# Reports of the Academy of Sciences of the USSR

I. Yu. Kozhevnikov, O. V. Travin, and E. N. Yarkho

1958

SovietRxiv

## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR
1958. Volume 122, No. 4

## PHYSICAL CHEMISTRY

I. Yu. Kozhevnikov, O. V. Travin, and E. N. Yarkho

# THE EFFECT OF $CaF_2$ ON THE DISTRIBUTION OF PHOSPHORUS BETWEEN LIQUID IRON AND FERROUS-LIME SLAGS

*(Presented by Academician G. V. Kurdyumov on 24 V 1958)*

From the practice of steelmaking it is known that the introduction of fluorite into slag promotes the formation of homogeneous slags, increases their fluidity and, consequently, accelerates the course of physicochemical processes in the metal–slag system, including the dephosphorization process. However, there are contradictory opinions on the question of the effect of $CaF_2$ on the distribution of phosphorus.

Thus, Winkler and Chipman ($^1$) consider calcium fluoride to be a simple slag diluent that has no appreciable effect on the equilibrium of phosphorus distribution. On the contrary, Gerasimenko and Speight ($^2$), proceeding from concepts of the complete ionization of compounds and oxides in liquid slags, on the basis of the data of work ($^1$) came to the conclusion that the introduction of $CaF_2$ significantly changes the value of the equilibrium constant of the phosphorus reaction. To explain this, the authors were forced to assume the formation in liquid slags of complex anions consisting of $F^-$ and $PO_4{}^{3-}$. As Flood and Grjotheim ($^3$) subsequently showed, this is not observed if, in calculating the ionic fractions of cations and anions, one uses the definition of the physical model of any ionic solution as two independent solutions of anions and cations inserted into one another ($^4$).

The purpose of the present work was to study the effect of additions of $CaF_2$ on the distribution of phosphorus between liquid iron and ferrous-lime slags.

Calcium fluoride gives, in the oxide melt, a singly charged anion $F^-$ ($R_F = 1.33$ Å), whose radius differs little from the radius of the oxygen ion ($R_{O^{2-}} = 1.32$ Å). Thus, in slags of the system $CaO-FeO-CaF_2$ there are two simple anions of the same size but different charge. Therefore the effect of $F^-$ on the distribution of phosphorus is fundamentally different from the effect of complex anions $SiO_4{}^{4-}$, $PO_4{}^{3-}$, and $AlO_2{}^-$.

In the present investigation the method of successive saturation was employed (5,6), the idea of which consists in saturating iron at constant temperature with radioactive phosphorus $P^{32}$, introduced beforehand into the slag. The method of successive saturation makes it possible: 1) to create isothermal conditions for the metal–slag system; 2) to fix the state of equilibrium reliably; 3) to determine the temperature dependence of the phosphorus distribution coefficient $L_P$ for a slag of constant composition. It can be shown that under these conditions

$$\frac{d \ln L_P}{dT} = \frac{\Delta H}{RT^2} = \frac{\Delta H^0 - \Sigma \Delta H_{\mathrm{cm}}}{RT^2}, \tag{1}$$

where $\Delta H$ is the heat effect of the transfer of phosphorus from liquid iron into slag of the given composition; $\Delta H^0$ is the heat effect under standard conditions (between pure substances), $\Sigma \Delta H_{\mathrm{cm}}$ is the sum of the heats of mixing of phosphorus with the metallic and FeO, $P_2O_5$ slag melts.

Integration of equation (1) gives

$$\lg L_{\mathrm{P}} = \lg \frac{I_{\mathrm{sh}}}{I_{\mathrm{m}}} = -\frac{\Delta H}{4.575T} + B, \tag{2}$$

where $I_{\mathrm{sh}}$ and $I_{\mathrm{m}}$ are the counting rates of slag and metal samples at equilibrium (imp/min); $B$ is the entropy term, numerically equal to the change in the entropy of the reaction when phosphorus passes from a 1% solution of phosphorus in the metal to a 1% solution in the slag. Consequently, $B = -\Delta S^0/4.575$.

The change in the quantities $\Delta H$ and $\Delta S^0$ depends only on the composition of the slag, since solutions of phosphorus in iron at concentrations up to 1% obey Henry’ s law (7,8). This makes it possible to compare the data for the system $CaO$–$FeO$–$CaF_2$ with the obtained values of the thermodynamic functions of the reaction of iron dephosphorization by ferrous-lime slags (6), and in this way to determine, in pure form, the influence of $CaF_2$.

**Table**

| Slag code | CaO | FeO | $Fe_2O_3$ | $CaF_2$ | $P_2O_5$ | MgO | $SiO_2$ |
|---|---|---|---|---|---|---|---|
| | Slag composition, wt.% | | | | | | |
| A | 28.0 | 41.02 | 21.97 | 6.00 | 0.030 | – | – |
| B | 35.0 | 34.80 | 20.71 | 9.26 | 0.040 | – | 0.10 |

The temperature dependence of $\lg L_{\mathrm{P}}$ for the slags investigated (see Table 1) is shown in Fig. 1. The experimental points fit satisfactorily on straight lines described by the equations

$$\text{for slag A} \qquad \lg L_{\mathrm{P}} = \frac{20900}{T} - 9.40. \tag{3}$$

$$\text{for slag B} \qquad \lg L_{\mathrm{P}} = \frac{21300}{T} - 9.25; \tag{4}$$

From these equations, and also from the equation

$$\lg L_{\mathrm{P}} = \frac{14000}{T} - 6.41 + 2.5N_{\mathrm{CaO}}, \tag{5}$$

which describes the distribution of phosphorus between liquid iron and slags of the CaO–FeO system ([6]), it is possible to determine the effect of partial replacement of CaO by $CaF_2$. The results of such a comparison for 1600° are presented

**Fig. 1**

**Fig. 2**

Fig. 1. Dependence of $\lg L_{\mathrm{P}}$ on the reciprocal temperature for slags of the CaO –FeO–$CaF_2$ system. $A$–6.0% $CaF_2$; $B$–9.26% $CaF_2$.

Fig. 2. Effect of partial replacement of CaO by fluorite in slags of the CaO–FeO –$CaF_2$ system on the value of the phosphorus distribution coefficient ($t = 1600°$). 1–$N_{\mathrm{CaO}} + N_{\mathrm{CaF_2}} = 0.534$; 2–$N_{\mathrm{CaO}} + N_{\mathrm{CaF_2}} = 0.452$.

in Fig. 2, from which it is evident that the introduction of $CaF_2$ in place of CaO leads to a decrease in the phosphorus distribution coefficients. To explain this fact

it is necessary to compare the values of $\Delta H$ and $\Delta S^0$ for the transfer of phosphorus from iron into slags of the systems CaO–FeO, CaO–FeO–$P_2O_5$, and CaO–FeO–$CaF_2$.

At low phosphorus concentrations, the reaction between iron and ferrous-lime slags proceeds as follows ([6,9])

$$2[\mathrm{P}] + 5(\mathrm{FeO}) + 3(\mathrm{CaO}) \rightleftharpoons 2(\mathrm{PO}_4^{3-}) + 3(\mathrm{Ca}^{2+}) + 5[\mathrm{Fe}]\,,$$
$$\Delta H_6 = -128000 \text{ cal.}, \tag{6}$$

the product of which is the phosphate ion. With an increase in the concentration of $P_2O_5$ in the ferrous-lime slag above 3%, a homogeneous reaction of calcium phosphate formation takes place

$$2(\mathrm{PO}_4^{3-}) + 3(\mathrm{Ca}^{2+}) \rightleftharpoons (\mathrm{Ca}_3(\mathrm{PO}_4)_2), \qquad \Delta H_7 = -56000 \text{ cal.} \tag{7}$$

or the overall reaction proceeding between iron and slags of the system CaO—FeO—$P_2O_5$

$$2[\mathrm{P}] + 5(\mathrm{FeO}) + 3(\mathrm{CaO}) \rightleftharpoons (\mathrm{Ca_3(PO_4)_2}), \qquad \Delta H_8 = -184000 \text{ cal.} \tag{8}$$

The entropy change in this reaction is equal to −37.5 cal/deg • g-atom. Comparing $\Delta H_8$ and $\Delta S_8^0$ with the values of the change in heat effect and entropy for the transfer of phosphorus from iron into slags of the system CaO—FeO—$CaF_2$ (Fig. 3), equal to −96000 cal/g-atom and −42.5 cal/deg • g-atom, we see that they are very close to one another. Thus, the introduction of $CaF_2$ into ferrous-lime slags leads to a decrease in $L_P$ owing to a sharp decrease in the value of $\Delta S^0$, i.e., strong associations of ions (cations and anions) are formed in the melt. The coincidence of the values of $\Delta H_8$ and of the heat effect of the phosphorus reaction in the case considered (calculated per 1 g-atom) makes it possible to assume the occurrence of reaction (8), proceeding with the formation of calcium phosphate.

In other words, the introduction of $CaF_3$ into the slag promotes the occurrence of reaction (7) at very low concentrations of $P_2O_5$ in the slag, i.e., stabilizes calcium phosphate. This is due to the fact that the presence of the electrostatically weak fluorine ion decreases the polarizability of the $Ca^{2+}$ cation, i.e., strengthens the field of the $Ca^{2+}$ cation in microregions of the slag melt containing $PO_4^{3-}$ anions. This is equivalent to strengthening the interaction of $PO_4^{3-}$ and $Ca^{2+}$ ions in the slag melt, which leads to associations of these ions into stable groupings even at insignificant concentrations of $P_2O_5$. Such groupings of ions in the present case may consist of $Ca^{2+}$, $PO_4^{3-}$, and $F^-$; in structure and composition they may correspond to fluorapatite $Ca_5(PO_4)_2F$—a magmatic mineral present in igneous rocks ([10]). The structure of the fluorapatite molecule is more complex than that of the calcium phosphate molecule. Accordingly, the entropy change upon transfer of phosphorus from iron into slags of the system CaO—FeO—$CaF_2$ is somewhat smaller than $\Delta S_8^0$, while the heat-effect value is greater than $\Delta H_8$.

**Fig. 3.** Effect of additions of $CaF_2$ and $P_2O_5$ to ferrous-lime slags on the values of the heat effect and entropy of the iron dephosphorization reaction

Thus, the introduction of $CaF_2$ into ferrous-lime slags leads to the formation, even at low $P_2O_5$ concentrations, of strong ionic groupings corresponding in composition to the chemical compound—fluorapatite. As was shown ([9]), in CaO—FeO—$P_2O_5$ melts, sta-

active groupings of ions correspond to the molecule of calcium phosphate. In such ionic groupings—molecules found in liquid slags—only the shielding principle operates with respect to the cations, which in the main provide current transfer (11–13). For calcium phosphate, for example, single-cation conductivity has been found (11). For the system CaO—MgO—$Al_2O_3$—$SiO_2$, the transport number of $Ca^{2+}$ is less than unity and decreases with increasing $Al_2O_3$ concentration, since in this case current transfer can be effected by the $Al^{3+}$ cation (12).

The data obtained make it possible to conclude that the theory of real metallurgical slags, when describing their physical model, which is the basis for further quantitative calculations, must proceed from the fact that stable groupings of ions are formed in the oxide melt, corresponding in composition to the formulas of definite chemical compounds. Therefore reactions should be written in "molecular form." This considerably facilitates interpretation of data on the thermodynamics of metallurgical reactions and simplifies calculations of the activities of components in slags. Such a model of liquid slags does not contradict the ionic nature of their structure, confirmed by numerous experimental studies of the electrochemical properties of liquid slags. Chemical compounds (phosphates, silicates), or stable groupings of ions in the slag, can dissociate into cations and complex anions only when the concentration of acidic oxides is considerably reduced. However, for real metallurgical slags such a case is not characteristic. The only exception is fluorspar, whose addition to the slag leads to stabilization of ionic groupings containing $PO_4^{3-}$ at very low concentrations of $P_2O_5$.

Considering that $CaF_2$ sharply lowers the solubility of $P_2O_5$ in citric acid, thereby reducing the value of phosphate slags as fertilizer, its use in processes for converting phosphoric pig iron should be deemed inadvisable. $CaF_2$ may be used only during the period of pure boiling in open-hearth smelting, provided that the process is conducted with complete emptying of the furnace.

Received
24 V 1958

## REFERENCES CITED

1. T. V. Winkler, J. Chipman, *Metals Technol.*, 13 April, Techn. Publ., No. 1987 (1946).

2. P. N. Nerasymenko, G. E. Speight, *J. Iron and Steel Inst.*, 166, p. 4, 289 (1950).

3. G. Futy, K. Grjotheim, *Probl. sovr. metallurg.*, No. 3, 3 (1953).

4. M. I. Temkin, *ZhFKh*, 20, issue 1, 105 (1946).

5. V. F. Surov, O. V. Travin, L. A. Shvartsman, *Probl. metalloved. i fiz. metall.*, collection 4, 616 (1955).

6. I. Yu. Kozhevnikov, L. A. Shvartsman, *DAN*, 113, No. 2, 376 (1957).

7. A. A. Granovskaya, A. P. Lyubimov, *Sborn. tr. Moskovsk. inst. stali*, 32, 79 (1954).

8. D. B. Buki, F. D. Richardson, A. Vel, *Probl. sovr. metallurg.*, No. 3, 18

(1953).

9. I. O. Kozhevnikov, I. S. Kulikov, *Izv. AN SSSR, OTN*, No. 11, 196 (1957).

10. A. G. Betekhtin, *Mineralogiya*, 1950.

11. V. I. Malkin, L. A. Shvartsman, *DAN*, 102, No. 5, 961 (1955).

12. V. I. Malkin, S. F. Khokhlov, *Izv. AN SSSR, OTN*, No. 3, 108 (1958).

13. V. I. Malkin, S. F. Khokhlov, L. A. Shvartsman, *Int. J. Appl. Rad. and Isotopes*, 2, No. 1, 19 (1957).

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

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*