# Chemistry

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1965

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## Abstract

## Full Text

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# INVESTIGATION OF THE PROCESS OF THERMAL DISSOCIATION OF CALCIUM PHOSPHATE IN A MIXTURE WITH SILICA

The question of the conditions and efficiency of the thermal dissociation of calcium phosphate in a mixture with silica, despite several laboratory studies, has remained unclear up to the present time. Meanwhile, its solution may be of great importance, since it would make it possible, directly—bypassing the stage of reduction and oxidation of phosphorus—to obtain phosphoric anhydride, which can readily be processed into phosphoric acid and highly concentrated fertilizers. In this case the need to use a reducing agent—coke—is eliminated, and, possibly, a saving of electric power is achieved in comparison with the existing process of reduction and sublimation of phosphorus in electric furnaces.

Studies of the direct dissociation of pure tricalcium phosphate according to the equation

$$Ca_3(PO_4)_2 = 3CaO + {}^1/_2 P_4O_{10} \tag{I}$$

at temperatures attainable in ordinary electric furnaces established the impracticability of such a process ([1,2]). The literature also contains information on studies of the decomposition reaction of tricalcium phosphate in the presence of silica:

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + {}^1/_2 P_4O_{10} \tag{II}$$

Some authors ([1–4]) came to the conclusion that the process according to reaction (II) cannot be carried out in an air medium, nor in a stream of inert gas. In other studies ([5–7]), however, the possibility of dissociation of tricalcium phosphate in a mixture with silica is indicated, and data are given on the yield of $P_2O_5$. Yet none of these works contains information on trapping and investigating the gaseous phase, i.e., the reaction product. The insufficiency and contradictory nature of the results of the cited works necessitate a detailed study of reaction (II) in order to clarify the possibility of its technical implementation.

In order to determine the equilibrium vapor pressure of $P_4O_{10}$ in the temperature interval 1800-3000° K, thermodynamic calculations were carried out for reactions (I) and (II), as well as calculations of possible reactions:

Fig. 1. Values of the isobaric-isothermal potential for reactions I–VI

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$$\mathrm{Ca_4P_2O_9 = 4CaO + {}^1\!/_2P_4O_{10}}, \tag{III}$$

$$\mathrm{Ca_3P_2O_8 + Ca_4P_2O_9 + 7SiO_2 = 7CaSiO_3 + P_4O_{10}}, \tag{IV}$$

$$\mathrm{Ca_4P_2O_9 + 4SiO_2 = 4CaSiO_3 + {}^1\!/_2P_4O_{10}}, \tag{V}$$

$$\mathrm{{}^1\!/_3Ca_{10}(PO_4)_6(OH)_2 + {}^{10}\!/_3SiO_2 = {}^{10}\!/_3CaSiO_3 + {}^1\!/_2P_4O_{10} + {}^1\!/_3H_2O}. \tag{VI}$$

The thermodynamic calculations available in the literature for the dissociation reaction of $\mathrm{Ca_3P_2O_8}$ were made either according to the approximate Nernst equation, which, because of its considerable inaccuracy, is no longer used at present, or in the first approximation.

Apparently, this is explained by the absence of certain initial thermodynamic data, mainly for $P_4O_{10\mathrm{(gas)}}$, which appeared in print at a later time. In addition, the value of the heat of formation of $SiO_2$ has undergone a change and, according to new data, is 217.7 kcal/mole ($^8$).

We determined the change in the isobaric-isothermal potential of the reactions as a function of temperature from the Temkin and Shvartsman equation:

$$\Delta Z_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T(\Delta a M_0 + \Delta b M_1 + \Delta C M_2).$$

The obtained values of $\Delta Z_T^0$ and $\lg K_p$ are presented in Figs. 1 and 2. For reaction (IV), the value of $\Delta Z_T^0$ was divided in half in order to compare these data with the other reactions.

**Fig. 1.** Values of the isobaric-isothermal potential for reactions $I$—$VI$

It should be noted that, because it is impossible to take into account the formation of solid solutions, the obtained values of the isobaric potential are overstated. The magnitude of this overstatement can be judged from the example of reaction (II), for which we experimentally determined the dissociation pressure at a temperature of 1700°$K$ by the effusion method on the apparatus of the Department of Radiochemistry of Moscow State University ($^9$). The values of the equilibrium pressure of $P_{P_4O_{10}}$ vapors obtained experimentally and by calculation are, respectively, $7.7 \cdot 10^{-7}$ and $4 \cdot 10^{-8}$ atm.

Fig. 2. Equilibrium constants for reactions I-IV

Figure 2: Fig. 2. Equilibrium constants for reactions I-IV

Figure 3

Figure 3: Figure 3

**Fig. 2.** Equilibrium constants for reactions $I$—$IV$

As thermodynamic calculation shows, the vapor pressure of $P_{P_4O_{10}}$ for reaction (II) does not reach atmospheric pressure even at $3000°K$. However, $Ca_3P_2O_8$ can be completely decomposed in vacuum, of the order of 0.15 mm Hg, and at a temperature of $1750°C$, i.e., under conditions accessible with modern technology.

The value of the isobaric potential of reaction (IV), the decomposition of defluorinated natural phosphate (apatite concentrate), consisting of a mixture of tri- and tetracalcium phosphate ([10]), is significantly lower under the same conditions. This can be explained by the presence of tetracalcium phosphate, which is completely decomposed by reaction (V) at atmospheric pressure already at a temperature of about $1800°C$. The calculated values of the dissociation pressures of hydroxylapatite according to reaction (VI) also indicate the real possibility of its decomposition in a mixture with silica under conditions analogous to those for reactions (II) and (IV).

In the experimental setup we studied the dependence of the yield of $P_4O_{10}$ on temperature at a vacuum of $1 \cdot 10^{-3}$ mm Hg over the course of 1 hour for mixtures of different composition.

The experiments were carried out in an improved TGV-1 vacuum electric furnace with a tungsten heater. The vacuum in the system was provided by an RVN-20 fore-vacuum pump and two TsVL-100 and N-5 oil diffusion pumps connected in series. The reaction products were captured by condensing them in a water-cooled quartz trap, which was located directly above the reaction zone. The temperature up to 1600° was measured using a Pt—PtRh thermocouple, and above 1600° using a tungsten-rhenium thermocouple VR 5/20. Boats for the initial mixture were made from sheet molybdenum 0.2 mm thick.

**Fig. 3. Effect of the $SiO_2$ content in the charge on the yield of $P_2O_5$.** 1 –36.73% $SiO_2$; 2 –27.55% $SiO_2$; 3 –18.36% $SiO_2$; 4 –9.18% $SiO_2$; 5 –3.67% $SiO_2$.

Defluorinated phosphate containing 40% $P_2O_5$ and pure quartz containing 100% $SiO_2$ were used as starting materials.

Defluorinated phosphate is currently produced in the USSR on a large industrial scale by the hydrothermal method—by treating apatite concentrate with water vapor at 1400-1500°C [10]. Both components were ground until particles smaller than 0.07 mm were obtained. A thoroughly mixed charge of calcium phosphate and silica in a molybdenum boat was placed in the vacuum electric furnace. Before the heater was switched on, the required vacuum was created in the furnace. The degree of distillation of $P_2O_5$ was judged from the amount of condensed product in the quartz trap. For control, the solid residue was analyzed for $P_2O_5$ and compared with the $P_2O_5$ content in the initial mixture.

The results of the experiments are presented in Fig. 3. As can be seen from the graph, the increase in the yield of $P_2O_5$ with increasing temperature is not the same for mixtures with different $SiO_2$ contents. Maximum $P_2O_5$ yields are obtained for a mixture of stoichiometric composition (according to reaction II), containing 36.75% $SiO_2$, whereas for a mixture containing 5.5% $SiO_2$, the yield in this same temperature range increases only slightly and at 1650°C did not exceed 35%. At temperatures below 1350° the change in the yields of $P_2O_5$ from mixtures of different composition is insignificant. The increase in yield with increasing $SiO_2$ content in the initial mixture is especially noticeable at temperatures of 1550-1650°. With an increase in the percentage of $SiO_2$, the melting temperature of the mixture increased. In our experiments, mixtures containing 10-50% $SiO_2$ melted below 1450°, whereas at contents of 75-100% $SiO_2$, at 1450-1500° a sintered mass was obtained, and melting occurred only at higher temperatures. Accordingly, upon transition to compositions with a higher $SiO_2$ content, the increase in the yield of $P_2O_5$ at low temperatures slowed somewhat.

The experimental results show that at a vacuum of $1 \cdot 10^{-3}$ mm Hg and at temperatures of 1600-1650° practically complete decomposition of tricalcium phosphate is possible only for mixtures containing $SiO_2$ in amounts close to the stoichiometric ratio.

Thus, as a result of laboratory experiments, the possibility has been established of sublimating phosphorus pentoxide from a mixture of defluorinated phosphate and silica to 98-99%. This result is achieved by heating a mixture containing 37% $SiO_2$ at 1550-1650° and a vacuum of $10^{-3}$ mm Hg, with a duration of up to 60 min.

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Received
8 IV 1965

## REFERENCES

1. W. H. Ross, A. L. Mehring, R. M. Jones, Ind. and Eng. Chem., **16**, 563 (1924).
2. A. P. Lyuban, *Metallurg*, No. 2, 54 (1936).

3. Nielsen, *Ferrum*, **10**, No. 4, 97 (1913).
4. N. N. Postnikov, in the collection *Studies in Applied Chemistry*, Publishing House of the USSR Academy of Sciences, 1955.
5. E. W. Guernsey, I. Y. Yee et al., Report No. 65, III, Fixed Nitr. Labor., Washington, 1921.
6. H. H. Franck, H. Füldner, *Zs. anorg. u. allgem. Chem.*, **204**, 97 (1932).
7. E. E. Babkin, K. I. Zagvozdkin, Yu. M. Rabinovich, *Scientific Notes of the Institute of Fertilizers*, **143**, 134 (1938).
8. S. S. Wise et al., *J. Phys. Chem.*, **66**, 381 (1962).
9. Yu. A. Priselkov, Yu. A. Sapozhnikov, A. V. Tseplyaeva, *Proceedings of the USSR Academy of Sciences, Department of Technical Sciences, Metallurgy and Fuel*, No. 1, 106 (1959).
10. S. I. Volfkovich et al., *Hydrothermal Processing of Phosphates into Fertilizers and Feed Materials*, Moscow, 1964.

*Note: Figure translations are in progress. See original paper for figures.*