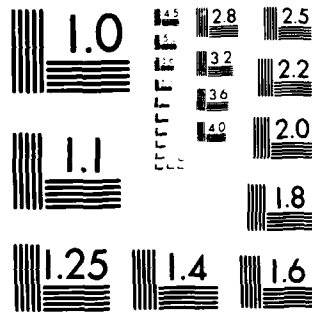


AD-A145 481 VAPORIZATION BEHAVIOR OF CHROMIUM PHOSPHIDES THE SOLID 1/1
TWO-PHASE REGIONS..(U) STATE UNIV OF NEW YORK AT
BINGHAMTON DEPT OF CHEMISTRY C E MYERS ET AL

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(kilokelvins): $1/2 \text{ CrP(s)}$, -5.69 ± 0.18 , 49.67 ± 0.2 ; $1/19 \text{ Cr}_{12}\text{P}_7\text{(s)}$, -4.48 ± 0.32 , 49.47 ± 0.3 ; $1/4 \text{ Cr}_3\text{P(s)}$, -3.18 ± 0.04 , 49.08 ± 0.04 . CrP was found to follow the trend in atomization enthalpy to valence state atoms established in the series MnP, FeP, CoP, and NiP.

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TECHNICAL REPORT NO. 1

VAPORIZATION BEHAVIOR OF CHROMIUM PHOSPHIDES:

THE SOLID TWO-PHASE REGIONS

$\text{CrP-Cr}_{12}\text{P}_7$, $\text{Cr}_{12}\text{P}_7\text{-Cr}_3\text{P}$, and $\text{Cr}_3\text{P-Cr}$

by

Clifford E. Myers, Greg A. Kisacky, and John J. Klingert

Prepared for Publication

in the

Journal of the Electrochemical Society

State University of New York at Binghamton
Department of Chemistry
Binghamton, New York 13901

September 1, 1984

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VAPORIZATION BEHAVIOR OF CHROMIUM PHOSPHIDES:
THE SOLID TWO-PHASE REGIONS
 $\text{CrP-Cr}_{12}\text{P}_7$, $\text{Cr}_{12}\text{P}_7\text{-Cr}_3\text{P}$, and $\text{Cr}_3\text{P-Cr}$ ^{a, b}

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^aSupported by U.S. Office of Naval Research

^bThermochemical data in this paper are given in "rational" units; values in other units may be obtained by multiplying by the appropriate value of the gas constant, R.

ABSTRACT

The vaporization reactions $24/5 \text{ CrP(s)} = 2/5 \text{ Cr}_{12}\text{P}_7\text{(s)} + \text{P}_2\text{(g)}$ (1194-1479K), $2/3 \text{ Cr}_{12}\text{P}_7\text{(s)} = 8/3 \text{ Cr}_3\text{P(s)} + \text{P}_2\text{(g)}$ (1421-1541K), and $2 \text{ Cr}_3\text{P(s)} = 6\text{Cr(s)} + \text{P}_2\text{(g)}$ (1543-1768K) have been studied by mass-loss effusion in the temperature ranges indicated. The reactions are kinetically inhibited. Enthalpies of formation and atomization respectively were found to be (kilokelvins): $1/2 \text{ CrP(s)}$, -5.69 ± 0.18 , 49.67 ± 0.2 ; $1/19 \text{ Cr}_{12}\text{P}_7\text{(s)}$, -4.48 ± 0.32 , 49.47 ± 0.3 ; $1/4 \text{ Cr}_3\text{P(s)}$, -3.18 ± 0.04 , 49.08 ± 0.04 . CrP was found to follow the trend in atomization enthalpy to valence state atoms established in the series MnP, FeP, CoP, and NiP.

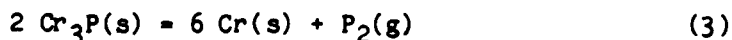
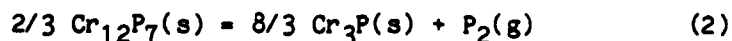
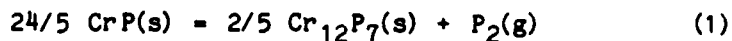
KEY DESCRIPTORS: Thermodynamics, Free Energy, Enthalpy

INTRODUCTION

The atomization enthalpy, ΔH°_{at} , of a solid compound may be used as a measure of its stability and of the strength of its chemical bonds. It has been shown¹, however, that the proper quantity is the atomization enthalpy to valence state atoms, ΔH^*_{at} . The stability of compounds in a series should increase with the number of bonding electrons per atom. As shown in Figure 1, $\Delta H^*_{at}/R(kK)$ exhibits a regular decrease in the series MnP (141.3), FeP (130.0), CoP (119.1), and NiP (104.4) as the number of bonding (unpaired) electrons per metal atom decreases from five in MnP to two in NiP for the presumed valence state $3d^{n-1}4s^1$, where n is the total number of valence electrons. Since Cr would have six bonding electrons in the valence state, one would expect $\Delta H^*_{at}/R$ for CrP to be proportionately larger, and an extrapolation produces an estimate of about 150kK. Trends in the enthalpies of sublimation of the metallic elements to valence state atoms, $\Delta H^*_s/R$, suggest an estimate of 147kK. A mass-loss effusion study of chromium phosphides was initiated to test the extrapolation.

The phase relations in the Cr-P system have been reviewed by Hansen,² Elliott,³ and Shunk.⁴ Well established compounds are Cr_3P , CrP, and CrP_2 which appear to have narrow ranges of homogeneity. Evidence for " Cr_2P " was conflicting, but Baurecht and coworkers⁵ have shown the composition to be $Cr_{12}P_7$ with a slight range of homogeneity.

It was established, as shown below, that the vaporization reactions were:



The enthalpy changes for these reactions, when combined with the enthalpy of formation⁶ of $P_2(g)$,



give the enthalpies of formation of the chromium phosphides:

$$\Delta H_5 = \Delta H^\circ_f(Cr_3P) = 1/2\Delta H^\circ_4 - 1/2\Delta H^\circ_3 \quad (5)$$

$$\Delta H_6 = \Delta H^\circ_f(Cr_{12}P_7) = 3/2\Delta H^\circ_4 + 4\Delta H^\circ_5 - 3/2\Delta H^\circ_2 \quad (6)$$

$$\Delta H_7 = \Delta H^\circ_f(CrP) = 5/24\Delta H^\circ_4 + 1/12\Delta H^\circ_6 - 5/24\Delta H^\circ_1 \quad (7)$$

EXPERIMENTAL

The samples used in this study were prepared in the manner described earlier⁷ by direct combination of chromium powder (99.99%) obtained from SPEX Industries, Inc., and red phosphorus (99.9%) obtained from CERAC/Pure, Inc. The products, as well as residues from effusion runs, were characterized by X-ray powder diffraction; the observed patterns were compared with computer generated patterns⁸ based on data from the literature: CrP,^{9,10,11} Cr₁₂P₇,⁵ Cr₃P.^{9,10,12} The channel-orifice effusion cells were machined from 1.59 cm graphite rod and were fitted with a tantalum liner to prevent the phosphide samples from coming into direct contact with the graphite. The effective orifice areas were measured with KCl as a vapor pressure standard; data for KCl(g) and K₂Cl₂(g) were taken from reference 13. The effusion apparatus, with calibration and operation procedures, has been described previously.^{7,14} It consists of a vacuum system, induction heater, and recording vacuum balance. For the experiments described here, the apparatus was fitted with an eddy current concentrator, and the temperatures were measured with a tungsten, 25% rhenium - tungsten, 3% rhenium thermocouple calibrated as described earlier.⁷

RESULTS AND DISCUSSION

The primary data were temperature, corrected for thermocouple calibration, and the rate of mass loss determined from the read-out of the recording vacuum balance. Individual experiments were of sufficient duration that the uncertainty in the slope of the mass vs. time plot was less than 5%. Partial pressures of $P_2(g)$ were calculated from the rate of mass loss, under the assumption that P_2 and P_4 are in equilibrium in the gas phase, with the modification of the effusion equation derived earlier:⁷

$$P(P_2) = \frac{K}{2\sqrt{2}} \left\{ \left[1 + \frac{8m}{aK} \left(\frac{\pi RT}{M} \right)^{1/2} \right]^2 - 1 \right\} \quad (8a)$$

$$= \frac{K}{2\sqrt{2}} \left\{ \left[1 + \frac{C'm}{aK} \left(\frac{T}{M} \right)^{1/2} \right]^2 - 1 \right\} \quad (8b)$$

When $P(P_2)$ is to be obtained in atmospheres from m (the rate of mass loss) in mg/min, T in Kelvins, M (the molecular weight of P_2), and a (the effective orifice area) in cm^2 , the constant is $C' = 2.127 \times 10^{-6}$. K is the equilibrium constant for $P_4(g) = 2 P_2(g)$; this constant was calculated for each temperature from data given in reference 13.

Initial heating of two of the samples resulted in apparent univariant behavior at temperatures near 800K. Further heating with loss of phosphorus developed univariant behavior in the range 1194-1479K, and the residues from these latter experiments were shown by X-ray powder diffraction to be a mixture of CrP and Cr_{12}P_7 . Further heating with additional loss of phosphorus developed a third univariant condition (1421-1541K) for which the residues were Cr_{12}P_7 and Cr_3P and a fourth (1543-1768) for which

the residues were Cr_3P and Cr . The first region was presumed to be due to the decomposition of small amounts of CrP_2 from the initial preparation, and it was not studied further. The remaining three invariant regions were studied in detail, and the resulting data are shown in Figure 2. Data taken during the evolution of the samples from one region to another have been omitted. For these two-phase regions, effective orifice areas of $2.39(\pm 0.06) \times 10^{-4} \text{ cm}^2$ and $8.91(\pm 0.2) \times 10^{-5} \text{ cm}^2$ gave the same results in each region within experimental uncertainty, and these runs were presumed to be at equilibrium. Larger orifices gave lower calculated pressures, presumably without achievement of equilibrium. The cross-sectional area of the sample was 1.76 cm^2 in all experiments. Only the equilibrium data from the three two-phase regions were used in subsequent thermodynamic calculations. These data are presented in Tables 1, 2, and 3, and the lines in Figure 2 result from a least squares treatment of each set of data. For the $\text{CrP-Cr}_{12}\text{P}_7$ and $\text{Cr}_{12}\text{P}_7\text{-Cr}_3\text{P}$ regions, phosphorus was assumed to be the only volatile component, whereas in the $\text{Cr}_3\text{P-Cr}$ region the rates of mass loss were corrected for the vapor pressure of elemental chromium.

There are neither entropy nor high temperature heat capacity data for chromium phosphides in the literature; hence these were estimated. Entropy estimates were based⁷ on data for chromium silicides^{15,16} and heat capacity estimates on data for manganese phosphides.¹⁷ These estimated values are given in Table 4. Second-law enthalpies, $\Delta H^{\circ\text{II}}$, were calculated for the temperature ranges of the measurements from the least squares slopes of $\log P(\text{P}_2)$ vs. $1/T$ and were corrected to 298.15K by means of $\Delta(H_T^{\circ} - H_{298.15}^{\circ})$ evaluated from C_p . Third-law enthalpies of reaction, $\Delta H^{\circ\text{III}}$ were obtained by means of free energy functions, $\Phi' \equiv -(G_T^{\circ} - H_{298.15}^{\circ})/T$, calculated from the entropy and heat capacity data. Tables 1, 2, and 3 summarize calculations for reactions (1), (2), and (3), respectively. The

agreement of respective second-law and third-law enthalpies is acceptable, particularly in view of the limited temperature ranges imposed by the difficulty in obtaining equilibrium. Enthalpies of formation calculated from the third-law enthalpies by Equations (5), (6), and (7) are given in Table 5, together with enthalpies of atomization. Uncertainty limits were assigned in the manner described earlier.¹ Also included in Table 5 are the enthalpies of formation and atomization of $\text{CrP}_2(\text{s})$ based on the static vapor pressure studies of Faller and Blitz¹⁹ and estimated free energy functions.

The enthalpy of atomization of CrP to valence state atoms was obtained by adding the valence state preparation energy¹⁸ of chromium (45.9kK) to the ground state atomization enthalpy. The resulting value, 145.3kK, is in excellent agreement with the estimate, 147kK, based on trends in $\Delta H^*_g/R$ of the metals. As was pointed out earlier,¹ this result confirms a similarity in bond type in the series CrP, MnP, FeP, CoP, NiP. The extrapolation to compounds such as ScP which have significant ionic character gives poor agreement with measured values.

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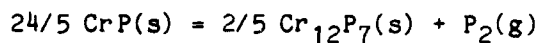
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TABLE 1

DATA FOR REACTION



T (K)	$\text{mx}10^3$ (mg/min)	$\text{Px}10^5$ (atm)	$\Delta G^\circ/\text{RT}$	$\Delta\phi'/\text{R}$	$\Delta H_{298.15}^{\circ\text{III}}/\text{R}$ (KK)
$(a_{\text{eff}} = 2.39 \times 10^{-4} \text{ cm}^2)$					
1380	33.1	24.5	8.31	22.27	42.21
1408	66.1	49.5	7.61	22.26	42.07
1377	33.2	24.6	8.31	22.27	42.11
1315	7.91	5.73	9.77	22.29	42.16
1365	25.0	18.4	8.60	22.28	42.15
1289	4.37	3.13	10.37	22.30	42.12
$(a_{\text{eff}} = 8.91 \times 10^{-5} \text{ cm}^2)$					
1479	118	242	6.02	22.25	41.81
1437	46.3	93.9	6.97	22.26	42.00
1398	20.8	41.6	7.79	22.27	42.01
1485	125	257	5.96	22.25	41.89
1355	8.21	16.2	8.73	22.28	42.02
1329	4.14	8.08	9.42	22.29	42.15

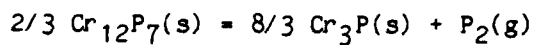
$$\Delta H_{1382}^{\circ\text{II}}/\text{R} = 43.5 \pm 1.4$$

$$\text{Mean } \Delta H_{298.15}^{\circ\text{III}}/\text{R} = 42.06 \pm 2.5$$

$$\Delta H_{298.15}^{\circ\text{II}}/\text{R} = 44.1 \pm 1.5$$

TABLE 2

DATA FOR REACTION



T (K)	$\text{m} \times 10^3$ (mg/min)	$\text{P} \times 10^5$ (atm)	$\Delta G^\circ / RT$	$\Delta \phi' / R$	$\Delta H_{298.15}^{\circ \text{III}} / R$ (KK)
$(a_{\text{eff}} = 2.39 \times 10^{-4} \text{ cm}^2)$					
1497	6.68	5.16	9.87	19.70	44.28
1512	9.29	7.22	9.54	19.70	44.21
1521	10.9	8.50	9.37	19.70	44.22
1506	8.75	6.79	9.60	19.70	44.13
1467	3.72	2.85	10.47	19.71	44.27
1488	5.66	4.36	10.04	19.71	44.26
1435	1.84	1.39	11.18	19.72	44.34
1508	7.9	6.13	9.70	19.70	44.34
1541	16.9	13.3	8.93	19.70	44.12
1512	8.33	6.48	9.65	19.70	44.37
1421	1.28	0.964	11.55	19.72	44.44
$(a_{\text{eff}} = 8.91 \times 10^{-5} \text{ cm}^2)$					
1513	3.46	7.22	9.54	19.70	44.24
1499	2.62	5.43	9.82	19.70	44.26
1516	3.68	7.68	9.48	19.70	44.23
1465	1.20	2.46	10.61	19.71	44.43
1530	4.61	9.67	9.25	19.70	44.29
1508	3.22	6.70	9.61	19.70	44.21
1539	5.70	12.0	9.03	19.70	44.21

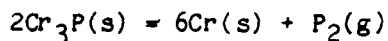
$$\Delta H_{1498}^{\circ \text{II}} / R = 46.6 \pm 2.7$$

$$\text{Mean } \Delta H_{298.15}^{\circ \text{III}} / R = 44.29 \pm 4.0$$

$$\Delta H_{298.15}^{\circ \text{II}} / R = 46.9 \pm 2.8$$

TABLE 3

Data For Reaction



T	$\text{mx}10^3$	$\text{Px}10^5$	$\Delta G^\circ/\text{RT}$	$\Delta\phi'/\text{R}$	$\Delta H_{298.15}^{\circ\text{III}}/\text{R}$
(K)	(mg/min)	(atm)			(KK)
$(a_{\text{eff}} = 2.39 \times 10^{-4} \text{ cm}^2)$					
1543	2.32	1.82	10.92	19.10	46.31
1601	5.70	4.57	9.99	18.95	46.35
1546	2.55	2.00	10.82	19.09	46.24
1581	3.18	2.52	10.59	19.00	46.79
1624	6.76	5.46	9.82	18.89	46.62
1650	10.45	8.46	9.38	18.82	46.53
1621	6.28	5.05	9.90	18.90	46.68
1599	4.48	3.56	10.24	18.96	46.69
1720	20.60	17.1	8.68	18.65	47.00
1753	27.10	22.7	8.39	18.59	47.29

$$(a_{\text{eff}} = 8.91 \times 10^{-5} \text{ cm}^2)$$

1690	6.33	14.0	8.88	18.72	46.63
1716	7.19	17.6	8.65	18.66	46.86
1744	9.68	21.7	8.44	18.60	47.16
1669	3.57	7.8	9.46	18.77	47.12
1738	7.60	17.0	8.68	18.61	47.44
1720	6.37	14.2	8.86	18.65	47.32
1697	4.83	10.6	9.15	18.70	47.25
1726	6.75	15.0	8.81	18.64	47.37
1768	10.99	24.8	8.30	18.56	47.49
1626	2.53	5.47	9.82	18.89	46.67
1651	2.96	6.44	9.65	18.82	47.01
1668	3.14	6.87	9.59	18.77	47.31

$$\Delta H_{1498}^{\circ\text{II}}/\text{R} = 32.0 \pm 2.7$$

$$\text{Mean } \Delta H_{298.15}^{\circ\text{III}}/\text{R} = 46.9 \pm 0.2$$

$$\Delta H_{298.15}^{\circ\text{II}}/\text{R} = 38.7 \pm 2.8$$

TABLE 4

ESTIMATED THERMOCHEMICAL DATA FOR CHROMIUM PHOSPHIDES

	$S_{298.15}^0/R$		A	$B \times 10^3$	$C \times 10^{-5}$
CrP	4.78	7.12	-0.06	-1.36	
Cr ₁₂ P ₇	50.33	60.67	12.42	-9.70	
Cr ₃ P	10.57	11.45	5.08	-1.42	

$$C_p/R = A + BT + CT^{-2}$$

TABLE 5

STABILITY DATA FOR CHROMIUM PHOSPHIDES AT 298.15K

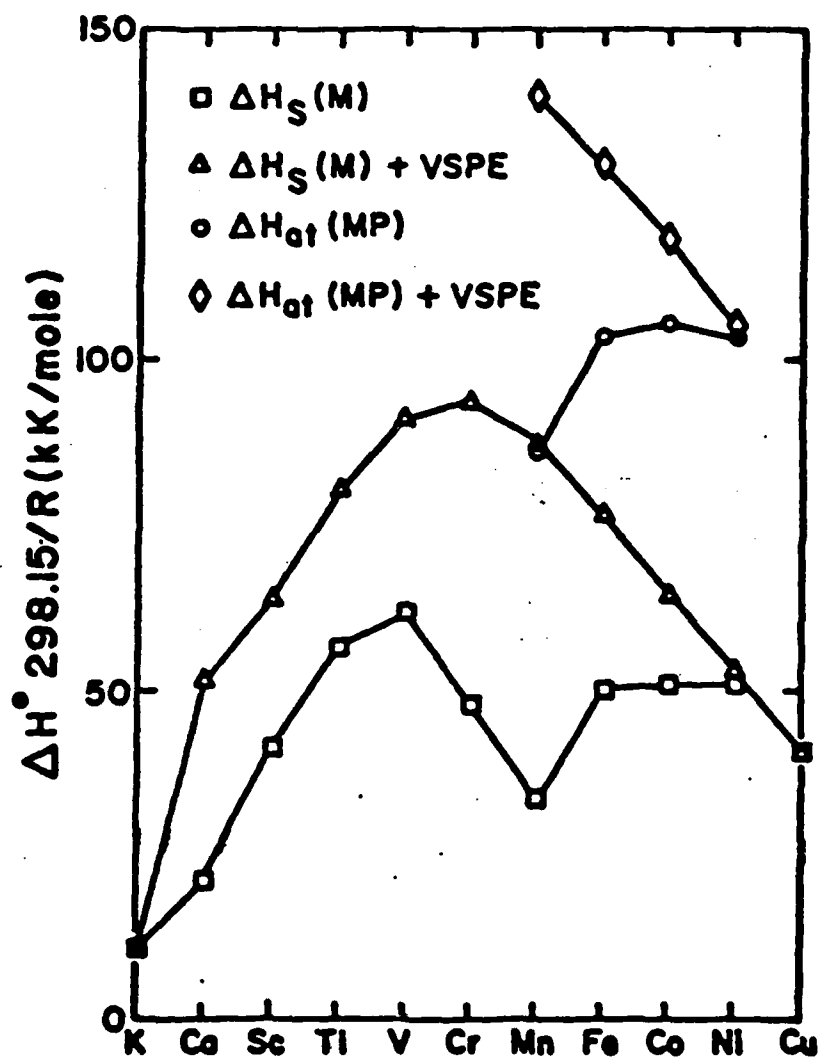
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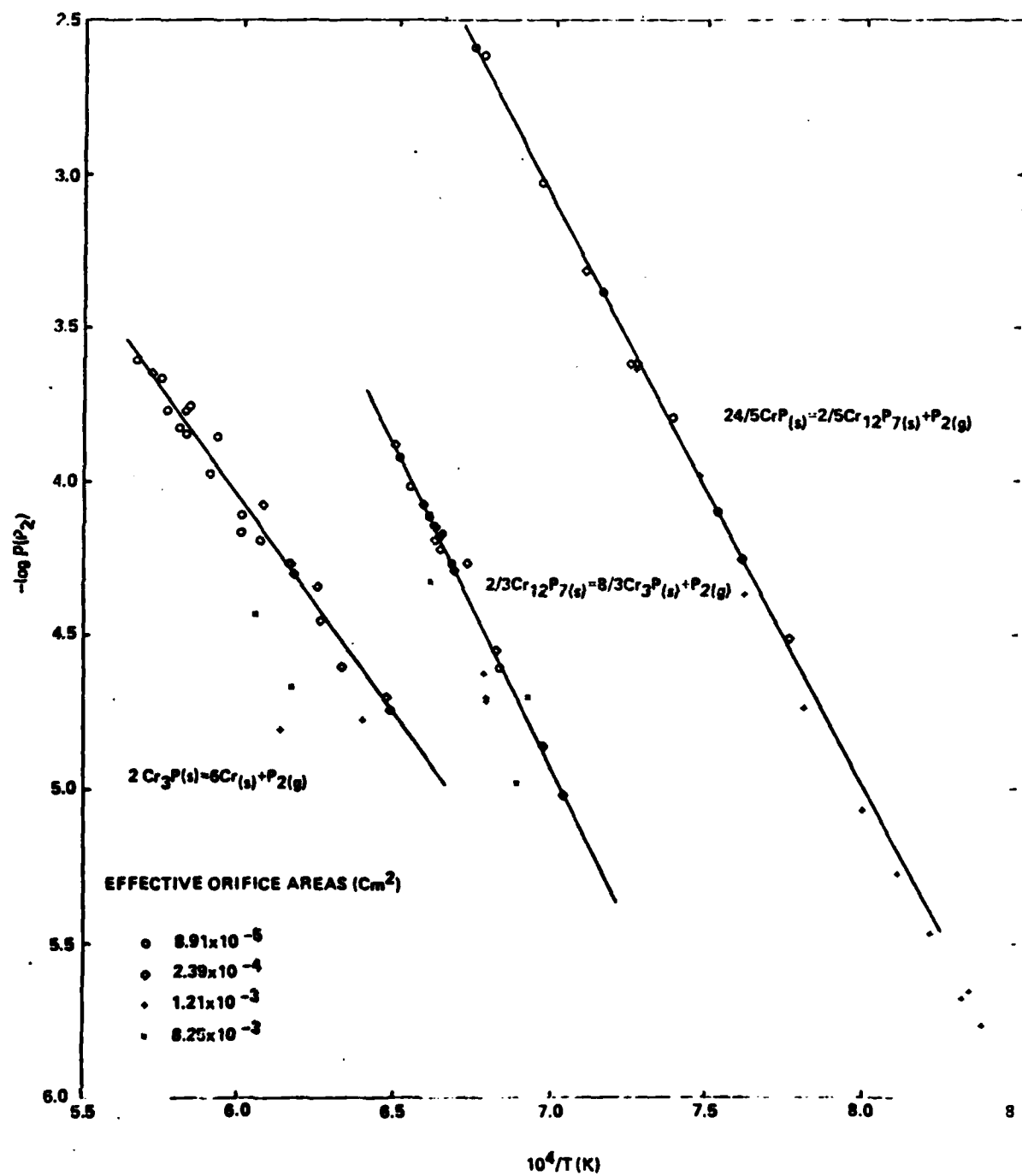
	$-\Delta H_f/R(\text{from red P})$	$\Delta H_{at}/R$
$1/2 \text{ CrP(s)}$	5.69 ± 0.18	49.67 ± 0.2
$1/19 \text{ Cr}_{12}\text{P}_7(\text{s})$	4.48 ± 0.32	49.47 ± 0.3
$1/4 \text{ Cr}_3\text{P(s)}$	3.18 ± 0.04	49.08 ± 0.04
$1/3 \text{ CrP}_2(\text{s})$	4.8 ± 0.7	47.5 ± 0.7

FIGURE CAPTIONS

1. Sublimation enthalpies of metals and atomization enthalpies(per mole) of some monophosphides to ground state atoms and to valence-state atoms.
2. Phosphorus dissociation pressures for chromium phosphides.

ENTHALPIES OF ATOMIZATION





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