

Thermodynamic properties of $\{x\text{Ca} + (1-x)\text{P}\}$

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A Knudsen-effusion technique in combination with a mass-spectral analysis of the vapour phase has been applied to study thermodynamic properties of $\{x\text{Ca} + (1-x)\text{P}\}$ alloys ($0.5 \leq x \leq 1$) over the temperature range 650 K to 1537 K. The compound CaP was found to be unstable and to decompose at low temperatures into Ca_3P_2 and gaseous phosphorus. Evaporation of the phosphide Ca_3P_2 was followed by congruent decomposition. The standard molar Gibbs energy of formation of Ca_3P_2 from red phosphorus and solid calcium has been expressed by the equation:

$$\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = -(527000 \pm 3300) + (35.93 \pm 2.36) \cdot (T/\text{K}).$$

Thermodynamic functions of $\{x\text{Ca} + (1-x)\text{P}\}(\text{l})$ have been estimated with help of $\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)$ values and the coordinates of a point on the line of the two-phase equilibrium ($\text{Ca}_3\text{P}_2 + \text{l}$). It has been shown that the liquid solution can be described by the ideal-associated-solution model if complexes of Ca_3P_2 type are assumed to exist.

1. Introduction

Removal of phosphorus from alloyed steels that contain metals with a high affinity for oxygen (Cr, Mn, Ti, Nb, V, Ta, Zr, Mo, *etc.*) is quite a problem. It cannot be solved by means of oxidizing dephosphorization as this process would promote simultaneous oxidation and considerable loss of expensive alloying elements.

An alternative and more attractive way of extracting phosphorus is by treatment of metallic melts with fluxes and alloys containing calcium and other alkali-earth elements under reducing conditions.^(1–19) Although there are numerous investigations in this direction, no reliable technological process of reducing-dephosphorization has been developed. The failure, in our opinion, is due to lack of fundamental knowledge concerning the mechanism of phosphorus transfer from metal to slag and the form in which it is transferred. It suffices to emphasize that even thermodynamic functions of formation for calcium phosphides, key-compounds in processes of reducing-dephosphorization, have not been established with the necessary precision.

It has been found^(6,20) that there exist in $\{xCa + (1-x)P\}$ three intermediate phases Ca_3P_2 , CaP , and CaP_2 though the conditions under which they form as well as their melting behaviour are not known.

At present only Ca_3P_2 has been subjected to thermodynamic study. Its formation thermodynamic functions have been obtained either by theoretical estimation^(22,23) or from indirect experiments while examining equilibria of Ca_3P_2 with iron⁽⁶⁾ or silver.⁽²¹⁾ The results are extremely contradictory. Equilibrium constants of the reaction:



at the temperature 1873 K, for example, vary by a factor of more than 10^{10} from $2.0 \cdot 10^6 \cdot Pa^{-1}$,⁽²³⁾ to $9.6 \cdot 10^{16} \cdot Pa^{-1}$.⁽⁶⁾

The facts presented may be explained to a great extent by difficulties that appear both in theoretical and experimental studies of $\{xCa + (1-x)P\}$. From the theoretical point of view compounds of calcium and phosphorus are characterized by a substantial fraction of covalent bond that makes it difficult to compute their energetic parameters. Complications one meets in experimental investigations are caused by a high affinity of the compounds, as well as of the pure components, for hydrolysis and oxidation. It suffices to say that hydrolysis of Ca_3P_2 that results in formation of calcium oxide and phosphine is completed in (3 to 8) h even in commercial argon media.

2. Experimental

In the present work a Knudsen-effusion method combined with mass-spectral analysis of the gaseous phase was applied to examine the vapour composition and pressure over (calcium + phosphorus) alloys.

The alloys for investigation were prepared from red phosphorus of the highest purity (99.995 mass per cent) and calcium with impurity content less than 0.1 mass per cent. In addition to the high chemical activity of the reagents the synthesis was complicated also by their very high volatility. The vapour pressure of phosphorus reaches atmospheric pressure at the temperature 550 K and that of calcium is 121.6 kPa at 1800 K and to 206.7 kPa at 1900 K. To avoid the loss of reagents because of evaporation the synthesis was carried out in quartz ampoules sealed under vacuum. Calcium was subjected to preliminary smelting in a purified-argon atmosphere. It was placed in a tantalum foil (0.1 mm) container and put into an alumina crucible. The latter was installed inside a quartz tube with a water-cooled jacket. After displacing air by purified argon the tube was heated to 1130 K and was held at that temperature for 15 min. Then it was withdrawn from the furnace and cooled. The tantalum foil was easily removed from the calcium ingot. The ingot was ground by drilling out chips. All these operations were carried out in a special box in a protective argon atmosphere. The chips were put into quartz ampoules. They were filled with argon, closed tightly, and weighed. Then necessary amounts of phosphorus were added to them in the box under an argon atmosphere. The ampoules were evacuated to a pressure of 10^{-3} Pa and sealed. The synthesis was

performed in a furnace that ensured the constancy of temperature along ampoules. They were slowly heated to a temperature which depended on the composition of the alloy being prepared and was equal to 1100 K to 1400 K. The highest temperature corresponded to alloys with compositions close to Ca_3P_2 , the lowest to alloys with high content of phosphorus. If the ampoules with the latter alloys were heated to a higher temperature they exploded because the phosphorus pressure developed inside them greatly exceeded the atmospheric pressure.

Alloys containing mole fractions 0.57 and 0.75 of Ca as well as those corresponding to the stoichiometry of the compounds Ca_3P_2 and CaP were synthesized.

The compound Ca_3P_2 was also prepared in a different way by reaction of calcium with an excessive amount of phosphorus followed by distillation of excessive phosphorus in vacuum. In all cases except the sample with mole fraction 0.75 of Ca no traces of interaction either of the reagents or of the products with quartz were observed. The sample mentioned contained excess of calcium as compared with the stoichiometry of Ca_3P_2 . In this case a reduction of silica with calcium and formation of silicon took place. The compounds synthesized were identified by means of X-ray diffraction analysis. The observed lattice spacings were in a good agreement with the values available.

Effusion experiments were carried out over the temperature range 650 K to 1537 K. Double effusion cells made from molybdenum, niobium, or tantalum were employed for the measurements. No influence of the material of the cell on either the composition of vapour or the partial pressures of vapour components was detected. Magnesium, copper, and strontium fluoride served as reference substances. In all cases reproducible results were obtained for temperature dependences of ion current (vapour pressures) of Mg, Cu, and SrF_2 that agreed with the thermodynamic values of both the IVTANTERMO bank and published studies.^(24, 25) For that reason the information on vapour pressures of Mg, Cu, and SrF_2 from these references has been used in the calculations.

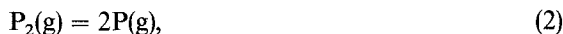
The experimental technique was the same as described in reference 25. Transference of prepared alloys into an effusion cell and fitting the cell into the evaporator of the ion source were carried out in the box under a protective atmosphere. After fitting, the evaporator was filled with argon, installed quickly in the mass-spectrometer, and evacuated. In the course of any experiment the pressure in the high-temperature ion source did not exceed $5 \cdot 10^{-5}$ Pa. The procedure described made it possible to avoid hydrolysis of alloys under investigation to any noticeable extent.

3. Calcium phosphides

Ions of Ca^+ , P_4^+ , P_2^+ , and P^+ have been registered in the mass spectra of the saturated vapour over the (calcium + phosphorus) alloys. Those ions were formed by ionization of calcium and phosphorus molecules. No ion including atoms of both components that could appear through the ionization of molecules (CaP_2 , CaP , Ca_2P , Ca_3P_2 , etc.) has been found in the mass spectra. This fact means that the

evaporation process of (calcium + phosphorus) compounds is followed by their dissociation into atoms of components. Ions of P_4^+ formed by ionization of molecules P_4 were discovered only in vapour over the phosphide CaP and alloys that belong to the two-phase field (CaP + Ca_3P_2) of the $\{x\text{Ca} + (1-x)\text{P}\}$ equilibrium diagram.

In order to determine whether ions P^+ are molecular (formed from molecules P) or fragmentary (appearing due to dissociative ionization of P_2 molecules) the equilibrium constants of the dissociation reaction:



have been calculated. The values from the IVTANTERMO bank were used for the purpose. The constants were found to be equal to $7.3 \cdot 10^{-22}$ Pa and $8.8 \cdot 10^{-5}$ Pa at the temperatures 800 K and 1700 K, respectively. The pressures of P_2 molecules in the vapour computed from the experimental results under the supposition that ionization of P_2 molecules caused formation of P_2^+ ions only constituted 10^{-4} Pa to 100 Pa at 800 K and 10 Pa to 100 Pa at 1700 K.

Substitution of these values into the expression for the equilibrium constant of reaction (2) gives the following results for monomer-species pressure: ($2.71 \cdot 10^{-13}$ to $2.71 \cdot 10^{-10}$) Pa at 800 K and ($2.96 \cdot 10^{-2}$ to $9.37 \cdot 10^{-2}$) Pa at 1700 K. It is obvious that the pressure of P_2 exceeds that of P by a factor more than 10^4 . Hence, ions of P^+ are formed mainly as a result of dissociative ionization of P_2 molecules. This conclusion is also proved by the constancy of the ratio of P_2^+ -to- P^+ ionic currents that was observed in all the mass spectra registered.

Calculations of calcium and phosphorus vapour pressures were carried out with the help of the conventional⁽²⁶⁾ equation:

$$p_j = K \cdot (\sum_j I_{ij}) \cdot (T/K) / \sigma_j, \quad (3)$$

where I_{ij} is an ionic current of i -type ions, formed from molecules j ; K is the sensitivity constant of the mass-spectrometer (determined from the vapour pressure of a reference substance); σ_j is the maximum ionization cross-section of molecules j . The ionization cross-sections of P_2 and P_4 molecules have been found in accordance with the additivity rule from the maximum atomic cross-sections presented in reference 27.

The experimental results showed that the vapour pressure of phosphorus over the compound CaP as well as over two-phase (CaP + Ca_3P_2) alloys reaches, even at temperatures close to 700 K, a value that corresponds to the upper limit of the effusion-method applicability (≈ 15 Pa). The vapour pressure of calcium lies beyond the lower level of sensitivity of the applied technique (10^{-5} Pa to 10^{-6} Pa). These facts demonstrate that the compound CaP is relatively unstable and decomposes even at low temperatures into Ca_3P_2 and gaseous phosphorus. This result corresponds to conclusions of the authors of reference 6 who showed that the phosphide CaP decomposes completely with formation of Ca_3P_2 at temperatures higher than 1473 K. The vapour pressure of calcium has measurable values only over the alloy that contained mole fraction 0.75 of Ca and belonged to the two-phase region (Ca + Ca_3P_2). The least-squares method treatment of the vapour-pressure

TABLE 1. Vapour pressures and the enthalpies of sublimation of calcium

$\frac{T}{\text{K}}$	$\frac{p_{\text{Ca}}}{\text{mPa}}$	$\frac{\Delta_s^{\circ}H_m^{\circ}(\text{III}, T \rightarrow 0)}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{p_{\text{Ca}}}{\text{mPa}}$	$\frac{\Delta_s^{\circ}H_m^{\circ}(\text{III}, T \rightarrow 0)}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{p_{\text{Ca}}}{\text{mPa}}$	$\frac{\Delta_s^{\circ}H_m^{\circ}(\text{III}, T \rightarrow 0)}{\text{kJ} \cdot \text{mol}^{-1}}$
633.8	0.169	176.9	687.2	2.19	177.0	747.5	23.8	177.4
633.8	0.174	176.7	705.6	4.73	177.1	748.9	26.2	177.1
652.7	0.449	176.8	707.1	5.17	177.0	753.3	30.1	177.2
654.3	0.486	176.8	710.0	5.54	177.3	756.3	31.9	177.6
657.8	0.576	176.8	710.8	5.57	177.4	758.5	37.6	177.0
660.0	0.647	176.7	712.2	5.97	177.4	760.0	41.3	176.8
662.3	0.677	177.1	714.4	6.36	177.4	762.9	47.0	176.6
669.6	0.916	177.3	715.9	6.57	177.7	790.1	112.0	177.0
681.4	1.74	176.8	717.4	7.22	177.5	795.3	133.0	177.1
682.1	1.89	176.5	721.8	10.5	176.3	797.4	144.0	177.0
682.8	1.91	176.6	732.1	14.5	176.8	811.2	214.0	177.3
683.5	2.03	176.4	735.8	15.6	177.2			
686.5	2.11	177.0	744.5	21.5	177.3			
Average value:								177.0 ± 0.7

values acquired (table 1) as a function of temperature led to the expression (634 K to 811 K):

$$\ln(p/\text{Pa}) = -(20693 \pm 191) \cdot (\text{K}/T) + (23.98 \pm 0.27), \quad (4)$$

that agrees within experimental errors with values presented in the IVTANTERMO bank for the vapour pressure of pure calcium. This coincidence means that there is no substantial region of primary solid solutions of phosphorus in calcium.

This result permitted to use the measured vapour pressures of calcium over the (0.75Ca+0.25P) alloy (table 1) for calculation of calcium sublimation enthalpy at $T \rightarrow 0$ according to the second and third laws of thermodynamics. The thermodynamic functions of Ca(g, s) from the IVTANTERMO bank have been employed for the purpose. The values obtained are

$$\Delta_s H_m^{\circ}(\text{II}, T \rightarrow 0) = (175.9 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$$

and

$$\Delta_s H_m^{\circ}(\text{III}, T \rightarrow 0) = (177.0 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}.$$

They agree within the experimental errors.

Evaporation of the phosphide Ca_3P_2 is followed by its congruent decomposition. At the beginning of this process calcium or phosphorus vapour predominated in the gaseous phase so that its composition differed from the stoichiometry of Ca_3P_2 . That is obviously connected with evaporation of a component excessive in respect to the congruently evaporating composition. The fact indicates that the compound Ca_3P_2 is characterized by a range of homogeneity.

The thermodynamic functions of Ca_3P_2 formation have been calculated from the measured vapour pressures of Ca and P_2 with respect to red phosphorus and solid calcium chosen as standard states for components. The following equations were

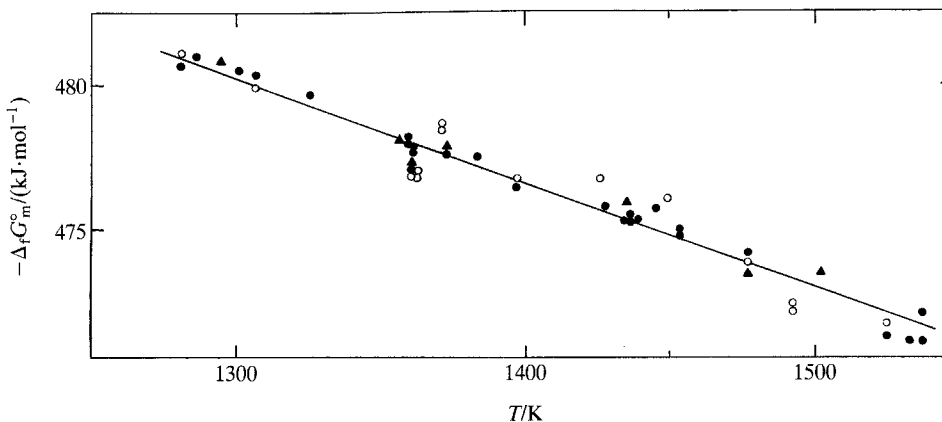


FIGURE 1. Standard molar Gibbs energies of formation of Ca_3P_2 from $\text{Ca}(\text{s})$ and $\text{P}(\text{red})$. ▲, Results obtained in experiments with a niobium effusion cell (diameter of the effusion holes, $4 \cdot 10^{-4}$ m; reference substance, Cu); ○, results obtained in experiments with a molybdenum effusion cell (diameter of the effusion holes, $4.06 \cdot 10^{-4}$ m; reference substance, SrF_2); ●, results established in experiments with a molybdenum effusion cell (diameter of the effusion holes, $2.04 \cdot 10^{-4}$ m; reference substance, SrF_2).

used for molar Gibbs energies of phase transitions:

$$\Delta_{\text{g}}^{\circ}G_{\text{m}}\{\frac{1}{2}\text{P}_2(\text{g}) = \text{P}(\text{red})\}/(\text{J} \cdot \text{mol}^{-1}) = -88874.18 + 81.3165 \cdot (T/\text{K}) \\ - 0.07246 \cdot (T/\text{K})^2 + 1.199 \cdot (T/\text{K}) \cdot \ln(T/\text{K}) - 104000 \cdot \text{K}/T, \quad (5)$$

$$\Delta_{\text{f}}^{\circ}G_{\text{m}}(\text{Ca})/(\text{J} \cdot \text{mol}^{-1}) = -8540 + 7.659 \cdot (T/\text{K}). \quad (6)$$

The former is based on the results of references 28 to 30 and the latter on the IVTANTERMO bank. The obtained molar Gibbs energies of the calcium phosphide formation are given in figure 1 and table 2. The least-squares treatment of these results as a function of temperature produced the equation:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = -(527000 \pm 3300) + (35.93 \pm 2.36) \cdot (T/\text{K}), \\ (1281 \text{ K} \leq T \leq 1537 \text{ K}). \quad (7)$$

For comparison of the present results with thermodynamic information available, the standard molar Gibbs energy of Ca_3P_2 formation from liquid calcium and P_2 gas has been computed too:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = -730365 + 221.54 \cdot (T/\text{K}) - 0.014492 \cdot (T/\text{K})^2 \\ + 2.398 \cdot (T/\text{K}) \cdot \ln(T/\text{K}) - 208000 \cdot \text{K}/T. \quad (8)$$

The thermodynamic quantities on Ca_3P_2 formation that have been obtained in all the studies carried out until now are demonstrated on figure 2. It is seen that the $\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Ca}_3\text{P}_2)$ values found in the present work lie considerably higher (in absolute value) than those of reference 23 and somewhat lower than the results of reference 21 and of estimation.⁽²²⁾ To determine the standard molar Gibbs energy of reaction (1) the authors of reference 21 studied an interaction between liquid silver and solid

TABLE 2. Standard molar Gibbs energies of formation of $\text{Ca}_3\text{P}_2(\text{s})$ from $\text{Ca}(\text{s})$ and $\text{P}(\text{red})$

$\frac{T}{\text{K}}$	$\frac{-\Delta_f G_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{-\Delta_f G_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{-\Delta_f G_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{-\Delta_f G_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$
I. Niobium effusion cell; copper as reference substance; diameter of the effusion hole is equal to $4\cdot 10^{-4}$ m							
1295	480919	1361	477458	1436	475967	1502	473710
1357	478164	1373	477942	1477	473662		
II. Molybdenum effusion cell; strontium fluoride as reference substance; diameter of the effusion hole is equal to $4.06\cdot 10^{-4}$ m							
1281	481164	1363	477110	1426	476783	1492	472332
1307	479776	1371	478656	1449	476191		
1361	476911	1371	478656	1487	474265		
1363	476922	1397	476796	1492	472435		
III. Molybdenum effusion cell; strontium fluoride as reference substance; diameter of the effusion hole is equal to $2.04\cdot 10^{-4}$ m.							
1281	480732	1361	477306	1434	475422	1477	473923
1286	481013	1361	477868	1436	475593	1525	471847
1301	480489	1361	477157	1436	475501	1525	471441
1307	480432	1373	477821	1439	475476	1533	471776
1326	479681	1383	477579	1445	475814	1537	472204
1359	478189	1397	476597	1453	474879	1537	471753
1359	478023	1428	475905	1453	475005		

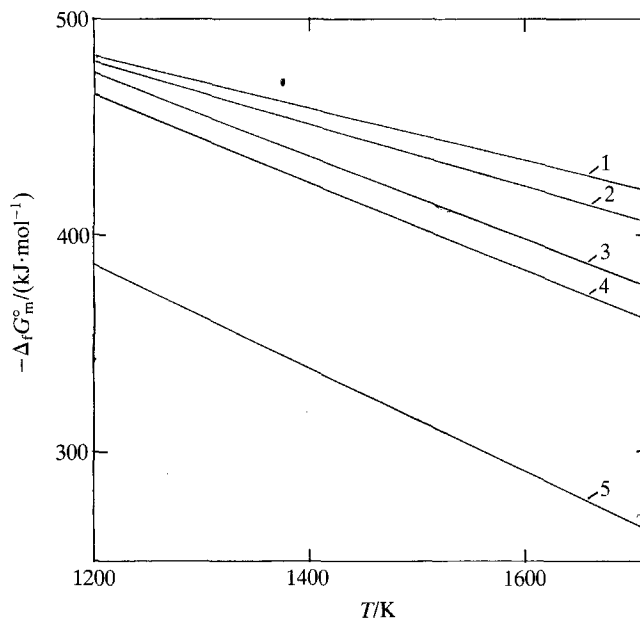


FIGURE 2. Standard molar Gibbs energies of formation of Ca_3P_2 from $\text{Ca}(\text{l})$ and $\text{P}_2(\text{g})$ as function of temperature: 1, according to present results; (2, results of Min and Sano;⁽²¹⁾ 3, results of Min and Sano⁽²¹⁾ with correction for the standard molar Gibbs energy of the reaction: $\frac{1}{2}\text{P}_2 = \text{P}(\text{in liquid Ag})$; 4, results of theoretical estimation; ⁽²²⁾ 5, results of Kubaschewski and Alcock.⁽²³⁾

phosphide Ca_3P_2 . They measured equilibrium constants of the reaction:



The values obtained and the molar Gibbs energies of solution of $\text{Ca}(\text{l})$,⁽³¹⁾ and $\text{P}_2(\text{g})$ in liquid silver,^(32, 33) allowed them to calculate the standard molar Gibbs energy changes of reaction (1). According to reference 21:

$$\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = -(653460 \pm 7110) + (144.01 \pm 4.98) \cdot (T/\text{K}), \quad (10)$$

(1273 K < T < 1573 K).

However, there is a possibility to calculate Gibbs energy changes for the solution reaction: $\frac{1}{2}\text{P}_2(\text{g}) = \text{P}(\text{in liquid Ag})$, on the basis of thermodynamic functions of $\text{P}_2(\text{g})$, $\text{P}(\text{l})$, and a solution of phosphorus in silver, recommended in references 28 to 30.

The computations carried out for the middle of the temperature range studied in reference 21 resulted in the equation:

$$\Delta_{\text{trs}} G_m^\circ\{\frac{1}{2}\text{P}_2(\text{g}) = \text{P}(\text{in liquid Ag})\}/(\text{J} \cdot \text{mol}^{-1}) = -46860 + 52.53 \cdot (T/\text{K}), \quad (11)$$

which is quite different from that of reference 21:

$$\Delta_{\text{trs}} G_m^\circ\{\frac{1}{2}\text{P}_2(\text{g}) = \text{P}(\text{in liquid Ag})\}/(\text{J} \cdot \text{mol}^{-1}) = -20500 + 28.5 \cdot (T/\text{K}). \quad (12)$$

Recalculation of the data in reference 21 with the use of equation (11) instead of (12) led to the expression for the standard molar Gibbs energy change of reaction (1) (line 3 in figure 1):

$$\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = -706180 + 192.08 \cdot (T/\text{K}), \quad (13)$$

which is in a better agreement with the present results.

The authors of reference 6 have studied an equilibrium between Ca_3P_2 and liquid iron at 1873 K and obtained for the reaction: $\text{Ca}_3\text{P}_2(\text{s}) = 3\text{Ca}(\text{mass per cent in Fe}) + 2\text{P}(\text{mass per cent in Fe})$; the equilibrium constant, $7.0 \cdot 10^{-14}$; and the standard molar Gibbs energy change, $472000 \text{ J} \cdot \text{mol}^{-1}$.

Combination of the latter value with the available molar Gibbs energies of solution of $\text{P}_2(\text{g})$,^(32, 34, 35) and $\text{Ca}(\text{l})$,⁽³⁶⁾ in liquid iron gives $\Delta_f G_m^\circ(\text{reaction 1}) = -608980 \text{ J} \cdot \text{mol}^{-1}$. This quantity (in absolute value) is twice as great as that found in all other investigations. This discrepancy may be explained by the complexity of precise chemical analysis of iron for low mole fractions of Ca and P.

In the present work the standard molar Gibbs energy of formation of Ca_3P_2 has been determined in direct experiments. It is essential that very reproducible results were obtained both for samples of Ca_3P_2 synthesized in various ways and for the same sample studied under different experimental conditions (various orifice areas and cell materials).

These facts permit us to regard the formation thermodynamic functions of Ca_3P_2 found here as reliable.

4. Liquid solutions: $\{x\text{Ca} + (1-x)\text{P}\}$

Information on thermodynamic properties of $\{x\text{Ca} + (1-x)\text{P}\}(\text{l})$ is necessary to establish technological quantities for reducing-dephosphorization of steel. Direct

experimental investigations of these melts are associated with great difficulties caused by high reactivity and high volatility of both components at temperatures of liquid-phase stability. For that reason thermodynamic functions of $\{x\text{Ca} + (1-x)\text{P}\}(\text{l})$ have been estimated with the help of the obtained standard molar Gibbs energy of the calcium phosphide formation and coordinates of points on the line of the two-phase equilibrium ($\text{Ca}_3\text{P}_2 + \text{l}$) found by the authors⁽¹⁹⁾ by d.t.a. The phase-transition molar Gibbs energies of calcium were described by equation (6) and that of phosphorus by the expression:

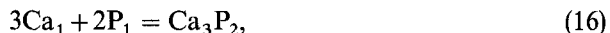
$$\Delta_1^{\text{red}}G_m(\text{P})/(\text{J} \cdot \text{mol}^{-1}) = -15926.18 - 38.1515 \cdot (T/\text{K}) - 0.7446 \cdot 10^{-2} \cdot (T/\text{K})^2 + 9.377 \cdot (T/\text{K}) \cdot \ln(T/\text{K}), \quad (14)$$

that has been obtained on the basis of published results.⁽²⁸⁻³⁰⁾

Thermodynamic properties of $\{x\text{Ca} + (1-x)\text{P}\}(\text{l})$ have been approximated by the regular-associated-solution model (RASM).⁽³⁷⁻⁴⁰⁾ Complexes Ca_3P_2 were supposed to exist in the melts and interactions only between monomer molecules were taken into consideration. The Gibbs energy of solution has been expressed in the form:

$$\Delta_{\text{sol}}G = n(\text{Ca}_3\text{P}_2) \cdot \Delta_f G_m^\circ(\text{Ca}_3\text{P}_2) + L_0 \cdot n(\text{Ca}_1) \cdot n(\text{P}_1)/n + RT \cdot [n(\text{Ca}_1) \cdot \ln\{x(\text{Ca}_1)\} + n(\text{P}_1) \cdot \ln\{x(\text{P}_1)\} + n(\text{Ca}_3\text{P}_2) \cdot \ln\{x(\text{Ca}_3\text{P}_2)\}]. \quad (15)$$

Here $n(i)$ and $x(i)$ are the amount of substance and mole fraction of associated-solution component i ; n is the total amount of substance of the associated-solution components; L_0 is a parameter of interaction between the monomer molecules; $\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)$ is the standard molar Gibbs energy of formation of associated complexes Ca_3P_2 . The latter value is connected with the equilibrium constant of the reaction of association:



by the equation:

$$\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2) = -RT \cdot \ln\{K(\text{Ca}_3\text{P}_2)\} = \Delta_f H_m^\circ(\text{Ca}_3\text{P}_2) - T \cdot \Delta_f S_m^\circ(\text{Ca}_3\text{P}_2), \quad (17)$$

where

$$K(\text{Ca}_3\text{P}_2) = a(\text{Ca}_3\text{P}_2)/[a(\text{Ca}_1)]^3 \cdot [a(\text{P}_1)]^2. \quad (18)$$

It is necessary to call attention to a contradictory feature of the RASM that seems essential for its application to liquid solutions. The difference between the ideal-associated-solution model (IASM) and the RASM is known to consist in the way the activities of associated-solution components are expressed. In the IASM they are put equal to the mole fractions of monomer molecules and in the RASM they are found in accordance with the equation:

$$a(i) = \gamma(i_1) \cdot x(i_1), \quad (19)$$

where $\gamma(i_1)$ is the activity coefficient of a monomer species ($i = \text{Ca}$ or P). Values of $\gamma(i_1)$ are completely determined by parameters of interaction between associated-solution components (e.g. by L_0 in equation 15).

TABLE 3. Mole fractions of associated-solution components and activities of calcium and phosphorus for the equilibrium constant of the reaction of association (16): $K(\text{Ca}_3\text{P}_2) = 9.37 \cdot 10^{12}$ and various values of the interaction parameter L_0 at $T = 1573$ K and $x = 0.9255$ for $\{x\text{Ca} + (1-x)\text{P}\}$

$L_0/(\text{kJ} \cdot \text{mol}^{-1})$	$x(\text{Ca}_1)$	$x(\text{P}_1)$	$10^2 \cdot x(\text{Ca}_3\text{P}_2)$	$a(\text{Ca})$	$10^8 \cdot a(\text{P})$
0	0.9562	$7.309 \cdot 10^{-8}$	4.377	0.9562	7.309
-1	0.9562	$7.309 \cdot 10^{-8}$	4.377	0.9562	7.309
-10	0.9562	$7.309 \cdot 10^{-8}$	4.377	0.9562	7.309
-25	0.9562	$4.547 \cdot 10^{-7}$	4.377	0.9562	7.309
-50	0.9562	$2.829 \cdot 10^{-6}$	4.377	0.9562	7.309
-75	0.9562	$1.759 \cdot 10^{-5}$	4.376	0.9562	7.309
-100	0.9562	$1.093 \cdot 10^{-4}$	4.371	0.9561	7.308
-125	0.9559	$6.747 \cdot 10^{-4}$	4.337	0.9557	7.305
-150	0.9526	$3.381 \cdot 10^{-3}$	4.143	0.9526	7.309
-175	0.9485	$1.882 \cdot 10^{-2}$	3.271	0.9362	7.350
-200	0.9351	$5.127 \cdot 10^{-2}$	1.365	0.9351	6.572
-250	0.9255	$7.442 \cdot 10^{-2}$	$4.751 \cdot 10^{-3}$	0.8325	0.575
-300	0.9255	$7.450 \cdot 10^{-2}$	$4.963 \cdot 10^{-6}$	0.8149	0.0218

The calculations based on the equations (15, 17, 18) that take into account interactions only between monomer molecules have revealed that both models give practically the same results for the component activities if the interaction parameter is small in comparison with the energy of the complex formation, the equilibrium constants for the association reaction being equal. The only difference observed is in the mole fraction of monomer species which does not seem important for approximation of a liquid-solution thermodynamic function. The activities computed with the help of the IASM and the RASM begin to differ substantially when the interaction parameter becomes comparable with interparticle interactions in the associated complex. These facts are illustrated by table 3 where activities of calcium and phosphorus calculated for various values of the parameter L_0 and $T = 1573$ K, $x = 0.9255$, and $K(\text{Ca}_3\text{P}_2) = 9.37 \cdot 10^{12}$, are given. Values of $a(\text{Ca})$ and $a(\text{P})$ calculated according to the RASM and IASM are seen practically to coincide in spite of the fact that the mole fraction of P_1 species in the solution varies substantially. The discussion presented makes it clear why in describing thermodynamic functions of melts with the help of the RASM one has to do with high absolute values of parameters of interaction between the associated-solution components (e.g. see reference 40). That does not agree of course with the main concept of the associated-solution model as these parameters should describe a residual interaction which is rather small in comparison with interparticle interaction in complexes. For this reason it is preferable to use the so-called model of quasi-ideal-associated solution.⁽⁴¹⁻⁴³⁾ In it, activity coefficients of components as well as the excess molar Gibbs energy are expressed through mole fractions of the initial components but not through that of the associated-solution components. As a result, rather small (in absolute value) parameters of interparticle interaction lead to substantial differences of the component activities from those calculated according to the IASM.

It has been demonstrated⁽⁴¹⁻⁴³⁾ that the application of the quasi-ideal-associated-

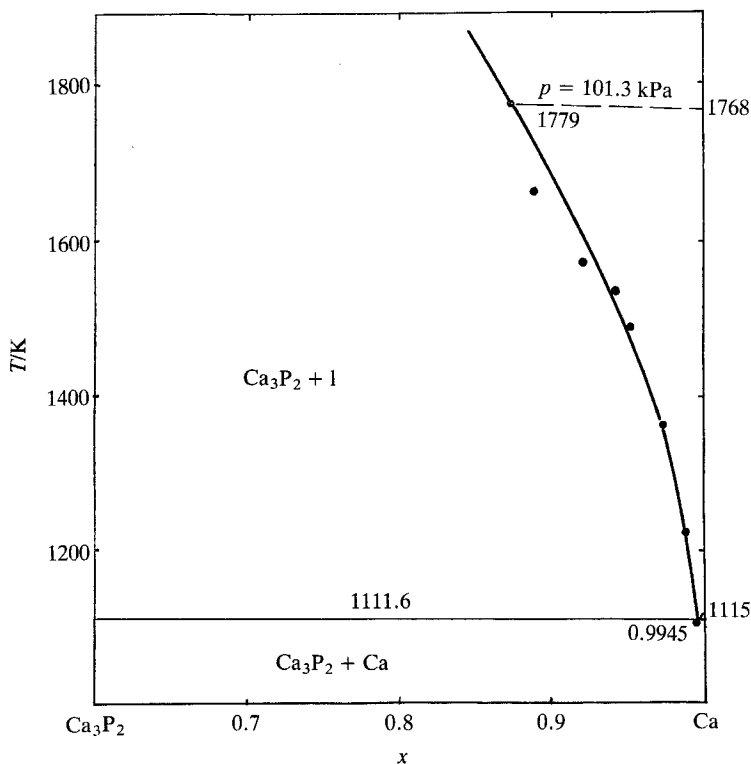


FIGURE 3. Phase diagram for $\{xCa+(1-x)P\}$, $x > 0.6$. —, Results of the present calculation; ●, Köhler and Engell⁽¹⁹⁾ by the d.t.a. method.

solution model is very effective for systems which are characterized by strong interparticle interactions between some components and by weak ones between the others.

As for the $\{xCa+(1-x)P\}(\text{l})$ an optimizing procedure has been devised to find the model parameters $\Delta_f H_m^\circ(\text{Ca}_3\text{P}_2)$, $\Delta_f S_m^\circ(\text{Ca}_3\text{P}_2)$, and L_0 . It consisted in a search for the minimum sum of squares of discrepancies between the standard molar Gibbs energy of formation of $\{xCa+(1-x)P\}(\text{l})$ at points of its equilibrium with Ca_3P_2 ,⁽¹⁹⁾ obtained through experimental values of $\Delta_f G_m^\circ(\text{Ca}_3\text{P}_2)$ and calculated by means of equation (15). The procedure allowed us to obtain the values:

$$\begin{aligned}\Delta_f H_m^\circ(\text{Ca}_3\text{P}_2) &= -(496560 \pm 12170) \text{ J} \cdot \text{mol}^{-1}, \\ \Delta_f S_m^\circ(\text{Ca}_3\text{P}_2) &= -(67.35 \pm 8.82) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1},\end{aligned}$$

and

$$L_0 = -(6200 \pm 13800) \text{ J} \cdot \text{mol}^{-1}.$$

It can be seen that the interaction between the monomer species in the associated solution might be neglected. This conclusion is confirmed by the fact that if $L_0 = 0$ is

supposed the values of $\Delta_f H_m^\circ(\text{Ca}_3\text{P}_2)$ and $\Delta_f S_m^\circ(\text{Ca}_3\text{P}_2)$ remain unchanged. Hence, the thermodynamic properties of $\{x\text{Ca} + (1-x)\text{P}\}(l)$ obey the rules of the ideal-associated-solution model.

The thermodynamic model discussed and the thermodynamic functions of Ca_3P_2 formation have been applied to compute the $\{x\text{Ca} + (1-x)\text{P}\}$ phase diagram for $x > 0.6$.

The results are given in figure 3 which contains also the experimental results⁽¹⁹⁾ used for determination of the model parameters. The coordinates of the eutectic point are $T = 1111.6$ K and $x = 0.9945$. The solubility of the calcium phosphide in liquid calcium constitutes at 1873 K $x = 0.846$ (36.3 mass per cent of Ca_3P_2), the vapour pressure of calcium being 167.6 kPa. The results of the calculation show that pure Ca_3P_2 cannot exist in the liquid state at atmospheric pressure. Its melting is preceded by sublimation to a gaseous mixture of Ca and P_2 . A comparison of the thermodynamic properties of the melt with the composition that corresponded to the stoichiometry Ca_3P_2 with that of the calcium phosphide allowed us to calculate the Gibbs energy of melting of Ca_3P_2 :

$$\Delta_s^1 G_m(\text{Ca}_3\text{P}_2)/(\text{J} \cdot \text{mol}^{-1}) = 22451 - 37.74 \cdot (T/\text{K}) + 3.894 \cdot (T/\text{K}) \cdot \ln(T/\text{K}). \quad (20)$$

(Calcium + phosphorus) melts are characterized by strong interparticle attractions and consequently by great values of the equilibrium constant for reaction (16). Therefore, if the melt contains an excess of calcium as compared with the stoichiometry of Ca_3P_2 then practically all the phosphorus will be bonded in associated complexes. For example, the mole fraction of monomer molecules of phosphorus is $2.5 \cdot 10^{-7}$ at $T = 1663$ K, $x = 0.902$ and $2.3 \cdot 10^{-9}$ at $T = 1363$ K, $x = 0.969$. This fact is rather important for analysis of phosphorus distribution between slag and metallic melts in processes of steel treatment with calcium-containing materials.

REFERENCES

1. Jha, A.; Abraham, K. P. *J. Iron Steel Inst. Jap.* **1989**, 29, 300.
2. Kusakawa, T. *Cast. Res. Lab. Waseda Univ.* **1983**, 34, 45.
3. Avato, T.; Uchida, T.; Omori, Y. *Trans. Iron Steel Inst. Jap.* **1985**, 25, 326.
4. Schüvmann, E.; Jacke, H. *Steel research* **1987**, 58, 406.
5. Masumitsu, N.; Ito, K.; Fruechan, R. J. *Met. Trans.* **1988**, 19B, 643.
6. Han, Q.; Zhang, X.; Chen, D.; Wang, P. *Met. Trans.* **1988**, 19B, 617.
7. Tabuchi, T.; Sano, N. *Met. Trans.* **1984**, 15B, 351.
8. Momokawa, H.; Sano, N. *Met. Trans.* **1982**, 13B, 643.
9. Engell, H. J.; Köhler, M.; Fleischer, H. J.; Thielmann, R.; Schürmann, E. *Stahl und Eisen* **1984**, 104, 443.
10. Nakamura, Y.; Tokumitsu, N.; Harashima, K.; Segawa, K. *Trans. Iron Steel Inst. Jap.* **1976**, 16, 623.
11. Kitamura, K.; Funazaki, M.; Iwanami, Y. *Trans. Iron Steel Inst. Jap.* **1984**, 24, 631.
12. Kawai, Y.; Nakao, R.; Mori, K. *Trans. Iron Steel Inst. Jap.* **1984**, 24, 509.
13. Tokumitsu, N.; Harashima, K.; Nakamura, Y. *Tetsu to Hagane* **1977**, 63, 2172.
14. Katayama, H.; Kajoka, H.; Inatomi, M.; Harashima, K. *Tetsu to Hagane* **1979**, 65, 1167.
15. Nakamura, Y.; Harashima, K.; Ito, M. *Tetsu to Hagane* **1977**, 63, 2287.
16. Kaneko, K.; Sano, N.; Takeuchi, S.; Shiomi, S. *Tetsu to Hagane* **1977**, 63, 2292.
17. Kusagawa, T.; Ohori, M.; Obana, T.; Taki, C.; Hanabusa, K. *Tetsu to Hagane* **1983**, 69, 1982.
18. Kusakawa, T.; Ohori, M.; Kondo, K.; Yoshioka, K. *Tetsu to Hagane* **1982**, 68, 1905.

19. Köhler, M.; Engell, H. J. *Second Int. Symp. on Metallurgical Slags and Fluxes*. 11 to 14 November 1984, at Lake Tahoe, NY. *TMS-AIME*. **1984**, 483.
20. Zhongbo, H. *Taiyangneng Xuebao* **1988**, 9, 80.
21. Min, D. J.; Sano, N. *Met. Trans.* **1988**, 19B, 433.
22. Ghosh, P. C.; Hess, E. G. *Science and Culture* **1962**, 28, 386.
23. Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry*. Pergamon Press: Oxford. **1979**. 449 pp.
24. Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*. Am. Soc. Met.: Metals Park, Ohio. **1973**.
25. Zaitsev, A. I.; Korolyov, N. V.; Mugotnov, B. M. *Teplofiz, Vys. Temper.* **1989**, 27, 465.
26. Sidorov, L. N.; Korobov, M. V.; Zhuravleve, L. N. *Mass-spektralnye termodinamicheskie issledovaniya*. Moscow University Press: Moscow. **1985**. 209 pp.
27. Mann, J. B. *Proc. Intern. Conf. Mass Spectroscopy*. T. Ogata; T. Hayakawa: Editors. Univ. Park Press: Tokyo. **1970**, p. 814.
28. Karakaya, J.; Tompson, W. T. *Bull. Alloys Phase Diagrams* **1988**, 9, 232.
29. Okamoto, H.; Massaiski, T. B. *Bull. Alloy Phase Diagrams* **1984**, 5, 490.
30. Barin, J.; Knacke, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances*. (Supplement). Springer-Verlag: Berlin. **1977**.
31. Fischbach, H. J. *Less Common Metals* **1985**, 108, 151.
32. Yamamoto, M.; Yamada, K.; Meshkov, L. L.; Kato, E. *Tetsu to Hagane* **1980**, 66, 2032.
33. Ban-ya, S.; Suzuki, M. *Tetsu to Hagane* **1975**, 61, 2933.
34. Schürmann, E.; Kaiser, H. P.; Hensgen, U. *Arch. Eisenhüttenwes.* **1981**, 52, 51.
35. Schenck, H. *Arch. Eisenhüttenwes.* **1966**, 37, 775.
36. Sigworth, G. K.; Elliott, J. F. *Metal Science* **1974**, 8, 298.
37. Jordan, A. S. *Met. Trs.* **1970**, 1, 239.
38. Sommer, F. *Z. Metallk.* **1982**, 73, 72.
39. Kellog, H. H. *Physical Chemistry in Metallurgy*. Fischer, R. M.; Oriani, R. A.; Turkdogan, E. T.: Editors. p. 49. U.S. Steel Research Lab.: Monroeville, PA. **1976**.
40. Sommer, F. *Z. Metallk.* **1982**, 73, 77.
41. Zaitsev, A. I.; Korolyov, N. V.; Mogutnov, B. M. *J. Chem. Thermodynamics* **1990**, 22, 513.
42. Krylov, A. S.; Katznelson, A. M.; Kashin, B. M. *Vzaimodeistviye Metallicheskih Rasplavov s Gazami i Shlakami*. Nauka Press: Moscow. **1986**, 57.
43. Zaitsev, A. I.; Korolyov, N. V.; Mogutnov, B. M. *High. Temp. Sci.* **1989**, 26.