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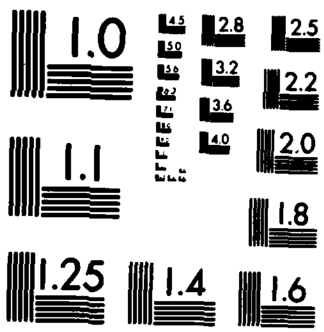

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The equilibrium vaporization reactions, 12 $Ni_2P(s)$ = 2 $Ni_{12}P_5(s)$ + $P_2(g)$ and 6.8 $Ni_{12}P_5(s)$ = 32 $Ni_{2.55}P(s)$ + $P_2(g)$, have been studied by mass-loss effusion in the temperature range 1237-1401 K. The results were combined with published calorimetric data for nickel-rich samples and static

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phosphorus dissociation pressure data for phosphorus-rich samples, with consideration of the requirements of the published phase diagram, to obtain enthalpies of formation (from red P), $\Delta H^o_f/R$, and enthalpies of atomization, $\Delta H^o_{at}/R$, respectively, in kilokelvins at 298.15 K: 1/4 $Ni_3P(s)$, -5.94±0.5, 54.8; 1/3.55 $Ni_{2.55}P(s)$, -6.65±0.5, 55.2; 1/17 $Ni_{12}P_5(s)$, -6.73±0.5, 55.1; 1/3 $Ni_2P(s)$, - 6.87±0.5, 54.8; 1/9 $Ni_5P_4(s)$, -6.39±0.5, 53.0; 1/2.22 $Ni_{1.22}P(s)$, -6.32±0.5, 52.9; 1/2 $NiP(s)$, -6.09±0.5, 52.1; 1/3 $NiP_2(s)$, -5.38±0.5, 49.4; 1/4 $NiP_3(s)$, -4.52±0.5, 47.6.

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TECHNICAL REPORT NO. 3

VAPORIZATION BEHAVIOR, PHASE EQUILIBRIA, AND THERMODYNAMIC STABILITIES OF NICKEL PHOSPHIDES

by

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VAPORIZATION BEHAVIOR, PHASE EQUILIBRIA, AND THERMODYNAMIC STABILITIES OF NICKEL PHOSPHIDES*‡

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*Energy 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.

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Key Words: Vapor pressure, enthalpy of formation, enthalpy of atomization

Running title: Vaporization of Nickel Phosphides

Delta H Sub F deg. Delta H deg.

ABSTRACT: The equilibrium vaporization reactions, 12 $Ni_2P(s) = 2\ Ni_{12}P_5(s) + P_2(g)$ and 6.8 $Ni_{12}P_5(s) = 32\ Ni_{2.55}P(s) + P_2(g)$, have been studied by mass-loss effusion in the temperature range 1237-1401 K. The results were combined with published calorimetric data for nickel-rich samples and static phosphorus dissociation pressure data for phosphorus-rich samples, with consideration of the requirements of the published phase diagram, to obtain enthalpies of formation (from red P), $\Delta H_f^o/R$, and enthalpies of atomization, $\Delta H_{at}^o/R$, respectively, in kilokelvins at 298.15 K: 1/4 $Ni_3P(s)$, -5.94 ± 0.5, 54.8; 1/3.55 $Ni_{2.55}P(s)$, -6.65 ± 0.5, 55.2; 1/17 $Ni_{12}P_5(s)$, -6.73 ± 0.5, 55.1; 1/3 $Ni_2P(s)$, -6.87 ± 0.5, 54.8; 1/9 $Ni_5P_4(s)$, -6.39 ± 0.5, 53.0; 1/2.22 $Ni_{1.22}P(s)$, -6.32 ± 0.5, 52.9; 1/2 $NiP(s)$, -6.09 ± 0.5, 52.1; 1/3 $NiP_2(s)$, -5.38 ± 0.5, 49.4; 1/4 $NiP_3(s)$, -4.52 ± 0.5, 47.6.

INTRODUCTION

The nickel-phosphorus phase diagram has been well-established in the definitive work of Larsson,[1] but published data do not permit a complete working out of the thermodynamics of the system. Weibke and Schrag[2] measured directly the heat of reaction of nickel and phosphorus at about 630°C, but their studies were limited to metal-rich compositions. Biltz and Heimbrecht[3] measured dissociation pressures of phosphorus over phosphorus-rich samples, but the static method they employed did not allow an overlap in composition with the calorimetric study.[2] Hence, a Knudsen effusion study of phosphorus dissociation pressures was initiated for the central portion of the phase diagram.

The compositions of the intermediate phases and their temperature ranges of stability were taken from Larsson's study;[1] the phase diagram is given in Figure 1. In terms of this diagram, the reactions studied by Weibke and Schrag[2] are:

$$3Ni(s) + P(s,red) = Ni_3P(s) \quad (1)$$

$$2.55Ni(s) + P(s,red) = Ni_{2.55}P(s) \quad (2).$$

Similarly, the reactions studied by Biltz and Heimbrecht[3] are:

$$4NiP_3(s) = 4NiP_2(s) + P_4(g) \quad (3)$$

$$\frac{10}{3}NiP_2(s) = \frac{2}{3}Ni_5P_4(s) + P_4(g) \quad (4)$$

$$\frac{8}{3}Ni_5P_4(s) = \frac{20}{3}Ni_2P(s) + P_4(g) \quad (5).$$

The effusion study reported here considered the reactions:

$$12Ni_2P(s) = 2Ni_{12}P_5(s) + P_2(g) \quad (6)$$

$$6.8Ni_{12}P_5(s) = 32Ni_{2.55}P(s) + P_2(g) \quad (7)$$

which provide a link between the two previous studies.

EXPERIMENTAL

The effusion apparatus used in this study, together with calibration and operation procedures, has been described previously.[4] It consists of a vacuum system, induction heater, temperature controller, and recording vacuum balance. The channel-orifice effusion cells were fabricated from 0.95 cm high density graphite rod. The effective orifice areas were determined by direct measurement as previously described.[4] The phosphide samples were prepared by direct combination of the elements in evacuated and sealed "Vycor" glass ampoules using the procedures and precautions described earlier.[4] The products of the preparations, as well as residues from the effusion runs, were characterized by X-ray powder diffraction.[5-7] Observed intensity and d-spacing data were compared with published data for Ni_2P,[5] $Ni_{12}P_5$,[7] and $Ni_{2.55}P$.[6]

RESULTS

The primary data were the temperature, corrected for thermocouple calibration, and the rate of mass loss, corrected for non-orifice effusion[4] (less than 20%), obtained from the recording vacuum balance. Tables 1 and 2 list the results for the Ni_2P-$Ni_{12}P_5$ and $Ni_{12}P_5$-$Ni_{2.55}P$ two-phase regions, respectively. The vaporization was found to be severely retarded, and long channels were required to reduce the effective orifice areas sufficiently to achieve equilibrium. Additionally, the measurements were greatly complicated by sintering of the samples which resulted in a decrease in the rate of effusion as the run progressed, even though two solid phases were still present. In order to cope with this difficulty, the sample was removed after every second or third point for regrinding. While this procedure appeared to overcome the difficulty, the very low rates of mass loss, particularly at lower temperatures, made detection of a decrease in the rate very difficult. The slopes of the mass-time records could be measured with a reproducibility of about ±10%. The total mass losses in runs A, B, and C were 3.3, 7.6, and 2.1 mg, respectively, which may be compared with about 16 mg loss needed to cross the Ni_2P-$Ni_{12}P_5$ two-phase region. For run D, the total loss was 2.3 mg, with about 3 mg loss needed to cross the $Ni_{12}P_5$-$Ni_{2.55}P$ two-phase region. Pressures of P_2 were calculated, assuming P_2 and P_4 to be in equilibrium in the vapor, with the modification of the effusion equation derived earlier:[4]

$$\begin{aligned} P(P_2) &= \frac{K}{2\sqrt{2}}\left\{\left[1+\frac{8m}{aK}\left(\frac{\pi RT}{M}\right)^{1/2}\right]^{1/2}-1\right\} \\ &= \frac{K}{2\sqrt{2}}\left\{\left[1+\frac{Cm}{aK}\left(\frac{T}{M}\right)^{1/2}\right]^{1/2}-1\right\} \end{aligned} \tag{8}$$

where K is the equilibrium constant[8] for $P_4(g) = 2P_2(g)$ and M is the molecular weight of P_2. When $P(P_2)$ is given in atmospheres, m (the rate of mass loss) in mg/min, T as Kelvin temperature, and a (the effective orifice area) in cm^2, the constant is $C = 2.127 \times 10^{-6}$. Since the calculated pressures do not show any apparent variation with effective orifice area, all the data were taken to represent equilibrium conditions. There are no entropy nor high temperature heat capacity data for the nickel phosphides in the literature, and it was necessary to estimate these. The procedure used earlier,[4] based on published data on transition metal silicides,[9-13] was used to generate the estimates given in Table 3. The value for the entropy of NiP was adjusted upward by 5% in order to obtain results consistent with the observed phase diagram.[1]

Third-law enthalpy changes for reactions (6) and (7) were calculated using free energy functions, $\Phi' \equiv -\frac{G^o_T - H^o_{298.15}}{T}$, based on the entropy and heat capacity estimates. The second-law enthalpy change for reaction (6) was calculated to be 58.8 kK at 298.15K, which is in poor agreement with the mean third-law value. The second-law value was rejected in favor of the third-law result. This choice was based on two considerations. First, the very low rates of mass loss at lower temperatures made detection of curvature in the mass vs. time record extremely difficult, and thus, the observed slopes in this range may be too small due to kinetic effects brought on by sintering of the sample. Second, attempts to force agreement of the second-law and third-law results would require increasing $\Delta\Phi'/R$ for reaction (6) by 13.9. It is unlikely that the entropy estimates for $Ni_{12}P_5$ and Ni_2P are in error by a sufficient amount to produce this difference since similar estimates for other systems[4,14] have produced acceptable agreement. Hence, the mean third-law value was used in subsequent calculations. The available temperature range for the study of reaction (7) was too small to permit determination of a meaningful second-law enthalpy change; hence, the mean third-law result was carried forward into subsequent calculations. Free energy functions based on the estimates in Table 3 were used to obtain third-law enthalpy changes for reactions (3), (4), and (5) from the data of Blitz and Heimbrecht.[3] The enthalpies reported by Weibke and Schrag[2] were corrected to 298.15K by means of the heat capacity estimates in Table 3. Enthalpies of reaction at 298.15K are summarized in Table 4. The appropriate combination of these with the enthalpies of formation[8] of $P_2(g)$ and $P_4(g)$,

$$2P(s,red) = P_2(g) \tag{9}$$

$$4P(s,red) = P_4(g) \tag{10}$$

yields enthalpies of formation:

$$\Delta H_1 = \Delta H_f(Ni_3P)$$

$$\Delta H_2 = \Delta H_f(Ni_{2.55}P)$$

$$\Delta H_{13} = \Delta H_f(Ni_{12}P_5) = \frac{1}{6.8}(\Delta H_9 + 32\Delta H_2 - \Delta H_7)$$

$$\Delta H_{14} = \Delta H_f(Ni_2P) = \frac{1}{12}(\Delta H_9 + 2\Delta H_{13} - \Delta H_6)$$

$$\Delta H_{15} = \Delta H_f(Ni_5P_4) = \frac{3}{8}(\Delta H_{10} + \frac{20}{3}\Delta H_{14} - \Delta H_5)$$

$$\Delta H_{16} = \Delta H_f(NiP_2) = \frac{3}{10}(\Delta H_{10} + \frac{2}{3}\Delta H_{15} - \Delta H_4)$$

$$\Delta H_{17} = \Delta H_f(NiP_3) = \frac{1}{4}(\Delta H_{10} + 4\Delta H_{16} - \Delta H_3)$$

which are tabulated, together with enthalpies of atomization, in Table 5. In this series of calculations it is assumed that ΔH^o, ΔS^o, ΔG^o of phase formation are essentially constant across the Ni_2P single-phase region.

The enthalpies of formation of NiP and $Ni_{1.22}P$ may be deduced from data in Table 5 and consideration of the phase diagram.[1] Since NiP(s) is formed spontaneously from Ni_5P_4 and NiP_2 above (but not below) about 850°C (1123K), its formation from these compounds must proceed with positive changes in both enthalpy and entropy at that temperature, and $\Delta H^o_{11} = T\Delta S^o_{11}$ at 1123K. Use of the estimated entropy and heat capacity data in Table 3 leads to the enthalpy of reaction recorded in Table 4 and the enthalpies of formation and atomization of NiP(s) given in Table 5. According to the phase diagram,[1] $Ni_{1.22}P$ is stable with respect to Ni_5P_4 and NiP_2 only between about 770°C

(1043K) and 825°C (1098K). This requires not only that $\Delta H^o_{12} = T\Delta S^o_{12}$ at both these temperatures, but also that both ΔH^o_{12} and ΔS^o_{12} be positive at the lower temperature and negative at the higher temperature. These considerations, together with the estimated entropy and heat capacity data in Table 3, were used to deduce the value for ΔH_{12} in Table 4 and the enthalpies of formation and atomization of $Ni_{1.22}P(s)$ given in Table 5. Uncertainty limits were assigned in the manner described earlier.[14]

It has been pointed out[14] that the atomization enthalpies per gram atom of the nickel phosphides are, at corresponding compositions, very nearly the same as those for the phosphides of iron,[15] and cobalt,[4] but, when valence state energies[16] of the metal atom are taken into account,[14] the atomization enthalpies to valence-state atoms per mole of monophosphides show a regular decrease in the series CrP(145.3kK),[17] MnP(141.3kK),[14] FeP(130.0kK),[15] CoP (119.1kK),[4] and NiP(104.2kK). This decrease parallels the decrease in the number of bonding electrons per metal atom from six in CrP to two in NiP and suggests that chemical bonding is similar in this series of compounds.

ACKNOWLEDGMENTS

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Table 1

Data for the Reaction: $12Ni_2P(s) = 2Ni_{12}P_5(s) + P_2(g)$

T	Cell	$10^3 m$(mg/min)	$P(P_2)\times 10^6$(atm)	-log P	$\Delta\Phi'/R$	$\Delta H^{oIII}_{298.15}/R$ (kK)
			Run A (~560 mg sample)			
1260	C-3	1.5	9.25	5.03	20.38	40.27
1360	C-3	21.0	134.	3.87	20.47	39.96
1285	C-3	3.8	23.7	4.63	20.40	39.91
1323	C-3	8.3	52.4	4.28	20.34	39.95
1331	C-192	1.83	121.	3.92	20.44	39.22
1304	C-192	0.61	40.0	4.40	20.41	39.83
1274	C-3	1.2	7.44	5.13	20.39	41.03
1286	C-3	1.44	8.97	5.05	20.31	41.07
			Run B (~565 mg sample)			
1338	C-192	2.0	133.	3.88	20.45	39.32
1322	C-192	1.1	72.6	4.14	20.43	39.61
1354	C-192	3.84	257.	3.59	20.46	38.90
1322	C-3	6.22	39.3	4.41	20.43	40.43
1360	C-3	20.0	128.	3.89	20.47	40.02
1347	C-4	7.39	158.	3.80	20.46	39.35
1324	C-4	2.73	58.1	4.24	20.43	39.98
1359	C-4	10.2	220.	3.66	20.47	39.27
1289	C-4	0.90	18.9	4.72	20.40	40.31
1302	C-4	1.1	23.2	4.63	20.41	40.46
1328	C-4	2.78	59.2	4.23	20.44	40.08
1302	C-4	1.50	31.6	4.50	20.41	40.07
1353	C-4	5.17	111.	3.95	20.46	39.99
1331	C-4	3.5	74.7	4.13	20.44	39.87
			Run C (~510 mg sample)			
1341	C-192	1.83	122.	3.91	20.45	39.50
1362	C-192	3.69	247.	3.61	20.47	39.20
1305	C-192	0.53	34.8	4.46	20.42	40.05
1237	C-4	0.17	3.50	5.46	20.36	40.74
1260	C-4	0.32	6.64	5.18	20.38	40.71

Effective orifice areas:
C-3 2.75×10^{-4} cm^2
C-4 8.17×10^{-5} cm^2
C-192 2.63×10^{-5} cm^2

Mean $\Delta H^{oIII}/R = 39.97$

Table 2

Data for the Reaction: $6.80Ni_{12}P_5(s) = 32.0Ni_{2.55}P(s) + P_2(g)$

T	Cell	10^3m(mg/min)	$P(P_2)x10^6$(atm)	-log P	$\Delta\Phi'/R$	$\Delta H^{oIII}_{298.15}/R$ (kK)
			Run D (~360 mg sample)			
1401	C-4	1.4	32.8	4.48	20.97	43.83
1400	C-4	1.3	28.4	4.55	20.97	44.03
1399	C-4	1.5	32.8	4.48	20.97	43.77
1399	C-192	0.48	32.6	4.49	20.97	43.80

Effective orifice areas: C-4 $8.17x10^{-5}cm^2$
C-192 $2.63x10^{-5}cm^2$

Mean $\Delta H^{oIII}_{298.15}/R$ = 43.86

Table 3

Estimated Entropies and Heat Capacities

	$S^o_{298.15}/R$	A	$B \times 10^3 K^{-1}$
Ni_3P	13.1	10.3	4.72
$Ni_{2.55}P$	11.8	9.10	4.00
$Ni_{12}P_5$	56.3	42.2	21.0
Ni_2P	9.9	7.50	3.20
Ni_5P_4	26.4	23.5	7.30
$Ni_{1.22}P$	6.6_3	5.69	1.75
NiP	5.6	5.23	1.41
NiP_2	6.4	7.85	1.91
NiP_3	8.4	10.5	2.26

$$C_p/R = A + BT$$

Table 4

Enthalpies of Reaction at 298.15K (kK)

Reaction		$\Delta H^o_{298.15}/R$	Notes
$3Ni(s) + P(s,red) = Ni_3P(s)$	(1)	-23.8±2	a
$2.55Ni(s) + P(s,red) = Ni_{2.55}P(s)$	(2)	-23.6±2	a
$4NiP_3(s) = 4NiP_2(s) + P_4(g)$	(3)	23.2±3	b
$\frac{10}{3}NiP_2(s) = \frac{2}{3}Ni_5P_4(s) + P_4(g)$	(4)	31.0±3	b
$\frac{8}{3}Ni_5P_4(s) = \frac{20}{3}Ni_2P(s) + P_4(g)$	(5)	31.6±3	b
$12Ni_2P(s) = 2Ni_{12}P_5(s) + P_2(g)$	(6)	40.0±3	c
$6.80Ni_{12}P_5(s) = 32.0Ni_{2.55}P(s) + P_2(g)$	(7)	43.9±3	c
$\frac{1}{6}Ni_5P_4(s) + \frac{1}{6}NiP_2(s) = NiP(s)$	(11)	0.1±0.1	d
$0.24Ni_5P_4(s) + 0.02NiP_2(s) = Ni_{1.22}P(s)$	(12)	0.1±0.1	d

a) Calculated from the data of Weibke and Schrag.[2]

b) Calculated from the data of Biltz and Heimbrecht.[3]

c) This work.

d) Calculated from phase diagram.[1]

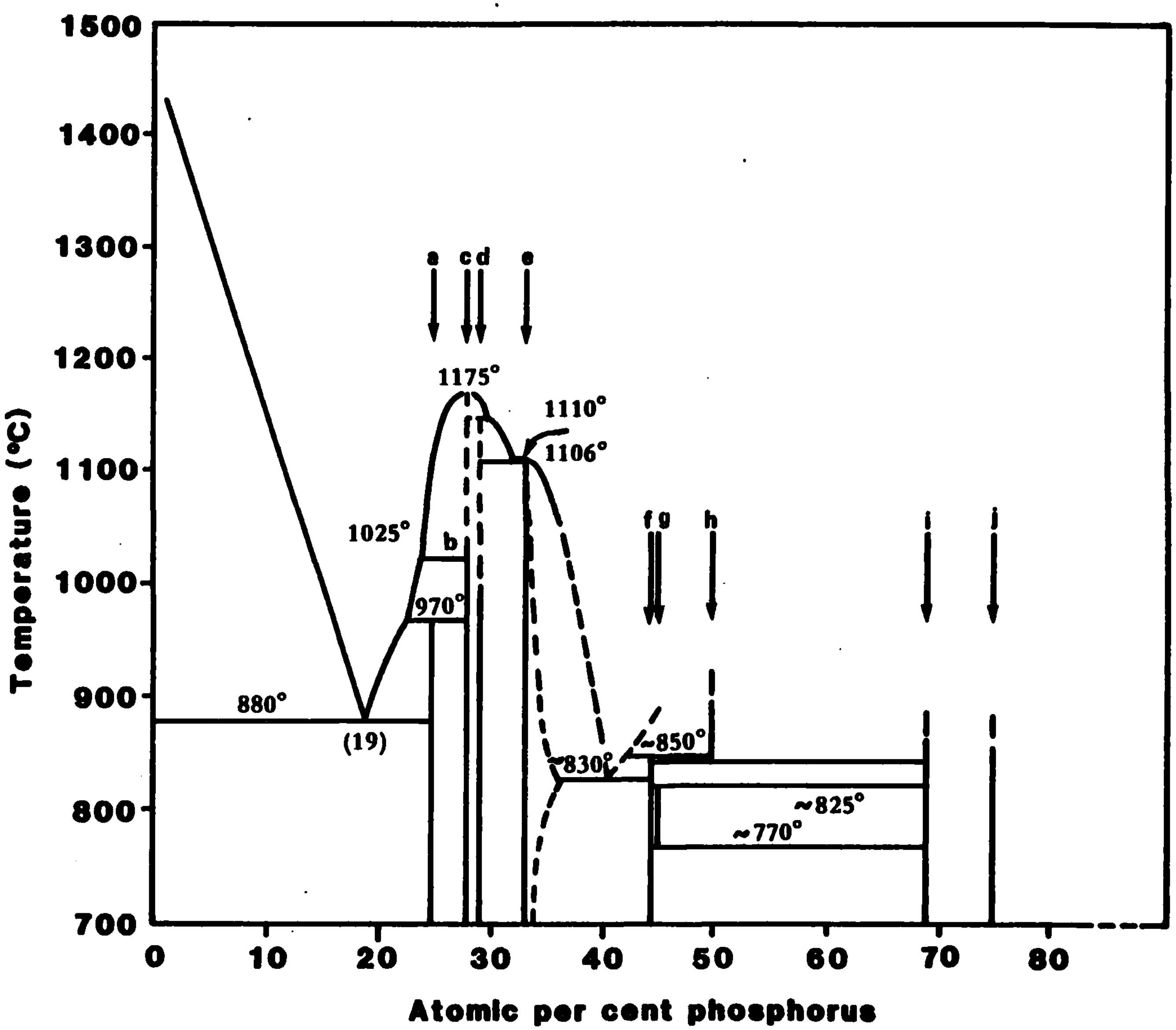
Table 5

Enthalpies of Formation (from red P) and Atomization (kK) at 298.15K

	$-\Delta H_f^o/R$	$\Delta H_{at}^o/R$
$\frac{1}{4}Ni_3P(s)$	5.94±0.5	54.8
$\frac{1}{3.55}Ni_{2.55}P(s)$	6.65±0.5	55.2
$\frac{1}{17}Ni_{12}P_5(s)$	6.73±0.5	55.1
$\frac{1}{3}Ni_2P(s)$	6.87±0.5	54.8
$\frac{1}{9}Ni_5P_4(s)$	6.39±0.5	53.0
$\frac{1}{2.22}Ni_{1.22}P(s)$	6.32±0.5	52.9
$\frac{1}{2}NiP(s)$	6.09±0.5	52.1
$\frac{1}{3}NiP_2(s)$	5.38±0.5	49.4
$\frac{1}{4}NiP_3(s)$	4.52±0.5	47.6

FIGURE CAPTION

FIGURE 1. Nickel-Phosphorus Phase Diagram (after Larsson, Ref. 1). Phases: a, Ni_3P; b, $Ni_5P_2(\beta)$; c, $Ni_{\sim 2.55}P$; d, $Ni_{12}P_5$; e, Ni_2P; f, Ni_5P_4; g, $Ni_{\sim 1.22}P$; h, NiP; i, NiP_2; j, NiP_3.



Temperature (°C)
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1400
1300
1200
1100
1000
900
800
700
0
10
20
30
40
50
60
70
80
Atomic per cent phosphorus
880°
(19)
1025°
970°
b
1175°
1110°
1106°
~830°
~850°
~825°
~770°
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