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Assessment of P_2O_5 Activity Coefficients in Molten Slags

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From a critical review of the existing experimental data, the free energy equations are presented. A new estimate is made of the standard free energy of formation of the hypothetical pure liquid P_2O_5, which is used in calculating the P_2O_5 activity coefficients from the experimental data of independent studies of slag–metal reactions. It is found that in low P_2O_5 slags, $\log(\gamma_{P_2O_5})$ is a linear function of CaO from 0 to 60 %, independent of temperature. Whereas, in slags containing $P_2O_5>10$ %, $\log(\gamma_{P_2O_5})$ is a linear function of CaO content>40 % only and increases with an increasing temperature. A novel concept of a slag–P_2O_5 emf sensor is presented for experimental evaluation.

KEY WORDS: Free energies of calcium phosphates and P_2O_5; P_2O_5 activity coefficients in slags; Slag–P_2O_5 sensor; Phosphate capacity of slags; Lime+calcium phosphate saturated slags.

1. Introduction

In metallurgical research publications of several decades, the terminology "…capacity" has been used in lieu of the thermodynamic term the "equilibrium constant" in formulating experimental equilibrium data on slag–gas and slag–metal reactions, *e.g.* sulphide capacity, phosphate capacity, nitride capacity. Because of limited existing data on the activities of reactants in slags, mass concentrations are used in the reaction equilibrium constant, which of course varies with the slag composition. Similarly, the "…capacity" of slag also varies with the slag composition.

Whether reactions with the slag are formulated in terms of compounds, *e.g.* oxides, sulphides, nitrides *etc*., or in ionic species, variation of the equilibrium constant or the "…capacity" with slag composition is a measure of the activity coefficient of the reactant in the slag. However, since no quantitative thermodynamic activity can be assigned to an ion in the slag, variation of the "…capacity" with slag composition will not yield a quantitative thermodynamic property of the slag.

The subject of this paper is to reassess the activity coefficients of P_2O_5 in complex steelmaking slags from available experimental data, which the author[1] compiled previously in terms of the phosphate capacity of slags.

2. Previous Assessment of P_2O_5 Activity Coefficient

In the late 1 940 s, Balajiva *et al.*[2,3] studied the iron–slag phosphorus reaction using a mini electric arc furnace with 600 g iron and 200 g slag. The experimental data were interpreted in terms of the equilibrium relation

$$k_P=\frac{(\%P_2O_5)}{[\%P]^2(\%FeO)^5} \quad \text{.........................(1)}$$

where the total iron oxide is represented as %FeO. In their experiments, MgO-saturated complex slags contained 40 to 60 wt% CaO for which the following empirical relation was derived from the experimental results.

$$\log k_P=11.80\log(\%CaO)-C \quad \text{....................(2)}$$

where C is a constant for a given melt temperature: $C=21.13$, 21.51 and 21.92 for the melt temperatures 1 550, 1 585 and 1 635°C respectively.

In the early 1 950 s, Turkdogan and Pearson[4] made an approximate evaluation of the activity coefficients of P_2O_5 in complex slags using the experimental data of Balajiva *et al.* This approximate evaluation was based on an approximate estimated standard free energy of formation of the hypothetical molten pure P_2O_5 as reproduced below.

$$P_2(g)+\frac{5}{2}O_2(g)=P_2O_5(l) \quad \text{......................(3)}$$

$$\Delta G^\circ_T=-1\,534\,482+506.26T \quad \text{J/mol} \quad \text{............(4)}$$

The known free energy equations for the solution of O_2 and P_2 in liquid iron are:

Reaction	ΔG°_s, J/g-atom
$\frac{1}{2}O_2(g)=[O]$ at 1wt%	$-115\,750-4.63T$.......(5)
$\frac{1}{2}P_2(g)=[P]$ at 1wt%	$-122\,173-19.25T$.....(6)

The above equations give for the estimated equilibrium constant

$$K_P=\frac{\alpha_{P_2O_5}}{[\%P]^2[\%O]^5} \quad \text{...........................(7)}$$

$$\log K_{\mathrm{P}}=\frac{37\,160}{T}-29.67 \quad\text{......................(8)}$$

With this equation and estimated [%O] for %FeO in the slag using compiled α_{FeO} data in Ref. 5), P_2O_5 activity coefficients $\gamma_{\mathrm{P_2O_5}}$ were derived from the data of Balajiva *et al.* The following empirical relation was obtained to describe the variation of $\gamma_{\mathrm{P_2O_5}}$ with melt temperature and slag composition.

$$\log(\gamma_{\mathrm{P_2O_5}})=-1.12(22N_{\mathrm{CaO}}+15N_{\mathrm{MgO}}+13N_{\mathrm{MnO}}+12N_{\mathrm{FeO}}-2N_{\mathrm{SiO_2}})-\frac{42\,000}{T}+23.58 \quad\text{.........(9)}$$

where N's are oxide mol fractions in the slag.

Thirty years later, a study of this subject was revived by Suito *et al.*[6] incorporating their own experimental data on phosphorus distribution between liquid iron and MgO-saturated slags of the system CaO–MgO–FeO–SiO_2. The slags used in these experiments contained CaO<40% for which

$$\log k_{\mathrm{P}}=7.6(\%\mathrm{CaO})-C' \quad\text{......................(10)}$$

differs from Eq. (2) for slags with CaO>40%. This difference suggests that log k_{P} *vs.* %CaO becomes non-linear, with an increasing slope, for CaO contents>about 35%.

Based on the former estimated ΔG°_{T} in Eq. (4), Suito *et al.* derived from their experimental data the following relation, describing the effects of temperature and slag composition on the value of $\gamma_{\mathrm{P_2O_5}}$.

$$\log(\gamma_{\mathrm{P_2O_5}})=-1.01(23N_{\mathrm{CaO}}+17N_{\mathrm{MgO}}+8N_{\mathrm{FeO}})-\frac{26\,300}{T}+11.2 \quad\text{...........................(11)}$$

The temperature effect shown in Eq. (11) is considerably less than that in Eq. (9).

3. Present Assessment of $\gamma_{\mathrm{P_2O_5}}$

In the present evaluation of P_2O_5 activities and activity coefficients in slags, the experimental data chosen as typical examples are for less complex slags as listed in **Table 1**.

The P_2O_5 activities calculated from the experimental data cited above, using Eqs. (7) and (8), are related to the CaO content of the slag in **Fig. 1**. In most of the experimental work of Wrampelmeyer *et al.*, liquid iron contained 5 to 20 ppm P. The analytical uncertainties at these very low phosphorus contents may account for the scatter of their data points in Fig. 1.

In **Fig. 2** the computed activities are related to BO=(%CaO+0.3×%MgO). There is more scatter in the data points in slags with 33 to 45% BO. However, over the entire composition range, in both Figs. 1 and 2, there is no distinct temperature effect on the activity values.

The data in Fig. 2 may be summarised as

$$\log a_{\mathrm{P_2O_5}}=-(14.5\pm0.45)-0.134\times\mathrm{BO} \quad\text{..........(12)}$$

For slags containing 0.2 to 1.0% P_2O_5, *i.e.* $N_{\mathrm{P_2O_5}}$ in the range ~0.001 to 0.004, the activity coefficients would be within the range

$$\log(\gamma_{\mathrm{P_2O_5}})=-(11.85\pm0.75)-0.134\times\mathrm{BO} \quad\text{........(13)}$$

Table 1. Typical examples of experimental data.

Experimental work by	
Suito, Inoue & Takada[6]	CaO–MgO–FeO–SiO_2–P_2O_5 0.2 to 40% CaO, 0.2 to 1.0% P_2O_5
Selin[7]	CaO–MgO–FeO–SiO_2–P_2O_5 35 to 45% CaO, 0.2 to 0.5% P_2O_5
Wrampelmeyer *et al.*[8]	CaO–FeO–SiO_2–P_2O_5 35 to 50% CaO, 0.2 to 3.0% P_2O_5
Knüppel and Oeters[9]	CaO–FeO–SiO_2–P_2O_5 37–60% CaO, 0.2 to 8% SiO_2, 0.2 to 40% P_2O_5

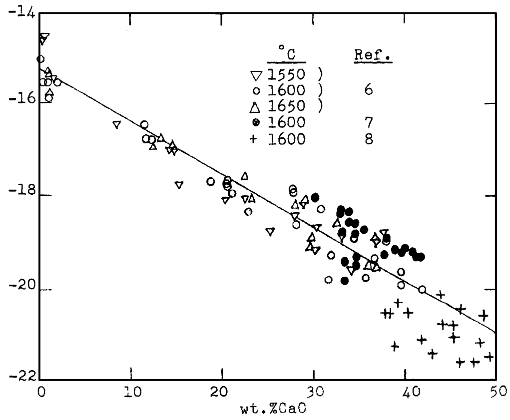

Fig. 1. P_2O_5 activities estimated from slag–metal equilibrium data for 1 550 to 1 650°C are related to CaO content of slags.

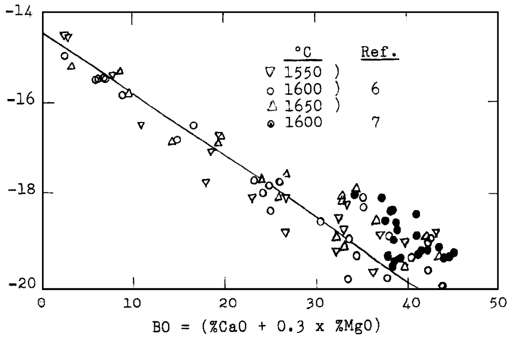

Fig. 2. P_2O_5 activities estimated from slag–metal equilibrium data for 1 550 to 1 650°C are related to CaO and MgO contents of slags.

4. Phosphate Capacity of Slags

As described by the author in a previous publication,[1] the slag composition effect on the phosphate capacity of the slag for low alloy steels, represented by the equation below

$$k_{\mathrm{PO}}=\frac{(\%\mathrm{P})}{[\%\mathrm{P}]}[\%\mathrm{O}]^{-2.5} \quad\text{........................(14)}$$

is governed primarily by the sum of the basic oxides.

$$\mathrm{BO}=\%\mathrm{CaO}+\%\mathrm{CaF_2}+0.3\times\%\mathrm{MgO} \quad\text{............(15)}$$

This is substantiated by the experimental data of many independent studies including Refs. 6), 8) and 9) shown in **Fig. 3**, reproduced from Ref. 1). The lines intersecting the

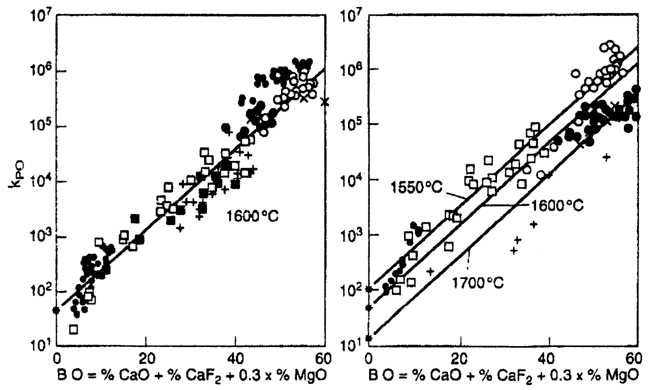

Fig. 3. Equilibrium data showing the decisive effects of CaO, CaF_2 and MgO on phosphate capacities of simple and complex slags. From Ref. 1).

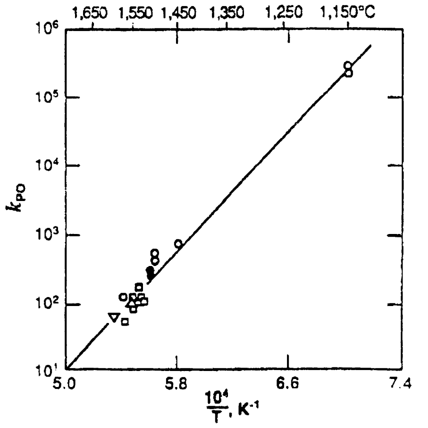

Fig. 4. Phosphate capacities of iron phosphate melts. From Ref. 1).

ordinate at BO=0 give k_{PO} values for iron phosphate melts as briefly described below.

Several studies were made in the 1 930 s[10–13] and subsequently by Trömel and Schwerdtfeger[14] of the phosphorus reaction between iron phosphate slags and liquid iron containing up to about 10% P. Ban-ya *et al.*[15] measured the activity of iron oxide in iron phosphate melts at temperatures of 1 200 to 1 450°C. In deriving the values of k_{PO} from these experimental data, due account was taken of the effect of phosphorus in iron on the activity coefficients f_P and f_O. Also in the phosphate melts containing MgO, the k_{PO} values were extrapolated to zero MgO. The results are given in **Fig. 4**, reproduced from Ref. 1).

From the previous critical reassessment of the slag–metal equilibrium data, reviewed above, the following equation was derived to describe the effects of temperature and slag composition on the phosphate capacity of steelmaking slags.

$$\log k_{PO}=\frac{21\,740}{T}-9.87+0.071\times\mathrm{BO}\quad\text{...........(16)}$$

where in mass percent BO=%CaO+%CaF_2+0.3×%MgO.

4.1. Derivation of $\gamma_{P_2O_5}$ from Phosphate Capacity

In terms of the oxide in wt% $PO_{2.5}$, dissolved in the slag as PO_4^{3-}, the activity of P_2O_5 with respect to pure liquid oxide is

$$\alpha_{P_2O_5}=\left(\frac{\%PO_{2.5}}{71\times1.65}\right)^2\gamma_{P_2O_5}\equiv\left(\frac{\%P}{31\times1.65}\right)^2\gamma_{P_2O_5}\quad\text{....(17)}$$

where 1.65 is an average total number of mols in 100 g steelmaking type slags, 71 and 31 are molecular and atomic weights. Substituting $\alpha_{P_2O_5}$ for %P in Eq. (14) squared $(k_{PO})^2$, gives the equilibrium constant K_P.

$$K_P=\frac{\alpha_{P_2O_5}}{[\%P]^2[\%O]^5}=\frac{(k_{PO})^2}{2\,616\gamma_{P_2O_5}}\quad\text{.............(18)}$$

Now, in terms of the equilibrium constant K_P, Eq. (16) is transformed to

$$\log K_P=\frac{43\,480}{T}-23.16+0.142\times\mathrm{BO}+\log(\gamma_{P_2O_5})\quad\text{...(19)}$$

4.2. New Estimate of ΔG_T° for Liquid P_2O_5

Since there is no detectable temperature effect on the computed values of $\alpha_{P_2O_5}$ in Figs. 1 and 2, it is surmised that the first term in Eq. (19) would be the temperature dependence of the equilibrium constant K_P. Therefore, the enthalpy change accompanying reaction

$$2[P]+5[O]=P_2O_5(l)\quad\text{.......................(20)}$$

would be

$$\Delta H^\circ=-832.38\ \mathrm{kJ/mol}\,.\quad\text{.....................(21)}$$

Inserting this in Eqs. (5) and (6) gives the new estimate of the standard enthalpy of formation of the hypothetical liquid P_2O_5.

$$\Delta H^\circ=-1\,655.5\ \mathrm{kJ/mol}\quad\text{......................(22)}$$

which is more negative by 121 kJ than that given in Eq. (4) which was the approximate estimate made initially by Turkdogan and Pearson.[1]

Whereas ΔH° is derived from the compiled experimental data on the temperature dependence of the phosphate capacity of slags, the ΔS° term for the formation of liquid P_2O_5 has to be estimated by other means.

It should be noted that for a given oxide formula and for the same type of reaction, ΔS° increases almost linearly with an increasing numerical value of ΔH°. Pertinent to the present case, the liquid oxides to be considered are of the type Me_2O_5 for which the ΔH° and ΔS° values, for Nb, Ta and V oxides, derived from the compiled thermochemical data,[16] are listed in **Table 2**.

As noted from the plot in **Fig. 5**, the previously estimated value of ΔH° and particularly of ΔS° for liquid P_2O_5 are not consistent with the data on the other three oxides. The dotted line on the linear relationship at $\Delta H^\circ=-1\,655.48$ kJ/mol derived from Eq. (19) gives the present estimate of $\Delta S^\circ=-571.0$ J/mol. On the basis of the foregoing analysis, the new estimate of the standard free energy of formation of liquid P_2O_5 is

$$\Delta G_T^\circ=-1\,655\,480+571.0T\ \ \mathrm{J/mol}\quad\text{............(23)}$$

which gives for the reaction equilibrium in Eq. (20)

$$\log K_P=\frac{43\,480}{T}-33.0\quad\text{.....................(24)}$$

Table 2. The standard $\Delta H°$ and $\Delta S°$ values for Nb, Ta and V oxides.*

Reaction	$-\Delta H°$, kJ/mol	$-\Delta S°$, J/mol
$2Nb(g)+\frac{5}{2}O_2(g)=Nb_2O_5(l)$	4 474.54	649.6
$2Ta(g)+\frac{5}{2}O_2(g)=Ta_2O_5(l)$	3 415.19	617.3
$2V(g)+\frac{5}{2}O_2(g)=V_2O_5(l)$	2 419.73	594.0
$P_2(g)+\frac{5}{2}O_2(g)=P_2O_5(l)$	(1 534.48 1 655.48[b]	506.3)[a] 571.0[c]

[a] Previous estimate, Eq. (4).

[b] Derived from Eq. (19).

[c] Derived from $\Delta H°$ *vs.* $\Delta S°$ correlation in Fig. 5.

[*] At elevated temperatures, the dominant vapour species of phosphorus is P_2; those of the Nb, Ta and V are monatomic.

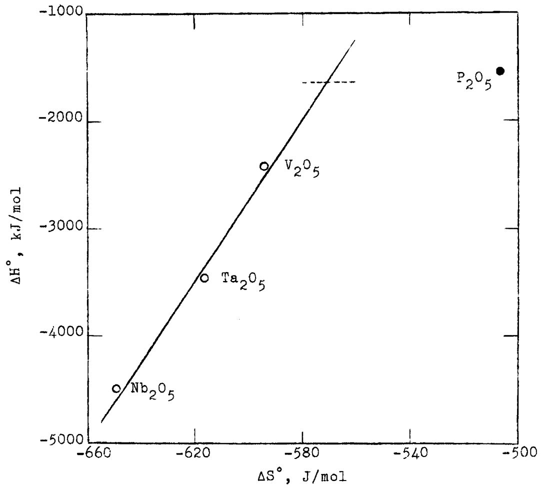

Fig. 5. Standard enthalpies and entropies of the formation of molten oxides from metal vapour and gaseous oxygen; (○) thermochemical data[16] and (●) earlier approximate estimate.[4]

Inserting this equation in (19) gives $\log(\gamma_{P_2O_5})$ independent of temperature as a linear function of BO, which in most cases is (%CaO+0.3×%MgO).

$$\log(\gamma_{P_2O_5})=-9.84-0.142(\%CaO+0.3\times\%MgO) \quad \text{...(25)}$$

In iron phosphate melts with other minor oxides, $\log(\gamma_{P_2O_5})$ will be close to −10, whereas in slags with about 60% CaO and 6% MgO, $\log(\gamma_{P_2O_5})\simeq -18$ to −19.

It should be noted that although the Eqs. (8) and (24) for the previous and present estimates of $\log K_P$ are different, they give similar $\log K_P$ values as shown in **Table 3**. Therefore, the values of $\log(\gamma_{P_2O_5})$ derived using Eq. (24) will differ very little from those given in Figs. 1 and 2, using Eq. (8).

4.3. Previous Work on $\gamma_{P_2O_5}$ in Soda Slags

Yamaguchi and Goto[17] and Tsukihashi *et al.*[18] derived indirectly the $\gamma_{P_2O_5}$ values from the experimental results on the phosphorus reaction between carbon-saturated iron and sodium silicophosphate melts low in iron oxide content. The calculations were again based on the author's earlier estimate[4] of ΔG_T° for liquid P_2O_5. Their $\log(\gamma_{P_2O_5})$ values are plotted in **Fig. 6**; the dotted line is from Eq. (25) for steelmaking slags. Considerable difference between the $\gamma_{P_2O_5}$ values in these two independent studies cannot be attributed to the temperature effect. Resolution of this anomaly awaits a further study.

Table 3. Comparison of the previous and present estimates of $\log K_P$.

Temperature °C	$\log K_P$	
	Previous	Present
1 500	−8.71	−8.48
1 600	−9.83	−9.79
1 700	−10.84	−10.96

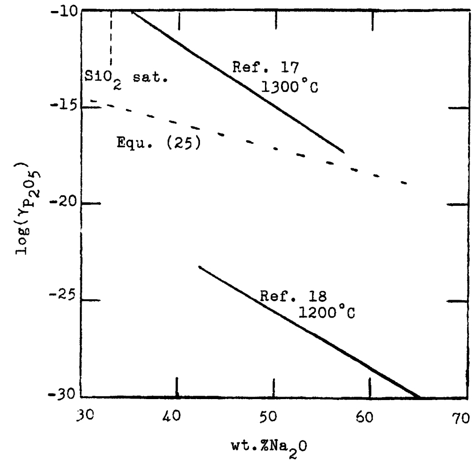

Fig. 6. Disparity in $\gamma_{P_2O_5}$ data for Na_2O–SiO_2–P_2O_5 melts.

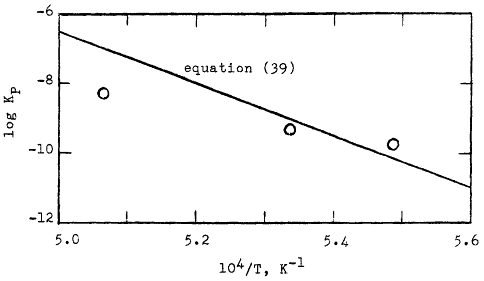

Fig. 7. Temperature dependence of the equilibrium constant K_P from data of Knüppel and Oeters[9] for $CaO+Ca_3P_2O_8$ saturated slags, are compared with Eq. (39) derived from reliable free energy data.

4.4. P_2O_5 Activity in Lime+Phosphate Saturated Slags

In slags saturated with both lime and calcium phosphate ($Ca_3P_2O_8$ or $Ca_4P_2O_9$), the equilibrium phosphorus and oxygen contents of liquid iron or low alloy steel are related by the equilibrium constant

$$K_{PO}=[\%P]^2[\%O]^5 \quad \text{.........................(26)}$$

In the experiments of Knüppel and Oeters,[9] the slags were saturated with both calcium oxide and tricalcium phosphate. The K_{PO} values derived from their data for slags containing $SiO_2<0.5\%$ are plotted in **Fig. 7**; the data point for 1 700°C is below the expected value, but those for 1 550 and 1 600°C are in general accord with the line derived from the free energy data discussed below.

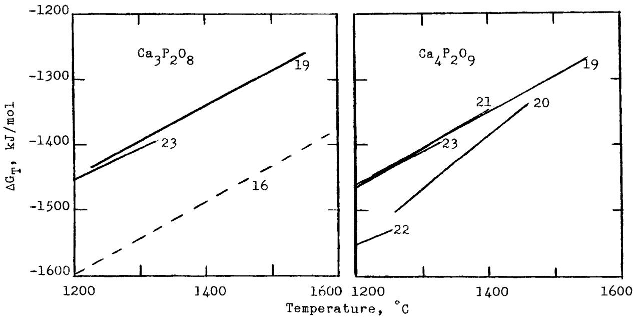

Fig. 8. Free energy data for the formation of calcium phosphates by reactions in Eqs. (27) and (28).

4.5. Compilation of Free Energy Data

Bookey[19)] determined the free energy change accompanying the reaction

$$3CaO(s)+P_2(g)+\frac{5}{2}O_2(g)=Ca_3P_2O_8(s) \quad ....(27)$$

$$4CaO(s)+P_2(g)+\frac{5}{2}O_2(g)=Ca_4P_2O_9(s) \quad ....(28)$$

by measuring the phosphorus vapour pressure in the reaction chamber, where the lime+phosphate mixture was equilibrated with various H_2O+H_2 gas mixtures at temperatures of 1 275 to 1 540°C. The experimental results were summarised as

$$\text{For } Ca_3P_2O_8: \quad \Delta G^\circ_T=-2\,246\,800+541T \text{ J/mol} \quad .....(29)$$

$$\text{For } Ca_4P_2O_9: \quad \Delta G^\circ_T=-2\,265\,000+547T \text{ J/mol} \quad .....(30)$$

These are compared in **Fig. 8** with the results of subsequent experimental work. The data of Refs. 21) and 23) are in complete accord with Bookey's ΔG_T values; approximate value from Ref. 16) is inaccurate.

Since the ΔG_T values are very similar for both phosphates, an average value would be adequate for the reactions

$$XCaO(s)+P_2(g)+\frac{5}{2}O_2(g)=XCaO\cdot P_2O_5(s) \quad .....(31)$$

$$\Delta G^\circ_T=-2\,250\,200+537.2T \text{ J/mol} \quad ....(32)$$

Gourishankar *et al.*[24)] measured the standard free energy of formation of CaO using the Knudsen effusion technique,

$$Ca(g)+\frac{1}{2}O_2(g)=CaO(s) \quad ....(33)$$

$$\Delta G^\circ_T=-753\,880+192.5T \text{ J/mol at } 1\,900-2\,000\text{K} \quad ...(34)$$

Noting that for the vaporisation of liquid Ca

$$\Delta G_V=153\,600-87.4T \quad ....(35)$$

the standard free energy of formation of CaO with respect to liquid Ca would be

$$\Delta G^\circ_T=-600\,300+105.1T \text{ J/mol} \quad ....(36)$$

As pointed out by Gourishankar *et al.*,[24)] ΔG°_T of Eq. (36) is +33 kJ/mol CaO higher than that given in JANAF Tables.[25)]

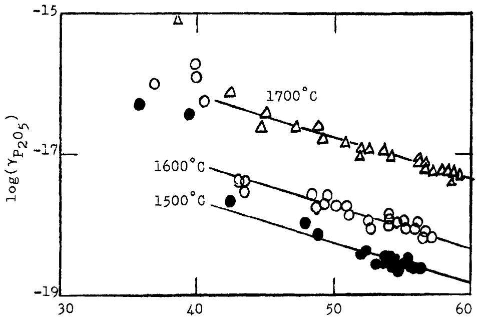

Fig. 9. Variations of $\gamma_{P_2O_5}$ with temperature and CaO content of slags saturated with $CaO+Ca_3P_2O_8$ from experimental data of Knüppel and Oeters.[9)]

Combining Eqs. (32) and (36) gives the standard free energies of formation of $Ca_3P_2O_5$ and $Ca_4P_2O_9$.

Reaction	ΔG°_T, J/mol
$3Ca(1)+P_2(g)+4O_2(g)$ $=Ca_3P_2O_8(s)$ ....(37)	$-4\,051\,100+852.5T$
$4Ca(1)+P_2(g)+\frac{9}{2}O_2(g)$ $=Ca_4P_2O_9(s)$ ....(38)	$-4\,651\,400+957.6T$

4.6. Lime+Phosphate Saturated Slags

For slags saturated with $CaO+Ca_3P_2O_8$ (or $Ca_4P_2O_9$), the temperature dependence of the equilibrium constant in Eq. (26) is obtained from the free energy values given in Eqs. (5), (6) and (32).

$$\log K_{PO}=-\frac{75\,546}{T}+31.28 \quad ....(39)$$

Sum of Eqs. (24) and (39) gives the following estimate of the P_2O_5 activities in slags saturated with lime+calcium phosphate.

$$\log(\alpha_{P_2O_5})=-\frac{32\,066}{T}-1.72 \quad ....(40)$$

Using this equation, $\log(\gamma_{P_2O_5})$ derived from the experimental data of Knüppel and Oeters for double saturated slags, are plotted in **Fig. 9**. In slags containing 40 to 60% CaO and 10 to 40% P_2O_5, $\log(\gamma_{P_2O_5})$ is a linear function of %CaO, which no longer holds for CaO<40% and the corresponding P_2O_5<10. For the stated composition range, the data are represented by the following equations,

$$1\,550°C: \quad \log(\gamma_{P_2O_5})=-15.32-0.058(\%CaO) \quad ....(41)$$

$$1\,600°C: \quad \log(\gamma_{P_2O_5})=-14.82-0.058(\%CaO) \quad ....(42)$$

$$1\,700°C: \quad \log(\gamma_{P_2O_5})=-13.86-0.058(\%CaO) \quad ....(43)$$

These equations are summarised by

$$\log(\gamma_{P_2O_5})=-\frac{34\,950}{T}+3.85-0.058(\%CaO) \quad .....(44)$$

5. Direct Measurement of P_2O_5 Activity in Molten Slags

In a paper due to be published,[26)] the author disclosed a theoretical concept of slag-oxygen sensors to measure oxide activities related to FeO, SiO_2 and CaO contents of steelmaking slags, for which a Patent Application was filed in the U.S. Patent and Trademark Office on 25 February, 2000. The concept of this sensor is based on the theoretical principle that two dis-similar electrodes immersed in a molten slag, will form a galvanic cell for which the open-circuit cell voltage E, in terms of mV, is a thermodynamic function of the chemical potential difference between the two dis-similar electrodes, for solely ionic conduction in the slag; this theoretical relation is

$$\frac{5.04E\cdot Z}{T}=\log(p_{\mathrm{i}})_{\mathrm{o}}^{1/2}-\log(p_{\mathrm{i}})_{\mathrm{r}}^{1/2} \quad\text{..............(45)}$$

where Z is a valency of the metallic element X, $(p_{\mathrm{i}})_{\mathrm{o}}$ the equilibrium X_2 gas partial pressure in atm at the slag–oxide electrode interface and $(p_{\mathrm{i}})_{\mathrm{r}}$ the X_2 gas reference electrode.

5.1. Electrodes

A rod or plate like electrode, about 3 to 5 mm thick, is made either by plasma spraying of the powder mixture of the ingredients onto a Mo wire or strip, or by sintering in oxygen-free dry argon, the compacted powder mixture. This is discussed in more detail in the author's paper.[26)]

5.1.1. P_2O_5 Electrode

With $(V+V_2O_5)$ mixture as the electrode, the phosphorus chemical potential at the electrode–slag interface, with respect to the P_2O_5 activity in the slag, is represented by the following reaction equilibrium,

$$\mathrm{V(s)}+\frac{1}{2}(\mathrm{P_2O_5})=\frac{1}{2}\mathrm{V_2O_5(s)}+\frac{1}{2}\mathrm{P_2(g)} \quad\text{..........(46)}$$

The equilibrium constant for this reaction is derived from the reliable value of $\Delta G^{\circ}_{\mathrm{T}}$ for V_2O_5[16)] and that estimated for liquid P_2O_5 in the present study, *i.e.* Eq. (23), giving

$$\log(p_{\mathrm{P_2}})_{\mathrm{o}}^{1/2}=-\frac{3\,753}{T}+4.73+\frac{1}{2}\log(\alpha_{\mathrm{P_2O_5}}) \quad\text{......(47)}$$

5.1.2. Reference Electrode

The only suitable reference electrode of a high melting point (1 775°C) is the mixture (Th+ThP). Using the estimated $\Delta G^{\circ}_{\mathrm{T}}$ values given by Barin and Knacke,[16)] the following approximate value of $\log(p_{\mathrm{P_2}})_{\mathrm{r}}^{1/2}$ is obtained,

$$\log(p_{\mathrm{P_2}})_{\mathrm{r}}^{1/2}\simeq-\frac{21\,709}{T}+4.48 \quad\text{.................(48)}$$

From Eqs. (45), (47) and (48) the following approximate relation is obtained for $\log(\alpha_{\mathrm{P_2O_5}})$ *vs.* sensor emf in mV.

$$\log(\alpha_{\mathrm{P_2O_5}})\approx-\frac{35\,912-30.24E}{T}+0.50 \quad\text{..........(49)}$$

This relation is shown graphically in **Fig. 10** for 1 600°C; the P_2O_5 contents shown on the right hand ordinate are calculated from Eq. (25) for slags containing 60% CaO and 6% MgO and $P_2O_5<1\%$.

It should be emphasised that the concept of the slag–oxide sensor proposed by the author is at present a conjecture, which has to be evaluated experimentally for its validity and for accuracy of the emf readings. Also, calculated oxide activity *vs.* sensor emf relations are only approximate, because of variations in the accuracy of the thermochemical data used in the calculations.

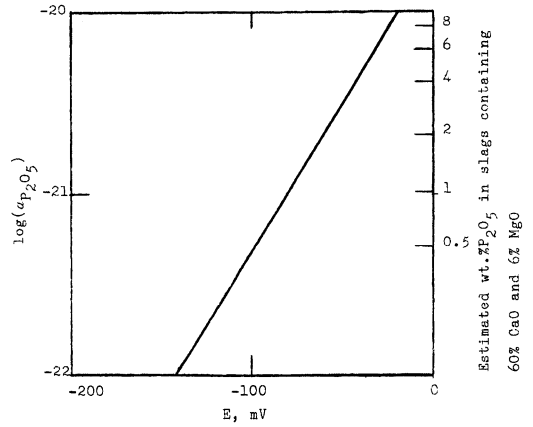

Fig. 10. $\log(\alpha_{\mathrm{P_2O_5}})$ in lime-base slags *vs.* emf at 1 600°C, by the proposed slag–P_2O_5 sensor.

6. Conclusions

The results of independent experimental work on the free energies of calcium phosphates may be summarised by the following equations.

$$\mathrm{XCaO(s)+P_2(g)}+\frac{5}{2}\mathrm{O_2(g)}=\mathrm{XCaO\cdot P_2O_5(s)}$$

$$\Delta G^{\circ}_{\mathrm{T}}=-2\,250\,200+537.2T\ \mathrm{J/mol}$$

$$\mathrm{3Ca(l)+P_2(g)+4O_2(g)=Ca_3P_2O_8(s)}$$

$$\Delta G^{\circ}_{\mathrm{T}}=-4\,051\,100+852.5T\ \mathrm{J/mol}$$

$$\mathrm{4Ca(l)+P_2(g)}+\frac{9}{2}\mathrm{O_2(g)}=\mathrm{Ca_4P_2O_9(s)}$$

$$\Delta G^{\circ}_{\mathrm{T}}=-4\,651\,400+957.6T\ \mathrm{J/mol}$$

From a theoretical analysis of the previously compiled experimental data on the phosphate capacities of simple and complex slags, a new estimate is made of the standard free energy of formation of the hypothetical pure liquid P_2O_5.

$$\mathrm{P_2(g)}+\frac{5}{2}\mathrm{O_2(g)}=\mathrm{P_2O_5(l)}$$

$$\Delta G^{\circ}_{\mathrm{T}}=-1\,655\,480+571.0T\ \mathrm{J/mol}$$

In terms of the gaseous phosphorus and oxygen dissolved in liquid iron, the new estimate of the ΔG_{T} values would be

$$\mathrm{2[P]+5[O]=P_2O_5(l)}$$

$$\Delta G_{\mathrm{T}}=-832\,384+632.65T\ \mathrm{J/mol}$$

The P_2O_5 activity coefficients derived from several experimental data on lime-base, low-P_2O_5 slags are summarised by

$$\log(\gamma_{\mathrm{P_2O_5}})=-9.84-0.142(\%\mathrm{CaO}+0.3\times\%\mathrm{MgO})$$

In slags containing 40 to 60% CaO and 10 to 40% P_2O_5,

$$\log(\gamma_{\mathrm{P_2O_5}})=-\frac{34\,950}{T}+3.85-0.058(\%\mathrm{CaO})$$

At present, for reasons not readily explainable, the variation of $\log(\gamma_{P_2O_5})$ with temperature and slag composition are different for slags of low and high P_2O_5 contents.

(i) With $P_2O_5 < 1\%$, $\log(\gamma_{P_2O_5})$ is a linear function of CaO content from 0 to 60% and independent of temperature.

(ii) With $P_2O_5 > 10\%$, $\log(\gamma_{P_2O_5})$ is a linear function of CaO content >40% only and increases with an increasing temperature.

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