

THERMODYNAMIC PROPERTIES OF CALCIUM AND BARIUM PHOSPHIDES

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The thermodynamic properties of calcium and barium phosphides have been determined in the temperature range 1178–1537 K by a Knudsen effusion technique combined with mass-spectral analysis of the evaporation products.

The specific heats of calcium and barium phosphides in the temperature range 118–863 K have been measured by means of a Mettler differential scanning calorimeter, TA-4000.

The thermodynamic functions obtained in the present work can be recommended for thermodynamic calculations for the compounds studied in the present work.

Keywords: calcium and barium phosphides, specific heat

Introduction

In order to obtain ferroalloys and alloyed steels of high quality it is necessary to reduce the phosphorus content to 0.005%. This problem cannot be solved by means of oxidizing dephosphorization because of the oxidation and loss of expensive alloying elements, having higher affinity for oxygen than iron. A treatment of metallic melts with fluxes and alloys containing alkaline earth elements was found to be promising. By this treatment the concentrations of nonmetallic and some harmful metallic impurities are considerably reduced. However, the interaction between alkaline earth metals and phosphorus has not been studied yet, and the thermodynamic functions of the formation of calcium and barium phosphides – key compounds in the processes of reducing dephosphorization – have not been determined with the required precision.

Experimental

In the present work the thermodynamic properties of calcium and barium phosphides have been determined in the temperature range 1178–1537 K by a Knudsen effusion technique combined with mass-spectral analysis of the evaporation products.

The specific heats of calcium and barium phosphides in the temperature range 118–863 K have been measured too by means of a Mettler Differential Scanning Calorimeter TA-4000.

The preparation method, data on the vapour composition and thermodynamic functions of the formation of calcium phosphides, received by means of high-temperature mass-spectral technique have been reported previously [1]. The preparation method for barium phosphide was the same. Measurements and calculations of the vapour pressures of the components over barium-phosphorus alloys were the same as reported in [1]. Strontium fluoride served as a reference substance. The orifice diameter varied from 0.36 to 0.404 mm while the effusion-cell diameter was 6 mm. No influence of the cell material (niobium, molybdenum, tantalum) and of the area of the effusion orifice on the composition of vapour over barium-phosphorus alloys has been detected.

A survey of the experimental results for the specific heats of calcium phosphide is given in Fig. 1. It can be seen that the specific heat vs. temperature function is almost linear at temperatures exceeding 298 K. The calculations performed by the method of least-squares yielded:

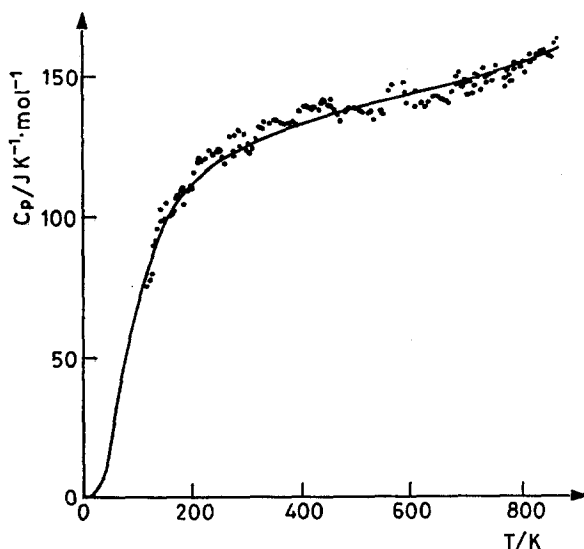


Fig. 1 Temperature dependence of the specific heat of Ca_3P_2 in the temperature range 118 to 863 K. Points — experimental data; line — approximated curve

$$C_p(\pm 3.3) = 115.3 + 0.0458 \cdot T, \text{ J/mol}\cdot\text{K} \quad (1)$$

In order to calculate the absolute entropy of calcium phosphide, the temperature dependence of the specific heat has been extrapolated to 0 K with the help of the method suggested in [2]. According to that method specific heats from 0 K up to the melting point can be described by an empirical equation:

$$C_p = K \cdot C_v(\theta/T) \cdot \exp(T/T_x) \quad (2)$$

where

$C_v(\theta/T)$ – specific heat of a substance in Debye approximation at $V = \text{const}$;

K – an empirical coefficient;

T_x – some temperature, characteristic of the substance and connected with its melting temperature.

In order to find the values of the three parameters θ , K and T_x an optimization procedure has been applied to the experimental data. It consists in a search for the minimum of sum of squares of the deviations of the experimental points from the smooth curve. The procedure has been carried out with all the experimental values of the specific heats of calcium phosphide from 118 to 863 K and allowed to get the following parameters for Eq. (2): $K = 1$, $\theta = 360$ K, $T_x = 3800$ K.

According to the conclusions of [1] calcium phosphide cannot exist in the liquid state at atmospheric pressure. Its melting is preceded by sublimation to a gaseous mixture of the components. The stability parameter of calcium phosphide [1] that corresponds to the Gibbs energy of melting allows to estimate the apparent melting temperature of calcium phosphide as equal to approximately 4500 K. This temperature exceeds the value of T_x obtained by a factor one and a half. The above mentioned parameters yield the following value for the absolute entropy of calcium phosphide at 298.15 K:

$$S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 153.36 \text{ J/mol}\cdot\text{K}.$$

As it can be seen from Fig. 1, the temperature dependence of the specific heats at temperatures above 400 K has an undulatory shape.

At the present time it is impossible to decide whether it is caused by some processes taking place in the samples of calcium phosphide at the mentioned temperature, or simply connected with the real precision of the measurements. To test the reliability of the extrapolation of the C_p vs. T function to 0 K we made an estimation of the three parameters of Eq. (2) using C_p values for temperatures below 400 K (Fig. 2) instead of the whole file of the specific heat data. As a result the following values have been obtained: $K = 1$, $\theta = 375$ K, $T_x = 3000$ K. The absolute entropy of calcium phosphide at 298.15 K was found to be equal to 150.18 J/mol·K. A comparison of the parameters of Eq. (2) and values $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_5)$, acquired in both computations shows that they agree. Therefore

the characteristic shape of the C_p vs. temperature function at $T > 400$ K, seems to be caused by the statistical scatter of the experimental results.

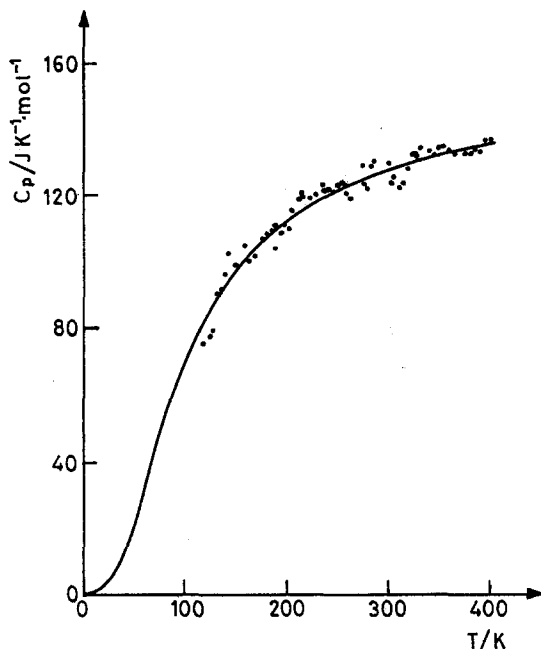


Fig. 2 Temperature dependence of the specific heat of Ca_3P_2 in the temperature range 118 to 400 K. Points — experimental data; line — approximated curve.

In [1] the Gibbs energy of the formation of calcium phosphide from liquid calcium and gaseous P_2 has been expressed by equation:

$$\Delta G_f(\text{Ca}_3\text{P}_2) = -730365 + 221.54 \cdot T - 0.014492 \cdot T^2 + 2.398 \cdot T \cdot \ln T - 208000/T, \text{ J/mol} \quad (3)$$

In accordance with this the formation entropy of calcium phosphide at 1409 K – the middle point of the temperature range investigated in [1] – is equal to $\Delta S_f = -200.59 \text{ J/mol}\cdot\text{K}$. This value, as well as data of the IVTANTERMO bank [3] yields for the absolute entropy of Ca_3P_2 at 1409 K the value: $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 369.13 \text{ J/mol}\cdot\text{K}$. Recalculation to the standard temperature 298.15 K carried out with the help of both Eq. (1) and Eq. (2) with the parameters found for the whole file of C_p data has given almost the same results: $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$, equal to 139.2 and 139.3 J/mol·K, respectively. The latter fact confirms once more that there is no anomaly in the temperature dependence of the

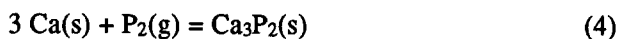
specific heats above 298.15 K, the undulatory shape of the curve being conditioned by the statistical scatter of experimental results.

In order to compare the values of $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$ calculated in different ways, errors of their determination should be estimated. The error of the values received from high-temperature experiments was obtained by taking into account the uncertainties of C_p measurements and extrapolation from 863 to 1409 K, the uncertainty of the determination of the formation entropy of calcium phosphide in [1] and the accuracy of the IVTANTERMO bank values [3]. It was found to reach 12–13 J/mol·K. It is more difficult to evaluate the error of the value $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$ obtained from low-temperature C_p measurements, because it depends not only on the scatter of C_p data, but on the choice of extrapolation formulae too. It is necessary to point out that the values of the specific heats of calcium phosphide below the point of inflection of the C_p vs. temperature curve have not been obtained in the present work. The uncertainty of the value of $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$ caused by all the factors mentioned can be estimated as equal to $\pm(15\text{--}17)$ J/mol·K. It means that the values of $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$ found in different ways are in a fair agreement with each other. The agreement indicates that there are no systematic errors in the high-temperature Knudsen effusion technique experiments and C_p -measurements in the whole temperature range. It also confirms the reliability of the thermodynamic data acquired.

In [4] the entropy of calcium phosphide formation from liquid calcium and gaseous phosphorus, equal to -144.01 J/mol·K, has been obtained while investigating the equilibria between calcium phosphides and liquid silver in the temperature range 1273–1573 K. Recalculation of this value to the standard temperature with the help of the present C_p data allowed us to obtain the value $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 195.24$ J/mol·K which is in an evident disagreement with the results discussed.

This fact may be explained by an incorrect choice of thermodynamic parameters for the reaction of dissolution of phosphorus in silver made by the authors [4]. If we use for this reaction the thermodynamic data referred to in [1] we can find $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 147.2$ J/mol·K which agrees well with the results of the present work.

Authors of [5] recommended for the reaction:



the following expression for the Gibbs energy change (J/mol):

$$\Delta G_f = -597475 + 94.14 \cdot T \quad (298 \leq T \leq 1123), \quad (5)$$

which is based on a theoretical evaluation.

Combined with data from the IVTANTERMO bank [3] it gives $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 248.67 \text{ J/mol} \cdot \text{K}$, that is almost twice as high as the present value.

The authors of reference-book [6] and monograph [7] recommend for the Gibbs energy of the reaction [4] the equation (J/mol) found in a theoretical way too:

$$\Delta G_f = 648520 + 216.31 \cdot T \quad (298 \leq T \leq 1112) \quad (6)$$

The calculation based on Eq. (6) produces $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2) = 126.5 \text{ J/mol} \cdot \text{K}$, which is lower than our value. Evidently, theoretical evaluations do not give satisfactory approximations of the thermodynamic functions of calcium phosphide. The results of all the experimental determinations coincide with each other and allow to recommend for $S_{298.15}^{\circ}(\text{Ca}_3\text{P}_2)$ the value $145 \pm 6 \text{ J/mol} \cdot \text{K}$.

Ba-P alloys with compositions corresponding both to the stoichiometry of barium phosphide and to the two-phase field $\text{BaP} + \text{Ba}_3\text{P}_2$ have been prepared for study by the Knudsen effusion technique combined with a mass-spectral analysis of the evaporation products. Barium and phosphorus were found to predominate in gaseous phase over the alloys within the investigated temperature range. Hence the evaporation of the Ba-P alloys is followed by their decomposition into the components. In contrast with calcium phosphide the decomposition of barium phosphide during evaporation is not congruent. The concentration of barium atoms is considerably higher than that of phosphorus particles. This is caused by a

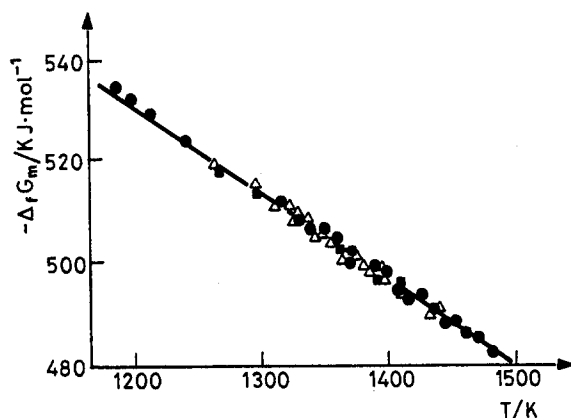


Fig. 3 Temperature dependence of the Gibbs energy of Ba_3P_2 formation from $\text{Ba}(1)$ and P_2 (g): ■ -homogeneous sample of Ba_3P_2 the effusion-orifice diameter is equal to $3.60 \cdot 10^{-4} \text{ m}$; Δ -homogeneous sample of Ba_3P_2 , the effusion-orifice diameter is equal to $3.97 \cdot 10^{-4} \text{ m}$; ● -sample of Ba_3P_2 with composition belonging to the two-phase equilibrium field $\text{Ba}_3\text{P}_2 + \text{BaP}(X_{\text{Ba}} = 0.55)$, the effusion-orifice diameter is equal to $4.04 \cdot 10^{-4} \text{ m}$

sufficiently higher relative stability of the BaP compound as compared with CaP in the Ca-P system.

The thermodynamic functions of barium phosphide formation have been calculated from measured vapour pressures of barium and phosphorus in respect to liquid barium and gaseous phosphorus chosen as standard states for the components. The values of vapour pressures over liquid barium have been taken from the IVTANTERMO bank [3]. The values of Gibbs energies of barium phosphide formation are presented in Fig. 3. They were approximated by the linear function $\Delta G_f = \Delta H_f - T\Delta S_f$, with the help of the method of least-squares. The calculations have resulted in the equation:

$$\Delta G_f = -(736700 \pm 3000) + (171.4 \pm 2.2) \cdot T \quad (1178 \leq T \leq 1483 \text{ K}), \text{ J/mol} \quad (7)$$

As it can be seen from Fig. 3, a good agreement was observed between the values of $\Delta G_f(\text{Ba}_3\text{P}_2)$, obtained both for homogeneous samples of barium phosphide and for the two-phase sample.

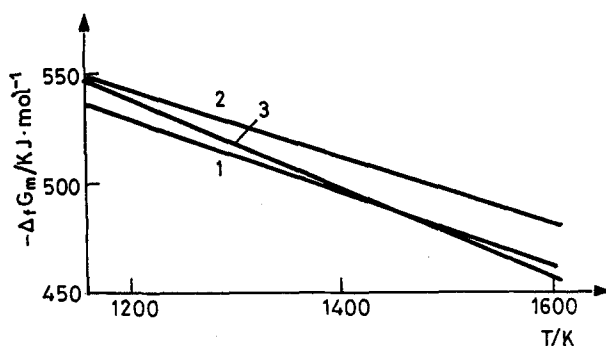
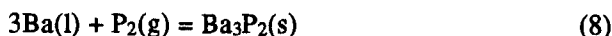


Fig. 4 Temperature dependences of the Gibbs energy of Ba_3P_2 formation from Ba(1) and $\text{P}_2(\text{g})$: 1-according to the present results; 2-data of [8]; 3-experimental results of [8] with the correction of the Gibbs energy of phosphorus dissolution in liquid silver

In Fig. 4 our results are compared with literature data on the thermodynamic functions of barium phosphide formation. It can be seen that the $\Delta G_f(\text{Ba}_3\text{P}_2)$ values found in the present work are somewhat lower (in absolute value) than that obtained in [8]. In order to determine the Gibbs energy of the reaction:



the authors of [8] studied an equilibrium between silver and solid barium phosphide by means of a technique reported in [5]. The equilibrium constants of the reaction:



have been determined directly. From these results the following expression for the Gibbs energy of reaction (9) has been received:

$$\Delta G_f = -691000 + 99.1 \cdot T, \text{ J/mol} \quad (10)$$

Gibbs energies for reaction (8) have been calculated from Eq. (10) with the help of data for the thermodynamic functions of solutions of barium and phosphorus in liquid silver. For the Gibbs energy of the reaction:



the authors of [8] used the expression reported in [5]. As a result for the temperature function of Gibbs energy of reaction (8) they have found:

$$\Delta G_f = -732000 + 156.1 \cdot T, \text{ J/mol} \quad (12)$$

Another expression for reaction (8) was shown to be more appropriate [1]. Taking into account the suggestions in [1] we can rewrite equation (12) in the form (line 3 in Fig. 4):

$$\Delta G_f = -785700 + 204.9 \cdot T, \text{ J/mol.} \quad (13)$$

which is in a better agreement with the present results for Gibbs energies, but strongly differs in slope from (11).

To decide which set of data is more correct and to determine thermodynamic functions for barium phosphide at lower temperatures, specific heat measurements have been carried out in the temperature range 113–763 K. The experimental results are plotted in Fig. 5. The method of extrapolation of the heat capacity function for barium phosphide to 0 K was the same as for calcium phosphide. Calculations based on the whole file of C_p data for barium phosphide yielded the following values for the parameters of Eq. (2): $K = 1$, $\theta = 230$ K, $T_x = 1700$ K. They lead to the absolute entropy of barium phosphide at 298.15 K: $S_{298.15}^0(\text{Ba}_3\text{P}_2)$ equal to 217.5 J/mol · K.

The temperature dependence of $C_p(\text{Ba}_3\text{P}_2)$ is practically linear above 298 K. A treatment of the experimental results by the method of least-squares has yielded the expression:

$$C_p(\text{Ba}_3\text{P}_2) = (122.5 \pm 3.4) + (0.0882 \pm 0.0062) \cdot T \quad (14)$$

Equation (7) and the heat capacities of barium phosphide extrapolated in accordance with (14) to 1330.5 K— the middle point of the mass-spectral measurements—resulted in $S_{298.15}^0(\text{Ba}_3\text{P}_2) = 210$ J/mol · K. The uncertainty of the latter was estimated to be 13–14 J/mol · K. The error in the absolute entropy connected with the extrapolation of the C_p function to 0 K is equal to 17–20 J/mol · K.

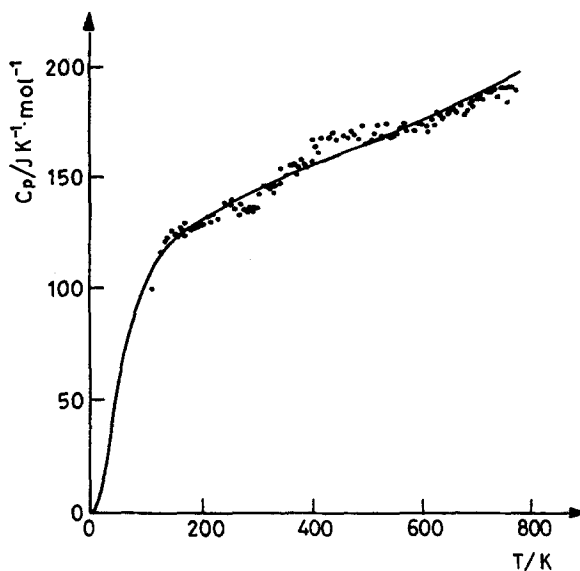
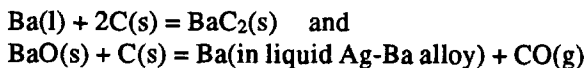


Fig. 5 Temperature dependence of the specific heat of Ba_3P_2 . Points—experimental data; line—approximated curve

Therefore the values of the absolute entropy computed in different ways are in agreement within the range of experimental errors. This allows us to recommend for $S_{298.15}^{\circ}(\text{Ba}_3\text{P}_2)$ a mean value $214.0 \pm 10.0 \text{ J/mol}\cdot\text{K}$. The absolute entropy of barium phosphide, obtained from the present C_p values and the results of [8] (Eq. (12)), was found to be equal to $223.6 \text{ J/mol}\cdot\text{K}$. It agrees within experimental errors with that obtained from the low-temperature specific heats. Equation (13) leads to $S_{298.15}^{\circ}(\text{Ba}_3\text{P}_2) = 174.8 \text{ J/mol}\cdot\text{K}$ which is much lower than the former values. Hence, the entropy term in equation (12) is much closer to the mean value of $S_{298.15}^{\circ}(\text{Ba}_3\text{P}_2)$ than the corresponding term in Eq. (13).

It should be emphasized that the entropy of formation of barium phosphide from solid barium and red phosphorus, calculated according to Eq. (12) for 1358 K — the middle of the temperature range investigated in [8] — gives a value $8.3 \text{ J/mol}\cdot\text{K}$ which exceeds the ideal configurational entropy of mixing by a factor of two. It is hardly probable for compounds with such high (in absolute value) formation enthalpies, as in case of the barium phosphide -736 kJ/mol .

The inaccuracy of the results in [8] can be explained by an uncertainty of the thermodynamic functions for the reactions:



applied in the calculations, carried out in the work.

This assumption permits to prefer the thermodynamic functions of barium phosphide obtained in the present work.

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Zusammenfassung — Mit Hilfe der Knudsen Effusionstechnik in Verbindungen mit MS-Analyse der Verdampfungsprodukte wurden im Temperaturbereich 1178-1537 K die thermodynamischen Eigenschaften von Calcium- und Bariumphosphiden bestimmt.

Die spezifische Wärme von Calcium- und Bariumphosphiden wurde im Temperaturbereich 118-863 K mittels eines Mettler-Differential-Scanningkalorimeters vom Typ TA-4000 bestimmt.

Die erhaltenen thermodynamischen Funktionen können für thermodynamische Berechnungen der hier untersuchten Verbindungen verwendet werden.