P(s)$  and  $V_2P(s)$  reported earlier [2,3] and continues work toward an evaluation of the thermodynamic stability of VP(s). Inasmuch as the earlier studies established that both  $V_3P$  and  $V_2P$  vaporize incongruently

under equilibrium effusion conditions with preferential loss of phosphorus, the vaporizations of  $V_{12}P_5$  and  $V_4P_3$  were presumed to be incongruent. The study reported here employed mass loss effusion.

## 2. Experimental details

Samples were prepared by direct combination of the elements in evacuated and sealed Vycor glass tubes as described earlier [5]. Starting materials were elemental vanadium (Alfa Products, 325 mesh, lot 081283) and red phosphorus (Fisher Scientific, lot 733149). The crude vanadium phosphide samples, contained in an open graphite crucible lined with tantalum, were annealed in the mass loss effusion apparatus in the temperature range 1400–1600 K. 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 [6] from published crystal structure data [7].

Effusion cells were fabricated from high density graphite and were lined with tantalum. The cells had cylindrical channel orifices, and effective orifice areas were

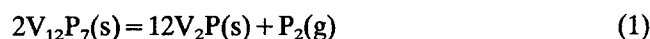
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obtained by a calibration which employed the known vapor pressure of silver [8]. A black-body hole was drilled into the lateral surface of the base of the cell in order to make accurate temperature measurement with the pyrometer. This hole did not penetrate the interior of the cell.

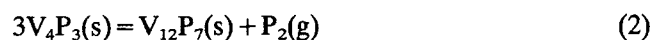
The apparatus and general procedures for the mass loss effusion studies have been described earlier [2]. Temperatures were monitored with a W-5 wt.%Re vs. W-26 wt.%Re thermocouple with digital read-out. The thermocouple was mounted beside the effusion cell. Temperatures were measured with an optical pyrometer (Pyrometer Instrument Company) with certificates of calibration traceable to the US National Bureau of Standards. Appropriate corrections were made for light absorption by the viewing window. Measurements in the  $V_{12}P_5$ - $V_2P$  two-phase region were made in the temperature range 1563–1762 K, and the range for the  $V_4P_3$ - $V_{12}P_5$  two-phase region was 1450–1650 K. Inasmuch as achieving equilibrium has proved to be a problem in effusion studies on transition metal phosphides [2,3,5], samples were routinely removed from the effusion cell and ground after collection of data at a given temperature. This was to minimize the effects of decreased surface area due to sintering.

The  $V_{12}P_7$ - $V_2P$  and  $V_4P_3$ - $V_{12}P_7$  two-phase regions were studied in the temperature ranges 1563–1762 K and 1450–1650 K respectively. The lower temperature limits were dictated by the limit of detection ( $10^{-5}$  mg  $\text{min}^{-1}$ ) of the mass loss apparatus while the upper limits were set by the partial reaction of the sample with the container or the melting point of the sample.

The initial work on the system was investigation of the nature of the vaporization. The study of  $V_{12}P_7$ - $V_2P$  two-phase region showed that, in samples exhibiting diffraction patterns of both  $V_{12}P_7$  and  $V_2P$ , the intensity of peaks assigned to  $V_{12}P_7$  decreased following an extensive effusion run; likewise the intensity of peaks owing to  $V_2P$  were enhanced. It was concluded that the vaporization of  $V_{12}P_7$  was incongruent yielding  $V_2P$  and phosphorus gas:



The  $V_4P_3$ - $V_{12}P_7$  two-phase region was similar:



The duration of each effusion run, generally 6–8 h, depended upon the rate of mass loss which was a function of orifice area and the temperature of the Knudsen cell. X-ray analysis of the residues was done routinely to ensure that the sample composition remained in the desired two-phase region. The rate of mass loss was usually 0.01–0.05 mg  $\text{h}^{-1}$  depending on the orifice area and the temperature of the Knudsen cell.

### 3. Results and treatment of data

The primary data were temperatures and rates of mass loss and were treated in terms of the reactions (1) and (2), 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. Phosphorus pressures were calculated from the effusion equation [2,5]

$$P_{P_2} = \frac{K}{8} \left\{ \left[ 1 + \frac{8m}{aK} \left( \frac{\pi RT}{M_P} \right)^{1/2} \right]^{1/2} - 1 \right\}^2 \\ = \frac{K}{8} \left\{ \left[ 1 + \frac{C'm}{aK} \left( \frac{T}{M_P} \right)^{1/2} \right]^{1/2} - 1 \right\}^2 \quad (3)$$

where  $K$  is the equilibrium constant for the dissociation of 1 mol of  $P_2$ ,  $m$  is the rate of mass loss,  $a$  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 milligrams per minute, the orifice area is in square centimeters, and the constant  $C'$  has the value  $2.155 \times 10^{-6}$ . The equilibrium constant  $K$  was calculated at each experimental temperature from data in the *JANAF Tables* [9]. Standard free energies of the vaporization reactions were calculated from the  $P_2$  pressures:

$$\Delta_r G_T^\circ = -RT \ln P_{P_2} \quad (4)$$

Standard enthalpies of reaction at 298.15 K were obtained from the relation

$$\Delta_r H_{298.15}^\circ = \Delta_r G_T^\circ - T \Delta_r \Phi'_T \quad (5)$$

where  $\Phi'_T = -(G_T^\circ - H_{298.15}^\circ)/T$  is the so-called free-energy function. This third-law treatment of the data required the standard molar entropies and heat capacity data to evaluate the free energy function  $\Phi'$ . For  $P_2(g)$  these data were available directly from published values in the *JANAF Tables* [9]. Since there are no published thermal data for  $V_{12}P_7$  and  $V_4P_3$ , it was necessary to estimate the needed values. These estimates, made in the manner described earlier [3], were based on published data for vanadium silicides [10,11] and the recently measured value for  $V_3P(s)$  [11]. Standard enthalpies of formation and of atomization were obtained from a Hess law type of thermochemical cycle which combined the results reported here with published data for the elements [9].

### 4. Results

The initial work on the system was done to investigate the nature of the vaporization. In samples exhibiting diffraction patterns of both  $V_{12}P_7$  and  $V_2P$ , the intensity

Table 1  
Vaporization data for  $V_{12}P_7(s)$ :  $2V_{12}P_7(s) = 12V_2P(s) + P_2(g)$

T (K)	$(dm/dt) \times 10^3$ (mg min <sup>-1</sup> )	$\log[P_{P_2}$ (bar)]	$\Delta_r G^\circ_T$ (kJ)	$\Delta\Phi'_T$ (J K <sup>-1</sup> )	$\Delta_r H_{298.15}^\circ$ (kJ)	$\Delta_r H_{298.15}^\circ$ <sup>a</sup> (kJ mol <sup>-1</sup> )
$a_{\text{eff}} = 1.760 \times 10^{-3} \text{ cm}^2$						
1604	1.01	-5.955	182.89	140.24	407.83	-1388.49
1627	1.18	-5.886	183.38	139.85	410.92	-1390.03
1646	1.29	-5.845	184.22	139.54	413.90	-1391.53
1647	3.14	-5.458	172.13	139.52	401.92	-1385.54
1671	2.93	-5.486	175.52	139.13	407.99	-1388.57
1685	3.40	-5.419	174.85	138.90	408.89	-1389.02
1696	3.25	-5.439	176.61	138.72	411.87	-1390.51
1709	3.93	-5.354	175.21	138.51	411.92	-1390.54
1715	3.58	-5.394	177.14	138.41	414.51	-1391.83
1723	6.16	-5.158	170.15	138.28	408.41	-1388.78
1736	6.59	-5.127	170.40	138.07	410.10	-1389.63
1739	7.49	-5.070	168.83	138.03	408.86	-1389.00
1745	6.55	-5.129	171.36	137.93	412.05	-1390.60
1762	13.1	-4.824	162.76	137.66	405.32	-1387.24
$a_{\text{eff}} = 2.173 \times 10^{-3} \text{ cm}^2$						
1563	0.971	-6.070	181.66	140.94	401.95	-1385.55
1627	1.65	-5.832	181.67	139.85	409.21	-1389.18
1640	1.74	-5.809	182.41	139.64	411.41	-1390.28
1650	1.81	-5.790	182.92	139.47	413.05	-1391.10
1655	2.14	-5.716	181.14	139.39	411.83	-1390.49
1657	2.24	-5.697	180.75	139.36	411.66	-1390.41
1660	2.37	-5.671	180.26	139.31	411.51	-1390.33
1670	2.59	-5.631	180.07	139.14	412.44	-1390.79
1690	3.91	-5.451	176.37	138.82	410.97	-1390.06
1722	4.60	-5.377	177.27	138.30	415.42	-1392.29
1737	7.21	-5.180	172.27	138.06	412.08	-1390.61
1748	5.60	-5.289	177.01	137.88	418.03	-1393.59
$a_{\text{eff}} = 5.52 \times 10^{-4} \text{ cm}^2$						
1630	0.351	-5.909	184.43	139.80	412.31	-1390.73
1650	0.412	-5.838	184.43	139.47	414.56	-1391.85
1700	0.895	-5.495	178.86	138.65	414.57	-1391.86
1750	2.76	-5.000	167.53	137.85	408.78	-1388.96
Mean $\Delta H_{298.15}^\circ$					410.8	-1390.0
Standard deviation					3.5	1.8

<sup>a</sup> Reference state for phosphorus: white P(s).

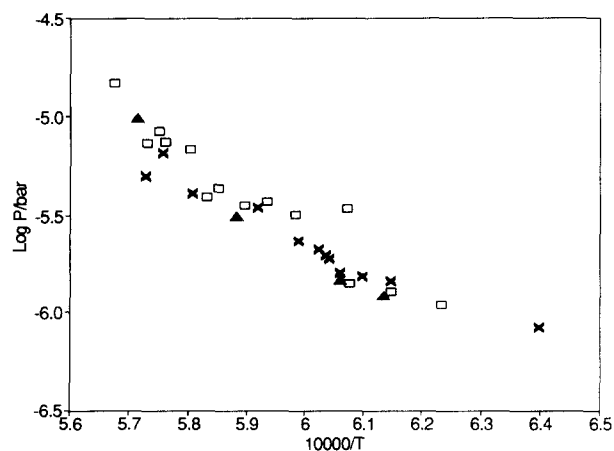


Fig. 1. Vaporization data for  $V_{12}P_7$ : dissociation pressures of  $P_2$  for various effective orifice areas.  $\square$ , 0.001 760  $\text{cm}^2$ ;  $\times$ , 0.002 173  $\text{cm}^2$ ;  $\blacktriangle$ , 0.000 552  $\text{cm}^2$ .

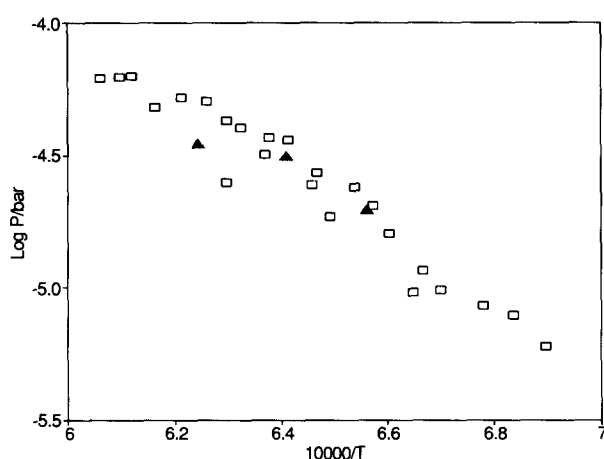
of peaks assigned to  $V_{12}P_7$  decreased following an extensive effusion run; likewise the intensity of peaks owing to  $V_2P$  was enhanced which led to the conclusion that the vaporization of  $V_{12}P_7$  was incongruent yielding  $V_2P$  and phosphorus gas according to Eq. (1), where  $P_2$  is presumed to be in equilibrium with other phosphorus species, principally  $P(g)$ . Similarly, in the  $V_4P_3$ - $V_{12}P_5$  two-phase region, phosphorus was shown to vaporize preferentially according to Eq. (2).

The results of the vaporization studies are given in Tables 1 and 2 and in Figs. 1 and 2. Inasmuch as a variation in the effective orifice areas of the effusion cells by a factor of about 4 gave no apparent difference in calculated pressures, it was concluded that equilibrium was achieved in these experiments. The standard enthalpies of formation for  $V_{12}P_7$  and  $V_4P_3$  as calculated from the heats of reaction are

Table 2

Vaporization data for  $V_4P_3(s)$ :  $3V_4P_3(s) = V_{12}P_7(s) + P_2(g)$ 

T (K)	$(dm/dt) \times 10^3$ (mg min <sup>-1</sup> )	$\log[P_{P_2}$ (bar)]	$\Delta_r G^\circ_\tau$ (kJ)	$\Delta\Phi'_\tau$ (J K <sup>-1</sup> )	$\Delta_r H^\circ_{298.15}$ (kJ)	$\Delta_r H^\circ_{298.15}^a$ (kJ mol <sup>-1</sup> )
$a_{\text{eff}} = 2.173 \times 10^{-3} \text{ cm}^2$						
1450	7.00	-5.227	145.11	142.69	352.00	-532.78
1463	9.22	-5.105	143.00	142.45	351.40	-532.58
1475	9.97	-5.069	143.17	142.23	352.95	-533.09
1492	11.3	-5.012	143.17	141.92	354.92	-533.75
1500	13.4	-4.937	141.79	141.78	354.46	-533.60
1504	11.1	-5.020	144.55	141.70	357.68	-534.67
1514	18.5	-4.795	138.99	141.52	353.26	-533.20
1521	23.5	-4.690	136.59	141.40	351.66	-532.66
1529	27.4	-4.622	135.32	141.26	351.30	-532.54
1540	21.3	-4.730	139.48	141.06	356.71	-534.35
1546	31.1	-4.565	135.13	140.95	353.05	-533.13
1548	27.9	-4.612	136.71	140.92	354.85	-533.73
1559	41.0	-4.443	132.63	140.72	352.02	-532.78
1568	41.7	-4.435	133.14	140.57	353.54	-533.29
1570	36.0	-4.498	135.22	140.53	355.85	-534.06
1581	45.1	-4.399	133.16	140.34	355.04	-533.79
1588	47.7	-4.374	132.98	140.22	355.64	-533.99
1588	28.1	-4.603	139.96	140.22	362.62	-536.32
1598	56.6	-4.298	131.50	140.04	355.28	-533.87
1610	58.2	-4.285	132.08	139.83	357.21	-534.51
1623	53.3	-4.321	134.27	139.61	360.86	-535.73
1634	70.1	-4.200	131.41	139.42	359.22	-535.18
1640	69.1	-4.206	132.07	139.32	360.55	-535.63
1650	68.1	-4.211	133.03	139.15	362.62	-536.32
$a_{\text{eff}} = 5.52 \times 10^{-4} \text{ cm}^2$						
1524	5.81	-4.702	137.19	141.35	352.60	-532.98
1560	9.13	-4.500	134.42	140.71	353.93	-533.42
1602	9.93	-4.458	136.75	139.97	360.99	-535.77
Mean $\Delta H^\circ_{298.15}$					355.6	-534.0
Standard deviation					3.4	1.1

<sup>a</sup> Reference state for phosphorus: white P(s).Fig. 2. Vaporization data for  $V_4P_3$ : dissociation pressures of  $P_2$  for various effective orifice areas:  $\square$ ,  $0.002173 \text{ cm}^2$ ;  $\blacktriangle$ ,  $0.000552 \text{ cm}^2$ .

$$\Delta_r H^\circ_{298.15}(V_{12}P_7) = -1390 \pm 5 \text{ kJ mol}^{-1}$$

and

$$\Delta_r H^\circ_{298.15}(V_4P_3) = -534 \pm 6 \text{ kJ mol}^{-1}$$

The enthalpies of atomization are

Table 3

Enthalpies of formation<sup>a</sup> and atomization of vanadium phosphides

	$\Delta_r H^\circ_{298.15}$ (kJ)	$\Delta_{\text{at}} H^\circ_{298.15}$ (kJ)
$\frac{1}{4} V_3P(s)$	-58.4	524
$\frac{1}{3} V_2P(s)$	-69.8	519
$\frac{1}{19} V_{12}P_7(s)$	-73.2	515
$\frac{1}{7} V_4P_3(s)$	-76.3	506
$\frac{1}{2} VP(s)^b$	-80.0	456

<sup>a</sup> Reference state for phosphorus: white P(s).<sup>b</sup> Lower and upper limits respectively; see text.

$$\Delta_{\text{at}} H^\circ_{298.15}(V_{12}P_7) = 9790 \pm 5 \text{ kJ mol}^{-1}$$

and

$$\Delta_{\text{at}} H^\circ_{298.15}(V_4P_3) = 3545 \pm 6 \text{ kJ mol}^{-1}$$

The uncertainty in these values was estimated by combining the statistical uncertainty in the standard enthalpy of the vaporization reaction with uncertainties in the published enthalpies of formation used in the thermochemical cycle. Uncertainties in the free-energy functions are not included.

The standard enthalpy of formation and the standard enthalpy of atomization of  $V_{12}P_7$  and  $V_4P_3$  together with  $V_3P$  [2] and  $V_2P$  [3] are listed in Table 3.

## 5. Discussion

The vaporization of  $V_{12}P_7$  and  $V_4P_3$  has been shown to be incongruent under equilibrium conditions using the standard mass loss Knudsen effusion method. The agreement of partial pressures of  $P_2(g)$  obtained with different effective orifice areas leads to the conclusion that equilibrium was maintained in the cell.

The enthalpies of formation (per gram atom) of vanadium phosphides as a function of atom fraction of phosphorus are given in Fig. 3. As noted earlier [3],

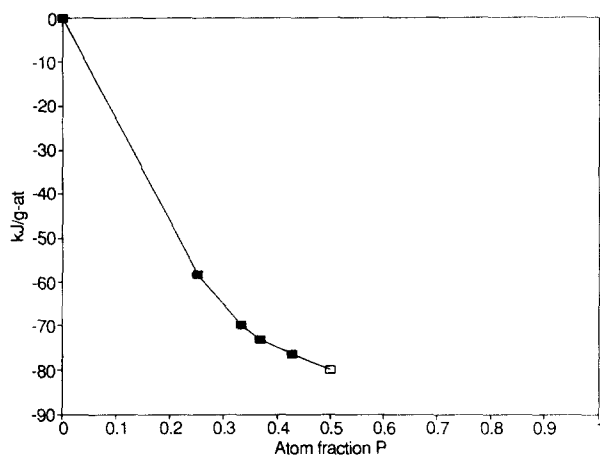


Fig. 3. Enthalpy  $\Delta_f H_{298.15}^\circ$  of phase formation of vanadium phosphides as a function of composition: ■, experimental results from this and earlier [2,3] work; □, limiting value for VP (obtained by extrapolation).

the estimate of the standard enthalpy of formation of VP by Glaum and Gruehn must be incorrect, and the standard enthalpy of formation of VP can be no more negative than  $\Delta_f H_{298.15}^\circ(VP) = -160 \text{ kJ mol}^{-1}$ , a value determined by extrapolation of the values for  $V_{12}P_7$  and  $V_4P_3$  to the atom fraction of VP.

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