The Thermodynamic Properties of Phosphorus and Solid Binary Phosphides

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I. Introduction

Although phosphorus forms solid compounds with nearly all the elements in the Periodic Table, the phosphides as a class are much less well-known than others. This is due in part to phosphides not being found in nature, and in part to the relatively sparse range of applications for these compounds. However, the semiconductive nature of several phosphides and a growing list of other applications have in recent years led to increased interest in these compounds,[1] as evidenced by growth in the literature on their preparation and properties.

Given the low level of interest, it is not surprising that the first investigations of the thermodynamic properties of phosphides were not reported until the 1930s.[2,3] Since then, the increased interest in these compounds has led to a slow but steady increase in the literature, and assessed thermodynamic properties for some compounds have appeared in recent compilations.[4−6] Occasional reviews of semiconducting phosphide thermodynamics have also appeared.[7−9] However, no complete thermodynamic review has yet appeared, perhaps due in part to the scarcity of data to review. The continued improvement in the size and

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reliability of the database has made such a general review feasible. This presentation will describe the experimental techniques used to determine the thermodynamic properties of solid binary phosphides, review and correct as necessary the existing database, and present recommended thermodynamic tables for those compounds as appropriate.

II. The Thermodynamic Properties of Elemental Phosphorus

Perhaps the most significant challenge in accurately assessing the thermodynamic properties of phosphides is the choice of reference state for elemental phosphorus. Phosphorus is available in a bewildering variety of physical states, and the thermodynamic stabilities of most are understood poorly at best. As Hultgren et al. admitted in 1973,[11] "The story is long, complex and confusing." Nevertheless, retelling it is necessary, since the reference state of elemental phosphorus used in phosphide thermodynamics investigations varies, and as a result the appropriate Gibbs energy and enthalpy changes for conversion from one reference state to another will be needed.

The allotropes of solid phosphorus can be divided into three "families". "White" phosphorus (sometimes known as yellow) was the first form of the element to be prepared, and it is still the best characterized. Its room-temperature crystal structure is a loosely

bonded cubic aggregation of condensed P_4 molecules, unique among the elements. White phosphorus transforms below 195 K to a triclinic structure;[10] despite this, the high-temperature form has generally been designated α.[11-13] White phosphorus melts at 317 K to the metastable liquid, which in turn boils at 552 K.

The most recently discovered family of phosphorus allotropes is "black" phosphorus, first isolated in 1915. Black phosphorus has been prepared at atmospheric pressure with both an amorphous and an orthorhombic crystal structure; it transforms at higher pressure to a rhombohedral and then a cubic structure.[1] Orthorhombic black phosphorus is likely the standard state of the element at ambient temperature, but this form transforms to red (V) phosphorus at or below 823 K.[14]

The third and most complex family of phosphorus allotropes is so-called "red" or "violet" phosphorus. Red phosphorus is prepared by the application of heat or light to white phosphorus, crystallization of the liquid, high-temperature condensation of the vapor, or precipitation from supersaturated solution in molten lead.[14,15] When prepared by the first two methods, it initially appears with an amorphous structure designated red (I).[11,16] Heating red (I) to 723 K generates two crystalline forms of red phosphorus, designated red (II) and red (III);[15-17] neither of these has been prepared in pure form, and their crystalline structures are unknown. Holding red (I), (II), or (III) at higher temperatures ($\sim$750–800 K) generates red (IV). The structure of this phase is uncertain; different investigators have claimed it to be hexagonal, tetragonal, triclinic, or monoclinic.[15,17-19] Finally, red phosphorus held at higher temperatures still ($\sim$823 K) or crystallized from molten lead has a red (V) structure.[15,16] This too was originally thought to be triclinic,[17] but it is currently thought to have a distinct monoclinic structure.[18,19] Regardless of crystalline structure, red phosphorus sublimes to P_4 vapor when heated;[15,16,20] the unit-pressure sublimation temperature varies according to structure type.

In addition to the various solid states, phosphorus has three significant gaseous species. Vaporizing red or liquid phosphorus forms a gas consisting primarily of P_4, which is the predominant form below 973 K.[1] Above this temperature, the presence of P_2 vapor becomes noticeable and increasingly predominant above 1533 K.[12] At still higher temperatures, monatomic phosphorus vapor begins to appear.[21] Triatomic P_3 is also present,[13] although its thermodynamic stability relative to those of P_2 and P_4 is negligible.

Current JANAF assessments of the thermodynamic properties of the allotropes of solid phosphorus were originally performed in 1961 for the white and red (V) modifications,[13] and in 1969 for orthorhombic black and red (IV). These assessments form the basis for most of the published tables of these properties.[4,5,22,23] An additional assessment was made in 1973 by Hultgren et al.[11] The accuracy of these assessed values is limited by several experimental difficulties associated with elemental phosphorus:

(*i*) the difficulty of preparing red and black phosphorus allotropes in pure form;[16,17,24]
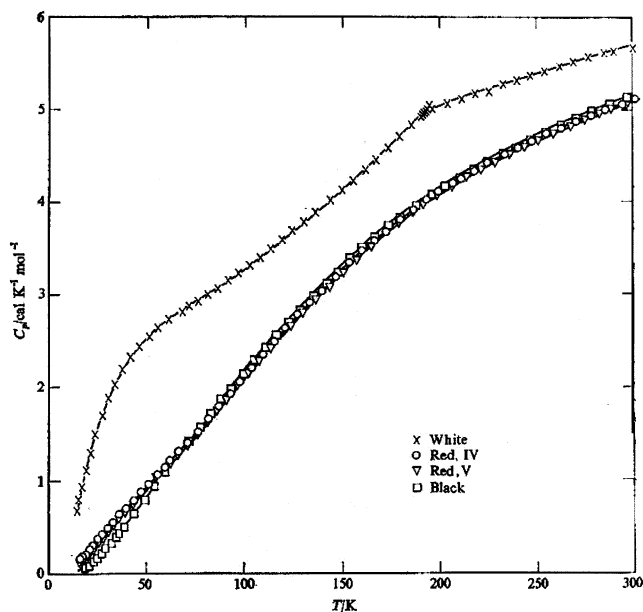

Figure 1. Heat capacities of solid allotropes of phosphorus vs temperature. Reproduced with permission from ref 16. Copyright 1969 Academic Press.

(*ii*) the poor ("retarded") vaporization kinetics of red and black phosphorus;[16,25] and

(*iii*) uncertainty over which form of red phosphorus early investigators were working with.[16,26]

Because of the difficulty in obtaining and performing experimental work with red and black phosphorus, the most reliable thermodynamic data has historically been obtained working with white phosphorus and the metastable liquid. That in turn has led to the choice of α-white/liquid phosphorus as the reference state for the element, despite experimental evidence showing that red (I), red (IV), red (V), and both black forms are all more thermodynamically stable.[16,24,27-29] (In fact, phosphorus is often the only chemical element for which the reference state is not the standard state.) However, several investigators have studied the thermodynamics of phosphide formation from "red" phosphorus,[30-47] and as a result, the Gibbs energy of "formation" of one or more of these forms will be needed. Using a form of red phosphorus as the room-temperature reference state for the element would also simplify the assessment of thermodynamic data for the phosphides, since all five types sublime directly to P_4 vapor without melting.

The most reliable thermodynamic measurements on solid phosphorus are the low-temperature calorimetry measurements of Stephenson et al.,[16] which determined the entropy at 298 K of the α-white (41.00 J/mol·K), red (IV) (23.17 J/mol·K), red (V) (22.84 J/mol·K), and orthorhombic black (22.59 J/mol·K) forms. The entropy value for black phosphorus is similar to that determined separately by the low-temperature calorimetry of Paukov et al.,[48] lending confidence to the other results (which are otherwise unconfirmed). Figure 1, reproduced from Stephenson's work, shows the four heat capacities as a function of temperature; it will be noted that the heat capacities of red (IV), red (V), and black phosphorus are virtually identical at room temperature.

Table 1. Enthalpies of Transformation between Solid Phosphorus Allotropes

	ΔH°_{298} (J/mol)				
reaction	O'Hare and Hubbard[24]	O'Hare et al.[27]	Jacobs[29]	Holmes[28]	present assessment
α-white−black		−21186			
α-white−red (I)	−16108			−7321	−4985
α-white−red (V)	−16263				−17557
α-white−red (IV)	−11313			−13074	
red (IV)−red (V)	−4950				
red (I)−red (IV)	4795			−5753	
red (I)−red (V)			−1100		−12572
red (I)−black			16400		
red (V)−black			17500		

The slow kinetics of the solid-state phase transformations of phosphorus make it infeasible to directly measure their enthalpy or Gibbs energy.[16] However, the enthalpies of transformation can be determined indirectly by comparing the enthalpies of reaction of different forms under identical conditions. Jacobs was the first to do this experimentally,[29] reacting white, red (I), and black phosphorus with bromine dissolved in carbon disulfide. Subsequently, Holmes compared the enthalpies of combustion at 298 K of white, red (I), and red (IV) phosphorus to form P_4O_{10},[28] and O'Hare and Hubbard measured the ambient-temperature enthalpies of combustion of white, red (I), red (IV), and red (V) in fluorine to form PF_5, later including orthorhombic black phosphorus.[24,27] The differences between these enthalpies of reaction are the enthalpy of transformation from one solid allotrope of phosphorus to another. Table 1 compares the experimental results of these investigations; the values obtained from Jacobs and from O'Hare and Hubbard are in closer agreement than those from the work of Holmes. However, the chemical and allotropic purities of the phosphorus phases used in these studies are uncertain.[24]

A second type of differential reaction thermodynamics results from studies of the vapor pressure of P_4 in equilibrium with different phosphorus allotropes. Farr has reported the most thorough research of this type,[15] describing the results of experiments measuring p_{P_4} (593−833 K) in equilibrium with red (I), (II), (IV), and (V). The experimental technique used to make these measurements was not reported, and Farr states that the allotropic purity of the red (II) and (IV) was questionable. If the data set is limited to results generating $p_{P_4} < 2.5$ atm, regression analysis of data for the reactions,

$$4P(red, I) = P_4(g) \qquad (1)$$

$$4P(red, V) = P_4(g) \qquad (2)$$
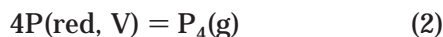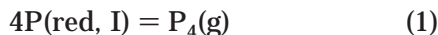
can be used to determine their standard Gibbs energy changes:

$$\Delta G^\circ = 77\,750 - 108.9\,T - 0.01047\,T^2 \text{ J/mol} \quad (3)$$

$$\Delta G^\circ = 130\,971 - 201.9\,T + 0.0225\,T^2 \text{ J/mol} \quad (4)$$

From eq 4, the entropy of reaction 2 is +188.5 J/mol·K at 298.15 K. Using the experimentally determined value of $S^\circ_{298.15}$ for red (V) mentioned above,[16] this leads to a calculated value of $S^\circ_{298.15}$ for $P_4(g)$ of 279.8

J/mol·K. This compares with the value of 280.0 J/mol·K determined from spectroscopic data.[16]

Several studies of the vapor pressure of P_4 in equilibrium with metastable liquid phosphorus have also been performed.[11] The most recent of these is that of Arita and Watanabe (373−500 K),[49] which combined with the results of previous work yields an expression for the Gibbs energy of formation of P_4 vapor from the liquid:

$$4P(l) = P_4(g) \qquad (5)$$

$$\Delta G^\circ = 52\,180 - 97.40\,T + 0.00565\,T^2 \text{ J/mol} \quad (6)$$

Last, the partial pressure of P_4 in equilibrium with solid α-white phosphorus has been determined by several researchers,[11] most notably Dainton and Kimberly (250−314 K).[50] From these data, the Gibbs energy of formation can be determined for the reaction:

$$4P(\alpha\text{-white}) = P_4(g) \qquad (7)$$
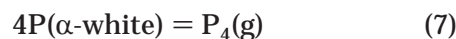
$$\Delta G^\circ = 62\,167 - 137.9\,T + 0.0385\,T^2 \text{ J/mol} \quad (8)$$

The entropy change of this reaction at 298.15 K is +115.0 J/mol·K; using the $S^\circ_{298.15}$ for P(α-white) determined by Stephenson et al.[16] results in a calculated value of $S^\circ_{298.15}$ for $P_4(g)$ of 279.0 J/mol·K, consistent with the other results.

From these expressions, the Gibbs energies of formation of red (I), α-white, and liquid phosphorus from red (V) can be determined as a function of temperature:

$$P(red, V) = P(red, I) \qquad (9)$$

$$\Delta G^\circ = 13\,305 - 23.25\,T + 0.00824\,T^2 \text{ J/mol} \quad (10)$$

$$P(red, V) = P(\alpha\text{-white}) \qquad (11)$$

$$\Delta G^\circ = 17\,201 - 15.99\,T - 0.00400\,T^2 \text{ J/mol} \quad (12)$$

$$P(red, V) = P(l) \qquad (13)$$
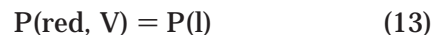
$$\Delta G^\circ = 19\,698 - 26.12\,T + 0.00421\,T^2 \text{ J/mol} \quad (14)$$

Table 2 lists the standard Gibbs energies of formation of red (I), α-white, and liquid phosphorus from standard-state red (V), along with $^1/_4 P_4(g)$. The upper limit of 704 K is the atmospheric sublimation temperature of red (V) to P_4. Using eqs 8, 10, 12, and 14, the enthalpies of these transformations can also be calculated; these have been added to Table 1, and can

Table 2. Standard Gibbs Energies of Formation of Phosphorus Allotropes from Red (V) (J/mol)

temp (K)	red (I)	α-white	liquid
298.15	7105	12078	12285
300	7072	12044	12241
400	5323	10165	9924
500	3740	8206	7691
600	2321	6167	5542
700	1068	4048	3477
704	1021	3962	3396

Table 3. Gibbs Energies of Formation of Phosphorus Species (Red (V) Reference, J/mol)

temp (K)	red (V)	$^1/_4P_4(g)$	$^1/_2P_2(g)$	P(g)
298.15	0	18194	64123	298183
300	0	18107	63965	297911
400	0	13453	55504	283282
500	0	8912	47171	268781
600	0	4483	38966	254408
700	0	167	30889	240163
704	0	0	30569	239596
704	0	0	30569	239596
800	4037	0	26976	230082
900	8129	0	23246	220184
1000	12107	0	19533	210303
1100	15974	0	15834	200436
1200	19727	0	12152	190586
1300	23369	0	8485	180751
1400	26897	0	4834	170932
1500	30314	0	1198	161128
1533	31416	0	0	157895
1533	31416	0	0	157895
1600	36039	2422	0	153762
1700	42835	6026	0	147594
1800	49502	9615	0	141426
1900	56041	13188	0	135258
2000	62452	16745	0	129090

be compared with the experimentally derived values. Equation 12 can also be used to calculate the entropy of reaction 11 at 298 K; the calculated value of +18.37 J/mol·K is similar to that calculated from the entropy measurements of Stephenson et al.,[16] +18.16 J/mol·K.

Considering higher-temperature phosphorus thermodynamics, several investigations have studied the equilibrium between P_4 and P_2 vapor.[11] The most recent of these is that of Arita and Watanabe (1073−1473 K),[49] which combined with similar results yields the following expression for the reaction:

$$2P_2(g) = P_4(g) \tag{15}$$

$$\Delta G^\circ = -229\,500 + 154.5\,T - 0.00313\,T^2 \text{ J/mol} \tag{16}$$

The enthalpy change for this reaction at 298 K is +229.2 kJ/mol, virtually identical to the +229 kJ/mol determined in an assessment of earlier experimental data.[22] Equation 16 allows derivation of an expression for the standard Gibbs energy of formation of P_2 vapor from red (V) phosphorus:

$$P(red, V) = {}^1/_2P_2(g) \tag{17}$$

$$\Delta G^\circ = 90\,118 - 89.10\,T + 0.00641\,T^2 \text{ J/mol} \tag{18}$$

From this expression and the experimentally determined value of $S^\circ_{298.15}$ for red (V),[16] the entropy of $P_2(g)$ at 298.15 K can be calculated as 216.2 J/mol·K. This compares with 218.1 J/mol·K determined from spectroscopic data.[22]

Finally, the Gibbs energy of formation of monatomic phosphorus vapor is needed. Because of the high temperatures required to dissociate P_2, only one investigation of this reaction has been performed;[11] the results reported by Gingerich over the temperature range 1916−2198 K can be used to determine ΔG° for the reaction:[21]

$$P_2(g) = 2P(g) \tag{19}$$

$$\Delta G^\circ = 504\,900 - 123.36\,T \text{ J/mol} \tag{20}$$

Although no experimental measurements have been made of the heat capacities of P_2 and P vapor, these values have been calculated in Gurvich et al.,[22,23] based on spectroscopically determined energy levels. Between 298 and 2500 K, regression against the calculated values generates the following heat capacity expressions:
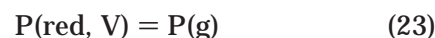
$$C_{P,P(g)} = 20.058 + 0.00063\,T + 57\,397\,T^{-2} \text{ J/mol·K} \tag{21}$$

$$C_{P,P_2(g)} = 34.097 + 0.00040\,T - 653\,288\,T^{-2} \text{ J/mol·K} \tag{22}$$

The differential heat capacity for reaction 19 can be used to calculate ΔG° for this reaction over a wider temperature range than that experimentally determined; the results compare well with those predicted using eq 20.

Using eq 20, ΔG° can be calculated for the equilibrium,

$$P(red, V) = P(g) \tag{23}$$

$$\Delta G^\circ = 342\,568 - 150.78\,T + 0.00641\,T^2 \text{ J/mol} \tag{24}$$

The standard Gibbs energies of formation of P_4, P_2, and P vapor from reference-state phosphorus (red (V) below 704 K, P_4 between 704 and 1533 K, and P_2 above 1533 K) are listed in Table 3. The uncertainties in the values in Tables 1−3 are on the order of 5 kJ/mol. They would be improved by (a) measurement of accurate high-temperature heat capacities for the various forms of red and black phosphorus and (b) redetermination of the enthalpies of reaction of the different solid phosphorus allotropes using purer starting materials. This would eliminate the need to use the vapor pressure data of Farr relied on for this assessment.[15]

Comparison of the thermodynamic properties of phosphorus allotropes calculated here with those listed in other compilations is hampered by the varying lists of phosphorus allotropes assessed elsewhere. The JANAF tables include data for α-white, liquid, black, red (IV), and red (V) phosphorus, along with P, P_2, and P_4 vapor, but not red (I).[13] Dinsdale

Table 4. Assessed Gibbs Energies of Formation of Phosphorus Allotropes from Red (V) at 298 K (J/mol, 1 atm)

	α-white	$^1/_4 P_4(g)$	$^1/_2 P_2(g)$	$P(g)$
present assessment	12078	18194	64123	298183
JANAF[13]	12026	18130	63598	292039
Elliott and Gleiser[6]	12074	18196	63682	292050
Pankratz[149]	12133	18296	63780	292138

includes data only for α-white, liquid, and "red";[12] Barin and Kubaschewski et al. list values for α-white, "red", and the three vapor species.[4,121] The tabulations of Elliott and Gleiser and of Pankratz include the three vapor species, along with α-white and a "red triclinic solid", possibly red (V).[6,149] Table 4 compares the Gibbs energies of formation at 298 K of α-white phosphorus, P(g), (g) $^1/_2 P_2(g)$, and $^1/_4 P_4(g)$ from red (V) calculated using this assessment with those of Elliott and Gleiser, Pankratz, and the JANAF tables (adjusting Gibbs energies of formation of gaseous species in the latter to 1 atm partial pressure.) The results are well within the degree of error of the experimental data from which they were derived.

III. Experimental Techniques and Modeling

A. Heat Capacity

The importance of experimental heat capacity measurements in the study of phosphide thermodynamics is more significant than for other compounds, due to increased difficulty of successfully modeling these values. As a result, the inadequacy of the existing database is more keenly felt. Most of those measurements which have been reported are relatively recent, and the improved experimental equipment used makes their reliability somewhat better than for other classes of compounds.

Most of the low-temperature heat capacity measurements reported for phosphides were made primarily to obtain their room-temperature entropy, although a few exhibit interesting low-temperature anomalies.[51-61] Most of the low-temperature work has been performed using adiabatic cryostatic calorimeters as described by Westrum;[62] a few differential scanning calorimetry (DSC) low-temperature results have also been reported.[51,63-66]

High-temperature heat capacity measurements have been made using a variety of instruments, beginning with traditional drop calorimetry.[67-70] Adiabatic calorimetry has also been used,[53,55,56,59,71] along with laser flash calorimetry,[60,61,72,73] DSC,[64-66,74] and AC calorimetry.[75] However, high-temperature measurements are somewhat rare, in part because of the tendency of phosphides to decompose when heated.

Because of the relative scarcity of experimental data, the modeling of heat capacities is potentially valuable for predicting phosphide thermodynamics. Unfortunately, modeling results are also scarce. Kagaya and Soma developed a model for calculating the heat capacities of chalcogenide compounds with tetrahedral orientations[76] with some success; however, this model does not appear to have wide applicability. The Neumann–Kopp equation, often

used for predicting the heat capacity of other compounds, is not applicable for phosphides, since it requires the availability of C_P data for elemental phosphorus which have not been determined (and cannot be obtained above 704 K, anyway). The ion-binding model proposed by Guosheng and Zhihong shows promise[77] but is valid only at 298 K. The model with the greatest value is that developed by Kubaschewski and Ünal,[78] which is based on compound stoichiometry, melting point, and "contributions" from the cation and anion in the compound. Kubaschewski and Ünal's model calculates a, b, and c values for the general heat capacity equation,

$$C_P = a + (b \times 10^{-3})T - (c \times 10^5)T^{-2} \text{ J/mol·K} \quad (25)$$

For the compound $A_x B_y$,

$$a = \frac{(T_m \times 10^{-3})(\sum \Theta + 1.125n) - (0.298n \times 10^5)T_m^{-2} - 2.16n}{(T_m \times 10^{-3}) - 0.298} \quad (26)$$

$$b = \frac{6.125n + 10^5 n T_m^{-2} - \sum \Theta}{(T_m \times 10^{-3}) - 0.298} \quad (27)$$

$$c = 4.12n \quad (28)$$

where $n = x/y$, T_m is the melting point in kelvin, and $\sum \Theta$ is the sum of the "contributions" of the compound cation and anion:

$$\sum \Theta = m\Theta_A + n\Theta_B \quad (29)$$

Using existing heat capacity data, Kubaschewski and Ünal have by regression analysis determined values of Θ_A and Θ_B for common cations and anions;[78] their value of 23.43 J/K for phosphorus is considered tentative.

Using eqs 26–29, values of a, b, and c have been determined for Mn_2P and Ba_3P_2. From these, the molar sensible heats ($H_T - H_{298}$) have been calculated; these are compared in Figure 2 with experimentally obtained values for these two compounds.[7,65]

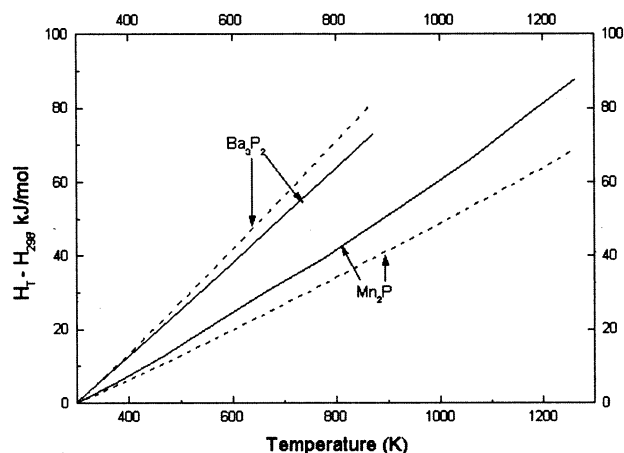

Figure 2. Experimentally determined heat capacities of Ba_3P_2 and Mn_3P_2 (solid lines) vs temperature,[7,65] plotted against values predicted using the model of Kubaschewski and Ünal (eqs 25–29, dotted lines).
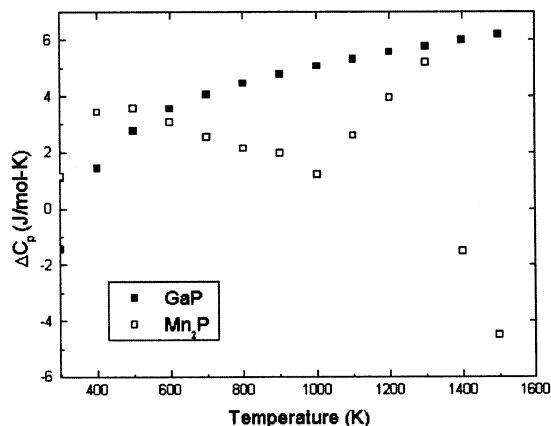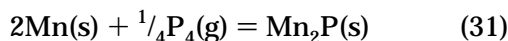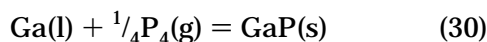
Figure 3. ΔC_p for the formation of GaP and Mn$_2$P from the elements (P$_4$(g) reference state) vs temperature, from experimental heat capacity data.[7,13,80]

Figure 4. Experimentally determined value of S°_{298} for phosphide compounds, plotted against values predicted using the model of Mills.[81]

As can be seen, the level of agreement leaves something to be desired. Beyond this, there are other difficulties with the use of eqs 26–29 for predicting high-temperature phosphide heat capacities. The equations become less valid for compounds with a melting point above 2000 K, eliminating many rare-earth phosphides from consideration;[79] furthermore, they require the availability of an accurate "melting point". As will be seen, most phosphides melt (or decompose) incongruently, with a decomposition temperature dependent on pressure. As a result, models of this type are not yet reliable enough to use in lieu of experimental data.

Another "model" of sorts used in lieu of high-temperature heat capacity measurements is the assumption that the differential heat capacity, ΔC_P, for the formation of phosphides is a constant. Figure 3 tests this assumption, using experimental high-temperature heat capacity data for GaP and Mn$_2$P,[7,80] along with heat capacities for the elements from JANAF.[13] In this temperature range, the reference state for elemental phosphorus is assumed to be P$_4$ vapor, and so the plotted points represent ΔC_P for the reactions,

$$\text{Ga(l)} + {}^1/_4\text{P}_4\text{(g)} = \text{GaP(s)} \qquad (30)$$

$$2\text{Mn(s)} + {}^1/_4\text{P}_4\text{(g)} = \text{Mn}_2\text{P(s)} \qquad (31)$$

As can be seen, the assumption of constant ΔC_P also leaves something to be desired. However, over relatively short temperature ranges, the errors introduced by its use may not be overly significant.

The low-temperature heat capacity database allows the testing of a third model, developed by Latimer for prediction of ionic compounds' entropies at 298 K. This model treats entropies as the sum of "contributions" made by the anion and cation, the contributions being determined by regression analysis of existing data. Spencer describes improvements made to this model by Mills which allow calculation of S°_{298} for less ionic compounds such as phosphides;[81] the contribution depends on compound stoichiometry as well as the choice of cation and anion. Figure 4 compares predicted values of S°_{298} for monophosphide compounds against experimen-
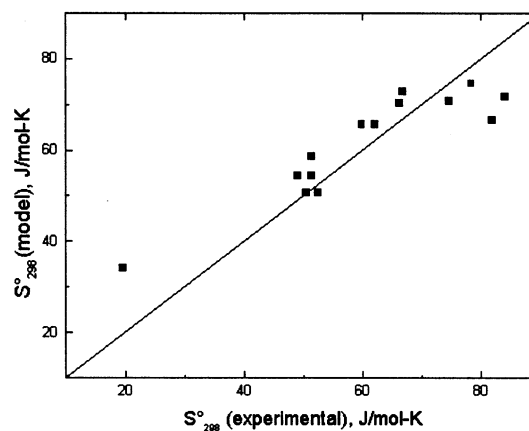
tally determined values obtained directly (i.e., using low-temperature calorimetry). While the agreement is reasonable, given the uncertainty of the experimental results, it is not sufficient to use in lieu of actual data.

B. Enthalpy of Formation

Most of the enthalpies of formation listed in the literature on phosphide thermodynamics are actually derived from second- and third-law analyses of Gibbs energy measurements. Actual experimental data for enthalpies of reactions involving phosphides are rare. Those experiments that have been performed fall into six categories:

(*i*) *Direct-reaction calorimetry*, in which mixtures of elemental phosphorus (usually red (I)) and the second element are ignited and the resulting heat generation is measured.[36,39,46,82–84] In addition to the usual concerns over calorimeter accuracy, the degree of completion of the reaction has been a potential limitation to this technique.

(*ii*) *Direct-synthesis drop calorimetry*, a variation of direct-reaction calorimetry, which has been used in recent years with more reliable results.[33–35]

(*iii*) *Precipitation calorimetry* from metallic solution, another type of direct-reaction calorimetry, demonstrated by Martosudirdjo and Pratt[40] with molten tin as the solvent. Possible concerns with this approach include the formation of binary or ternary tin phosphides and inaccurate enthalpies of mixing in the molten tin, especially in equilibrium with a compound. The heat effect caused by the decomposition of a phosphide has also been measured on one occasion.[85]

(*iv*) *Oxide reaction calorimetry*, in which the enthalpy of combustion of the compound is measured and compared with the enthalpy of combustion of a mixture of elemental phosphorus and the second element.[43,45,47,83,86,87] Again, the degree of completion of the reaction is a potential limitation; a more significant concern is ensuring that the reaction products are the same in both cases, since the enthalpies of formation of most phosphates are not well-known. The sameness of the products has often been assumed rather than verified.

(*v*) *Halide reaction calorimetry*, in which the combustion previously performed in oxygen is now carried out in bromine, chlorine, or fluorine gas.[37,42,88–91] There is considerable variety among this general technique, depending on the compound being studied and the possible reaction products; the reaction of boron phosphide to generate BCl_3–PCl_3 has been especially popular.

(*vi*) *Aqueous solution calorimetry* is rare in the study of phosphides[42,92–96] and has not been performed since the early 1960s. Hydrochloric and sulfuric acids have been used as solvents, the reaction products presumably being a dissolved metal chloride or sulfate and phosphine (PH_3) gas. The gaseous product is one of the experimental difficulties confronting this technique; it is also not clear whether all of the phosphorus in the compound reacts to form PH_3.

The enthalpy of formation of phosphides has proven difficult to model, in part because phosphides are not easily classified. They are not truly ionic compounds in the manner of sulfides or halides, so models of ΔH° for metal salts are rarely applicable.[81] Gruza has extended an ionic compound model to predict ΔH° for "stoichiometric" alkali and alkaline-earth phosphides (i.e., M_3P, N_3P_2),[97] but the accuracy is not always impressive. Nguyen and Dang's model applies only to M_3P compounds.[98] On the other hand, phosphides are not truly metallic compounds either, so models for estimating ΔH° for intermetallic phases are also not readily applied. Niessen and de Boer have extended Miedema's semiempirical model to deal with less metallic phases such as carbides, silicides, and phosphides,[99,100] but this requires adding an additional enthalpy term to "transform" these elements to a metallic state. (For phosphorus, this equals 17 kJ/mol.) Although this model can theoretically predict ΔH° for any metallic phosphide, the accuracy of the results compared with experimental data is inconsistent.[100] (This may be as much a reflection on the quality of the experimental data as on the model.) Additionally, none of the models uses a specific reference state for elemental phosphorus, further reducing their reliability. Calculated estimates of ΔH° for phosphides generated using these models will be presented for comparison with other results but will not be used for calculation of recommended thermodynamic properties.

C. Gibbs Energies

Studies of phase equilibria leading directly to calculation of Gibbs energies of formation are by far the most common type of thermodynamic investigation of phosphides. They can be categorized into four types:

(*i*) *EMF studies* are performed less commonly on phosphides than on other classes of chemical compound. Reasons for this include the lack of a condensed phase of phosphorus that is stable above 704 K, which makes the element less useful as a reference electrode, and the instability of many phosphides at higher temperatures. The need for lower temperatures in turn requires the use of chemically stable low-melting-point electrolytes, which are difficult to find. Because of this, higher-temperature studies
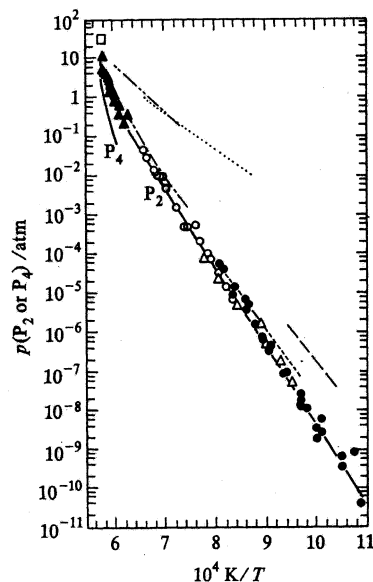

Figure 5. Use of phosphorus vapor pressures along the liquidus line in the Ga–P system to calculate ΔG_T° for GaP. Reproduced with permission from ref 116. Copyright 1974 Academic Press.

have occasionally used solid-state electrolytes instead, particularly calcium fluoride.[101–104] Otherwise, chloride-based solutions have been the electrolyte of choice.[30–32,44,105–110] The metallic element in the compound has usually been the reference electrode, although Voleinik and Shabdenov used solid silver instead.[110]

(*ii*) *Reaction equilibria* studies are also uncommon, although they are possibly more viable than EMF measurements. Several different reaction types have been tried; generally the goal is to react the solid phosphide to form a gaseous compound and use mass loss rates to determine compound partial pressures and thus K_{eq} for the reaction. Khukhryanskii et al. and Thurmond and Frosch have used hydrogen to generate PH_3 from phosphides,[111–113] and Glaum and Gruehn have formed PI_3 as a reaction product using I_2 at lower temperatures.[114] Other investigators have used reactions in which a solid phosphide was the reaction product.[2,115] However, there are fewer examples of this type of experimental approach than might be suspected.

(*iii*) *Phase equilibria* have been reported occasionally, often in combination with vapor pressure or reaction equilibria measurements. There are two types of phase equilibria studies. The first involves calculation of liquidus line activities of one or both elements in the binary system, thus determining the equilibrium constant for the formation reaction; Panish and co-workers were particularly active using this method.[116,117] Figure 5, which depicts the liquidus line in the Ga–P system, illustrates the technique;[116] at lower temperatures, the activity of gallium can be assumed to equal one, so measuring the partial pressure of P_2 or P_4 vapor in a GaP-saturated melt is all that is needed to determine the Gibbs energy of formation of the compound. The second type of phase equilibria study involves equilibria between the compound and both elements dissolved in a solvent, either molten iron[118] or silver.[119,120] If the

activities of the elements in the solvent can both be set, then the Gibbs energy of formation of the compound can be determined. The accuracy of this latter method is limited by the accuracy of the dilute solution activity expression.

(*iv*) *Vapor pressure* measurements are by far the most numerous of the thermodynamic investigations of phosphides, and they are sometimes the most controversial. They can be divided according to the classification used by Kubaschewski et al.:[121]

(*a*) *Static Methods.* Perhaps the oldest method of measuring the vapor pressures generated by a decomposing compound involves the use of a manometer, sometimes known as a "tensimetric" apparatus. Numerous investigators have used manometric methods to study phosphides, most commonly the Bourdon gauge. As with other static methods, the applicability of manometric methods is generally best at higher partial pressures of phosphorus vapor, meaning that higher temperatures are required. This in turn causes concern over the accuracy of the quartz gauge indicator, which loses elasticity above 1073 K.[4] Bachmann and Buehler dealt with this concern by using liquid boric oxide as the manometer fluid and reading the increased argon pressure required to maintain the meniscus in a constant position.[20] Vasil'eva and Mironov have used a membrane manometer in place of the Bourdon gauge.[122,123]

Dew-point methods have also been used on an occasional basis, particularly by Nashel'skii and co-workers.[122,124-128] The choice of this technique for experiments with phosphides is dubious, for two reasons. First is the uncertainty over the form of phosphorus which actually condenses; Marina et al. reported that the white phosphorus which initially appeared in their experiments quickly changed to "red".[125] As a result, the assumption of equilibrium, which dew-point measurements require, cannot be made. Second, the partial pressure of P_4 in systems such as these is dependent not only on the choice of phosphorus allotrope, but also on temperature, and small temperature errors cause larger than usual uncertainties in p_{P_4}, given the relatively low sublimation temperatures for this element.

A few investigators have used a vapor density approach,[122,129-132] in which a sealed ampule containing a known initial mass of compound is equilibrated at a given temperature and quenched. The loss in mass of the sample (presumably caused by the formation of P_4 vapor), divided by the ampule volume, yields the equilibrium partial pressure. The technique has also been used by Stephenson to measure the equilibrium partial pressure of red (IV) elemental phosphorus.[16] Again, use of this technique is limited to systems with high vapor pressures, to ensure accurate measurement of mass loss, and condensation during cooling of the ampule may result in lower than actual reported vapor pressure measurements. Ugai and co-workers developed a similar system for measuring vapor pressures generated by decomposing CuP_2,[133] based on real-time mass losses in a sealed system. This approach which may merit more consideration.

The last of the static vapor pressure measuring devices is that described by Kubaschewski et al. as a "tensi-eudiometer".[121] This device was used frequently by Biltz and co-workers during the 1930s and 1940s to measure the partial pressure generated by decomposing phosphides (particularly refractory metal), the results of which have stood up well over time.[3,174,176-178,198,201,214,219,258,260]

(*b*) *Dynamic Methods.* By far the vast majority of dynamic vapor pressure measurements of phosphides have been made using Knudsen effusion, but there are a few others. The only reported transportation study is that of Stone et al.,[134] who studied the decomposition of boron phosphide. This technique usually requires higher vapor pressures to be effective. Two Langmuir evaporation studies have also been published;[135,136] as will be seen, both results are controversial. Schoonmaker and co-workers used torsion effusion for investigations of cadmium, gallium, and zinc phosphides;[137-139] this was coupled with mass spectrometry for the last two studies. Most Knudsen effusion studies have been coupled with mass spectrometry, but there are several exceptions.[140-142] Mass spectrometry was less needed particularly in higher-temperature studies, where the predominance of P_2 as the primary vapor species could be assured. Franzen and co-workers supplemented mass spectrometry with target collection for the measurement of metal vapor pressures at higher temperatures.[143,144] The reader is referred to the excellent review by Tmar et al. for a complete exposition of the experimental concerns associated with effusion/mass spectrometry;[145] the most significant concern is parasitic re-evaporation of phosphorus deposits on hotter parts of the furnace, which generates erroneous levels of P_4. The use of a collimating device helps minimize this problem,[116,135,146,147] along with other improvements in the arrangement of the cell and spectrometer. Attempts to model the Gibbs energy of formation of phosphides are not known.

IV. Specific Systems: Notes on Assessment Techniques

Most of the thermodynamic assessments in this review rely primarily on high-temperature measurements of elemental vapor pressures in equilibrium with solid phosphides. Where possible, these results have been combined with experimentally determined high-temperature heat capacities and room-temperature entropies to generate enthalpies and Gibbs energies of formation for the compound by a third-law method. The differential heat capacity required for this analysis was obtained using the heat capacity of $P_2(g)$ from eq 22, and that of the element, obtained from the compilation of Pankratz.[149] The data in this compilation were also used to change the reference state of the element at transition temperatures. The reference state of elemental phosphorus was converted to $P_4(g)$ (704–1533 K) and red (V) (298–704 K) using eqs 4 and 16. The reference pressure is one standard atmosphere (101 325 Pa), and all quantities are expressed in joules per mole (gram formula weight).

In addition to the uncertainties in the experimental data, possible errors in third-law analysis center on the occasionally inadequate temperature ranges for the high-temperature heat capacity data and the frequent use of "high" (>100 K) low-temperature limits for the data from which S°_{298} was determined. These will be pointed out as they occur. For some compounds, S°_{298} values provided in the literature have not been experimentally determined, but instead have been estimated on the basis of those of similar compounds. Given the lack of confidence in the ability to model this property mentioned earlier, the use of estimated values of S°_{298} for third-law analysis has been rejected.

Where the heat capacity data are insufficient to allow the third-law analysis of data, second-law analysis has been used to calculate thermodynamic properties. If high-temperature heat capacity data are available for the compound, the differential heat capacity has been used to improve the accuracy of second-law calculations. Second-law analysis is inherently less accurate than third-law calculations; in addition, the sizable temperature intervals over which extrapolations of data were occasionally made for second-law analysis increased the uncertainty level, especially at lower temperatures. A rough measure of the reliability of second-law calculations is the calculated value of ΔS°_{298} for the formation of the particular phosphide from red (V) and the element. Calculation of this value from experimentally determined entropies of phosphides typically produces a value between -10 and $+10$ J/mol·K.

V. The Alkali Metals

In some ways, the alkali metal–phosphorus systems are characteristic of most metal–phosphorus systems, in that (a) no phase diagram exists and (b) the complete list of phases may not yet be known. To date, the Li–P, Na–P, K–P, Rb–P, and Cs–P systems have only two compounds in common: a M_3P_7 phase with an orthorhombic room-temperature structure, changing to cubic at higher temperatures,[150] and an MP_{15} stoichiometry that decomposes to M_3P_7 and P_4 vapor when heated.[151,152] The expected M_3P composition has been prepared for Li, K, and Na, but not for Rb or Cs. K, Rb, and Cs form a sesquiphosphide (M_2P_3) that is not prepared using the first two elements. Several other alkali phosphides have been reported; their relative stability is uncertain.

The most thorough thermodynamic investigations in the alkali-metal systems have been performed by von Schnering and co-workers,[64,150,151] using Knudsen effusion to measure the vapor pressure generated by decomposing phosphides. It was found that M_3P_7 compounds decompose congruently to the metal vapor and P_4 (730–1066 K);[150] results depended on the size of the effusion cell aperture, indicating kinetically limited decomposition. Although mass spectrometry was initially used for vapor pressure determination, decomposition of P_4 to P_2 caused by the beam made accurate vapor pressure measurements difficult, and ultimately mass loss calculations were relied on instead. The P_4 pressures generated

Table 5. Experimental and Estimated Enthalpies of Formation for Alkali-Metal Phosphides

	ΔH°_{298} (kJ/mol)				
compd	Santandrea et al.[150,151]	Marek et al.[152]	Gruza[97]	Nguyen and Dang[98]	Morozova et al.[92]
Li$_3$P			-290	-240	
Na$_3$P			-99	-202	-134
Na$_3$P$_7$	-119				
NaP$_{15}$	-139				
K$_3$P			-70	-177	
K$_3$P$_7$	-114				
KP$_{15}$	-118	-87			
Rb$_3$P			-41	-189	
Rb$_3$P$_7$	-118				
RbP$_{15}$	-110				
Cs$_3$P			-27		
Cs$_3$P$_7$	-66				
CsP$_{15}$	-109				

by the decomposition of MP_{15} compounds to P_4 and M_3P_7 were also measured using this approach (443–620 K).[151] Marek et al. used a Bourdon gauge to measure the P_4 pressure generated by decomposing KP$_{15}$ (578–803 K),[152] with results somewhat different from those of the Knudsen effusion work. The only experimental work done with M_3P compounds is the enthalpy of formation measurement for Na$_3$P reported by Morozova et al.,[92] obtained using hydrochloric acid solution calorimetry. Results determined using this approach for other phosphides are controversial, as will be seen.

Assessment of these experimental results is made difficult by the fact that measured heat capacities exist only for LP$_{15}$ and KP$_{15}$[64] and by the temperatures (730–1066 K) used for the Knudsen effusion studies. The lack of heat capacity data meant that second-law estimations of Gibbs energies and enthalpies of formation of the M_3P_7 compounds were made using heat capacities calculated using the Neumann–Kopp law. This in turn required extrapolating the measured heat capacity for red (I) phosphorus (the chosen reference state) to temperatures well above the experimentally measured range. Furthermore, the high experimental temperatures meant that P_4 partial pressures were measured in equilibrium with the high-temperature cubic form of the M_3P_7 compounds rather than the low-temperature form; this adds uncertainty to the calculated enthalpies and entropies of formation. Table 5 presents enthalpies of formation for various alkali phosphides, estimated from the experimental results or calculated using the models of Gruza and of Nguyen and Dang,[97,98] The reference state for elemental phosphorus is not known, but this is insignificant, given the uncertainty level for both the experimental and modeled results. The need for further experimental work with these compounds is evident.

VI. The Alkaline-Earth Metals

Phosphides of these elements are of some interest due to their potential formation during phosphorus removal from steels. However, this has not resulted in a substantial increase in knowledge about these systems. Figure 6 shows the Ba–P phase diagram,[153] the only one of the five extensively studied to date. M_3P_2 compounds have been identified for all five
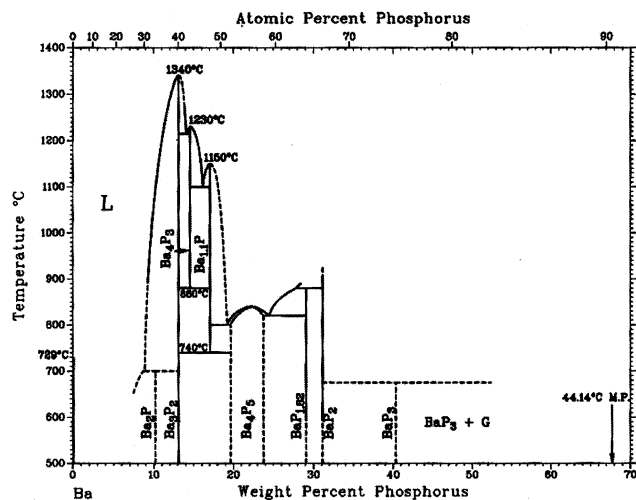
Figure 6. The Ba−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

elements and are the most stable of the alkaline-earth phosphides; higher phosphides have also been identified in the Mg−P (MgP_4), Ca−P (CaP, CaP_3, CaP_5), Sr−P (SrP_3, Sr_3P_{14}), and Ba−P systems. Ba_2P is currently the only known compound in this group with a P/M ratio less than 2:3.

Most of the thermodynamic investigations of these compounds have been performed on Ca_3P_2 and Ba_3P_2. An exception is the work of Shchukarev et al.,[93] who measured the enthalpy of formation of Sr_3P_2 and Mg_3P_2 using hydrochloric acid solution calorimetry; ΔH°_{298} (red (I) reference) was −670 kJ/mol for Sr_3P_2 and −498 kJ/mol for Mg_3P_2. A subsequent study by this group on Ca_3P_2 generated $\Delta H^\circ_{298} = -523$ kJ/mol.[94] Investigations of Ba_3P_2 include those of Min and Sano,[120] who determined the concentrations of barium and phosphorus dissolved in liquid silver in equilibrium with the compound, and Zaitsev and co-workers,[65,154,155] who measured its heat capacity (113−873 K) and the decomposition vapor pressure (Knudsen effusion/mass spectrometry) over a composition range in the Ba−P system. Several investigations of Ca_3P_2 have been conducted:

(*i*) Franck and Füldner[2] studied the vapor pressures generated by the reduction of calcium phosphate by graphite to CO and Ca_3P_2, and the further reduction of Ca_3P_2 to CaC_2 and P_2 vapor (1573−1943 K).

(*ii*) Han et al.[118] studied the equilibrium between solid Ca_3P_2 and calcium and phosphorus dissolved in molten iron (1873 K).

(*iii*) Min and Sano[119] used liquid silver as the solvent instead of molten iron, similar to their work with Ba_3P_2 (1273−1573 K).

(*iv*) Zaitsev and co-workers[65,154,156] performed heat capacity measurements and Knudsen effusion/mass spectrometry work similar to that performed on Ba_3P_2 (650−1537 K).

Both of the Gibbs energy studies on Ba_3P_2 have potential causes of inaccuracy. In the case of Min and Sano's work,[120] the activities of barium dissolved in the molten silver were calculated from the equilibrium reached with a graphite crucible:

$$\underline{Ba}_{Ag} + 2C(gr) = BaC_2 \qquad (32)$$

This requires accurate values for the Gibbs energy of formation of barium carbide, a source of some uncertainty. In addition, there is disagreement over the equilibrium constant for the reaction,

$$2\underline{P}_{Ag} = P_2(g) \qquad (33)$$

Zaitsev et al. have shown that the disagreement between their results and those of Min and Sano decreases considerably when equilibrium constants for eq 33 different from those used in the original paper are applied.[155]

The most significant concern about the work of Zaitsev et al. stems from the use of "alloys" with mole fractions of barium equal to 0.58 and 0.55 to measure the vapor pressures of Ba(g) and P_2(g). Zaitsev et al. claim that these compositions lie in a BaP−Ba_3P_2 two-phase field, and they calculated Gibbs energies of formation of both "BaP" and Ba_3P_2 from the experimental results. These values show no effect from the choice of alloy composition. However, Figure 6 shows the existence of two additional compounds (Ba_4P_3 and $Ba_{1.1}P$) in this region and the absence of BaP. As a result, it is difficult to state just which compounds were actually in equilibrium in these experiments. However, the consistency of the results suggests that these data can be used to calculated assessed Gibbs energies of formation for Ba_3P_2, if not for a higher phosphide.

Table 6 lists values for the Gibbs energy and enthalpy of formation of Ba_3P_2, calculated by a third-law method using the vapor pressure measurements of Zaitsev et al.[155] and the high-temperature and low-temperature heat capacity measurements reported by Dobrokhotova et al.[154] The uncertainties in this table are on the order of 10 kJ/mol. This is due to (i) the previously discussed concern over what phases were actually present in the vaporization experiments, (ii) possible errors resulting from extrapolation of the high-temperature heat capacity data (maximum experimental temperature 863 K), and (iii) uncertainty in the experimentally determined value of S°_{298} for Ba_3P_2 (217.5 J/mol·K) due to the low-temperature experimental minimum of 118 K. Extension of the heat capacity measurements for Ba_3P_2 to temperatures both below and above the 113−873 K limits of Dobrokhotova et al. would

Table 6. Enthalpies and Gibbs Energies of Formation of Ba_3P_2 (J/mol)

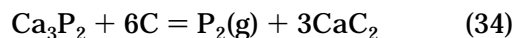| temp (K)	ΔH°_f	ΔG°_f	temp (K)	ΔH°_f	ΔG°_f
298.15	−561541	−556998	1000	−610257	−524481
300	−561513	−556970	1002	−610155	−524308
400	−560065	−555691	1002	−633418	−524308
500	−560283	−554623	1100	−628631	−513850
582	−562534	−553547	1200	−622595	−503673
582	−562514	−553582	1300	−615507	−494044
600	−562229	−553310	1400	−607445	−484997
700	−561000	−551929	1500	−598467	−476558
704	−560964	−551861	1533	−595311	−473954
704	−620899	−551861	1533	−706301	−473954
768	−619398	−545635	1600	−699271	−463994
768	−619374	−545635	1700	−688053	−449628
800	−618433	−542580	1800	−675991	−435947
900	−614839	−533304	1814	−674236	−434087
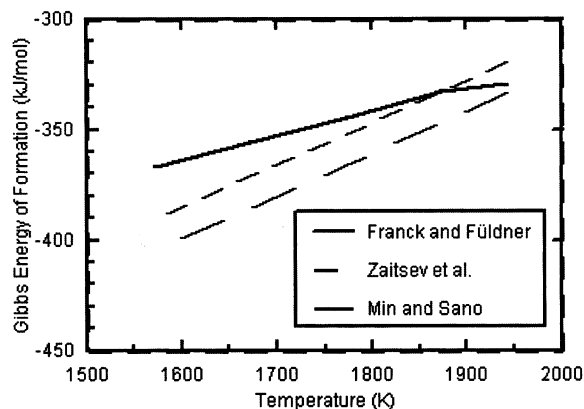
Figure 7. Experimentally determined Gibbs energies of formation of Ca_3P_2, from the investigations of Zaitsev et al.,[156] Min and Sano (corrected by Zaitsev et al.),[119] and Franck and Füldner (corrected by the author).[2]

Table 7. Enthalpies and Gibbs Energies of Formation of Ca_3P_2 (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−499734	−493716	1100	−556363	−449097
300	−328458	−493678	1112	−556479	−447922
400	−328114	−491897	1112	−581996	−448022
500	−327747	−490430	1200	−578422	−437550
600	−327594	−489129	1300	−573971	−425988
700	−327755	−487891	1400	−569103	−414785
704	−327769	−487836	1500	−563818	−403944
704	−556430	−487836	1533	−561981	−400443
720	−556194	−486294	1533	−673065	−400443
720	−558917	−486294	1600	−668869	−388613
800	−557372	−478335	1700	−662230	−371298
900	−556200	−468534	1757	−658244	−361609
1000	−555865	−458819			

improve the calculated thermodynamic data for this compound.

The concerns expressed over the investigations of Ba_3P_2 by Min and Sano also extend to investigations of Ca_3P_2 by the same authors.[119] Zaitsev et al. demonstrated that applying the same correction to the data of Min and Sano for the equilibrium constant of eq 35 improved the agreement between the results as it had for Ba_3P_2.[156] Figure 7 compares the standard Gibbs energies of formation of Ca_3P_2 determined by Zaitsev et al. with the "corrected" results of Min and Sano, and with Gibbs energies of formation derived from the 1932 results of Franck and Füldner.[2] The latter results are based on equilibrium partial pressures of P_2 generated by the reaction,

$$Ca_3P_2 + 6C = P_2(g) + 3CaC_2 \qquad (34)$$

Calculating ΔG° for Ca_3P_2 from these results requires using extrapolated Gibbs energies of formation for

CaC_2; it also requires assuming that all the vapor generated by the reaction was in fact P_2, a dubious proposition at lower temperatures. Nevertheless, there is a reasonable level of agreement. Han et al. have published results stating that the Gibbs energy of formation of Ca_3P_2 from calcium and phosphorus dissolved in molten iron at 1873 K equals +472 000 J/mol.[118] Subtracting the Gibbs energy of formation of Ca_{Fe} and P_{Fe} at this temperature from this calculates a standard Gibbs energy of formation of +608 000 J/mol, an outlandish result.

Consequently, the results of Zaitsev et al. have again been selected as the basis for third-law calculation of the thermodynamic properties of Ca_3P_2, tabulated in Table 7.[154,156] The ambient-temperature entropy of this compound (150.18 J/mol·K) is based on heat capacity measurements with a low-temperature limit of 118 K, and the high-temperature heat capacity expression is extrapolated from an upper data limit of 863 K; extending both of these limits would improve the reliability of the calculated values, which again have an estimated uncertainty of 10 kJ/mol.

Table 8 compares the enthalpy of formation of the alkaline-earth M_3P_2 compounds at 298 K, using both experimental results and model-predicted values.[94,97] The reference state for phosphorus used in calculating these values varies, but the level of disagreement among them is such that this is not overly significant.

VII. Group IIIB, the Lanthanides and the Actinides

Figure 8 shows the Pr−P phase diagram,[153] the only one determined to date for the elements in this
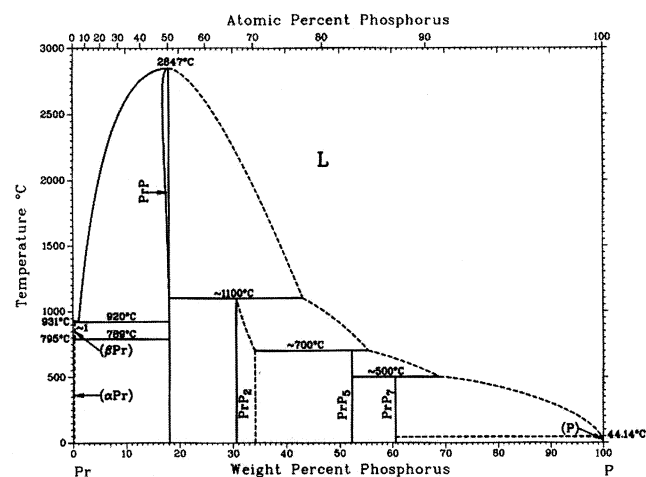
Figure 8. The Pr−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

Table 8. Experimental, Assessed, and Modeled Enthalpies of Formation of Alkaline-Earth Phosphides (298 K, kJ/mol)

compd	assessed	Shchukarev et al.[93,94]	Min and Sano[119]	Gruza[97]	Ghosh and Hess[199]	Kubaschewski et al.[121]	Barin et al.[4]
Be_3P_2				−517			
Mg_3P_2		−498		−413	−453		
Ca_3P_2	−500	−523	−706	−494	−420	−506	−506
Sr_3P_2		−635		−586			
Ba_3P_2	−562			−492			

Table 9. Enthalpies and Gibbs Energies of Formation of ScP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−347354	−345391	1500	−393007	−290004
300	−347369	−345377	1533	−393626	−287729
400	−348210	−344593	1533	−449168	−287729
500	−349282	−343570	1600	−450301	−280647
600	−350588	−342309	1608	−450440	−279798
700	−352129	−340810	1608	−454454	−279798
704	−352195	−340745	1700	−456576	−269745
704	−382148	−340745	1800	−458880	−258688
800	−383044	−335041	1812	−459156	−257350
900	−384098	−328978	1812	−473251	−257350
1000	−385275	−322792	1900	−475275	−246813
1100	−386575	−316482	2000	−477571	−234729
1200	−387998	−310048	2100	−479863	−222531
1300	−389544	−303490	2200	−482152	−210223
1400	−391214	−296809	2300	−484436	−197812

Table 10. Enthalpies and Gibbs Energies of Formation of YP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298	−374831	−375862	1500	−418591	−334226
300	−374841	−375868	1533	−419122	−332362
400	−375504	−376120	1533	−474664	−332362
500	−376458	−376169	1600	−475614	−326120
600	−377664	−376002	1700	−477101	−316732
700	−379103	−375615	1752	−477908	−311818
704	−379165	−375591	1752	−482888	−311818
704	−409123	−375591	1799	−483524	−307221
800	−409914	−370965	1799	−494921	−307221
900	−410844	−366042	1800	−494943	−307113
1000	−411879	−361009	1900	−497112	−296619
1100	−413018	−355868	2000	−499290	−286011
1200	−414259	−350618	2100	−501475	−275293
1300	−415602	−345261	2200	−503669	−264471
1400	−417046	−339797	2300	−505871	−253549

Table 11. Experimentally Measured Entropies of Lanthanide Monophosphides

compd	S_{298}° (J/mol·K)	ref	compd	S_{298}° (J/mol·K)	ref
CeP	70.66	79	NdP	83.26	79
EuP	101.83	79	PrP	84.05	161
	74.72	159		79.45	79
GdP	96.90	79		75.39	158
	81.88	157, 163	SmP	74.64	162
LaP	66.82	160		90.66	79
	69.53	79		87.78	158

Table 12. Values of a, b, and c (Eq 25) for Calculation of Heat Capacities of Lanthanide Monophosphides[79]

compd	a	b	c	temp range (K)
CeP	54.884	2.67	6.965	298−3200
EuP	50.284	2.88	−1.44	298−2400
GdP	49.755	4.262	1.276	298−2200
LaP	49.726	2.819	1.904	298−3400
NdP	54.945	2.864	6.475	298−2900
PrP	54.333	3.016	6.237	298−3100
SmP	57.58	1.329	6.802	298−2500

group. The most significant feature of this diagram is the monophosphide PrP. All of the elements in this group form such a compound, with a NaCl cubic structure and a very high melting point, rarely found in phosphides formed by other elements. The small stoichiometry range of PrP is also found in a few other lanthanide monophosphides.

In addition to the monophosphide, several lanthanide elements (Ce, Gd, La, Nd, Pr, Sm) form a pentaphosphide,[153] and others form diphosphide (Ce, La, Pr) and heptaphosphide (Eu, La, Pr) compounds as well. Less typical compounds are also formed by europium (Eu_3P_2, EuP_3) and scandium (Sc_3P_2, Sc_3P, Sc_7P_3). In addition to the monophosphide, common phosphides formed by the actinide elements include diphosphides (Pa, Th, U) and M_3P_4 (Np, Pa, Th, U). Additional compounds have been prepared for thorium (Th_2P_{11}, ThP_7) and uranium (UP_{10}). It is likely that this list will grow, as many of the systems in this group have not been thoroughly investigated.

Studies of the thermodynamic properties of phosphides in this group are evenly divided between those of the lanthanide and actinide elements, with two exceptions. These are the studies of high-temperature decomposition of ScP and YP reported by Franzen and co-workers.[143,144] In both cases, congruent decomposition to the monatomic metal vapor and a mixture of $P_2(g)$ and $P(g)$ was reported; partial pressures of $Sc(g)$ and $Y(g)$ were directly measured using Knudsen effusion/mass spectrometry. The partial pressures of $P_2(g)$ and $P(g)$ were subsequently calculated by combining a mass balance and the equilibrium for eq 19. This in turn allowed calculation of the Gibbs energies of decomposition over the experimental temperature range (1767−2209 K for ScP, 2107−2300 K for YP). These partial pressures have been recalculated using the experimentally determined Gibbs energy change for the decomposition of $P_2(g)$ (eq 20) instead of the JANAF values, and they have been converted to standard enthalpies and Gibbs energies of formation of ScP and YP by a second-law approach. Tables 9 and 10 show the results, which have an uncertainty of ±10 kJ/mol. De Boer et al. have estimated that ΔH_{298}° for both ScP and YP equals −344 kJ/mol.[100] The standard entropies at 298 K for ScP and YP calculated from these results are 50.9 and 70.7 J/mol·K, respectively.

Nearly all of the reported thermodynamic data for lanthanide phosphides is focused on the monophosphides. Low-temperature heat capacity data have been generated by two groups;[79,157−163] the room-temperature entropies of seven lanthanide monophosphides resulting from this work are compared in Table 11. As can be seen, the differences in some cases are considerable. High-temperature heat capacities for several lanthanide monophosphides have been measured by Gordienko and Gol'nik.[79] Table 12 lists values for a, b, and c for these compounds (see eq 25), calculated by regression against their tabulated values.

There are two Knudsen effusion studies of the decomposition of LaP, by Gol'nik and Gordienko (2098−2450 K) and by Franzen and Hariharan (2096−2316 K).[143,158] Both conclude that LaP decomposes congruently to a mixture of $La(g)$ and $P(g)$ + $P_2(g)$, and both use the same method for calculating partial pressures as previously described for ScP and YP. The information provided by Gol'nik and Gordienko is not sufficient to allow for calculation of assessed thermodynamic properties of LaP; however, the results of Franzen and Hariharan can be adjusted using eq 20 to recalculate p_P and p_{P_2}, which in turn

Table 13. Enthalpies and Gibbs Energies of Formation of LaP (J/mol)

| temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−363724	−359879	1193	−396599	−328044
300	−363716	−359853	1193	−402796	−328044
400	−363427	−358615	1200	−402799	−327604
500	−363307	−357429	1300	−402846	−321335
550	−363301	−356838	1400	−402886	−315064
550	−363661	−356838	1500	−402917	−308790
600	−363680	−356215	1533	−402926	−306717
700	−363892	−354957	1533	−458290	−306717
704	−363905	−354906	1600	−458149	−300085
704	−393857	−354906	1700	−457918	−290203
800	−393482	−349620	1800	−457662	−280336
900	−393220	−344155	1900	−457381	−270483
1000	−393091	−338711	2000	−457076	−260647
1100	−393096	−333274	2100	−456746	−250827
1134	−393129	−331426	2200	−456392	−241024
1134	−396253	−331426	2300	−456013	−231237

allows calculation of assessed values. Table 13 shows the calculated enthalpies and Gibbs energies of formation of LaP, calculated by a third-law method using the S_{298}° value of Mironov et al.,[160] the high-temperature heat capacities reported by Gordienko and Gol'nik,[79] and the effusion results of Franzen and Hariharan. The enthalpy of formation in Table 13 can be compared with values of ΔH_{298}° (corrected for red (V) reference state) suggested by Franzen and Hariharan (−379 kJ/mol),[143] Gol'nik and Gordienko (−310 kJ/mol),[158] and de Boer et al. (−340 kJ/mol).[100]

The vapor pressure generated by decomposing PrP has been measured by Gingerich (1273−1973 K),[164,165] Gol'nik and Gordienko (2028−2360 K),[158] Torbov et al. (673−1273 K),[166] and Vasil'eva and Mironov (1173−1573 K).[122] The latter of these is of particular interest, since it demonstrates the impact of experimental method on the obtained vapor pressures. As previously mentioned, PrP has a significant composition range, so the decomposition product at lower temperatures is a mixture of P_2 and/or P_4 vapor, along with phosphorus-deficient $Pr_{1-x}P$. The higher-temperature Knudsen effusion work of Gol'nik and Gordienko apparently measured the partial pressures of Pr(g) and P(g) + P_2(g) as before; again, not enough data are provided to generate assessed thermodynamic properties for this compound. This is also the case for the Knudsen effusion investigation of SmP conducted by these authors.[158,167] Torbov et al. have also measured the lower-temperature (473−1273 K) vapor pressures of P_2 and P_4 generated by decomposing DyP, GdP, NdP, SmP, and TbP, without stating the composition of the solid product.

Schmettow et al. have measured the vapor pressures of P_2 and P_4 generated by the stepwise decomposition of higher europium phosphides EuP_7, EuP_3, EuP_2, and Eu_3P_4 to EuP;[168] there are, however, no reported thermodynamic data for EuP. Finally, two investigations have been performed for GdP: the lower-temperature (873−1273 K) work of Vasil'eva and Mironov,[123] and the high-temperature Knudsen effusion study of Gordienko et al.[157] Again, neither investigation reports sufficient data for the development of assessed thermodynamic properties for GdP.

Four investigations have dealt with the thermodynamic properties of thorium phosphides. Low-temperature heat capacity measurements have been used to determine S_{298}° for ThP (66.34 J/mol·K) and Th_3P_4 (222.0 J/mol·K).[51,169] At higher temperatures, Gingerich and Efimenko used Knudsen effusion/mass spectrometry to measure the partial pressures of P_2 generated by the decomposition of Th_3P_4 to ThP (actually $ThP_{0.96}$) at 1213−1452 K, and by phosphorus effusion from the (ThP) solid solution at 1447−2245 K.[170] Subsequently, a solid-state EMF technique (CaF_2 electrolyte) was used (1073−1223 K) to measure the Gibbs energy change of the reactions,[103]

$$Th + Th_3P_4 = 4ThP \qquad (35)$$

$$Th + yThP_{0.55} = (1 + y)Th_\alpha$$
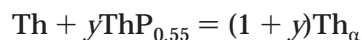
where Th_α is a phosphorus-saturated solid solution in metallic thorium. On this basis, Gibbs energies of formation were calculated for "ThP" (−299.1 kJ/mol) and Th_3P_4 (−970.6 kJ/mol) at 1173 K. However, the considerable stoichiometry range of the "monophosphide" ($ThP_{0.55}$−$ThP_{0.96}$) makes calculations of this sort subject to considerable uncertainty. As a result, no assessed values are presented here.

Low-temperature heat capacity studies for uranium phosphides have yielded S_{298}° for UP (78.3 J/mol·K[53,61]), U_3P_4 (267.7,[51] 260.4,[57] and 258.7 J/mol·K[53]), and UP_2 (101.8 J/mol·K[58]). The high-temperature heat capacity curve for U_3P_4 established by Ono et al.[71] agrees more closely with the low-temperature results of Counsell et al.[53] than with other results,[51,57] suggesting that the lowest reported value of S_{298}° for this compound is the most accurate. High-temperature heat capacity data are available only for UP and U_3P_4. Figure 9, reproduced from the results of Yokokawa et al.,[61] compares the low- and high-temperature results for UP; the high-temperature disagreement is apparent. Moser and Kruger (curve 2) report a constant value heat capacity unsupported by other results;[73] Men'shikova et al. (curve 5) claim a second-order phase transition at about 973 K,[171] not since confirmed. The agreement of the low-
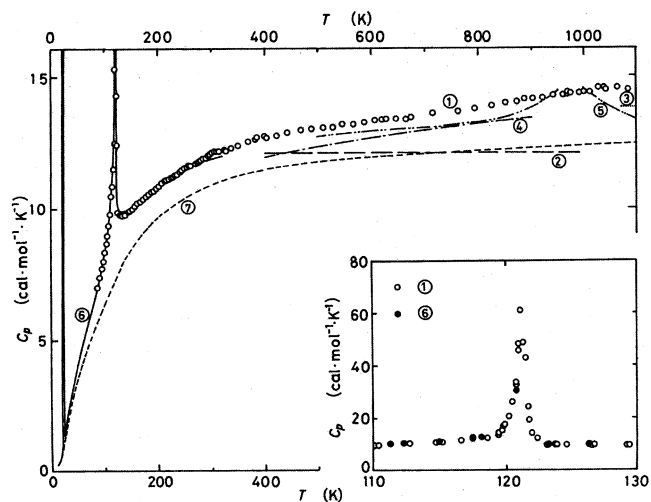

Figure 9. Experimentally measured heat capacities for UP. Reproduced with permission from ref 61. Copyright 1974 IAEA. Experimentally results include those Yokokawa et al.,[61] Moser and Kruger,[73] Ono, et al.,[71] Men'shikova et al.,[171] and Counsell et al.[53]

Table 14. Enthalpies and Gibbs Energies of Formation of UP (J/mol)

temp (K)	ΔH_f	ΔG_f°	temp (K)	ΔH_f	ΔG_f°
298.15	−308314	−306694	1100	−340547	−285738
300	−308314	−306683	1200	−337688	−280880
400	−308314	−306140	1300	−334368	−276279
500	−308314	−305596	1400	−330585	−271950
600	−308314	−305052	1408	−330263	−271615
700	−308314	−304509	1408	−339404	−271615
704	−308314	−304491	1500	−336436	−267278
704	−338267	−304491	1533	−335276	−265756
800	−337454	−299941	1533	−390790	−265756
900	−336497	−295307	1600	−388116	−260334
942	−336061	−293387	1700	−383725	−252480
942	−338872	−293387	1800	−378854	−244898
1000	−337959	−290606	1900	−373503	−237600
1049	−337067	−288308	2000	−367671	−230595
1049	−341828	−288308	2100	−361359	−223895

Table 15. Enthalpies and Gibbs Energies of Formation of U_3P_4 (J/mol)

temp (K)	ΔH_f	ΔG_f°	temp (K)	ΔH_f	ΔG_f°
298.15	−1172159	−1139771	1100	−1283156	−1008270
300	−1172121	−1139604	1200	−1272268	−983755
400	−1170520	−1131217	1300	−1259815	−960212
500	−1169241	−1122814	1400	−1245797	−937686
600	−1168094	−1114466	1408	−1244608	−935925
700	−1167001	−1106198	1408	−1272032	−935925
704	−1166957	−1105887	1500	−1260502	−914325
704	−1286768	−1105987	1533	−1256044	−906705
800	−1282478	−1081923	1533	−1478101	−906705
900	−1277558	−1057473	1600	−1467875	−881894
942	−1275350	−1047336	1700	−1451252	−845771
942	−1281406	−1047336	1800	−1433000	−810673
1000	−1277519	−1033013	1900	−1413121	−776634
1049	−1273826	−1021126	2000	−1391614	−743684
1049	−1288107	−1021126			

temperature results of Yokokawa et al. with those of Counsell et al. suggest that curve 1 in Figure 9 is the most reliable of the high-temperature results,[53,60,61] and as a result these values are recommended over those of Ono et al.[71] Ono et al. have published the only high-temperature heat capacity data for U_3P_4.

The enthalpy of formation of uranium monophosphide has been measured by O'Hare et al.[91] using fluorine reaction calorimetry. O'Hare et al. reported an enthalpy of formation for UP (specifically $UP_{0.992}$) at 298.15 K of −325.8 kJ/mol, using α-white phosphorus as the reference state for the element; applying the data in Table 3, the enthalpy of formation from red (V) and standard-state uranium is −308.3 kJ/mol. The entropy of formation of UP at 298.15 K from red (V) and standard-state uranium is +5.44 J/mol·K, making ΔG_{298}° equal to −306.7 kJ/mol. At higher temperatures, the decomposition of UP to U(g) and $P_2(g) + P_4(g)$ has been studied by Gingerich and Lee (1750−2250 K)[172,173] and by Men'shikova et al. (1920−2230 K).[171] The reported partial pressure of U(g) in equilibrium with UP at 2000 K was 3.92 × 10^{-7} atm from the first of these investigations and 5.74 × 10^{-7} atm from the second; both of these are higher than the currently accepted partial pressure of U(g) in equilibrium with pure liquid uranium at this temperature, 1.05 × 10^{-7} atm.[11,149] As a result, the results of O'Hare et al. have been used to calculate thermodynamic properties for UP, along with the entropy measurement of Counsell et al.[53] Lacking high-temperature heat capacity data for red (V), only a second-law analysis is possible. Table 14 lists the results.

Two investigations have measured the enthalpies of formation of U_3P_4 and UP_2 using direct reaction calorimetry. Dogu et al. measured the area under the DTA peak which occurred when uranium and "red" (presumably I) phosphorus powder reacted at about 673 K.[36] Presuming that the ratio of peak areas resulting from the formation of U_3P_4 or UP_2 to that generated by the formation of UP equaled the ratio of the enthalpies of reaction, enthalpies of formation at 673 K (red (I) reference) were calculated for U_3P_4 (−1 093 600 J/mol) and UP_2 (−387 400 J/mol). Baskin and Smith used a more traditional calorimeter to measure the enthalpies of reaction of uranium and

phosphorus (unspecified form)[82] at a nonspecific temperature; their reported enthalpy of formation for UP is noticeably less exothermic than that of O'Hare et al.,[91] but it depends on an assumed value of ΔH° for UP_2 to solve simultaneous equations. If the enthalpy of formation for UP listed above is used to analyze these results instead, then the enthalpy of formation for U_3P_4 from this work can be recalculated as −260 800 ± 39 800 J/mol, a clearly unreliable result. As a result, the work of Dogu et al. is preferred. For the reaction,

$$U_3P_4 + U = 4UP \qquad (37)$$

$\Delta H_{673}^\circ = -107\,900$ J/mol. The entropies of U_3P_4, UP, and U at 673 K are 408.42, 121.93, and 75.83 J/mol·K, respectively; as a result, ΔG_{673}° for reaction 37 equals −110 200 J/mol. Applying the thermodynamic functions tabulated in Table 14, the standard Gibbs energy of formation of U_3P_4 at 673 K equals −1 108 300 J/mol. Since the heat capacities of U_3P_4, UP, and U are known, calculation of ΔH° and ΔG° for U_3P_4 is possible using the data in Table 14; Table 15 lists the results. The uncertainties in these values are considerable, given the reliance on the second-law values for UP and the limited temperature range (<1000 K) for the uranium phosphide heat capacity data.

One final investigation of uranium phosphide thermodynamics exists, the tensimetric study of UP_2 decomposition to U_3P_4 and P_4 vapor investigated between 805 and 1155 K by Heimbrecht et al.[174] Steady-state vapor pressures were achieved at only two temperatures in this range, and the lack of additional data makes the calculation of thermodynamic properties for UP_2 unwise.

VIII. Groups IVB and VB

Figure 10 presents the titanium−phosphorus phase diagram, the only one produced to date for an element in these two groups.[153] As before, the Ti−P diagram and its compounds are similar to those of the other elements. Common compounds include M_3P, MP_2, MP, and M_2P. Each of the six elements features additional, less common compounds as well; the stability, crystal structure, and stoichiometry
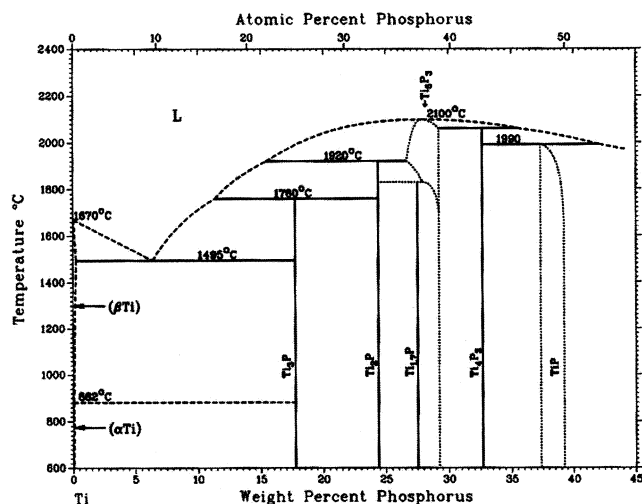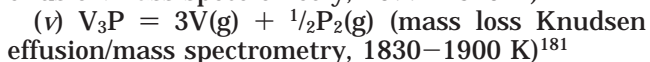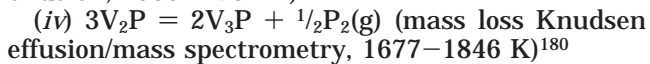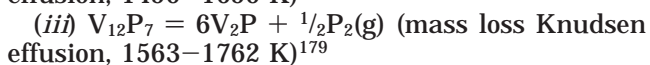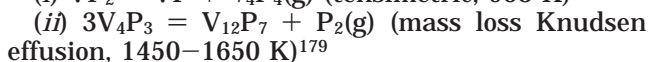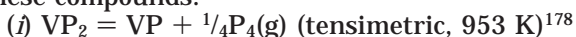
Figure 10. The Ti–P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

range of several are still uncertain and are easily influenced by contamination.

Given the multitude of compounds (and their relative lack of importance), determining their thermodynamic properties has proven difficult, and only the vanadium phosphides have been the subject of extensive investigation. Gingerich used Knudsen effusion/mass spectrometry to measure the P_2 vapor pressure from decomposing NbP, TiP, and ZrP.[175] The only other investigation of titanium phosphides is that of Shchukarev et al.,[86] who used oxide combustion calorimetry to determine the enthalpy of formation of TiP (red (I) reference), −265.3 kJ/mol. This result differs considerably from the value estimated by de Boer et al.,[100] −324 kJ/mol. Strotzer et al. performed tensiometric measurements of the partial pressure of P_4 from the decomposition of ZrP to ZrP_2 at 1099 K,[176] and Zumbusch and Biltz did the same for TaP_2 decomposition to TaP at 1089 K.[177] Otherwise, no published thermodynamic data for the Hf–P, Nb–P, Ta–P, Ti–P, or Zr–P systems exist.

Much of the thermodynamic literature on vanadium phosphides reports the phosphorus vapor pressures generated by the stepwise decomposition of these compounds:

(*i*) $VP_2 = VP + {}^1/_4P_4(g)$ (tensimetric, 953 K)[178]

(*ii*) $3V_4P_3 = V_{12}P_7 + P_2(g)$ (mass loss Knudsen effusion, 1450–1650 K)[179]

(*iii*) $V_{12}P_7 = 6V_2P + {}^1/_2P_2(g)$ (mass loss Knudsen effusion, 1563–1762 K)[179]

(*iv*) $3V_2P = 2V_3P + {}^1/_2P_2(g)$ (mass loss Knudsen effusion/mass spectrometry, 1677–1846 K)[180]

(*v*) $V_3P = 3V(g) + {}^1/_2P_2(g)$ (mass loss Knudsen effusion/mass spectrometry, 1830–1900 K)[181]

Myers et al. have used their results to calculate ΔH_{298}° (α-white reference) for V_4P_3, $V_{12}P_7$, V_2P, and V_3P. These values depend on estimated free-energy functions, which in turn depend on experimental heat capacity measurements for V_3P made using DSC by White et al.[74] The heat capacity measurements cover the temperature range 160–330 K, meaning that entropy values for V_3P are calculated using a substantial temperature extrapolation. An additional difficulty with these calculations is their dependence

Table 16. Estimated Values of ΔH_{298}° for Vanadium Phosphides (Red (V) Reference, kJ/mol)

compd	Myers et al.[179–181]	de Boer et al.[100]	Glaum and Gruehn[114]
V_3P	−216	−320	
V_2P	−191	−306	
$V_{12}P_7$	−1267	−2066	
V_4P_3	−481	−799	
VP	−142	−234	−243
V_4P_7		−1056	
VP_2		−176	
VP_4		−239	

on the experimental results for the decomposition of V_3P as an "anchor", since the uncertainty level attached to these latter results is considerable.[181] As a result, assessed values for the enthalpies and Gibbs energies of formation of the vanadium phosphides based on these results are not tabulated.
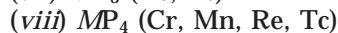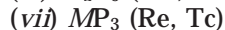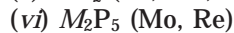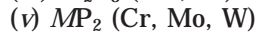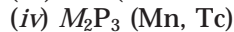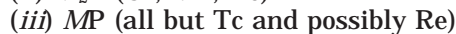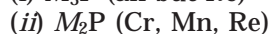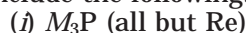
Two other studies of vanadium monophosphide have been performed. Glaum and Gruehn have looked at reaction rates for the transport of vanadium by reaction at 1073–1173 K with iodine vapor:[114]

$$VP + {}^7/_2I_2 = VI_4(g) + PI_3(g) \qquad (38)$$
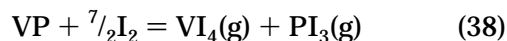
Assuming an equilibrium process, an estimated enthalpy of formation of −252 kJ/mol (red (I) reference state) was calculated for VP. Voleinik and Shabdenov used a molten salt electrochemical cell to determine the standard Gibbs energy of formation for VP;[110] according to these results, $\Delta G_T^{\circ} = -227\,600 + 75.89T$ J/mol (reference state unknown). The reliability of these results is uncertain at best. Table 16 compares the reported enthalpies of formation for vanadium phosphides (converted to red (V) reference), along with the model-generated values of de Boer et al.[100]

IX. Groups VIB and VIIB

The presence of elements from these groups in ferrous alloys means there is increasing interest in their interaction with other impurities in steels, and as a result the systems of these elements and phosphorus are better characterized. Figures 11 and 12 show the Mn–P and Mo–P partial phase diagrams;[153] a tentative Cr–P phase diagram has also been generated. Reported compound stoichiometries include the following:

(*i*) M_3P (all but Re)

(*ii*) M_2P (Cr, Mn, Re)

(*iii*) MP (all but Tc and possibly Re)

(*iv*) M_2P_3 (Mn, Tc)

(*v*) MP_2 (Cr, Mo, W)

(*vi*) M_2P_5 (Mo, Re)

(*vii*) MP_3 (Re, Tc)

(*viii*) MP_4 (Cr, Mn, Re, Tc)

Other compounds include $Cr_{12}P_7$, Mo_4P_3, Re_3P_4, and Re_6P_{13}. All of these compounds appear to have negligible solubility ranges.

Most of the thermodynamic data for phosphides of these elements have been obtained for the Cr–P and Mn–P systems. Exceptions include the Knudsen effusion study of the decomposition of MoP to Mo_4P_3 (1190–1450 K) and of WP to W_3P (950–1250 K) by Gingerich,[175] the tensiometric analysis of P_4 partial
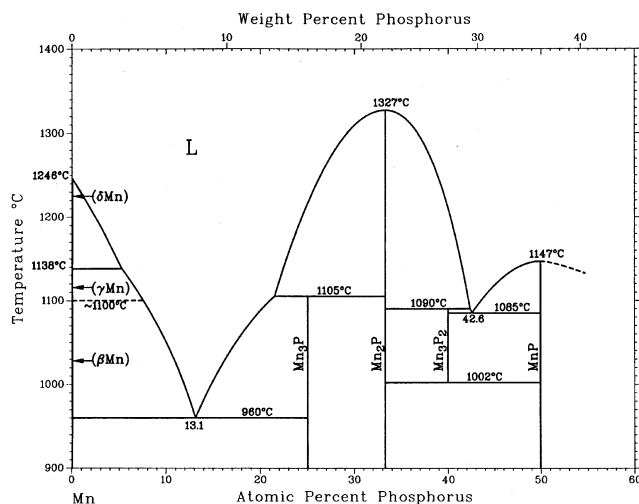
Figure 11. The Mn−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.
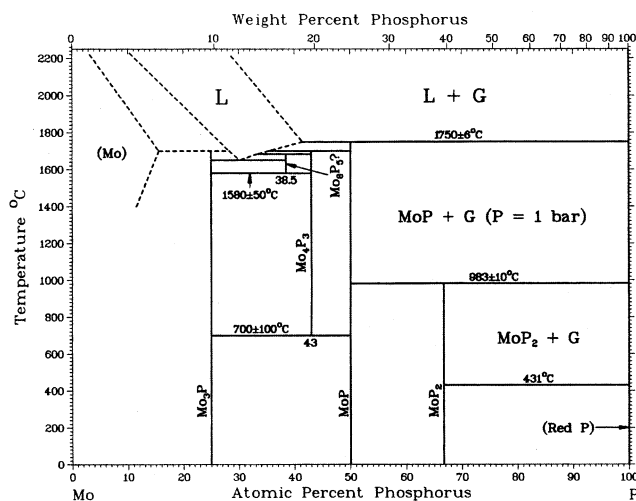

Figure 12. The Mo−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

pressure generated by the decomposition of MoP_2 to MoP (1148 K) and of WP_2 to WP (833 K) performed by Faller et al.,[182] and the tensiometric measurement of $(P_4 + P_2)$ vapor pressures in equilibrium with Re_2P/Re_3P_4 (1383−1487 K), Re_3P_4/Re_6P_{13} (1208−1332 K), and Re_6P_{13}/ReP_3 (1136−1229 K) reported by Haraldsen.[183] None of these measurements are sufficient to allow calculation of thermodynamic properties for compounds in the Mo−P, Re−P, or W−P systems. As might be suspected, no thermodynamic studies have been performed on compounds in the Tc−P system.

The thermodynamic data for the Cr−P system consist primarily of three Knudsen effusion investigations of equilibrium vapor pressures generated by decomposing lower phosphides. These include studies of Cr/Cr_3P (1543−1768 K), $Cr_3P/Cr_{12}P_7$ (1435−1541 K), and $Cr_{12}P_7/CrP$ (1289−1485 K) equilibria performed by Myers et al.,[141,184] Cr/Cr_3P (1350−1640 K) equilibria reported by Pogorelyi et al.,[185,186] and Cr/Cr_3P (1440−1630 K) and $Cr_3P/Cr_{12}P_7$ (1341−1704 K) equilibria investigated by Zaitsev et al.[65,66] Zaitsev et al. also measured the heat capacities (113−873 K) of Cr_3P and $Cr_{12}P_7$. The results of the three investi-

gations are very different. For the reaction,

$$3Cr(c) + {}^1/_2P_2(g) = Cr_3P(c) \qquad (39)$$
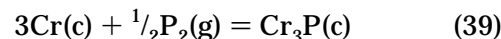
the reported standard Gibbs energy expressions are

$$\Delta G° = -132\,418 + 40.48\,T\,\text{J/mol}$$
$$\text{(Myers et al.[184]) (40)}$$

$$\Delta G° = -253\,844 + 225.09\,T\,\text{J/mol}$$
$$\text{(Pogorelyi et al.[185]) (41)}$$

$$\Delta G° = -244\,112 + 70.95\,T\,\text{J/mol}$$
$$\text{(Zaitsev et al.[66]) (42)}$$

Zaitsev et al. point out that eq 41 would result in atmospheric decomposition of Cr_3P to elemental chromium and P_2 vapor at 1127 K (and at even lower temperatures to P_4 and elemental Cr). Furthermore, the partial pressures of Cr(g) in equilibrium with Cr_3P and elemental chromium reported by Pogorelyi et al. are several times the accepted value for pure chromium. The cause of the discrepancy between eqs 40 and 42 is less obvious, but Zaitsev et al. (who so far have the last word) point out that the Cr−Cr_3P eutectic is roughly 1643 K, below the experimental temperature used in several of Myers et al.'s experiments. As a result, eq 42 is adopted for assessment purposes, although it should be pointed out that the publication by Zaitsev et al. does not include their original data. Table 17 presents the enthalpy and Gibbs energy of formation of Cr_3P, calculated by the third-law method using the heat capacity and vapor pressure measurements of Zaitsev et al.[66]

Myers et al. and Zaitsev et al. have measured the vapor pressure in equilibrium with Cr_3P and $Cr_{12}P_7$.[65,66,141,184] For the reaction,

$$^8/_3Cr_3P + P_2(g) = {}^2/_3Cr_{12}P_7 \qquad (43)$$
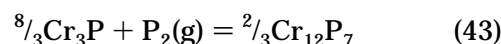
the following standard Gibbs energies of reaction were obtained:

$$\Delta G°_T = -387\,404 + 176.94\,T\,\text{J/mol}$$
$$\text{(Myers et al.[184]) (44)}$$

$$\Delta G°_T = -391\,487 + 104.53\,T\,\text{J/mol}$$
$$\text{(Zaitsev et al.[66]) (45)}$$

Again, the difference is substantial. Zaitsev et al.

Table 17. Enthalpies and Gibbs Energies of Formation of Cr_3P (J/mol)

temp (K)	$\Delta H_f°$	$\Delta G_f°$	temp (K)	$\Delta H_f°$	$\Delta G_f°$
298.15	−163052	−162947	1000	−188547	−153165
300	−163037	−162946	1100	−187779	−149664
311	−162966	−162944	1200	−187052	−146231
311	−162966	−162944	1300	−186367	−142858
400	−162294	−163031	1400	−185723	−139535
500	−161730	−163284	1500	−185120	−136257
600	−161344	−163634	1533	−184930	−135183
700	−161125	−164036	1533	−240472	−135183
704	−161119	−164049	1600	−239935	−130590
704	−191077	−164049	1700	−239156	−123780
800	−190213	−160417	1783	−238527	−118162
900	−189358	−156745			

Table 18. Enthalpies and Gibbs Energies of Formation of $Cr_{12}P_7$ (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−988497	−1007942	1100	−1170053	−966871
300	−988393	−1008063	1200	−1168164	−948489
311	−987870	−1008796	1300	−1167119	−930231
311	−987868	−1008796	1400	−1166924	−912022
400	−983284	−1015409	1500	−1167578	−893797
500	−979373	−1023922	1533	−1167980	−887779
600	−976933	−1033086	1533	−1556727	−887779
700	−976038	−1042538	1600	−1556679	−858554
704	−976035	−1042947	1700	−1557229	−814909
704	−1185738	−1042847	1800	−1558522	−771209
800	−1180749	−1023728	1900	−1560560	−727417
900	−1176352	−1004373	1996	−1563217	−685259
1000	−1172784	−985464			

Table 19. Enthalpies and Gibbs Energies of Formation of CrP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−120604	−120738	1100	−149539	−104940
300	−120598	−120738	1200	−149457	−100889
311	−120573	−120744	1300	−149453	−96843
311	−120573	−120744	1400	−149525	−92794
400	−120360	−120824	1500	−149676	−88737
500	−120274	−120954	1533	−149742	−87395
600	−120364	−121084	1533	−205268	−87406
700	−120637	−121185	1600	−205264	−82255
704	−120652	−121188	1700	−205310	−74566
704	−150610	−121182	1800	−205418	−66872
800	−150242	−117194	1900	−205588	−59171
900	−149932	−113082	1996	−205809	−51768
1000	−149697	−109001			

suggest that one possible reason for the difference is the decision by Myers et al. to treat the mass loss from their experiments in this portion of the system as consisting entirely of $P_2 + P_4$ vapor, without any significant Cr(g) content. The lack of published $p_{Cr(g)}$ data for their experimental results makes the significance of this difference difficult to judge. Nevertheless, the results of Zaitsev et al. will again be used for $Cr_{12}P_7$ assessment. Table 18 shows the standard enthalpy and Gibbs energy of formation of $Cr_{12}P_7$, again calculated using a third-law approach. The only measurement of equilibrium partial pressures over $Cr_{12}P_7$–CrP mixtures is that of Myers et al. (1289–1485 K).[184] For the reaction,

$$^2/_5Cr_{12}P_7 + P_2(g) = {}^{24}/_5CrP \qquad (46)$$
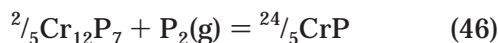
$$\Delta G^\circ = -362\,596 + 194.49\,T\,\text{J/mol} \qquad (47)$$

As before, the partial pressures of $P_2(g)$ from which this expression was obtained were calculated assuming that the vapor given off by the mixture consisted entirely of P_2 and P_4, a source of possible error. However, the likelihood of significant Cr(g) presence in this composition range seems remote, especially

given the relatively low temperature range (1289–1485 K). As a result, eq 47 can be used to calculate assessed thermodynamic properties for CrP by a second-law method, using the results for $Cr_{12}P_7$ in Table 18. Table 19 shows the assessed enthalpy and Gibbs energy of formation of CrP. Glaum and Gruehn estimated ΔH_{298}° for CrP on the basis of the results of transport experiments using iodine as the transport agent.[276] Converting their estimate to the red (V) reference state produces a value of −117.6 kJ/mol, comparable to the calculated value in Table 19. The value of S_{298}° for CrP calculated from Table 19 is 46.9 J/mol·K.

The only other thermodynamic study of chromium phosphide thermodynamics is that of Faller et al.,[182] who used tensiometric analysis to measure the $P_4(g)$ vapor pressure in equilibrium with CrP and CrP_2 at 933 K. The results are not sufficient for further thermodynamic analysis. Table 20 illustrates the assessed values of ΔH_{298}° for Cr_3P, $Cr_{12}P_7$, and CrP, compared with those predicted using Miedema's revised model.[100]

The presence of manganese in alloy steels and the need to remove phosphorus from ferromanganese have resulted in greater interest in the Mn–P system than any of the others reviewed so far, and a much more extensive thermodynamic database as well. Most of the published results concern the lower phosphides Mn_3P, Mn_2P, Mn_3P_2, and MnP, although some data have appeared for the higher phosphide MnP_3 as well. Low-temperature heat capacity measurements have generated S_{298}° values for Mn_2P (75.7[187] and 91.01 J/mol·K[54]) and MnP (49.16[187] and 48.96 J/mol·K[59]). In a previous review of the published data,[188] Lee reported that the low-temperature heat capacities reported by Grandjean et al. for Mn_2P were compatible with higher-temperature measurements,[54] and Zaitsev et al. also found their experimental results compatible with this work.[189] As a result, the higher experimental value of S_{298}° for Mn_2P is recommended. Within experimental error limits, the reported values of S_{298}° for MnP are identical. At higher temperatures, heat capacity measurements have been made for Mn_3P (298–1182 K[101,190]), Mn_2P (377–1264[7,101] and 298–1300 K[54]), and MnP (383–1185,[7,101] 298–330,[197] and 298–800 K[59]). Figure 13 compares the measured high-temperature heat capacities, which in general are in reasonable agreement.

A difficulty in using the existing thermodynamic database for developing assessed enthalpies and Gibbs energies of formation for manganese phosphides is that most of the reported high-temperature experimental results feature equilibria between two of the compounds, e.g., Mn_3P/Mn_2P or Mn_2P/MnP. An "anchor" measurement of the enthalpy or Gibbs energy of formation of one of the compounds from the

Table 20. Published Values of ΔH_{298}° for Chromium Phosphides (Red (V) Reference, kJ/mol)

compd	assessment	Zaitsev et al.[66]	Pogorelyi et al.[186]	Myers et al.[184]	de Boer et al.[100]	Glaum and Gruehn[276]
Cr_3P	−163	−154	−164	−93	−183	
$Cr_{12}P_7$	−988	−919		−620	−1590	
CrP	−121			−82	−170	−118

elements is needed to obtain these properties for the other compounds. This was accomplished in the Cr−P system by using the measured phosphorus vapor pressure in equilibrium with Cr_3P and elemental chromium (eq 41). However, experimental attempts to accomplish the same for Mn_3P/Mn mixtures generated a vapor containing only Mn(g),[189,191−193] eliminating this approach. Instead, four other possible anchors are available:

(*ix*) the determination of ΔH°_{298} for MnP performed by Shchukarev et al.,[43] using oxide combustion calorimetry;

(*x*) the measurement by Knudsen effusion/mass spectrometry of Mn(g) and P_2(g) vapor pressures in congruently decomposing Mn_3P (1200−1380 K), originally reported by Chizikov et al.;[191−193]

(*xi*) the measurement by Knudsen effusion/mass loss of Mn(g) and P_2(g) vapor pressures in congruently decomposing Mn_2P (1246−1500 K), made by Myers et al.;[194] and

(*xii*) the measurement by Knudsen effusion/mass loss of Mn(g) and P_2(g) vapor pressures in Mn_3P/Mn_2P (1298−1374 K) and Mn_2P/MnP (1088−1272 K) mixtures performed by Zaitsev et al.[189]

Zaitsev et al.[189] have criticized the results of Chizikov et al.,[191−193] noting that the Gibbs energies of formation for Mn_3P and Mn_2P obtained from these results imply that Mn_3P should decompose at temperatures above 1200 K, which is clearly not the case. In particular, the partial pressures of P_4(g) measured in this work seem to be too high. The parasitic re-evaporation problem described previously may be the cause.[145] The oxide calorimetry data appear to be less controversial but may be less reliable. The two remaining vapor pressure studies give somewhat similar results. For the reaction,

$$4Mn(g) + P_2(g) = 2Mn_2P(s) \tag{48}$$

$$\Delta G^{\circ} = -1\,560\,306 + 647.78\,T \text{ J/mol}$$
$$\text{(Zaitsev et al.}^{189}) \tag{49}$$

$$\Delta G^{\circ} = -1\,679\,866 + 757.10\,T \text{ J/mol}$$
$$\text{(Myers et al.}^{194}) \tag{50}$$

Using these and the high-temperature heat capacity data for Mn_2P obtained by Makharadze et al.,[7,54] ΔS°_{298} for reaction 50 can be calculated. The value using eq 49 is −729.6 J/mol·K, and the value using eq 51 is −839.0 J/mol·K. These compare with a value of −728.6 J/mol·K obtained using experimentally determined entropies at 298.15 K, suggesting that the experimental results of Zaitsev et al. are the more reliable of the two. Table 21 presents calculated enthalpies and Gibbs energies of formation for Mn_2P, calculated by a third-law method using the vapor pressure results of Zaitsev et al., the low- and high-temperature heat capacity data presented by Grandjean et al.,[54] and the tabulated properties of the elements.

In addition to the enthalpy of formation determination by Shchukarev et al.,[43] four other investigations have considered the high-temperature phase equilibria of MnP. These include EMF studies (CaF_2 electrolyte) of the equilibrium between MnP and
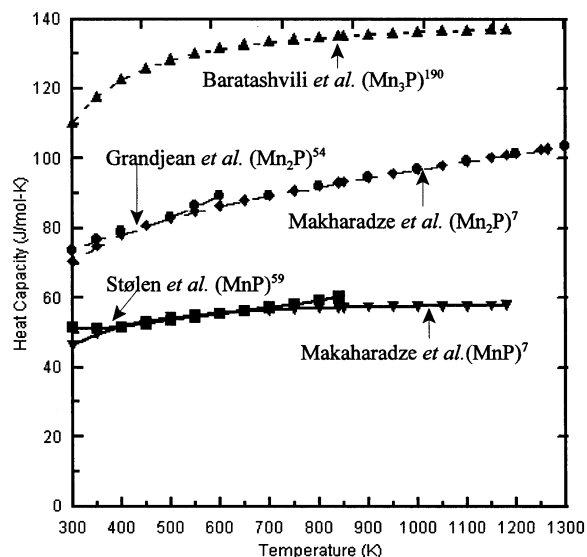

Figure 13. Measured high-temperature heat capacities of manganese phosphides.

Table 21. Enthalpies and Gibbs Energies of Formation of Mn_2P (J/mol)

temp (K)	ΔH°_f	ΔG°_f	temp (K)	ΔH°_f	ΔG°_f
298.15	−157425	−158664	1200	−189472	−141837
300	−157418	−158671	1300	−188854	−137892
400	−157110	−159139	1360	−188426	−135555
500	−156943	−159668	1360	−192656	−135555
600	−156944	−160216	1400	−192663	−133881
700	−157122	−160750	1410	−219019	−133460
704	−157133	−160770	1410	−222786	−133460
704	−187086	−160770	1500	−223076	−129429
800	−186624	−157212	1517	−223126	−128668
900	−186215	−153561	1517	−220892	−128668
980	−185943	−150670	1533	−220933	−127693
980	−190399	−150670	1533	−276385	−127693
1000	−190340	−149860	1600	−276339	−121189
1100	−189968	−145829			

Mn_2P, conducted by Baratashvili et al. (851−1067 K) and by Myers and Simpson (867−1067 K),[102,104] and the measurement of P_2 vapor pressure in equilibrium with MnP and Mn_2P reported by Myers et al. (1071−1192 K) and by Zaitsev et al. (1088−1272 K).[189,196] Based on a third-law analysis, Myers and Simpson suggest that the results of the first three investigations are similar, generating an enthalpy of formation more negative than that determined by Shchukarev et al. However, rigorous analysis using the EMF data is difficult, since the temperature range of both studies crosses the α-Mn−β-Mn transition temperature (980 K). The results of the two vapor pressure studies appear to be similar; for consistency, the data reported by Zaitsev et al. will serve as the basis for calculations. From these results, for the reaction,

$$Mn(g) + \tfrac{1}{2}P_2(g) = MnP \tag{51}$$
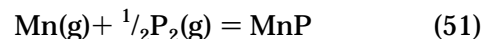
$$\Delta G^{\circ} = -462\,434 + 202.46\,T \text{ J/mol} \tag{52}$$

The expression for the heat capacity of MnP reported by Makharadze et al.[7] does not appear to fit their data as accurately as it might. A new regression analysis against the data results in the

Table 22. Enthalpies and Gibbs Energies of Formation of MnP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−119667	−117916	980	−155214	−100977
300	−119659	−117905	1000	−155388	−99868
400	−119502	−117358	1100	−156304	−94272
500	−119772	−116798	1200	−157299	−88590
600	−120399	−116150	1300	−158371	−82821
700	−121352	−115354	1360	−159052	−79322
704	−121397	−115354	1360	−161166	−79322
704	−150132	−115335	1400	−161793	−76908
800	−150684	−110400	1410	−161953	−76301
900	−151412	−105196	1410	−163837	−76301
980	−152110	−100977	1424	−164086	−75430

Table 23. Enthalpies and Gibbs Energies of Formation of Mn₃P (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−179801	−174057	980	−197959	−157988
300	−179772	−174022	980	−204644	−157988
400	−177925	−172373	1000	−204402	−157038
500	−175961	−171214	1100	−203204	−152360
600	−174176	−170436	1200	−202038	−147790
700	−172697	−169935	1300	−200913	−143315
704	−172646	−169918	1360	−200262	−140680
704	−202598	−169918	1360	−206608	−140680
800	−200727	−165586	1378	−206627	−139817
900	−199065	−161297			

revised expression:

$$C_{p,MnP} = 48.622 - 0.00122\,T - 37\,606/T \text{ J/mol·K} \quad (53)$$

Using this expression, the enthalpies and Gibbs energies of formation of MnP have been calculated by the third-law method, using the vapor pressure data of Zaitsev et al.,[189] the heat capacity measurements of Makharadze et al. and Stølen et al.,[59] and the tabulated properties of elemental manganese and phosphorus. These are presented in Table 22.

As is the case with MnP, the thermodynamic properties of Mn₃P have been obtained in equilibrium with Mn₂P, and the research can be divided into EMF studies and vapor pressure measurements. EMF studies (CaF₂ electrolyte) have been reported by Baratashvili (830−1080 K) and Myers and Simpson (867−1035 K);[101,104] vapor pressure measurements have been performed by Chizikov and co-workers (1200−1380 K)[191−193] and by Zaitsev et al. (1096−1374 K).[189] As before, the temperature ranges for both EMF studies cross the α-Mn−β-Mn transition point; regression analysis of the data provided by Myers and Simpson shows an extremely weak dependence on temperature. The objection to the vapor pressure results of Chizikov et al. has already been mentioned. As a result, the results of Zaitsev et al. will again be used for assessment of Mn₃P. For the reaction,

$$3Mn(g) + {}^1\!/_2P_2(g) = Mn_3P \quad (54)$$
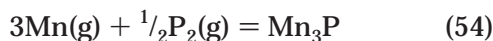
$$\Delta G^\circ = -1\,061\,828 + 451.181\,T \text{ J/mol} \quad (55)$$

Lacking an experimentally determined value of S_{298}° for Mn₃P, only second-law treatment of the data can be performed. Table 23 lists tabulated enthalpies and Gibbs energies of formation, calculated using eq 55

Table 24. Enthalpies and Gibbs Energies of Formation of Mn₃P₂ (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−199257	−224256	980	−289298	−239033
300	−199303	−224410	980	−295995	−239033
400	−202209	−232290	1000	−297079	−237886
500	−205866	−239313	1100	−302594	−231691
600	−210223	−245496	1200	−308270	−224989
700	−215258	−250860	1300	−314111	−217806
704	−215474	−251054	1360	−317694	−213285
704	−276276	−251054	1360	−324112	−213285
800	−280398	−247347	1354	−323682	−213782
900	−285155	−242934			

and the high-temperature heat capacity measurements reported by Baratashvili et al.[195] The calculated value of S_{298}° for Mn₃P from Table 23 is 99.6 J/mol·K.

The only reported thermodynamic investigation for Mn₃P₂ is the measurement of Mn(g) and P₂ partial pressures in equilibrium with Mn₂P reported by Zaitsev et al. (1276−1337 K).[189] For the reaction,

$$3Mn(g) + P_2(g) = Mn_3P_2 \quad (56)$$
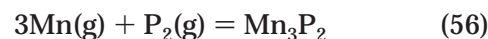
$$\Delta G^\circ = -1\,220\,945 + 509.304\,T \text{ J/mol} \quad (57)$$

As a result, for

$$Mn_2P + MnP = Mn_3P_2 \quad (58)$$

$$\Delta G^\circ = 21\,655 - 16.98\,T \text{ J/mol} \quad (59)$$

This expression equals zero at 1275 K, the lower-temperature stability limit for Mn₃P₂ in Figure 11. Lacking heat capacity data for Mn₃P₂, a second-law approach is required to calculate the thermodynamic properties tabulated in Table 24. S_{298}° for Mn₃P₂ is calculated as 225.5 J/mol·K, higher than expected. Heat capacity measurements for this compound would be of value.

The only existing thermodynamic investigation of MnP₃ is that of Biltz et al.,[198] who measured the partial pressure of P₄(g) in equilibrium with MnP and MnP₃ at 891, 931, and 951 K. Based on these results, for the reaction,

$$MnP_3 = MnP + {}^1\!/_2P_4(g) \quad (60)$$
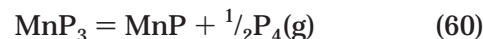
$$\Delta G^\circ = 111\,231 - 113.14\,T \text{ J/mol} \quad (61)$$

Although the phase diagram in the P-rich end of Figure 11 is unknown, eq 60 shows that MnP₃ decomposes to MnP and unit-pressure P₄(g) at 983 K. No measurements of the heat capacity are known, so a second-law approach is required to calculate thermodynamic properties for MnP₃. Table 25 presents the results, which are subject to more uncertainty than those of the other manganese phosphides. From Table 25, S_{298}° for MnP₃ is calculated as 75.8 J/mol·K.

Table 26 compares the published room-temperature enthalpies of formation of manganese phosphides with those calculated here and those predicted by de Boer et al.[100] (Values from other tabulations have been converted to a red (V) reference state using the data in Table 1.) The variety of results is due to

Table 25. Enthalpies and Gibbs Energies of Formation of MnP_3 (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−166412	−159026	980	−266445	−101330
300	−166417	−158980	1000	−266619	−97959
400	−167047	−156427	1100	−267535	−81049
500	−168330	−153636	1200	−268530	−64053
600	−170194	−150531	1300	−269602	−46970
700	−172610	−147070	1360	−270283	−36682
704	−172718	−146920	1360	−272397	−36682
704	−261363	−146920	1400	−273024	−29743
800	−261915	−131119	1410	−273184	−28004
900	−262643	−114601	1410	−275068	−28004
980	−263341	−101330	1424	−275317	−25549

the use of different data for ΔG° determination, the use in earlier assessments of assumed entropies rather than subsequent experimental determinations, and the use of different thermodynamic properties for elemental phosphorus than those calculated here.

X. Group VIIIB

Partial metal–phosphorus phase diagrams have been published for seven of the nine elements in this group. In most cases the accuracy of these diagrams improves as the phosphorus content declines. The sixth-row elements (Ir, Os, Pt) form a limited number of phosphides, while the fourth- and fifth-row elements are more prolific. Common stoichiometries include the following:

(*i*) M_3P (Fe, Ni, Pd)
(*ii*) M_2P (Co, Ir, Fe, Ni, Rh, Ru)
(*iii*) MP (Co, Fe, Ni, Ru)
(*iv*) MP_2 (all nine elements)
(*v*) MP_3 (Co, Ir, Ni, Pd, Rh, Ru)
(*vi*) MP_4 (Fe, Os, Ru)

The stoichiometry of several compounds is uncertain, particularly in the Ni–P and Pd–P systems.

As might be expected, most of the thermodynamic investigations of VIIIB phosphides deal with those of Co, Ni, and Fe. There are three exceptions. Boone and Kleppa used direct synthesis drop calorimetry to determine the standard enthalpy of formation of Pd_3P at 298 K (red (I) reference state),[33] reporting a value of −203 kJ/mol. From phase equilibria considerations in the In–Pt–P system, Lin et al. estimated a value of ΔH_{298}° for PtP_2 of −350 kJ/mol.[200] Last, Biltz et al. measured the partial pressure of phosphorus generated by the decomposition of OsP_2 to elemental osmium and phosphorus vapor at 1463 K,[201] and RuP to Ru_2P at the same temperature. It was assumed by Biltz et al. that the generated phosphorus vapor consisted entirely of $P_2(g)$, which is not accurate at this temperature. Using the equilibrium constant for reaction 15 at 1463 K generates
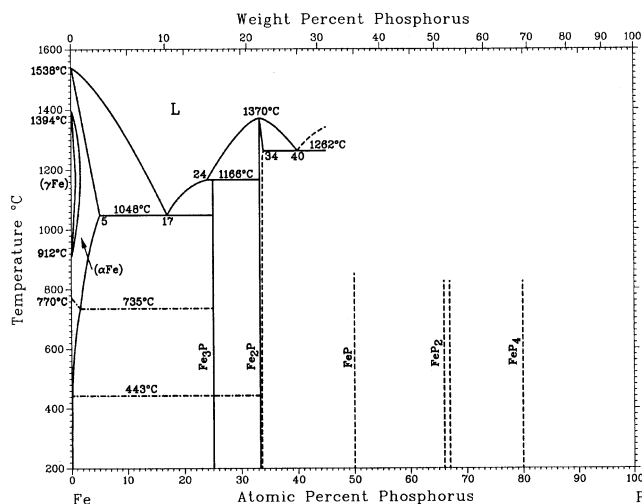

Figure 14. The Fe–P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

a partial pressure for P_4 of 2.44×10^{-4} atm for the decomposition of OsP_2, and 3.46×10^{-3} atm for the decomposition of RuP. This converts to a standard Gibbs energy of formation of −50 600 J/mol for OsP_2 at 1463 K. Beyond these, no experimental data exist for the thermodynamic properties of the platinum group metal phosphides.

Figure 14 illustrates the assessed Fe–P phase diagram.[153] In addition to the compounds shown, higher phosphides in the system include FeP, FeP_2, and FeP_4. No polymorphism is known, but Fe_3P, Fe_2P, and FeP all have Curie temperatures (706, 266, and 215 K, respectively). The solubility ranges of the compounds appear to be negligible. Although the thermodynamic database for this system is more substantial than for most phosphide systems, there are some gaps. Heat capacity values are particularly scarce, consisting almost entirely of measurements made between 113 and 873 K by Zaitsev et al.[65,202–205] The below-ambient results were used to determine values of S_{298}° for Fe_3P (109.4 J/mol·K), Fe_2P (90.5 J/mol·K), and FeP (57.0 J/mol·K). The only other reported heat capacity measurements are those of Beckman et al.,[52] who examined Fe_2P at low temperatures (2–20 and 80–300 K). From these results, a value of S_{298}° for Fe_2P of 84.0 J/mol·K has been calculated by the present author. No heat capacity measurements for FeP_2 or FeP_4 have been reported.

The only direct measurement of enthalpies of formation in the system is that of Weibke and Schrag,[46] who determined ΔH_{903}° (red (I) reference state) for Fe_3P (−147.3 kJ/mol), Fe_2P (−144.3 kJ/mol), FeP (−105.6 kJ/mol), and FeP_2 (−143.3 kJ/mol). Roth et al. measured the enthalpy of ferrous phosphate formation from both the elements and from Fe_2P,[41]

Table 26. Published Values of ΔH_{298}° for Manganese Phosphides (Red (V) Reference, kJ/mol)

compd	present assessment	Lee [188]	Barin et al.[4]	Baratashvilli et al.[102,190]	Schukarev et al.[43]	Biltz et al.[198]	Myers et al.[104,196]	Grandjean et al.[54]	Zaitsev et al.[189]	deBoer et al.[100]
Mn_3P	−180	−158		−160			−194		−160	−289
Mn_2P	−157			−138			−138	−141	−141	−241
MnP	−120		−66		−84		−91		−94	−173
MnP_3	−166		−84			−151				−145

Table 27. Enthalpies and Gibbs Energies of Formation of Fe$_3$P (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−142841	−146169	900	−178608	−143694
300	−142834	−146189	1000	−182127	−139636
400	−142497	−147363	1043	−183959	−137769
500	−142544	−148586	1043	−183973	−137769
600	−143218	−149742	1100	−186270	−135174
700	−144624	−150729	1185	−187219	−131156
704	−144697	−150764	1185	−189915	−131156
704	−174650	−150764	1200	−189635	−130400
716	−174779	−150354	1300	−187658	−125543
716	−174779	−150354	1400	−185502	−120845
800	−176110	−147420	1493	−183338	−116619

Table 28. Enthalpies and Gibbs Energies of Formation of Fe$_2$P (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−130821	−134730	1043	−167015	−129539
300	−130817	−134755	1100	−168458	−127447
400	−130413	−136124	1185	−168967	−124236
500	−130174	−137588	1185	−170764	−124236
600	−130446	−139055	1200	−170556	−123639
700	−131380	−140426	1300	−169108	−119788
704	−131432	−140477	1400	−167555	−116051
704	−161385	−140477	1500	−165901	−112430
800	−162189	−137580	1533	−165332	−111257
900	−163677	−134421	1533	−220874	−111257
1000	−165854	−131060	1600	−219524	−106493
1043	−167006	−129539	1643	−218630	−103468

Table 29. Enthalpies and Gibbs Energies of Formation of FeP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−95224	−97281	1043	−125994	−88746
300	−95219	−97294	1100	−126370	−86697
400	−94859	−98038	1185	−126087	−83630
500	−94606	−98867	1185	−126986	−83630
600	−94633	−99722	1200	−126784	−83078
700	−95011	−100546	1300	−125389	−79492
704	−95034	−100576	1400	−123906	−76017
704	−124989	−100576	1500	−122335	−72650
800	−124920	−97252	1533	−121797	−71561
900	−125139	−93784	1533	−177339	−71561
1000	−125665	−90274	1600	−176055	−66964
1043	−125989	−88746	1643	−175207	−64043

and from the difference they calculated a value of ΔH_{298}° for Fe$_2$P (red (I) reference) of −156.1 kJ/mol. Neither of these results is considered sufficiently reliable for assessment purposes.

All of the Gibbs energy determinations in the Fe−P system are measurements of the vapor pressure generated by reacting or decomposing phosphides. As with the manganese phosphides, the most thorough investigations are those of Zaitsev and co-workers.[203,205,206] These investigations measured the partial pressures of Fe(g) and P$_2$ over single- and two-phase alloys in the system (1243−1549 K), from which the Gibbs energies of formation of the different phosphides from γ-Fe and P$_2$ were calculated by the authors. These Gibbs energies have been reported, but not the raw data from which they were calculated. For the reaction,

$$3\text{Fe}(\gamma) + {}^1\!/_2\text{P}_2(\text{g}) = \text{Fe}_3\text{P} \qquad (62)$$
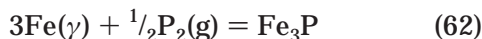
$$\Delta G^\circ = -239\,080 + 80.44\,T \text{ J/mol} \qquad (63)$$

This, along with the heat capacity data reported by Dobrokhotova et al.,[207] allows third-law calculation of the thermodynamic properties of Fe$_3$P, tabulated in Table 27. An uncertainty of ±10 kJ/mol is attached, due mostly to the narrow temperature range for the heat capacity data (113−873 K); since the heat capacity of nonmagnetic Fe$_3$P is known only between 716 and 873 K, the extrapolation to both lower and higher temperatures required for Table 27 is troublesome.

A similar approach was used to determine the Gibbs energy of formation for Fe$_2$P.[205,206] For the reaction,

$$2\text{Fe}(\gamma) + {}^1\!/_2\text{P}_2(\text{g}) = \text{Fe}_2\text{P} \qquad (64)$$
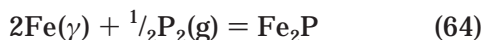
$$\Delta G^\circ = -231\,730 + 79.95\,T \text{ J/mol} \qquad (65)$$

Again, using the heat capacity data of Dobrokhotova et al.[207] and the tabulated thermodynamic properties of the elements, enthalpies and Gibbs energies of formation for Fe$_2$P can be calculated; these are presented as Table 28. The sources of uncertainty are the same as for Table 27. The partial pressure of phosphorus vapor in equilibrium with Fe$_2$P and Fe$_3$P has also been determined by Lewis and Myers (1295−1384 K);[208] lacking the raw data from Dobrokhotova et al., the degree of agreement between these investigations cannot be assessed.

Three investigators measured the vapor pressures generated by the decomposition of FeP to Fe$_2$P: Franke et al.,[209] using a static method (1448−1488 K), Lewis and Myers,[208] using Knudsen effusion/mass loss calculations (1000−1157 K), and Zaitsev et al.,[203] using Knudsen effusion/mass spectrometry (1041−1257 K). Lewis and Myers showed that their results are compatible with those of Franke et al.; however, Zaitsev et al. found that their calculated p_{P_2} values were lower, especially at higher temperature. It was suggested that the difference resulted from the presence in the vapor of FeP$^+$ and Fe$_2$P$^+$ ions, which would have been counted as phosphorus for partial pressure calculations in the previous two investigations. Given the better agreement at lower temperatures, this recommends the use of Zaitsev et al.'s results for assessment purposes. For the equation,

$$\text{Fe}_2\text{P} + {}^1\!/_2\text{P}_2(\text{g}) = 2\text{FeP} \qquad (66)$$
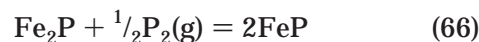
$$\Delta G^\circ = -153\,006 + 81.95\,T \text{ J/mol} \qquad (67)$$

This allows calculation of the enthalpies and Gibbs energies of formation of FeP by a third-law method, using the data for Fe$_2$P in Table 28 and the heat capacity results of Zaitsev et al.[203] for the two compounds. The results are displayed in Table 29.

The decomposition of FeP$_2$ to FeP and P$_2$(g) has been studied by Franke et al. (1165−1246 K) and Lewis and Myers (787−926 K),[208,209] using the techniques previously described. In addition, Flörke investigated the chemical transport of FeP$_2$ by reaction with iodine to generate FeI$_2$ and P$_4$ vapor (923−1123 K).[210] The lower temperatures and higher

Table 30. Enthalpies and Gibbs Energies of Formation of FeP_2 (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−153363	−147854	900	−216086	−118632
300	−153365	−147820	1000	−216761	−107770
400	−153453	−145960	1043	−217153	−103076
500	−153776	−144057	1043	−217158	−103076
600	−154507	−142052	1100	−217630	−96825
700	−155717	−139888	1185	−217500	−87484
704	−155775	−139792	1185	−218398	−87484
704	−215690	−139792	1200	−218225	−85823
800	−215734	−129437	1300	−217026	−74838

phosphorus potential of FeP_2/FeP mixtures make the previous concerns about non-phosphorus vapor species insignificant, and the results of the first two investigations are in good agreement.[208] Combining the two data sets and using linear regression, for the reaction,

$$FeP + {}^1/_2 P_2(g) = FeP_2 \qquad (68)$$
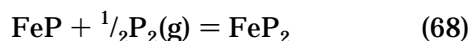
$$\Delta G^\circ = -147\,688 + 110.66\,T\ \text{J/mol} \qquad (69)$$

If eq 15 is applied to convert the reference state of phosphorus to the standard state, FeP_2 decomposes to FeP and $P_4(g)$ at 1237 K. Using the values for FeP in Table 29, enthalpies and Gibbs energies of formation have been calculated for FeP_2 and are displayed in Table 30. S_{298}° for FeP_2 is calculated as 54.5 J/mol·K.

As previously mentioned, ΔG° values for FeP_2 can also be calculated from the results of the iodide transport experiments of Flörke.[210] These are in excellent agreement with the assessed values at higher temperatures (>1100 K), but they increasingly diverge as the temperature falls. (The assessed values are about 6 kJ/mol less negative at 923 K.) As a result, the experimental results obtained in the same investigation for the iodide transport of FeP_4 are not sufficiently reliable to be used for assessment purposes. Using the thermodynamic data for $FeI_2(g)$ provided by Pankratz,[211] ΔG° can be calculated for FeP_4 at two temperatures: 873 K (−184.6 kJ/mol) and 973 K (−170.0 kJ/mol). Obviously, more data would be desirable.

In addition to the experimental work on the system, several modelers estimated the thermodynamic properties of iron phosphides, including a complete assessment of the system by Spencer and Kubaschewski.[100,199,212] Table 31 compares the estimated, experimental, and assessed values of ΔH_{298}° for the five compounds.

Figure 15 illustrates the tentative Co−P phase diagram; the higher phosphides CoP_2 and CoP_3 also exist in the system.[153] The thermodynamic database
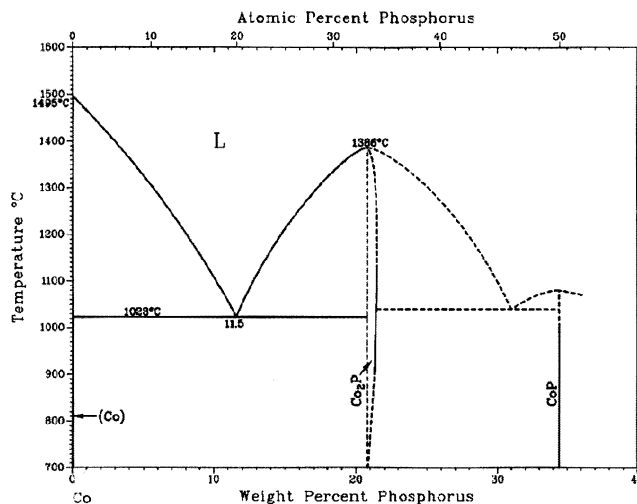

Figure 15. The Co−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

for this system is also minimal. Sarsenbaev et al. measured the heat capacity of Co_2P,[213] but only between 298 and 450 K. Weibke and Schrag used direct reaction calorimetry to measure the enthalpy of formation of Co_2P (−179.5 kJ/mol, red (I) reference state),[46] but the reported reaction temperature of 1003 K is well above the unit-pressure volatilization temperature of elemental phosphorus. Biltz and Heimbrecht measured the phosphorus vapor pressure generated by the decomposition of CoP_3 to CoP (1207 and 1310 K) and CoP to Co_2P (1488 K).[214] The most thorough investigation of the system is that of Myers,[215] who used Knudsen effusion/mass loss to measure the partial pressures of $P_2(g)$ in equilibrium with CoP_3/CoP (929−1072 K) and CoP/Co_2P (1125−1328 K). For the reaction,

$$CoP_3 = CoP + P_2(g) \qquad (70)$$
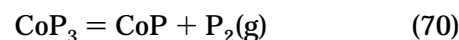
$$\Delta G^\circ = 275\,459 - 198.86\,T\ \text{J/mol} \qquad (71)$$

For

$$2CoP = Co_2P + {}^1/_2 P_2(g) \qquad (72)$$
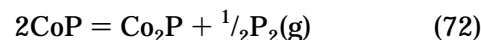
$$\Delta G^\circ = 150\,054 - 87.32\,T\ \text{J/mol} \qquad (73)$$

Table 32 compares the Gibbs energies for these reactions with those experimentally determined by Biltz and Heimbrecht and with values obtained from the estimated Gibbs energies of formation of the three phosphides by Ghosh and Hess.[199] (The values of p_{P_2} used to calculate ΔG_T from the results of Biltz and Heimbrecht were recalculated using eq 15.) The agreement between the experimentally obtained results is reasonable but not sufficient to justify

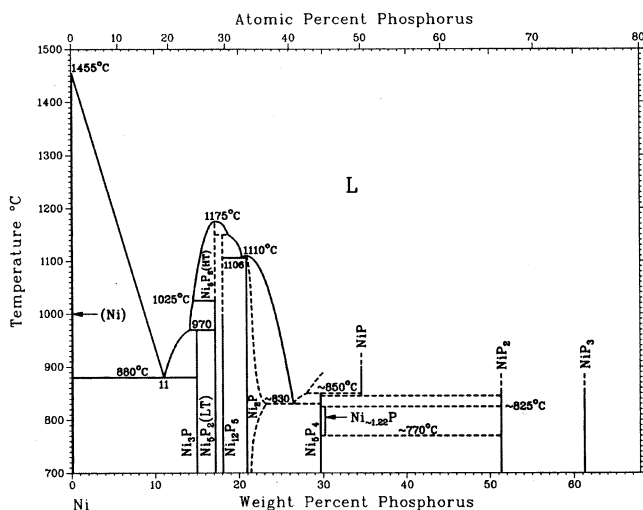**Table 31. Published Values of ΔH_{298}° for Iron Phosphides (Red (V) Reference, kJ/mol)**

compd	assessment	Spencer and Kubaschewski[212]	Dobrokhotova et al.[206]	Lewis and Myers[208]	Weibke and Schrag (908 K)[46]	Roth et al.[41]	de Boer et al.[100]	Elliott and Gleiser[6]	Kubaschewski et al.[121]
Fe_3P	−143	−146	−128		−130		−200	−133	−146
Fe_2P	−131	−144	−126	−132	−128	−161	−189	−130	−143
FeP	−95		−110	−109	−95	−108	−140	−93	
FeP_2	−153				−122	−135	−150	−135	
FeP_4							−118		

Table 32. Experimental and Estimated Gibbs Energies of Reaction for Equilibria between Cobalt Phosphides and $P_2(g)$ (J/mol)

source	eq 71, 1207 K	eq 71, 1310 K	eq 73, 1488 K
Biltz and Heimbrecht[214]	40427	21399	21439
Ghosh and Hess[199]	73811	101771	98677
Myers[215]	35435	14952	24122

Table 33. Estimated Values of ΔH_{298}^o for Cobalt Phosphides (Red (V) Reference, kJ/mol)

compd	Elliott and Gleiser[6]	Barin et al.[4]	Kubaschewski et al.[121]	de Boer et al.[100]	Weibke and Schrag (1003 K)[46]
Co_2P	−166	−171	−170	−174	−169
CoP	−130	−130	−108	−126	
CoP_3	−205	−231	−152	−120	

Figure 16. The Ni−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

generating assessed thermodynamic values for these compounds. Table 33 compares the estimated ΔH_{298}^o (converted to red (V) reference state) of cobalt phosphides compiled from various sources.[4,6,100,121]

Figure 16 shows the most recent assessed Ni−P phase diagram, from the review of Lee and Nash.[216] Much of the diagram is controversial, in particular the high-temperature phases. The low-temperature form of "Ni_5P_2" may in fact be Ni_8P_3;[217] both the low- and high-temperature forms of Ni_5P_2 and $Ni_{12}P_5$ apparently have some stoichiometry range, along with (Ni_2P). Because of this uncertainty, the existing thermodynamic database, although more extensive than for the Co−P system, is insufficient to allow

calculation of assessed thermodynamic data for any nickel phosphides. The only heat capacity measurement is that of Sarsenbaev et al. for Ni_2P,[213] limited as before to 298−450 K. Weibke and Schrag determined the enthalpy of formation of Ni_3P and "Ni_5P_2" (red (I) reference state) by direct reaction calorimetry as before,[46] reporting values of −202.5 and −401.2 kJ/mol, respectively; the concern over these results has been previously mentioned. A second experimental measurement of ΔH^o for Ni_5P_2 is that of Boone and Kleppa,[35] who reported a value at 298 K of −181 kJ/mol (red (I) reference state) for "$Ni_{2.55}P$".

Three investigations of equilibrium vapor pressures in the system have been reported. Viksman and Gordienko used Knudsen effusion/mass spectrometry to determine p_{P_2} in equilibrium with Ni_3P and elemental nickel;[218] for the reaction,

$$3Ni + {}^{1}/_{2}P_2 = Ni_3P \qquad (74)$$

ΔG^o was −73 887 J/mol at 1744 K and −79 306 J/mol at 1761 K. Biltz and Heimbrecht measured the partial pressure of P_4 in equilibrium with NiP_3/NiP_2 and NiP_2/Ni_5P_4 mixtures;[219] for the reaction,

$$NiP_3 = NiP_2 + {}^{1}/_{4}P_4(g) \qquad (75)$$
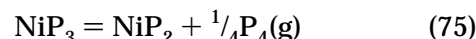
ΔG^o was +3125 J/mol at 870 K and +969 J/mol at 917 K. (It should be noted that NiP_3 is not stable at these temperatures in Figure 16; this further emphasizes the tentative nature of the diagram.) For the reaction,

$$5NiP_2 = Ni_5P_4 + {}^{1}/_{4}P_4(g) \qquad (76)$$
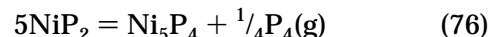
ΔG^o was +2957 J/mol at 1034 K.

The third vapor pressure measurement is that of Myers and Conti,[220] who used Knudsen effusion/mass loss measurements to measure p_{P_2} in equilibrium with $Ni_2P/Ni_{12}P_5$ (1260−1362 K) and $Ni_{12}P_5/Ni_5P_2$ (1400 K). For the reaction,

$$12Ni_2P = 2Ni_{12}P_5 + P_2(g) \qquad (77)$$

$$\Delta G^o = 476\,810 − 279.55\,T \text{ J/mol} \qquad (78)$$

For the reaction,

$$5Ni_{12}P_5 = 12Ni_5P_2 + {}^{1}/_{4}P_2(g) \qquad (79)$$

$\Delta G^o = +60\,300$ J/mol at 1400 K. The Gibbs energies of formation of nickel phosphides were also estimated by Ghosh and Hess[199] and by Miodownik (quoted by Lee and Nash).[216] Table 34 lists the enthalpies of

Table 34. Published Values of ΔH_{298}^o for Nickel Phosphides (Red (V) Reference, kJ/mol)
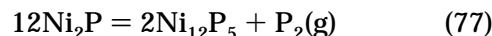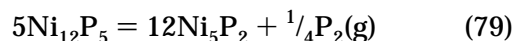
compd	Myers and Conti[220]	Boone and Kleppa[35]	Viksman and Gordienko[218]	Miodownik[216]	Press et al.[227]	Kubaschewski et al.[121]	de Boer et al.[100]	Barin et al.[4]	Elliott and Gleiser[6]
Ni_3P	−187		−196	−161	−337	−203	−140	−203	−186
Ni_5P_2	−387	−351		−314		−401	−350	−402	−365
$Ni_{12}P_5$	−940			−765	−2241				
Ni_2P	−161			−136	−190	−167	−168	−168	−151
Ni_5P_4	−467			−461					
NiP	−90						−122		
NiP_2	−123						−126		−100
NiP_3	−139						−112		−99

formation of nickel phosphides (converted to red (V) reference state) estimated by different sources. An obvious need exists for further experimental measurements in this system.

XI. Group IB

In contrast to other transition metal−phosphorus systems, the Ag−P, Au−P, and Cu−P systems are relatively simple. Figure 17 illustrates the currently assessed Cu−P phase diagram,[153] which under nonisobaric conditions features the compounds Cu_3P, CuP_2, and Cu_2P_7. Silver forms the stable phosphides AgP_2 and Ag_3P_{11}, and gold forms Au_2P_3. No other stable compounds have been reported.

Of the three elements in this group, the most thermodynamic information exists for the Cu−P system, research interest being driven by the use of phosphorus in commercial copper alloys. No low-temperature heat capacity measurements have been made in the system, but high-temperature heat capacities were measured for Cu_3P (298−1295 K) and CuP_2 (298−1164 K) by Gordienko and Viksman.[221] Two experimental determinations of ΔH° (red (I) reference state) were also made for Cu_3P, using direct reaction calorimetry: Weibke and Schrag[46] reported a value of −133.9 kJ/mol at 903 K, and Boone and Kleppa[34] determined a value of −166.1 kJ/mol at 298 K. The unusual temperature used by Weibke and Schrag (discussed previously), along with other concerns over the accuracy of their calorimeter,[34] recommends the results of Boone and Kleppa as more accurate.

Studies of Gibbs energy changes associated with copper phosphide formation consist entirely of vapor
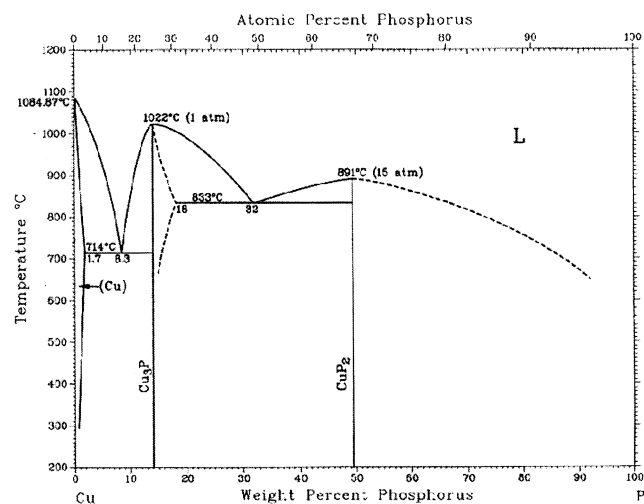
Figure 17. The Cu−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

pressure studies. The partial pressure of P_4 in equilibrium with CuP_2 and Cu_3P has been measured by Haraldsen (873−1073 K) and by Ugai et al. (963−1173 K)[133,222] using static method techniques; the agreement between the results is impressive. Combining the two results, for

$$3CuP_2 = Cu_3P + {}^5/_4P_4(g) \tag{80}$$
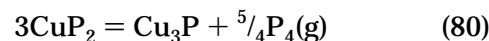
$$\Delta G^\circ = 267\,600 - 257.5\,T\ \text{J/mol} \tag{81}$$

In addition to this, Gordienko and Viksman reported the partial pressure of P_4 generated by the decomposition of Cu_3P.[221] However, the temperatures at which values are reported (1178, 1238, and 1292 K) are higher than the Cu/Cu_3P eutectic in Figure 17, making the data unusable for calculating assessed thermodynamic properties for Cu_3P (and thus for CuP_2 as well). No reported thermodynamic data are available for Cu_2P_7. On the basis of the available thermodynamic data for the solid compounds as well as results for liquid Cu−P solutions, an Mey and Spencer determined "optimized" enthalpies and entropies of formation for the three copper phosphides;[223] these differ considerably from previously estimated values. Table 35 compares the various estimated and experimental values of ΔH_{298}° for the copper phosphides. Low-temperature heat capacity measurements would be of considerable value in improving the database for this system, along with an EMF study of the Cu/Cu_3P equilibrium.

The only two thermodynamic investigations involving gold and silver phosphides are measurements of P_4 vapor pressure generated by their decomposition, measured using a static method by Haraldsen and Biltz[3] and by Myers et al. using mass loss effusion.[224] As Myers et al. showed, the results of the two investigations are consistent, despite differences in experimental method and temperature range (about 200 K lower for Haraldsen and Biltz). For the reaction,

$$2AgP_2 = 2Ag + P_4(g) \tag{82}$$

$$\Delta G^\circ = 139\,400 - 168.69\,T\ \text{J/mol} \tag{83}$$

For the reaction,

$$4Au_2P_3 = 8Au + 3P_4(g) \tag{84}$$
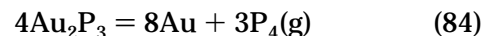
$$\Delta G^\circ = 553\,300 - 569.00\,T\ \text{J/mol} \tag{85}$$

On the basis of these equations, second-law calculations can be made of the enthalpies and Gibbs energies of formation of AgP_2 and Au_2P_3; these are listed in Table 36. It should be noted that eq 85 generates a unit-pressure decomposition temperature

Table 35. Experimental and Assessed Values of ΔH_{298}° for Copper, Silver, and Gold Phosphides (Red (V) Reference, kJ/mol)

compd	assessed	Barin et al.[4]	Elliott and Gleiser[6]	Kubaschewski et al.[121]	Myers et al.[224]	Boone and Kleppa[34]	Weibke and Schrag[46]	Karakaya and Thompson[228]	Gordienko and Viksman[221]	an Mey and Spencer[223]
AgP_2	−7	−10	17		14			76		
Ag_3P_{11}	−41		82					−47		
Au_2P_3	−42	−53		−45	−16					−38
Cu_3P		−135	−121	−133		−52	−123		−54	−58
CuP_2		−88	−39							−109

Table 36. Enthalpies and Gibbs Energies of Formation of Gold and Silver Phosphides (J/mol)

temp (K)	AgP$_2$		Ag$_3$P$_{11}$		Au$_2$P$_3$	
	ΔH_f°	ΔG_f°	ΔH_f°	ΔG_f°	ΔH_f°	ΔG_f°
298.15	−7251	−8141	−40556	−49216	−41604	−41338
300	−7257	−8160	−40624	−49270	−41622	−41336
400	−7628	−9033	−44956	−51533	−42804	−41072
500	−8105	−9681	−50525	−52558	−44323	−40471
600	−8688	−10104	−57332	−52346	−46180	−39531
700	−9377	−10302	−65376	−50896	−48374	−38254
704	−9766	−10302	−65724	−50894	−48469	−38192
704	−69676	−10302	−395228	−50794	−138332	−38192
800	−69676	−2202	−395228	−3805	−138332	−24532
808	−69676	−1527	−395228	109	−138332	−23394
826	−69676	−9			−138332	−20834
900					−138332	−10307
972					−138332	−65

for Au$_2$P$_3$ of 972 K (699 °C), considerably different from that suggested in the published phase diagram. The entropies at 298 K of AgP$_2$ and Au$_2$P$_3$ calculated from these results are 91.2 and 162.4 J/mol·K, respectively.

The vapor pressure measurements by Haraldsen and Biltz also include measurement of the partial pressure of P$_4$ in equilibrium with AgP$_2$ and a phase identified as "AgP$_3$", which likely has the actual stoichiometry Ag$_3$P$_{11}$.[3] If the latter stoichiometry is used, for the reaction,

$$Ag_3P_{11} = 3AgP_2 + {}^5/_4P_4(g) \quad (86)$$
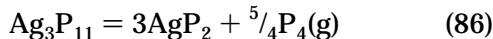
$$\Delta G^\circ = 186\,200 - 236.25\,T\ \text{J/mol} \quad (87)$$

This allows second-law calculation of thermodynamic values for Ag$_3$P$_{11}$, also shown in Table 36. Equation 87 is based on all of three data points, so considerable uncertainty should be attached to these results. Table 35 includes the assessed enthalpies of formation (converted to red (V) reference state) of the three phosphides and those predicted from previous estimations.

XII. Group IIB

Phase equilibria in both the Cd−P and Zn−P systems are well-characterized, due to interest generated by the semiconducting nature of the compounds. Figure 18 illustrates the assessed Zn−P phase diagram;[225] the high- and low-temperature forms of Zn$_3$P$_2$ and ZnP$_2$ are the only stable compounds at unit pressure. Stable cadmium phosphides include Cd$_3$P$_2$, Cd$_2$P$_3$, CdP$_2$, and CdP$_4$; unconfirmed claims were also made for Cd$_6$P$_7$.[226] CdP$_2$ undergoes a phase transition at 693 K;[108] no other polymorphism has been reported. No mercury phosphides are known.

Cadmium and zinc phosphides are semiconductors, and as a result there is considerable interest in their thermodynamic properties. An extensive experimental database includes measurements of low- and high-temperature heat capacities, enthalpies of formation, and phase equilibria determinations. In the zinc−phosphorus system, low-temperature heat capacity measurements were made for α-Zn$_3$P$_2$ (S_{298}° = 177.2 J/mol·K[229]), α-ZnP$_2$ (S_{298}° = 77.9[229] or 87.1[55] J/mol·K), and β-ZnP$_2$ (S_{298}° = 77.65 J/mol·K[230]). The measurements of Sheleg et al. on α-ZnP$_2$ extend to 400
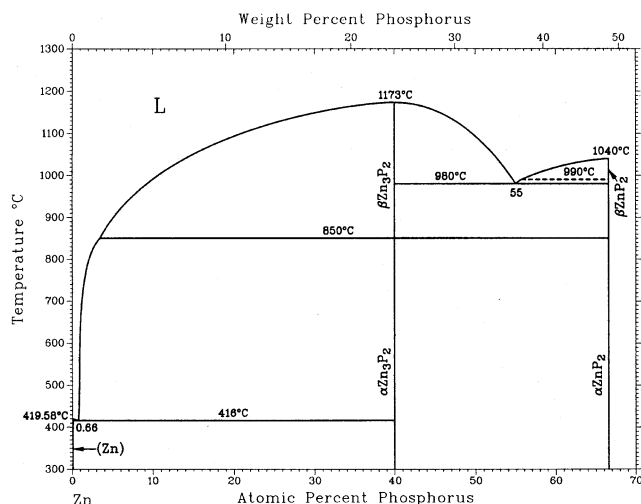

Figure 18. The Zn−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

K;[55] high-temperature heat capacities for α-Zn$_3$P$_2$ and α-ZnP$_2$ (300−1000 K) were also measured by Sirota et al.[44] There are no high-temperature heat capacity measurements for β-Zn$_3$P$_2$ or β-ZnP$_2$, in part because of their volatility.

The enthalpy of formation of α-Zn$_3$P$_2$ from red (I) phosphorus has been measured by three investigators. Shchukarev et al. and Zaheeruddin used oxide combustion calorimetry,[47,231] arriving at different values of ΔH_{298}° (−410 and −377.8 kJ/mol, respectively). Karvelis tried two different approaches, direct reaction calorimetry and comparative enthalpies of hydrolysis;[39,84] these yielded values for ΔH_{298}° of −230.2 and −223.3 kJ/mol. Dutkiewicz points out that all of these values are substantially more negative than those indirectly obtained from ΔG_{298}° measurements.[225]

Schoonmaker et al. were the first to show that α-Zn$_3$P$_2$ decomposes congruently to a mixture of Zn-(g) and P$_2$(g) + P$_4$(g) when heated,[139] requiring solution of a complex equilibrium calculation (or the use of mass spectrometry) to convert mass loss measurements (620−820 K) to component partial pressures. Within a short period of time following this investigation, reports from several other groups appeared, including Korb and Hein (Bourdon gauge, 1100−1350 K),[232] Valov and Ushakova (isolated-volume mass loss, 888−1337 K),[132] Greenberg et al. (Bourdon gauge, 890−1130 K),[233] Borshchevskii et al. ("isoteniscope," 1100−1410 K),[130] Lazarev et al. (970−1150 K),[234] and Golodushko et al. (726−833 K).[235] An EMF investigation (molten chloride electrolyte, 330−498 K) of the equilibrium 2Zn + ZnP$_2$ = α-Zn$_3$P$_2$ was also reported by Sirota et al.[44] Most of these investigations produced similar results, with the exception of that of Valov and Ushakova, whose total system pressures appear to be higher than those reported elsewhere.[232] If the torsion effusion results of Schoonmaker et al. are used for assessment purposes, for the reaction,

$$3Zn(g) + {}^1/_2P_4(g) = \alpha\text{-}Zn_3P_2 \quad (88)$$
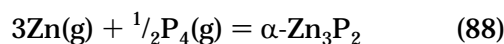
$$\Delta G^\circ = -602\,844 + 450.06\,T\ \text{J/mol} \quad (89)$$

Table 37. Enthalpies and Gibbs Energies of Formation of Zn_3P_2 (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−147124	−147699	800	−244771	−129168
300	−147162	−147702	900	−247949	−114527
400	−149467	−147549	1000	−251127	−99531
500	−152294	−146753	1100	−254305	−84218
600	−155668	−145337	1180	−256847	−71766
692	−159266	−143508	1180	−602844	−71766
692	−181235	−143508	1200	−602844	−62772
700	−181615	−143082	1300	−602844	−17766
704	−181805	−142855	1400	−602844	27240
704	−241720	−142855	1446	−602844	47943

Table 38. Enthalpies and Gibbs Energies of Formation of ZnP_2 (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−71332	−68815	800	−146873	−50803
300	−71353	−68799	900	−147933	−38731
400	−72646	−67761	1000	−148992	−26540
500	−74262	−66360	1100	−150051	−14244
600	−76211	−64602	1180	−150899	−4340
692	−78300	−62677	1180	−266231	−4340
692	−85624	−62677	1200	−266231	97
700	−85833	−62415	1300	−266231	22291
704	−85939	−62274	1313	−266231	25176
704	−145856	−62274			

The experimental entropy change for this reaction is virtually identical with the value of ΔS_{298}° calculated from the room-temperature entropies of α-Zn_3P_2 and gaseous Zn and P_4 (−445.3 J/mol·K). As a result, second-law calculation of enthalpies and Gibbs energies of formation for α-Zn_3P_2 is a reliable approach. Table 37 shows the results. No allowance is made in Table 37 for the transformation of α-Zn_3P_2 to β-Zn_3P_2 at 1123 K; higher-temperature investigations show that the impact of this change on the relationship between decomposition vapor pressure and temperature is apparently less than the overall level of uncertainty in the experimental results.[130,230,232] It should also be noted that β-Zn_3P_2 apparently decomposes to $P_4(g)$ and $Zn(g)$ at temperatures below the apparent melting point of 1446 K (and at even lower temperatures to P_4 and the zinc-rich liquid). Measurement of the enthalpy of transformation and the heat capacity of β-Zn_3P_2 would improve the accuracy of Table 37.

The phase stability of ZnP_2 in Figure 18 is a source of some controversy; Sirota et al. claim a second phase transition at 375 K (98 °C).[107] The most thorough thermodynamic investigation of this compound was the vapor pressure measurements of Alikhanyan and co-workers (Knudsen effusion and Bourdon gauge, 700−860 K);[236,237] other vapor pressure measurements include those of Golodushko et al. (786−889 K)[235] and Borshchevskii et al. (isoteniscope, 1020−1250 K).[130] The results of the first two investigations are similar; for the reaction,

$$Zn_3P_2 + P_4(g) = 3ZnP_2 \qquad (90)$$

$$\Delta G^\circ = -195\,849 + 215.76\,T \text{ J/mol}$$
$$\text{(Alikhanyan et al.}[236]) \quad (91)$$

$$\Delta G^\circ = -249\,091 + 207.13\,T \text{ J/mol}$$
$$\text{(Golodushko et al.}[235]) \quad (92)$$

These suggest that ZnP_2 decomposes to Zn_3P_2 and $P_4(g)$ above 907−917 K. The entropy of reaction calculated at 298 K from the measured room-temperature entropies of the species is −214.1 or −223.3 J/mol·K, depending on the choice of S_{298}° for ZnP_2. On the other hand, the results of Sirota et al. suggest that the entropy of formation of ZnP_2 from red (I) and solid zinc is +83.2 J/mol·K,[107] an impossible value given the experimentally determined values of S_{298}° for ZnP_2 listed above. Table 38 lists values of ΔH° and ΔG° for ZnP_2, based on the values in Table 37 and second-law treatment of the results of

Table 39. Published Values of ΔH_{298}° for Zinc Phosphides (Red (V) Reference, kJ/mol)

	compd	
source	Zn_3P_2	ZnP_2
present assessment	−147	−71
Alikhanyan et al.[235]		−60
Lazarev et al.[234]	−75	−67
Schoonmaker et al.[139]	−140	−97
Jordan[238]		−77
Sirota et al.[44]	−148	−98
Golodushko et al.[235]	−140	
Barin et al.[4]	−162	−69
Greenberg et al.[233]	−143	
Shchukarev et al.[86,231]	−384	
Karvelis[39,84]	−205, −198	
Zaheeruddin[47]	−352	
Korb and Hein[232]	−142	
Valov and Ushakova[132]	−174	
Kubaschewski et al.[121]	−124	−67

Alikhanyan et al. Table 39 compares reported values of ΔH_{298}° for the zinc phosphides, converted to the red (V) reference state.

Low-temperature calorimetry has been used to determine values of S_{298}° for the cadmium phosphides Cd_3P_2 (200.8 J/mol·K[229]), CdP_2 (86.63,[56] 87.7,[229] and 87.82 J/mol·K[230]), and CdP_4 (135.7 J/mol·K[239]). The heat capacity measurements for CdP_2 of Sheleg et al. extend to 400 K;[56] high-temperature heat capacities were also reported for CdP_2 (<693 K), Cd_2P_3 (<1019 K), and Cd_3P_2 (<1013 K) by Sirota et al.[108] The only direct measurement of enthalpies of formation for cadmium phosphides is that of Shchukarev et al.,[42] who used bromide solution calorimetry to determine ΔH_{298}° for Cd_3P_2 (red (I) reference), −114 600 J/mol. This is considerably less negative than the comparable value reported by Shchukarev et al. for Zn_3P_2,[231] obtained using oxide combustion calorimetry.

Several of the groups who reported Gibbs energy-related data for the zinc phosphides also performed experiments on cadmium phosphides. These include low-temperature (320−500 K) chloride−electrolyte EMF data obtained by Sirota et al.[108] and a series of vapor pressure investigations. The vapor pressure results vary considerably. Schoonmaker and Rubinson used torsion effusion/mass loss calculations to determine the partial pressures of Cd(g) and $P_4(g)$ in equilibrium with Cd_3P_2 (530−650 K);[138] however, they were unable to establish partial pressures independent of the cell orifice diameter. The total partial pressures above solid Cd_3P_2, determined by Süss et al. with a Bourdon manometer (~785−990 K),[242] are similar to those measured by Borshchevskii

et al. (823−998 K)[240] using an isoteniscope; Süss et al. treat the decomposition of Cd_3P_2 as noncongruent, a choice contradicted by Borshchevskii et al. The decomposition of Cd_3P_2 is also treated as congruent in analyzing the Bourdon gauge experiments of Lazarev et al. (760−990 K).[234,241] Comparing the reported experimental results (Cd reference state as noted), for the reaction,

$$3Cd + {}^{1}/_{2}P_4(g) = Cd_3P_2(c) \qquad (93)$$

$$\Delta G° = -518\,442 + 558.58\,T\,\text{J/mol}$$
$$\text{(Schoonmaker and Rubinson,}^{138}\,Cd(g))\quad (94)$$

$$\Delta G° = -477\,467 + 228.32\,T\,\text{J/mol}$$
$$\text{(Lazarev et al.,}^{241}\,Cd(g))\quad (95)$$

$$\Delta G° = -452\,694 + 250.36\,T\,\text{J/mol}$$
$$\text{(Borshchevskii et al.,}^{240}\,Cd(g))\quad (96)$$

$$\Delta G° = -100\,000 + 107.10\,T\,\text{J/mol}$$
$$\text{(Sirota et al.,}^{108}\,Cd(s))\quad (97)$$

$$\Delta G° = -324\,709 + 300.80\,T\,\text{J/mol}$$
$$\text{(Süss et al.,}^{242}\,Cd(l))\quad (98)$$

To compare these results, $\Delta G°_{298}$ is calculated for all five equations and converted to the Cd(s) reference state as needed using Tables 2 and 3; the resulting values are −120.0,[138] −177.5,[241] −146.2,[240] −68.1,[108] and −226.2 kJ/mol.[242] $\Delta S°_{298}$ for reaction 93 calculated from room-temperature entropies of the components equals −94.5 J/mol·K (Cd(s) reference state); if the enthalpy of formation determined by Shchukarev et al.[42] is converted to a P_4 reference state, then a sixth $\Delta G°_{298}$ value for reaction 93 of −47.1 kJ/mol is calculated. Given this level of disagreement, no table of calculated thermodynamic properties for Cd_3P_2 would be reliable.

The thermodynamic database for CdP_2 is similar to that for Cd_3P_2, with the EMF study of Sirota et al. (330−470 K)[108] added to vapor pressure measurements by Borshchevskii et al. (833−984 K),[240] Süss et al. (673−923 K),[242] Lazarev et al. (785−1000 K),[226] and Gadzhiev et al. (570−740 K).[237] Again, all but Süss et al. treat the decomposition as congruent. The results published by Gadzhiev et al. are insufficient for further analysis; for the others, a similar comparison of results can be provided. For the reaction (Cd reference state as noted),

$$Cd + {}^{1}/_{2}P_4(g) = CdP_2(s) \qquad (99)$$

$$\Delta G° = -218\,361 + 204.44\,T\,\text{J/mol}$$
$$\text{(Lazarev et al.,}^{226}\,Cd(g))\quad (100)$$

$$\Delta G° = -187\,368 + 179.94\,T\,\text{J/mol}$$
$$\text{(Borshchevskii et al.,}^{240}\,Cd(g))\quad (101)$$

$$\Delta G° = -187\,896 + 181.60\,T\,\text{J/mol}$$
$$\text{(Süss et al.,}^{242}\,Cd(l))\quad (102)$$

$$\Delta G° = -92\,300 + 113.90\,T\,\text{J/mol}$$
$$\text{(Sirota et al.,}^{108}\,Cd(s))\quad (103)$$

Calculating $\Delta G°_{298}$ for reaction 99 for the four equations, and converting to the Cd (s) reference state
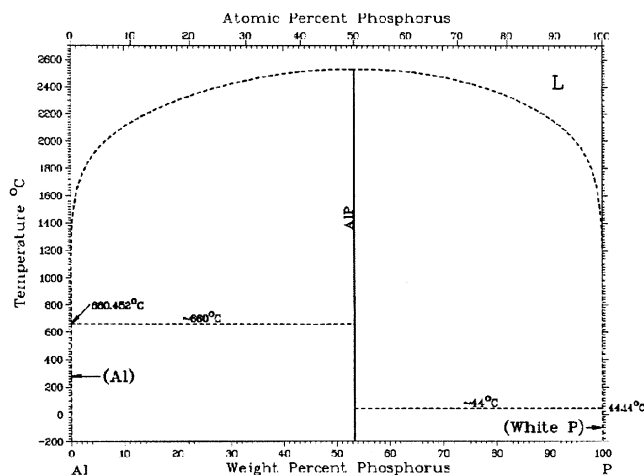

Figure 19. The Al−P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

as needed, produces values of −80.1,[226] −56.4,[240] −131.0,[242] and −58.3 kJ/mol.[242] It should be noted that the values calculated from the work of Sirota et al. are for the low-temperature form of CdP_2, while the others are for the high-temperature form; this difference is insignificant compared with the wide overall variation. As a result, no table of thermodynamic properties for CdP_2 is included.

Lazarev et al. and Süss et al. also investigated the noncongruent decomposition of CdP_4, which generates a mixture of Cd(g) and $P_4(g)$.[226,242] The EMF investigation of Sirota et al. has also looked at the Gibbs energy of formation of CdP_4.[108] None of these results are reliable enough to justify calculating thermodynamic properties for this compound. The same applies to the thermodynamic data for Cd_2P_3 obtained from the results of Sirota et al.

XIII. Group IIIA

The phosphides of four of these five elements are the best known and most thoroughly investigated of this class of compound. Boron, aluminum, gallium, and indium all form a highly stable semiconducting monophosphide with minimal stoichiometry range. Boron also forms a lower phosphide, originally thought to be B_6P but more recently corrected to $B_{13}P_2$.[243] The only other compounds in this group are the phosphides of thallium, which are poorly known but may include TlP_3 and/or TlP_5. Figure 19 shows the Al−P phase diagram, typical of the group.[244]

Boron phosphide is unusual among the phosphides in that its thermodynamic properties are based on C_p and $\Delta H°$ measurements, rather than vapor pressure determinations. Heat capacity measurements for BP include those of Kischio (143−323 K),[96] Koshchenko and co-workers (5−310 K),[80,245,246] David et al. (298−627 K),[247] Ohsawa et al. (300−850 K),[75] and Kumashiro et al. (333−773 K).[72] The value of $S°_{298}$ for BP of 19.69 J/mol·K provided by Koshchenko et al. is recommended over that of Kischio, whose low-temperature limit is too high. The high-temperature heat capacities determined by Kumashiro et al. are preferred to those of Ohsawa et al., which show

greater levels of uncertainty. The enthalpy of formation of BP has been measured by

(*i*) Kischio and Gal'chenko et al. (298 K),[37,88,96] who compared the enthalpies of reaction of BP and of the elements with chlorine to form solid $BCl_3 \cdot PCl_5$;

(*ii*) Gross et al. (298 K),[38] who compared the enthalpies of reaction of BP and of the elements with fluorine to form a mixture of $BF_3(g)$ and $PF_5(g)$;

(*iii*) Thevenot,[87] who measured the enthalpy of reaction of BP with oxygen to form BPO_4 and calculated ΔH_{298}° for BP from a previously measured enthalpy of formation for the phosphate; and

(*iv*) Zaheeruddin (298 K),[47] who used oxide combustion calorimetry.

In addition, the Gibbs energy of formation of BP has been determined by Stone et al. (1193−1543 K),[134] who measured the equilibrium partial pressures for the reaction,

$$BCl_3(g) + {}^3/_2H_2(g) + {}^1/_4P_4(g) =$$
$$BP + 3HCl(g) \quad (104)$$
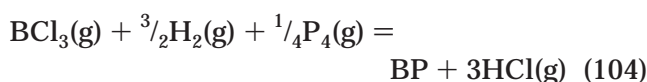
and by Medvedeva and Grinberg (>1200 K),[115] who performed similar analysis of the reaction,

$$2H_2(g) + 4BBr(g) + P_4(g) = 4BP + 4HBr(g) \quad (105)$$
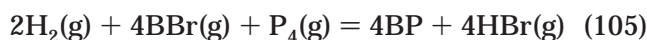
Table 40 lists the experimentally determined and estimated values of ΔH_{298}° for BP, converted to β-B and red (V) phosphorus reference state. The variety of results is discouraging, and even the two results obtained using the most reliable technique (halide combustion calorimetry) disagree. As a result, reliable thermodynamic properties for BP cannot be calculated.

When heated, BP decomposes to $B_{13}P_2$ and $P_2 + P_4$ vapor. The partial pressures generated by this decomposition were measured by Williams and Ruehrwein ("gas saturation" method, 1473−1573 K)[249] and by Alikhanyan et al. (Knudson effusion/mass spectrometry, 1150−1428 K).[248] Kelder et al. used the results of Alikhanyan et al. to calculate thermodynamic properties for the lower phosphide;[243] these values rely on the enthalpy of formation determined by Gross et al.,[38] along with the high-temperature heat capacity data of either Ohsawa et al. or Kumashiro et al.[72,75] Given the ΔH_{298}° data illustrated in Table 40, the thermodynamic properties for $B_{13}P_2$ calculated by Kelder et al. are uncertain at best.

There are no low-temperature heat capacity measurements for AlP, but values predicted by the model of Kagaya and Soma may be fairly accurate,[76] given

Table 40. Experimental and Estimated ΔH_{298}° for BP (βB and Red (V) Reference, kJ/mol)

source	
Gross et al.[38]	−103
Kischio[96]	−106
Gardner[89]	−235
Gal'chenko et al.[37,88]	−82
Stone et al.[134]	−71
Thevenot[87]	−464
Zahreeruddin[47]	−239
Kubaschewski et al.[121]	−98
Barin et al.[4]	−63

Table 41. Experimental and Estimated ΔH_{298}° for AlP (Red (V) Reference, kJ/mol)

source	
present assessment	−112
Wang et al.[45]	−109
Kischio[90]	−109
Peviak and Sandulova[95]	−168
Martusodirdjo and Pratt[40]	−61
Zaheeruddin[47]	−109
Panish et al.[117]	−133
De Maria et al.[250]	−100
McAlister[244]	−98
Kubaschewski et al.[121]	−147
Barin et al.[4]	−148
Terpiłwski et al.[8]	−123
Marina and Nashel'skii[251]	−104

the good degree of agreement of this model with the experimentally determined low-temperature heat capacities of similar compounds. Terpiłowski et al. list theoretically calculated values of S_{298}° for AlP of 38.06, 39.36, and 46.89 J/mol·K[8] and suggest a value of 50.35 J/mol·K themselves. High-temperature drop calorimetry measurements were made by Cox and Pool (298−1150 K)[67] and by Yamaguchi and co-workers (800−1400 K).[68,70] Cox and Pool reported only an average heat capacity over the range, making their results unusable, but their molar sensible heat for AlP at 1100 K is within 1% of the value calculated from the latter work.

ΔH_{298}° measurements for AlP include the following:

(*v*) Wang et al.,[45] oxygen combustion calorimetry;

(*vi*) Kischio,[90] hydrochloric acid solution calorimetry;

(*vii*) Peviak and Sandulova,[95] sulfuric acid solution calorimetry;

(*viii*) Martosudirdjo and Pratt,[40] metal solution precipitation calorimetry; and

(*ix*) Zaheeruddin,[47] oxide combustion calorimetry.

The results (converted to red (V) reference state) are compared with other estimated and compiled values in Table 41. The values in the table attributed to De Maria et al. stem from the measurement by Knudsen effusion/mass spectrometry of the vapor pressures of Al(g) and $P_2(g)$ generated by decomposing AlP (1276−1784 K);[250] for the reaction,

$$Al(g) + {}^1/_2P_2(g) = AlP(s) \quad (106)$$
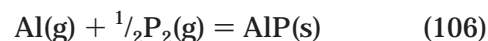
$$\Delta G^{\circ} = -517\,186 + 198.59\,T \text{ J/mol} \quad (107)$$

Gibbs energies of formation were also estimated from the liquidus line measurements (1317−1466 K) of Panish et al. in the ternary Al−Ga−P system.[117] For the reaction,

$$Al(l) + P(l) = AlP(s) \quad (108)$$

$$\Delta G^{\circ} = -101\,527 + 38.56\,T \text{ J/mol} \quad (109)$$

If the "standard" (Al(l) and $P_4(g)$ reference) Gibbs energy of formation of AlP is calculated from eqs 107 and 109, values of −82 864 and −29 266 J/mol result. However, eq 109 is the result of a substantial extrapolation of ternary system equilibria with small ($X_{Al} < 0.06$) levels of aluminum. As a result, eq 107 is more trustworthy.

Table 42. Enthalpies and Gibbs Energies of Formation of AlP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−111664	−113477	1100	−154124	−98278
300	−111665	−113488	1200	−154266	−93195
400	−111736	−114087	1300	−154409	−88100
500	−111926	−114656	1400	−154556	−82994
600	−112306	−115170	1500	−154707	−77877
700	−112908	−115603	1533	−154757	−76184
704	−112937	−115615	1533	−210299	−76184
704	−142895	−115615	1600	−210240	−70322
800	−142894	−111893	1700	−210142	−61580
900	−143024	−108012	1800	−210033	−52844
934	−143099	−106687	1900	−209914	−44115
934	−153890	−106687	2000	−209784	−35392
1000	−153984	−103349			

Table 43. Enthalpies and Gibbs Energies of Formation of GaP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
303	−101252	−90015	1100	−126440	−45613
400	−100542	−86198	1200	−125453	−38403
500	−99812	−82448	1300	−124556	−31264
600	−99180	−78837	1400	−123748	−24186
700	−98688	−75321	1500	−123028	−17158
704	−98672	−75178	1533	−122810	−14846
704	−131298	−75178	1533	−177585	−14846
800	−129972	−67824	1600	−177040	−7743
900	−128696	−60307	1700	−176280	2814
1000	−127520	−52909	1730	−176065	5973

Table 44. Enthalpies and Gibbs Energies of Formation of InP (J/mol)

temp (K)	ΔH_f°	ΔG_f°	temp (K)	ΔH_f°	ΔG_f°
298.15	−59333	−53826	704	−93588	−43883
300	−59334	−53792	800	−93188	−37128
400	−59429	−51936	900	−92731	−30147
430	−59508	−51366	1000	−92237	−23220
430	−62755	−51366	1100	−91709	−16343
500	−62948	−49492	1200	−91148	−9516
600	−63254	−46773	1300	−90556	−2738
700	−63615	−43999	1335	−90341	−376
704	−63631	−43883			

Table 42 lists enthalpies and Gibbs energies of formation for AlP, calculated by a second-law method using eq 107 and the high-temperature heat capacities of Yamaguchi et al.[68,70] The entropy of AlP at 298.15 K, calculated from these results and the room-temperature entropies of red (V) phosphorus and aluminum, is 57.3 J/mol·K. The calculated enthalpy of formation has been added to Table 41; the results could be improved by experimental determination of S_{298}° and by determination of the high-temperature heat capacity over a wider range than that previously used.
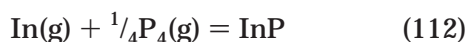
The thermodynamic research database for GaP and InP is voluminous enough to justify a review of its own. Fortunately, this has already been done, most impressively, by Tmar et al.[145] This review includes a thermodynamic optimization for both compounds, using critically assessed data for both the solid phosphides and liquid Ga−P and In−P solutions. The results were used to calculate the partial pressures for P$_2$, P$_4$, and the metal vapor in equilibrium with the solid phosphide as a function of temperature; from these, thermodynamic functions can be obtained. For the reaction,

$$Ga(g) + \tfrac{1}{2}P_2(g) = GaP \qquad (110)$$
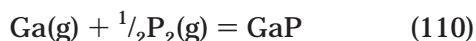
$$\Delta G^\circ = -467\,292 - 13.663\,T\ln T + 326.943\,T \text{ J/mol} \quad (111)$$

The experimental data relied on most heavily to obtain this expression include the vapor pressure measurements of Ilegems et al.,[116] Marina et al.,[126] Lee and Schoonmaker,[137] Johnston,[140] and Richman;[252] the high-temperature heat capacity measurements of Pankratz;[69] and the ΔH_{298}° determination of Martosudirdjo and Pratt.[40] Table 43 lists reference enthalpies and Gibbs energies of formation for GaP calculated using eq 111 as a basis. The entropy at 303 K of GaP calculated from Table 43 and the thermodynamic properties of Ga(l) and P (red (V)) is 44.8 J/mol·K; this compares with the experimentally determined value at 298.15 K of 51.1 J/mol·K.[253]

For the reaction,

$$In(g) + \tfrac{1}{4}P_4(g) = InP \qquad (112)$$

the optimized equilibrium vapor pressures deter-

mined by Tmar et al. yield[145]

$$\Delta G^\circ = -337\,547 - 9.064\,T\ln T + 242.106\,T \quad (113)$$

Primary influences in this optimization include the vapor pressure measurements of Bachmann and Buehler,[20] Panish and Arthur,[147] Drowart and Goldfinger,[146] and Richman;[252] the high-temperature heat capacity measurements of Pankratz;[69] and the ΔH_{298}° determinations of Martosudirdjo and Pratt and of Pool (quoted by Tmar et al.).[40,145] Table 44 lists calculated reference enthalpies and Gibbs energies of formation for InP based on eq 113. S_{298}° for InP calculated from this table (62.2 J/mol·K) compares with the value of 59.7 J/mol·K from low-temperature heat capacity measurements.[254] ΔH_{298}° for InP from Table 44 (−59.3 kJ/mol) compares with experimental values (converted to red (V) reference state) obtained by Martosudirdjo and Pratt (−43.9 kJ/mol),[40] Pool (−48.0 kJ/mol, quoted by Tmar et al.),[145] Sharifov and Gadzhiev (−57.8 kJ/mol),[85] and Sirota (−59.9 kJ/mol).[9]

Tmar et al.'s review was published in 1984.[145] Since that time, the only new thermodynamic information on these systems consists of the high-temperature heat capacity measurements of Itagaki and Yamaguchi for GaP and InP (800−1400 K).[68] No thermodynamic data have been reported for thallium phosphides.

XIV. Group IVA

Of the five elements in this group, phosphorus forms stable solid compounds only with Si and Sn. The Si−P phase diagram published by Ugai et al. differs considerably from the assessed diagram of Olesinski et al. (Figure 20),[255,256] showing two congruently melting compounds (SiP, SiP$_2$) rather than the single peritectic decomposition of SiP in the assessed version. Olesinski et al. claim that SiP$_2$ is metastable; arbiter work is needed to resolve this
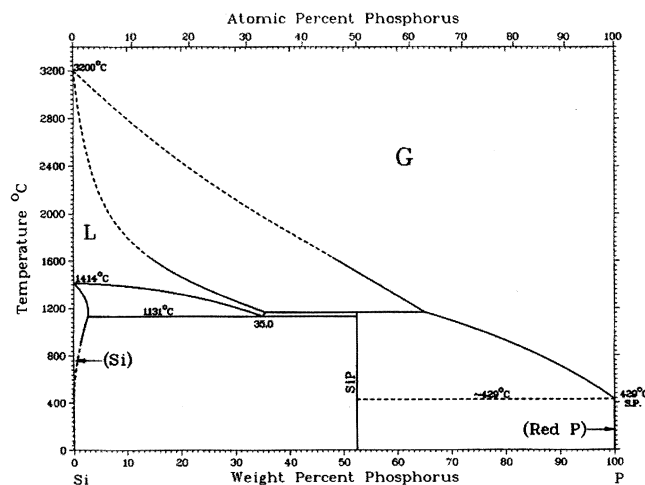
Figure 20. The Si–P phase diagram. Reprinted with permission from ref 153. Copyright 1990 ASM International.

Table 45. Enthalpies and Gibbs Energies of Formation of SiP and GeP (J/mol)

temp (K)	SiP		GeP	
	ΔH_f°	ΔG_f°	ΔH_f°	ΔG_f°
298.15	−38844	−38441	27316	16558
300	−38850	−38438	27310	16492
400	−39244	−38244	26916	12942
500	−39750	−37938	26410	9505
600	−40369	−37520	25791	6180
700	−41100	−36988	25060	2968
704	−41132	−36963	25028	2844
704	−71087	−36963	−4927	2844
800	−71087	−32308	−4927	3905
900	−71087	−27460	−4927	5009
1000	−71087	−22613	−4927	6113
1100	−71087	−17766	−4927	7217
1200	−71087	−12918	−4927	8321
1300	−71087	−8071	−4927	9425
1400	−71087	−3223	−4927	10529
1500	−71087	1624	−4927	11633

issue. The Ge–P phase diagram has a single solid compound,[257] GeP, stable only at elevated pressures. The Sn–P diagram is more complicated and more controversial. A partial phase diagram reported by Arita and Kamo includes the compounds Sn_4P_3 and Sn_3P_4;[262] Suleimanov and Kuliev also list a Sn_5P composition.[109]

As might be suspected, the thermodynamic database for compounds in this group is limited. Three investigators studied the decomposition of SiP to elemental silicon (more accurately, a phosphorus-saturated solid solution) and $P_2(g) + P_4(g)$: Biltz et al. (1299 and 1328 K)[258] using their previously described static device, Korb and Hein (1173–1373 K)[232] using a Bourdon gauge, and Ugai et al. (1313–1483 K)[259] using a static manometric method. The results are in reasonable agreement, especially between the first two results. About half of Ugai et al.'s results were obtained at temperatures above the eutectic temperature (Figure 20), and so these data are discounted for assessment purposes. Using the remaining data, for the reaction,

$$Si + {}^1\!/_4 P_4(g) = SiP \qquad (114)$$

$$\Delta G^\circ = -71\,087 + 48.47\,T\,\text{J/mol} \qquad (115)$$

Lacking heat capacity data, a second-law analysis is required to calculate enthalpies and Gibbs energies of formation for SiP. The results are detailed in Table 45. S_{298}° for SiP calculated from these values is 40.3 J/mol·K.

The same three groups that analyzed the vapor pressure of decomposing SiP also performed this analysis for GeP.[242,260,261] All three sets of results are in very good agreement and can be used for assessment purposes. For the reaction,

$$Ge + {}^1\!/_4 P_4(g) = GeP \qquad (116)$$

$$\Delta G^\circ = -4927 + 11.04\,T\,\text{J/mol} \qquad (117)$$

This produces a unit-pressure decomposition temperature of 446 K, well below the atmospheric sublimation temperature of solid red (V). As a result,

the calculated thermodynamic properties of GeP listed in Table 45 show no temperature at which this phase is stable under unit-pressure conditions. S_{298}° for GeP calculated from these values is 90.0 J/mol· K. Low- and high-temperature heat capacity measurements for SiP and GeP would improve the accuracy of both sets of thermodynamic values.

Two investigations of tin phosphide thermodynamics have been reported. Arita and Kano measured the vapor pressure of P_4 in equilibrium with Sn–P melts using a dew point technique (703–973 K);[262] the results were used to plot a liquidus line in the Sn-rich end of the system and to calculate the Gibbs energy of formation of Sn_4P_3. For the reaction,

$$4Sn(l) + {}^3\!/_4 P_4(g) = Sn_4P_3 \qquad (118)$$
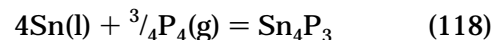
$$\Delta G^\circ = -13\,580 + 11.26\,T\,\text{J/mol} \qquad (119)$$

This equation is based on three data points and should be regarded skeptically. Suleimanov and Kuliev reported the results of EMF measurements at 673 K of the Gibbs energy of formation of Sn_5P, Sn_4P_3, and Sn_3P_4[109] using a "liquid electrolyte"; the lack of detail makes their results difficult to assess, but their Gibbs energies of formation appear to be more negative than those of Arita and Kamo, regardless of reference state. Obviously, more experimental work is needed in this system.

XV. Groups VA and VIA

The only solid compound formed by phosphorus and any of the other VA elements is a low-temperature "AsP" solid solution, with a stoichiometry more accurately described as As_3P_2.[263] Ugai et al. analyzed the vapor composition in equilibrium with the As_3P_2-saturated liquid (893–923 K);[264] On the basis of these results and an optimization performed by Karakaya and Thompson,[263] thermodynamic properties for the phase can be estimated. For the reaction,

$$3As(\text{orthorhombic}) + 2P\,(\text{red, I}) = As_3P_2 \qquad (120)$$
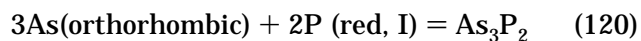
$$\Delta G^\circ = 70\,000 + 1.0\,T\,\text{J/mol} \qquad (121)$$

It should be noted that neither orthorhombic arsenic nor red (I) phosphorus is the standard state of the element.

Of the five VIA elements, phosphorus forms stable solid compounds with oxygen (P_2O_5), sulfur (P_4S_2, P_4S_3, P_4S_4, P_4S_5, P_4S_7, P_4S_9, P_4S_{10}), and selenium (P_4Se_4, P_4Se_3, P_4Se_5).[63] White phosphorus reacts with tellurium to form metastable PTe and/or P_2Te_3; neither compound is formed when the black or red allotropes of phosphorus are used.[265] The thermodynamic properties of P_2O_5 are well-known[149] and will not be discussed here.

Measurement of the thermodynamic properties of phosphorus sulfides is complicated by the sheer number of compounds, the low melting points, and controversies over which allotrope of some compounds is in fact the standard state. Vapor pressure measurements were made for solid P_4S_{10} by Förthmann and Schneider (496 K),[266] Gigli et al.(493–543 K),[267] and Demarcq (485–548 K).[268] The compound apparently decomposes to P_4S_9 and sulfur vapor; measured vapor pressures depend considerably on the chemical and allotropic purity of the initial sample.[268] The vapor pressure generated by decomposing P_4S_3 and P_4S_5 has also been measured at 425 K by Förthmann and Schneider.[266] In all of these cases, only the total vapor pressure was measured; determining the partial pressures of any one vapor species was apparently not feasible. As a result, these results cannot be used for calculation purposes.

Heat capacity measurements for solid phosphorus sulfides include those of Blachnik and Hoppe (P_4S_3, 5–550 K; P_4S_4, 130–400 K; P_4S_5, 130–430 K; P_4S_9, 130–530 K; P_4S_{10}, 130–550 K),[63] Clever et al. (P_4S_3 and P_4S_{10}, 5–350 K),[269] Peters and Muscheites (P_4S_{10}, 273–561 K),[270] and Chattopadhyay et al. (P_4S_3, 130–450 K).[271] The lower-temperature limits from these investigations are not sufficient for reliable calculation of compound entropies, with the exception of $S°_{298}$ for P_4S_3 (203.3 J/mol·K) and P_4S_{10} (381.7 J/mol·K) reported by Clever et al. Cueilleron and Vincent measured the enthalpy of formation of some of the sulfides, using direct reaction calorimetry[273] and benzoic acid solution calorimetry;[272] $\Delta H°_{298}$ for P_4S_3, P_4S_5, P_4S_7, and P_4S_{10} (red (I) and orthorhombic αS reference) are −154.4, −235.1, −253.5, and −228.0 kJ/mol, respectively. These differ considerably from previous results;[274,275] the reason may be in part the use of different allotropes of the sulfides. The only thermodynamic studies of phosphorus selenides are the heat capacity measurements of Blachnik and Hoppe (P_4Se_3 and P_4Se_4, 130–700 K)[63] and Clever et al. (P_4Se_3, 5–350 K).[269] The latter work yields a value of $S°_{298}$ for P_4Se_3 of 239.6 J/mol·K.

XVI. Conclusions and Recommendations

Although the thermodynamic database for phosphorus is more extensive than might be suspected, this review has revealed obvious needs for further work. Most significant among these are the following:

(*i*) An improved thermodynamic database for elemental phosphorus. Particularly needed are "high"-temperature heat capacities for red (I), red (V), and black phosphorus and more accurate measurements of the vapor pressure of P_4 in equilibrium with these allotropes.

(*ii*) Development of reliable methods for measuring enthalpies of formation. Most of the experimentally measured $\Delta H°$ values for phosphides were found to be not usable for assessment purposes or in strong disagreement with values calculated by other means. Improved direct reaction calorimetry may be the best response to this need.

(*iii*) Improved EMF measurement techniques. Accurate measurement of high-temperature heat capacities for many phosphides is difficult, due to decomposition; as a result, EMF studies may be the best way to obtain reliable Gibbs energies of formation for these compounds. However, the relatively few EMF investigations reported in the literature were generally found to give results that were unreliable or in serious disagreement with thermodynamic properties obtained by other experimental methods. The biggest challenge appears to lie in finding a suitable electrolyte.

XVII. Supporting Information

Coefficients for calculation of $\Delta G°$ and $\Delta H°$ are available for alkaline-earth phosphides (Table S1), lanthanide and actinide phosphides (Table S2), chromium phosphides (Table S3), manganese phosphides (Table S4), iron phosphides (Table S5), group 11 and 12 phosphides (Table S6), and group 13 and 14 phosphides (S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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