An Assessment of Thermodynamic Parameters for Deoxidation of Molten Iron by Cr, V, Al, Zr and Ti*

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Synopsis

Critical review of thermodynamics of deoxidation of molten iron by Cr, V, Al, Zr, and Ti has been made. Experimental [wt. % O] vs. [wt. % M] data in these systems have been used to estimate first and second order cross-interaction parameters (e_O^M, r_O^M) employing five different calculation models. It was found that r_O^M should be considered for best fit. On the basis of this exercise, a simple analytical equation relating [wt. % O] and [wt. % M] has been proposed and values of e_O^M, r_O^M recommended. Assessments have also been made of deoxidation constants (K). Values of K for the above systems have been proposed based on selected experimental data and thermodynamic estimates. [wt. % O] vs. [wt. % M] solubility curves for molten iron in equilibrium with oxide product calculated from the accepted values of thermodynamic parameters, have been presented.

1. Introduction

Let us consider solubility of an oxide (M_aO_b) in molten steel *vide* the reaction:

where, [M], [O]: respectively metal and oxygen dissolved in liquid iron.

The equilibrium constant for reaction (1) is given as:

$$K = [a_M]^a [a_O]^b, \text{ if the oxide is pure } \dots\dots\dots(2)$$

K is known as 'deoxidation constant' in connection with deoxidation of liquid steel. M is the deoxidizer element and M_aO_b is deoxidation product. a is Henrian activity.

If the steel is considered otherwise pure, then thermodynamically the alloy system is a ternary, Fe-M-O. In such a system, neglecting higher order interaction coefficients,

$$\log [a_M] = \log [\text{wt. \% M}] + e_M^O [\text{wt. \% M}] + e_M^O [\text{wt. \% O}] \dots\dots\dots(3)$$

$$\log [a_O] = \log [\text{wt. \% O}] + e_O^O [\text{wt. \% O}] + e_O^M [\text{wt. \% M}] \dots\dots\dots(4)$$

Combining Eqs. (2), (3) and (4), at constant temperature,

$$\log K = a \text{ constant} = (a \log [\text{wt. \% M}] + b \log [\text{wt. \% O}] + [\text{wt. \% M}] \dots\dots\dots(5)$$

$$(ae_M^M + be_O^M) + [\text{wt. \% O}](ae_O^O + be_O^O) = \log K' + [\text{wt. \% M}](ae_M^M + be_O^M) + [\text{wt. \% O}](ae_O^O + be_O^O) \dots\dots\dots(6)$$

where, K' : 'apparent deoxidation constant'.

The traditional method of determination of the interaction coefficient, e_O^M , from experimental data has been to plot $\log K'$ as function of [wt. % M], construct a best fit line through the points or determine the limiting slope in $\log K'$ vs. [wt. % M] data points as [wt. % M] $\rightarrow 0$. e_O^M is estimated from the slope, making certain assumptions about contributions from other terms of Eq. (6).

The determination of limiting slope this way suffers from uncertainty in view of scatter in data especially for strong deoxidizers such as Al, Zr, etc.^{1,2)} Therefore it is better to estimate e_O^M by considering all data points of [wt. % O] vs. [wt. % M] in liquid iron in equilibrium with the oxide, M_aO_b . This is a superior method mathematically also, since the significance of the term e_O^M [wt. % M] increases with increasing [wt. % M] making the estimate more reliable.

Again, for many deoxidizers, [wt. % O] vs. [wt. % M] in molten iron in equilibrium with M_aO_b were found to exhibit minima in solubility of oxygen. Averin and Samarin³⁾ first examined this issue. St. Pierre and Blackburn⁴⁾ did a more rigorous analysis and arrived at the relationship:

$$X_M(\text{min}) = -\frac{1}{\epsilon_M^M + r\epsilon_O^M} \dots\dots\dots(7)$$

where, X_M : mole fraction of M at solubility minimum (min)

ϵ : interaction coefficient in Raoultian scale

r : oxygen-to-metal ratio in oxide (*i.e.* b/a).

This thermodynamic analysis was further generalized by Smith and Kirkaldy⁵⁾ to include oxides of variable composition.

Knowing $X_M(\text{min})$, ϵ_M^M , and r , one can find out ϵ_O^M from Eq. (7) and hence e_O^M , because of the standard relation:

$$\epsilon_O^M = 230 \frac{m_M}{m_{Fe}} \cdot e_O^M + \frac{m_{Fe} - m_M}{m_{Fe}} \dots\dots\dots(8)$$

where, m : molecular weight.

However $X_M(\text{min})$ for most systems is not well-defined and has a range of uncertainty. Therefore Feldman and Kirkaldy¹⁾ decided to estimate ϵ_O^M and $X_M(\text{min})$ by curve fitting all experimental data points of [wt. % O] vs. [wt. % M]. Agreements were reasonably good. However they encountered mismatch between calculated curves and experimental data at higher [wt. % M] presumably due to the fact that they ignored the second-order interaction coefficients.

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St. Pierre⁶⁾ considered both first order (e_O^M , e_M^M) as well as second-order interaction coefficients (r_O^M , r_M^M) for the system Fe-[Al]-[O]-Al₂O₃. He accepted the values of e_O^{Al} , r_O^{Al} , e_{Al}^{Al} and r_{Al}^{Al} as compiled by Sigworth and Elliott⁷⁾ and calculated [wt.% O] *vs.* [wt.% Al] curve. The curve exhibited both minima and maxima as expected mathematically. However agreement with experimental data was not good. In a recent paper, Rao⁸⁾ has presented a method of analyzing experimental solubility data in order to arrive at analytical correlation in a ternary system, and to extract first and second-order interaction coefficients. The treatment is comprehensive in nature but is applicable to simpler reactions such as dissolution of nitrogen in molten iron from nitrogen bearing gases.

Reviewing the situation it appeared that further efforts are desirable to extract the values of interaction coefficients in the systems Fe-[M]-[O]-M_aO_b. It was also recognized that there is a need also to test the significance of the various assumptions on the resulting estimated values.

II. Estimation Procedure

It was decided to:

- 1) carry out curve fitting of all or most experimental data points from investigations considered reliable, and evaluate interaction coefficients from best fit curves,
- 2) carry out all calculations in the weight percent and Henrian activity scale for [M] and [O],
- 3) consider both first-order and second-order interaction coefficients, and
- 4) test out significance of some simplifying assumptions in calculation procedures.

If second-order interaction coefficients are included, then Eqs. (3) and (4) are modified as follows:

$$\log [a_M] = \log [\text{wt.}\% M] + e_M^M [\text{wt.}\% M] + e_O^M [\text{wt.}\% O] + r_M^M [\text{wt.}\% M]^2 + r_O^M [\text{wt.}\% O]^2 \dots\dots\dots (9)$$

$$\log [a_O] = \log [\text{wt.}\% O] + e_O^O [\text{wt.}\% O] + e_M^O [\text{wt.}\% M] + r_O^O [\text{wt.}\% O]^2 + r_M^O [\text{wt.}\% M]^2 \dots\dots\dots (10)$$

The numerical curve-fitting procedure is highly complex with so many terms. It poses problem as well. Therefore it was considered desirable to omit terms that are not so significant. It leads to improved estimation of the more significant terms.

Since r_M^M is expected to be much lower compared to r_O^M , the term r_M^M [wt.% M]² was dropped. Again, [wt.% O] ≪ [wt.% M] at higher values of [wt.% M].

Hence the terms containing [wt.% O]² were dropped. With these simplifications, combination of Eqs. (9) and (10) with Eq. (2) leads to the equation:

$$\log K = a(\log [\text{wt.}\% M] + e_M^M [\text{wt.}\% M] + e_M^O [\text{wt.}\% O]) + b(\log [\text{wt.}\% O] + e_O^O [\text{wt.}\% O] + e_O^M [\text{wt.}\% M] + r_O^M [\text{wt.}\% M]^2) \dots\dots\dots (11)$$

Altogether 5 models were employed for computations. Their salient features are summarized in Table 1. An examination of the table shows that these calculation models have been designed to test significance of using data points range in terms of [wt.% M], of course within availability of experimental values. Significance of e_O^O , e_M^O as well as the second order interaction coefficient (r_O^M) were also to be tested. Logically speaking, e_M^O is related to e_O^M by the equation:

$$e_M^O = e_O^M \left(\frac{m_M}{m_O} \right) + \frac{1}{230} \frac{m_O - m_M}{m_O} \dots\dots\dots (12)$$

However in order to make computations feasible, some value of e_M^O had to be used *a-priori*. Errors arising out of all these would be discussed later.

Equation (11) is a multivariable, nonlinear one. All computations were carried out by computer using various numerical methods. The calculation steps consisted of:

- 1) estimation of parameters, K , e_O^M and r_O^M , which gave best fit to the experimental data points used (Gauss Newton Method);
- 2) calculation of [wt.% O] *vs.* [wt.% M] curve using the above estimated parameters (Newton Raphson Method); and
- 3) estimation of the minima in oxygen solubility curves (Golden Search Method).

The systems on which this study was carried out are Fe-[Al]-[O], Fe-[Zr]-[O], Fe-[Cr]-[O], Fe-[Ti]-[O] and Fe-[V]-[O] in equilibrium with their respective stable oxides.

While selecting values of e_O^O , e_M^O and e_M^M , efforts were made to ascertain the approximate reliabilities of the values chosen from literature. There is very little controversy about e_O^O in literature and hence the value reported in compilation of Sigworth and Elliott⁷⁾ were taken. Same comment applies to values of e_M^M . However literature sources for some systems revealed large scale discrepancy in e_O^M and hence e_M^O values. Here e_M^O values for Fe-Cr-O, Fe-V-O and Fe-Al-O were taken from Sigworth and Elliott,⁷⁾ for Fe-Zr-O from Buzek,⁹⁾ For Fe-Ti-O it was

Table 1. Characteristic features of various models for computation.

Model	Values of coefficients used			Range of [wt.% M] used	Whether r_O^M considered	Parameters estimated
	e_O^O	e_O^M	e_M^M			
1	0	0	Literature value	Lower; including up to solubility minimum	No	K , e_O^M
2			Literature values	do.	No	K , e_O^M
3	0	0	Literature value	Full range of data points available	Yes	K , e_O^M , r_O^M
4			Literature values	do.	Yes	K , e_O^M , r_O^M
5	0	0	Literature value	do.	No	K , e_O^M

decided to take average of the more acceptable values.¹⁰⁾ These have been presented in Table 2.

As Table 2 shows that 1 600 °C has been selected as the working temperature for all the systems except for Fe–Zr–O, where proper data were available at 1 680 °C only.

III. Discussion

1. Fe–[Cr]–[O] System

This system exhibits several oxides and there have been controversies about the stabilities of the same. On the basis of literature review, it was decided to accept the following as stable oxides at 1 600 °C: FeCr₂O₄ at less than 3 % Cr, Cr₂O₃ at 3~8 % Cr, Cr₃O₄ above 8 % Cr.^{11–13)}

Calculations were performed with the data of Fruehan¹⁴⁾ as well as of Janke and Fischer¹³⁾ assuming Cr₃O₄ as the stable oxide in equilibrium. For all purposes, Models 1 and 2 yielded approximately the same values of parameters and same curves. Similarly models 3 and 4 gave almost the same results.

Table 2. Literature values of e_O^0 , e_M^0 , e_M^M employed for computation.

System	Temperature (°C)	e_O^0	e_M^0	e_M^M
Fe–Cr–O	1 600	–0.2	–0.14	–0.0003
Fe–V–O	1 600	–0.2	–0.9	0.015
Fe–Al–O	1 600	–0.2	–6.6	0.045
Fe–Zr–O	1 680	–0.162	–2.6 ⁹⁾	0.023
Fe–Ti–O	1 600	–0.2	–1.8 ¹⁰⁾	0.013

All values from Ref. 7) except those indicated.

These demonstrated that it does not give any significant errors if e_O^0 and e_{Cr}^0 are taken as zero. Therefore it is good enough to consider only models 1,3, and 5 for further discussion, and out of these model 3 gave the best fit. Figure 1 shows curve fitting of the data of Janke and Fischer¹³⁾ to demonstrate it. It is being clarified that existence of two oxides in the different ranges of chromium concentration posed problems. In Fig. 1, the curve for model 1 assumed Cr₂O₃ as the stable oxide. Model 5 as well as model 3 assumed Cr₃O₄ as the stable oxide.

As Table 3 shows the parameters obtained on the basis of the two sets of data differed somewhat. Since the value of $e_{Cr}^0 = -0.038$ on the basis of Fruehan's data agree with several others, it is being recommended. There is another reason for recommending the above. Table 3 shows values of K estimated in the present study. It also presents recommended values of K at 1 600 °C (to be discussed

Fig. 1. The solubility of oxygen in Fe–Cr melts in equilibrium with Cr₂O₃ and Cr₃O₄ at 1 600 °C.

Table 3. Estimated thermodynamic parameters at 1 600 °C.

System	Reference	Assumed oxide phase	Conc. range [wt% M]	Parameters estimated by model 3				Recommended value of K (also K reported by investigators in bracket)
				K	e_O^0 (Std. dev.)	γ_O^0 (Std. dev.)	wt.% O (min)	
Fe–V–O	Fruehan ¹⁷⁾	V ₂ O ₃	0.43~36.3	6.76×10^{-6}	–0.117 (0.003)	0	0.018	—
	Kay and Kontopoulous ¹⁶⁾	V ₂ O ₃	upto 12.0	3.09×10^{-6}	–0.14 (0.008)	0	0.015	2.2×10^{-6} (2.71×10^{-6})
Fe–Cr–O	Fruehan ¹⁴⁾	Cr ₃ O ₄	9.5~50.0	2.69×10^{-5}	–0.038 (0.005)	0.0002 (9.5×10^{-5})	0.0275	— (2.23×10^{-5})
	Janke and Fischer ¹³⁾	Cr ₃ O ₄	8.0~45.0	1.02×10^{-5}	–0.044 (0.002)	0.00028 (3×10^{-5})	0.0267	(1.07×10^{-5})
Fe–Al–O	Fruehan ¹⁹⁾	Al ₂ O ₃	0.02~1.4	5.0×10^{-13}	–2.86 (0.24)	1.08 (0.17)	0.00069	(5.6×10^{-14}) 3.32×10^{-14}
	Janke and Fischer ²⁰⁾	Al ₂ O ₃	0.0004~1.5	9.3×10^{-14}	–2.81 (0.32)	1.03	0.0004	(2.41×10^{-14})
Fe–Zr–O*	Fruehan ²⁾	ZrO ₂	0.005~0.1	3.25×10^{-8}	–3.41 (0.67)	1.91 (0.69)	0.0011	5.43×10^{-10}
Fe–Ti–O	Kojima <i>et al.</i> ²²⁾ **	Ti ₃ O ₅	0.0001~0.4	4.07×10^{-19}	–1.0 (0.39)	—	—	5.45×10^{-20} (3.5×10^{-18})
	Janke and Fischer ²⁰⁾	Ti ₂ O ₃	0.4~8.0	8.9×10^{-11}	–0.42 (0.08)	0.026 (0.009)	—	2.06×10^{-12} (2.72×10^{-12})

* at 1 680 °C, ** estimated by model 1

later). It may be noted that these two agreed much better when Fruehan's data were used.

2. Fe-[V]-[O] System

Like Fe-Cr-O system, a number of oxides of vanadium have been reported in literature. Kojima *et al.*¹⁵⁾ and Kay *et al.*¹⁶⁾ carried out X-ray and other investigations to identify the oxides. FeV_2O_4 is stable below 0.2 % V in Fe, and V_2O_3 is stable above 0.2 %. These have received acceptance as well, and here also it has been accepted. Computations were carried out with data of Fruehan¹⁷⁾ and Kay *et al.*¹⁶⁾

Again, like Fe-Cr-O system, models 1 and 2 yielded approximately the same results, and models 3 and 4 also matched with each other leading to the same conclusions as earlier. Again, model 3 gave the best fit as demonstrated by Fig. 2. Values of e_o^v and r_o^v estimated on the basis of data of Kay and Kontopoulos¹⁶⁾ are being recommended, since K estimated by this procedure and K recommended agreed well (Table 3). Table 3 presents values of K , e_o^v and r_o^v as estimated by model 3. However r_o^v exhibited high standard deviation (*i.e.*, 0.003 ± 0.008). Hence it should be taken as zero.

Fig. 2. The solubility of oxygen in Fe-V melts in equilibrium with V_2O_3 at 1600 °C.

Fig. 3. The solubility of oxygen in Fe-Al melts in equilibrium with Al_2O_3 at 1600 °C.

3. Fe-[Al]-[O] System

Here there is only one oxide (Al_2O_3) in the range of dissolved oxygen concentration of interest in steel-making. FeAl_2O_4 is not of interest since that is found only at very high oxygen content in molten iron.¹⁸⁾ Considerable discrepancy, ranging from -0.22 to -12.0 , exists in literature for the value of e_o^{Al} . Computations were carried out using data of Fruehan¹⁹⁾ as well as Janke and Fischer.²⁰⁾ Again conclusions are similar to the previous systems and model 3 gave the best fit out of all. Figure 3 demonstrates it. As Table 3 shows that e_o^{Al} estimated from Fruehan's and Janke and Fischer's data are respectively -2.86 and -2.81 and hence they do not differ much. Similarly, r_o^{Al} also are close. Janke and Fischer have collected a large quantity of data. Also the recommended value of K (3.32×10^{-14}) is much closer to that estimated from data of Janke and Fischer than that from data of Fruehan. Therefore the former is being recommended.

4. Fe-[Zr]-[O] System

Only one oxide, *viz.* ZrO_2 , has been identified in this system. Not many investigators have determined the value of e_o^{Zr} and that too there is considerable discrepancy, ranging from -0.44 ⁹⁾ to -3.0 ²⁾. The only experimental investigation that appeared suitable for analysis is that of Fruehan²⁾ at 1680 °C. The data exhibit scatter at higher zirconium concentrations. The data of Janke *et al.*²⁰⁾ exhibit a high degree of scatter and hence were not selected.

Like previous systems, models 1 and 2 yielded almost identical results. Same is true of comparison between models 3 and 4. Therefore Fig. 4 shows a comparison amongst models 1,3, and 5 only and it demonstrates again that model 3 tends to give best curve fitting. For computations, the experimental point enclosed by square bracket has not been considered since Fruehan himself doubted its reliability.

5. Fe-[Ti]-[O] System

This system is characterised by the presence of a large number of oxides.²¹⁻²³⁾ From the point of view of conditions prevailing in steelmaking, formation of some of them are not likely. Kojima²²⁾ found Ti_3O_5 to be stable below 0.4 wt.% Ti in molten

Fig. 4. The solubility of oxygen in Fe-Zr melts in equilibrium with ZrO_2 at 1 680 °C.

Fig. 5. The solubility of oxygen in Fe-Ti melts in equilibrium with Ti_3O_5 and Ti_2O_3 at 1 600 °C.

iron and Ti_2O_3 above 0.4 wt% Ti. This conclusion seems to be most acceptable. Formation of TiO is possible only at high titanium concentrations and $\text{FeO} \cdot \text{TiO}_2$ or $\text{FeO} \cdot \text{Ti}_2\text{O}_3$ at very low concentrations. Again, considerable controversies exist in literature amongst investigators on the values of e_{O}^{Ti} (-0.37^{22} to -5.0^{24}).

Computations were carried out with data of Fruehan,¹⁴⁾ Janke and Fischer²⁰⁾ as well as Kojima *et al.*²²⁾ Fruehan's data could not be fitted with any model well. Moreover it gave an abnormally high estimate of K (about 10^{-15}) in the range where Ti_3O_5 is stable in contrast to the recommended value of 5.45×10^{-20} . Therefore these estimates have not been included in Table 3. A large number of data points are available in the work of Kojima *et al.*²²⁾ at 1 600 °C, of course only up to 0.4 wt.% Ti. Models 1,2 and 5 yielded almost identical results. Similarly models 3 and 4 were approximately the same. It may be noted that there was virtually no difference between the two sets. In view of low concentrations of Ti, r_{O}^{Ti} was considered to be unreliable. e_{O}^{Ti} based on fitting of data of Kojima *et al.* was found to be -1.0 (± 0.39) in contrast to their reported value of -0.37 . As mentioned in introduction, the term $e_{\text{O}}^{\text{M}}[\text{wt. \% M}]$ is comparatively very small at low concentrations of M. Therefore presence of scatter in data makes the estimate of e_{O}^{M} uncertain. This is reflected by high standard deviation of ± 0.39 . Therefore the above value of e_{O}^{Ti} is not being recommended.

Janke and Fischer investigated at titanium concentrations ranging from 0.001 wt. % to 8.8 wt. %. Fit of data with model 3 and assuming Ti_2O_3 as the stable oxide yielded a value of $e_{\text{O}}^{\text{Ti}} = -0.42$ (± 0.08) and $r_{\text{O}}^{\text{Ti}} = 0.026$ (± 0.009). Model 1 with Ti_3O_5 as stable oxide fitted only in the lower range with $e_{\text{O}}^{\text{Ti}} = -1.43$. This discrepancy in the two estimates revealed the unsatisfactory state of data. The investigators themselves failed to evaluate e_{O}^{Ti} . However in view of earlier discussions it is being concluded that estimates based on model 3 be accepted. Figure 5 shows the fit. It is not as good as in the other systems. However it is about the best that can be achieved.

6. Overall Assessment

In all the 5 systems studied, models 1 and 2

yielded approximately the same results. Similarly models 3 and 4 also behaved almost the same. Therefore, one may ignore the contributions of the terms $e_{\text{O}}^{\text{O}}[\text{wt. \% O}]$ and $e_{\text{M}}^{\text{O}}[\text{wt. \% O}]$, *i.e.*, e_{O}^{O} and e_{M}^{O} may be taken as zero without incurring any significant error in estimation. This is due to the fact that $[\text{wt. \% O}] \ll [\text{wt. \% M}]$. Hence Eq. (11) may be further simplified into:

$$\begin{aligned} \log K = & a(\log [\text{wt. \% M}] + e_{\text{M}}^{\text{M}}[\text{wt. \% M}]) \\ & + b(\log [\text{wt. \% O}] + e_{\text{O}}^{\text{M}}[\text{wt. \% M}]) \\ & + r_{\text{O}}^{\text{M}}[\text{wt. \% M}]^2 \dots\dots\dots(13) \end{aligned}$$

This is a simple analytical equation. If thermodynamic parameters are known, $[\text{wt. \% O}]$ *vs.* $[\text{wt. \% M}]$ relationship is uniquely determined.

In Fe-Cr-O and Fe-V-O systems, standard deviations are very low (Table 3). The values of K obtained by present estimate also match fairly well with those recommended through separate assessment (Table 3). e_{O}^{M} estimated in the present study agreed very well with those estimated by investigators themselves (Table 4). All these are due to the fact that the $[\text{wt. \% O}]$ and $[\text{wt. \% M}]$ are large enough in Fe-Cr-O and Fe-V-O systems to allow accuracy in sampling and chemical analysis. As stated earlier that $r_{\text{O}}^{\text{M}} \gg r_{\text{M}}^{\text{M}}$. Therefore only $r_{\text{O}}^{\text{M}}[\text{wt. \% M}]^2$ term would be additionally significant at large $[\text{wt. \% M}]$ and very little purpose would be served by including $r_{\text{M}}^{\text{M}}[\text{wt. \% M}]^2$ term in Eq. (13). However, even then, if one wishes to include it he may do so at his own discretion.

The situations with respect to Fe-Al-O, Fe-Zr-O and Fe-Ti-O are otherwise. Standard deviations are high. The values of K obtained by present estimate do not match well with those determined by investigators directly (Table 3). e_{O}^{M} estimated in the present study do not agree well with those estimated by the investigators themselves, wherever they attempted the same. All these are due to scatters in experimental data (Figs. 3 to 5) caused by small values of $[\text{wt. \% O}]$ and $[\text{wt. \% M}]$ and consequent difficulties

Table 4. Comparisons of interaction coefficients at 1600 °C.

System	Source of data for recommended values	e_O^M estimated by investigators	Recommendations from present study			Sigworth and Elliott ⁷⁾		
			e_O^M	e_M^O	r_O^M	e_O^M	e_M^O	r_O^M
Fe-Cr-O	Fruchan ¹⁴⁾	-0.037	-0.038	-0.13	0.0002	-0.04	-0.14	0
Fe-V-O	Kay <i>et al.</i> ¹⁶⁾	-0.14	-0.14	-0.46	0	-0.3	-0.97	—
Fe-Al-O	Janke <i>et al.</i> ¹³⁾	—	-2.81	-4.77	1.03	-3.9	-6.6	1.7
Fe-Zr-O	Fruchan ²⁾	(-3.0)	(-3.41)	(-19.5)	(1.91)	-3.0	—	0
Fe-Ti-O	Janke <i>et al.</i> ²⁰⁾	—	-0.42	-1.27	0.026	-0.6	-1.8	0.031

( ) at 1680 °C

Table 5. Data for estimation of deoxidation constant.

System	Oxide	ΔG_{14}° (cal/mol)	ΔG_{15}° (cal/mol) (from Ref. 7))	ΔG_{16}° (cal/mol) (from Ref. 7))
Fe-Cr-O	Cr ₂ O ₃	270 550-61.35 $T^{25)}$	-4 600+11.20 T	28 000+0.69 T
	Cr ₃ O ₄	323 900-63.25 $T^{25)}$	do.	do.
	FeCr ₂ O ₄			
Fe-V-O	V ₂ O ₃	-287 000+54.0 $T^{25)}$	4 950+10.9 T	do.
Fe-Al-O	Al ₂ O ₃	401 500-76.91 $T^{25)}$	15 000+6.67 T	do.
Fe-Zr-O	ZrO ₂	258 000-42.5 $T^{25)}$	8 300+11.95 T	do.
Fe-Ti-O	Ti ₃ O ₅	-577 500+97.69 $T^{25)}$	7 440+10.75 T	do.
	Ti ₂ O ₃	-354 000+58.36 $T^{25)}$	do.	do.

in determination of chemical compositions.

Discrepancies in the values of K as reported by investigators themselves (within bracket in Table 3) and as estimated in the present study for Fe-Al-O and Fe-Ti-O systems may be noted in Table 3. This is due to the fact that investigators employed limiting slope method or linear regression analysis (see *Chapter I*) and in the present study K values are based on curve fitting by model 3 covering all data points in [wt.% O] *vs.* [wt.% M] experimental data and using second-order interaction coefficient as well. These are entirely different estimation procedures. Scatters in experimental data therefore led to the discrepancy.

So far as the deoxidation constant, K , is concerned there have been many more experimental investigations, which ought to be considered for recommending its value. It has been done through a separate exercise¹⁰⁾ as outlined below.

IV. Assessment of Deoxidation Constants

There are two methods of finding out deoxidation constant, K .

1. Thermodynamic Estimation

Consider the reactions:

$$M_aO_b(s, l) = aM(s, l) + \frac{b}{2}O_2(g); \quad \Delta G_{14}^\circ \dots\dots\dots(14)$$

$$[M]_{1 \text{ wt.\% std. state}} = M(s, l); \quad \Delta G_{15}^\circ \dots\dots\dots(15)$$

$$[O]_{1 \text{ wt.\% std. state}} = \frac{1}{2}O_2(g); \quad \Delta G_{16}^\circ \dots\dots\dots(16)$$

Multiplying Eq. (15) by a and Eq. (16) by b and then

subtracting from Eq. (14) leads to:

$$M_aO_b(s, l) = a[M]_{1 \text{ wt.\% std. state}} + b[O]_{1 \text{ wt.\% std. state}} \Delta G_{17}^\circ \dots\dots\dots(17)$$

Reaction (17) is the same as reaction (1) with the difference that in Eq. (1) the $[M]$ and $[O]$ are at any arbitrary state, where as in Eq. (17) they are at 1 wt.% standard states in the Henrian Scale.

$$\Delta G_{17}^\circ = \Delta G_{14}^\circ - a\Delta G_{15}^\circ - b\Delta G_{16}^\circ \dots\dots\dots(18)$$

It may also be noted that:

$$\Delta G_{17}^\circ = -2.303RT \log K \dots\dots\dots(19)$$

Since fairly reliable experimental values of ΔG_{14}° , ΔG_{15}° and ΔG_{16}° are available for most deoxidizer systems, K can be estimated on the basis of these with the help of Eqs. (18) and (19).

Table 5 presents the values of ΔG_{14}° , ΔG_{15}° and ΔG_{16}° (taken from Ref. 25)) as well as estimated equations of $\log K$ for the systems Fe-Cr-O, Fe-V-O, Fe-Al-O, Fe-Zr-O and Fe-Ti-O. For estimation of the deoxidation constant for the reaction:

the additional data have been taken from Turkdogan.²⁶⁾

2. Direct Experimental Values

Numerous experimental investigations have been reported in literature where the deoxidation constants were determined directly by studying the equilibria

of reactions represented by Eq. (1). Direct determination of K is, in principle, a more accurate method. However there are difficulties, especially when the deoxidizer is very reactive such as in Fe-Al-O, Fe-Zr-O and Fe-Ti-O systems. These have already been discussed. They arise from the following:

- 1) errors in sampling and analysis at low concentrations of [wt.% O] and [wt.% M].
- 2) difficulty of containing metal and oxide in the same crucible; also crucible-deoxidizer reaction,
- 3) existence of several oxides and hence the resulting uncertainty in some systems, and
- 4) other problems specific to systems.

Literature review revealed considerable discrepancies amongst investigators. Even compilers^{25,27} differed amongst themselves. Therefore it was decided to assess the data critically.

The procedure consisted of selecting some experimental data and then find out the best fit equation of the type:

$$\log K = \frac{A}{T} + B \dots\dots\dots(21)$$

where T is temperature in degrees Kelvin, by linear regression analysis.

It is to be recognized that discrepancies amongst investigators arise due to:

- 1) experimental errors, and
- 2) errors involved in extrapolation of data beyond the experimental temperature range. Quite often K had been determined in a limited temperature range only and the $\log K$ vs. $1/T$ relation determined from it.

The following procedure was adopted in selection of experimental values of K from literature.

(1) They should lie within an approximately acceptable range established by several reliable investigations.

(2) They are not extrapolated values.

(3) Experimental details were available for examination.

These accepted values along with thermodynamically estimated deoxidation constants were used for finding out the best fit values of A and B in Eq. (21).

Table 6 presents the list of data sources selected for this exercise. It shows that while for some systems data are sufficient, for some others, such as Fe-Zr-O and Fe-Ti-O there is a scarcity of reliable experimental values of K .

As an illustration, Fig. 6 presents a comparison of various sources of data for the deoxidation constant for the reaction:

in the form of $\log K$ vs $1/T$ plots. The thermodynamically estimated as well as the best fit line are also shown.

Table 7 presents deoxidation constants estimated in this study. The best fit set is the recommended one. Figure 7 gives the [wt.% O] vs. [wt.% M] relationship for the different systems calculated on the basis of Eq. (13) and with the help of estimated values

Table 6. Sources of experimental data selected for deriving best fit of Eq. (21).

System	Oxide in equilibrium	Source of selected data (year)	Ref. No.	Temperature range selected (°C)
Fe-Cr-O	Cr ₂ O ₃	Chen and Chipman (1947)	28)	1595
		Turkdogan (1954)	29)	1565 ~ 1600
		Nakamura <i>et al.</i> (1971)	30)	1500 ~ 1700
		Janke <i>et al.</i> (1976)	13)	1600
	Cr ₃ O ₄	Sakao <i>et al.</i> (1962)	31)	1600
		Janke <i>et al.</i> (1976)	13)	1600
	FeCr ₂ O ₄	Chen <i>et al.</i> (1947)	28)	1595
		Sakao <i>et al.</i> (1962)	31)	1600
		Kojima <i>et al.</i> (1968)	12)	1600
		Buzek <i>et al.</i> (1972)	32)	1600
		Janke (1978)	33)	1500 ~ 1700
		Kim and McLean (1979)	34)	1500 ~ 1700
Fe-V-O	V ₂ O ₅	Chipman <i>et al.</i> (1951)	35)	1600
		Narita <i>et al.</i> (1969)	36)	1500 ~ 1700
		Kay <i>et al.</i> (1971)	16)	1500 ~ 1700
		Kojima <i>et al.</i> (1971)	15)	1600
	FeV ₂ O ₄	Buzek <i>et al.</i> (1972)	32)	1600
		Chipman <i>et al.</i> (1951)	35)	1600
		Narita <i>et al.</i> (1969)	36)	1500 ~ 1700
		Kay <i>et al.</i> (1971)	16)	1500 ~ 1700
		Kojima <i>et al.</i> (1971)	15)	1600
Fe-Al-O	Al ₂ O ₃	Gokcen <i>et al.</i> (1953)	37)	1680 ~ 1866
		McLean <i>et al.</i> (1965)	38)	1723 ~ 1823
		Schenck <i>et al.</i> (1970)	39)	1600
		Fruehan (1970)	19)	1600
		Rohde <i>et al.</i> (1971)	40)	1600 ~ 1700
		Buzek (1971)	41)	1600
		Janke <i>et al.</i> (1976)	20)	1600
Fe-Zr-O	ZrO ₂	Buzek <i>et al.</i> (1972)	32)	1600
		Jacquemot <i>et al.</i> (1974)	9)	1500 ~ 1700
		Janke <i>et al.</i> (1976)	20)	1600
Fe-Ti-O	Ti ₃ O ₅	Smellie <i>et al.</i> (1972)	24)	1500 ~ 1700
		Janke <i>et al.</i> (1976)	20)	1600
	Ti ₂ O ₃	Janke <i>et al.</i> (1976)	20)	1600

of e_{O}^{M} , r_{O}^{M} and K (Tables 4 and 7) and literature values of e_{M}^{M} (Table 2). All curves are at 1 600 °C. For Fe-Zr-O the interaction coefficients of 1 680 °C have been assumed to be valid at 1 600 °C.

V. Conclusions

(1) Numerical, computer-oriented curve-fitting exercises have been carried out on experimental [oxygen] solubility, *i.e.*, [wt.% O] *vs.* [wt.% M] data for molten Fe–Cr–O, Fe–V–O, Fe–Al–O, Fe–Zr–O and Fe–Ti–O systems, in order to extract values of first and second order cross-interaction coefficients (e_0^M , r_0^M).

Fig. 6. Comparison of various data on deoxidation constant for the reaction: $\text{Al}_2\text{O}_3(s) = 2[\text{Al}] + 3[\text{O}]$.

(2) Five different calculation models based on different assumptions were used for the above exercise in order to assess significance of various interaction coefficients.

(3) Consideration of second order interaction coefficient (r_0^M) always gave the best fit.

(4) Based on the results obtained, a simplified relation between [wt.% O] *vs.* [wt.% M] in molten iron in equilibrium with oxide, M_aO_b , has been proposed. It is claimed to be sufficiently precise and also amenable to analytical solution.

(5) Accepted values of e_0^M , r_0^M , e_0^O , e_M^O and e_M^O at 1 600 °C (1 680 °C for Fe–Zr–O) have been presented for these deoxidation systems.

Fig. 7. Deoxidation equilibria in liquid iron at 1 600 °C.

Table 7. Deoxidation constants estimated in the present study.

System	Oxide (Conc. range (%M))	Log K Thermodynamic estimated	Log K Best fit (Recommended set)	$K_{1600^\circ\text{C}}$ Thermodynamic estimate	$K_{1600^\circ\text{C}}$ Best fit
Fe–Cr–O	FeCr_2O_4 (<3.0)	$-\frac{53\,922}{T} + 23.1$	$-\frac{45\,796}{T} + 18.83$	2.12×10^{-6}	2.39×10^{-6}
	Cr_2O_3 (3.0~8.0)	$-\frac{42\,777}{T} + 18.75$	$-\frac{45\,531}{T} + 20.25$	8.15×10^{-5}	8.73×10^{-5}
	Cr_3O_4 (>8.0)	$-\frac{49\,322}{T} + 21.77$	$-\frac{48\,850}{T} + 21.43$	2.73×10^{-5}	2.23×10^{-5}
Fe–Al–O	Al_2O_3	$-\frac{62\,784}{T} + 20.17$	$-\frac{58\,473}{T} + 17.74$	4.46×10^{-14}	3.32×10^{-14}
Fe–Zr–O	ZrO_2	$-\frac{42\,329}{T} + 12.2$	$-\frac{41\,258}{T} + 11.86$	3.98×10^{-11} (3.36×10^{-10}) ^φ	6.8×10^{-11} (5.43×10^{-10}) ^φ
Fe–V–O	FeV_2O_4 (<0.2)	—	$-\frac{46\,452}{T} + 17.92$	—	1.32×10^{-7}
	V_2O_3 (>0.2)	$-\frac{42\,198}{T} + 17.0$	$-\frac{44\,422}{T} + 18.06$	2.95×10^{-6}	2.2×10^{-6}
Fe–Ti–O	Ti_3O_5 (<0.4)	$-\frac{90\,727}{T} + 29.15$	$-\frac{91\,034}{T} + 29.34$	5.13×10^{-20}	5.45×10^{-20}
	Ti_2O_3 (>0.4)	$-\frac{55\,751}{T} + 17.9$	$-\frac{55\,751}{T} + 18.08$	1.36×10^{-12}	2.06×10^{-12}

( )^φ Values at 1 680 °C

(6) Deoxidation constants (K) for the above systems have been assessed. Log K vs. $1/T$ relations have been proposed by linear regression analysis of selected experimental values and thermodynamic estimates.

(7) [wt.% O] vs. [wt.% M] solubility curves in molten iron in equilibrium with oxide products have been calculated from the accepted values of thermodynamic parameters.

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