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Equilibrium Constant of Reaction $Al_2O_3(s)=2\underline{Al}+3\underline{O}$ in Liquid Iron

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After inspecting the results of the experimental investigations hitherto published regarding the equilibrium constant of the reaction $Al_2O_3(s)=2\underline{Al}+3\underline{O}$, the Gokcen and Chipman's result was considered to be more reliable than those of other investigators. The reason for it was that their result agrees exactly with that of the thermodynamic calculation of Chipman. The Geller and Dicke's experimental result and the result of the thermodynamic calculation of Chipman were revised, using the new thermodynamic data. It was confirmed that the agreement between the revised Geller and Dicke's result and the Gokcen and Chipman's result above stated is very good, and the discrepancy between the original Chipman's result and the result revised by the present authors is very small.

The average of the following three results may be expressed by:

$$\log K_2 = \log a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3 = -\frac{65{,}200}{T} + 21.33$$

1) The experimental result of Geller and Dicke revised by the present authors.

2) The experimental result of Gokcen and Chipman.

3) The result of the thermodynamic calculation of Chipman revised by the present authors.

Introduction

The following reaction

$$Al_2O_3(s) = 2\underline{Al}+3\underline{O} \qquad \cdots\cdots\cdots(1)$$

in liquid steel is very important for steelmaking. Hence the experimental works regarding the equilibrium constant of this reaction $K_1=[\%\,\mathrm{Al}]^2[\%\,\mathrm{O}]^3$ or $K_2=a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3$ were carried out by many investigators, especially by Wentrup and Hieber¹⁾, Geller and Dicke²⁾, Hilty and Crafts³⁾ and Gokcen and Chipman⁴⁾. Thermodynamic calculations on the same subject were also attemped by Schenck⁵⁾, Kubaschewsky⁶⁾, Richardson⁽⁷⁾, Chipman⁽⁸⁾ and other investigators, because the equilibrium constant in question might be found by thermodynamic calculations more reliably than by experiments on account of experimental difficulties at high temperatures. The purpose of this investigation is to determine the reliable equilibrium constant K_2 by inspecting the results of investigations hitherto published on this problem.

1. Experimental Results

The results of experimental works by the investigators above mentioned are expressed by the following equations:

$$\log K_1 = \log [\%\,\mathrm{Al}]^2[\%\,\mathrm{O}]^3 = -\frac{71{,}200}{T} + 27.98 \quad \text{(Wentrup–Hieber, 1939)} \quad \cdots\cdots(2)$$

$$\log K_1 = \log [\%\,\mathrm{Al}]^2[\%\,\mathrm{O}]^3 = -\frac{58{,}600}{T} + 18.90 \quad \text{(Geller–Dicke, 1943)} \quad \cdots\cdots\cdots(3)$$

$$\log K_1 = \log [\%\,\mathrm{Al}]^2[\%\,\mathrm{O}]^3 = -\frac{58{,}600}{T} + 22.75 \quad \text{(Hilty–Crafts, 1950)} \quad \cdots\cdots\cdots(4)$$

$$\log K_2 = \log a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3 = -\frac{64{,}000}{T} + 20.48$$

$$\text{(Gokcen–Chipman, 1950)} \cdots(5)$$

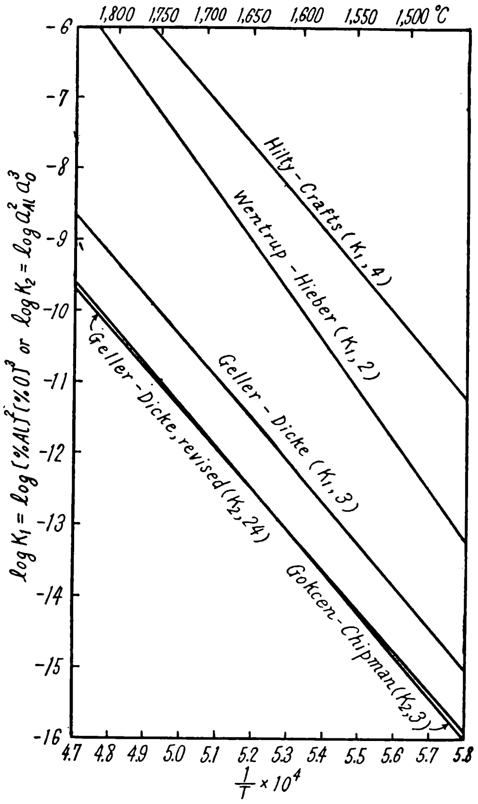

Fig. 1 Relalionship between $\log K_1$ or $\log K_2$ and temperature. Number in bracket indicates number of equation.

where a_{Al} and a_{O} represent respectively the activity of aluminium and oxygen in iron solutions, standard state being one pct Henry solution of aluminium or oxygen in iron-aluminium or iron-oxygen melts. Figs. 1 and 2 show the above equations graphically. Among these equations, Wentrup and Hieber's one seems to be unreliable as pointed out by Geller and Dicke⁽⁹⁾. The result of Hilty and Crafts deviates far from the result of Gokcen and Chipman which agrees exactly with the result of thermodynamic calculations carried out by Chipman as explained later. According to Chipman⁽¹⁰⁾, the explanation of the experimental errors of Hilty and Crafts must be sought in the nature of the products of deoxidation. The result of Geller and Dicke is also unsatisfactory, as errors are involved in the method of treating their experimental data notwithstanding the fact that their experiments were carried out under the procedure in which experimental errors might be avoided to a great degree.

The present authors considered their experimental data reliable and attemped to determine a revised equation representing the relationship between the equilibrium constant K_2 and temperature, using those and recent thermodynamic data regarding iron solutions.

Many investigators treated with the equilibrium constant of the reaction $\underline{C}+\underline{O}=CO\,(gas)$ in iron solution. The results of Geller[11], Marshall and Chipman[12] and Turkdogan et al[13]. are given below:

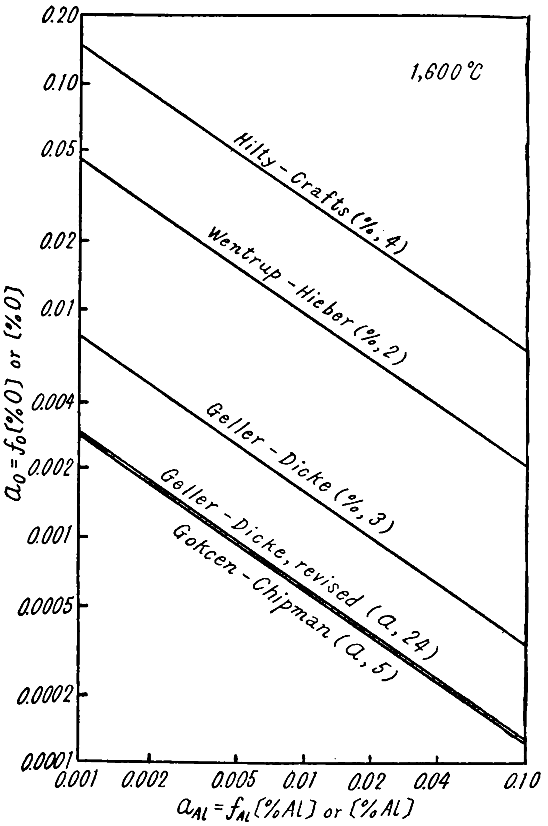

Fig. 2 Relationship between a_{Al} or $[\%\,Al]$ and a_O or $[\%O]$ at 1,600°C. Number in bracket indicates number of equation.

$$\log K_1' = \log[\%\,C][\%\,O] = -\frac{790}{T}-2.182 \quad \text{(Geller, 1942)} \qquad \cdots\cdots\cdots(6)$$

$$\log K_2' = \log a_C a_O = -\frac{1{,}860}{T}-1.643 \quad \text{(Marshall-Chipman, 1942)} \qquad \cdots\cdots\cdots(7)$$

$$\log K_2' \doteqdot \log a_C a_O = -\frac{1{,}056}{T}-2.131 \quad \text{(Turkdogan et al., 1955)} \qquad \cdots\cdots\cdots(8)$$

where a_C and a_O are the activity of carbon and oxygen respectively, standard state being one pct Henry solution of carbon or oxygen in iron-carbon or iron-oxygen melts. From Eq. (6), Geller and Dicke indirectly determined the oxygen contents of the equilibrated iron solutions, which contained carbon from about 0.4 to about 1.1 pct. However, they did not take into account the activities of carbon and oxygen in their calculations.

For the similar purpose, the present authors adoped here Eq. (8) given by Turkdogan et al., as this equation was estimated to be more reliable than Eq. (6), and the activities of aluminium and oxygen in the equilibrated melts established by Geller and Dicke were calculated in the following manner.

Now, the melts in this case are the iron solutions containing carbon except aluminium and oxygen as solutes. Hence Eq. (8) is expressed by the following formula:

$$\log K_2' = \log f_C[\% C]\, f_O\, [\% O] = \log f_C^{(C)} f_C^{(O)} f_C^{(Al)}[\% C] f_O^{(O)} f_O^{(C)} f_O^{(Al)}[\% O] = -\frac{1,056}{T} - 2.131 \qquad \cdots\cdots\cdots(9)^*$$

where f_C and f_O are the activity coefficients of carbon and oxygen respectively in iron-carbon-aluminium-oxygen melts, $f_C^{(C)}$ is the activity coefficiefnt of carbon in iron-carbon melts, and the following equation was obtained by Turkdogan et al.[14]:

$$\log f_C^{(C)} = 0.233[\% C] \quad \text{when} \quad C < 1.0\% \quad \text{at} \quad 1,560-1,760°C \qquad \cdots\cdots\cdots(10)$$

$f_O^{(O)}$ is the activity coefficient of oxygen in iron-oxygen melts, and according to Daster and Chipman[15] $f_O^{(O)} = 1$ in wide steelmaking temperature range.

$f_C^{(O)}$ and $f_O^{(C)}$ are the interaction coefficients in iron-carbon-oxygen melts, and according to Turkdogan et al[16].

$$\log f_C^{(O)} = -0.364[\% O] \quad \text{at} \quad 1,560-1,760°C \qquad \cdots\cdots\cdots(11)$$

$$\log f_O^{(C)} = -0.485[\% C] \quad \text{when} \quad C < 1\% \quad \text{at} \quad 1,560-1,760°C \qquad \cdots\cdots\cdots(12)$$

$f_O^{(Al)}$ is the interaction coefficient in iron-aluminium-oxygen melts. It may be determined when interaction parameter $e_O^{(Al)} (= \partial \log f_O^{(Al)} / \partial [\% Al])$ is known, because aluminium contents in the melts at the equilibrium state in the experiments of Geller and Dicke is very low and the following equation may be estimated to be valid in this case:

$$\log f_O^{(Al)} = e_O^{(Al)}[\% Al] \qquad \cdots\cdots\cdots(13)$$

The relationship between the value of $e_O^{(Al)}$ and temperature is given by Gokcen and Chipman[17].

$f_C^{(Al)}$ is the interaction coefficient in iron-carbon-aluminium melts.

The following expression represents the relationship between interaction parameters $\varepsilon_{Al}^{(C)}$ and $e_{Al}^{(C)}$:

$$\varepsilon_{Al}^{(C)} = \frac{\partial l_n \gamma_{Al}^{(C)}}{\partial N_C} = e_{Al}^{(C)} \cdot \frac{M_C}{0.2425} \qquad \cdots\cdots\cdots(14)$$

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* As to the notation of activity coefficient, f will be used when activity coefficient is related to composition in weight pct, and when composition is represented in terms of atom fraction, γ will be employed.

where N_C is the atom fraction of carbon in the melts, $\gamma_{Al}^{(C)}$ is the interaction coefficient in the melts, M_C is the atomic weight of carbon. From the Wagner's theory[18], the following equation may be valid:

$$e_C^{(Al)}=e_{Al}^{(C)}\cdot\frac{M_C}{M_{Al}} \quad \cdots\cdots\cdots(15)$$

where $e_C^{(Al)}$ is the interaction parameter in the melts, and M_{Al} is the atomic weight of aluminium.

Furthermore, because of the very low contents of aluminium in the melts, the following formula can be obtained:

$$\log f_C^{(Al)}=e_C^{(Al)}[\%\,Al] \quad \cdots\cdots\cdots(16)$$

From Eqs. (14), (15) and (16), the values of $f_C^{(Al)}$ may be determined when the value of $\varepsilon_{Al}^{(C)}$ and the contents of aluminium in the melts are known. Recently Chipman and Floridis[19] found the value of $\varepsilon_{Al}^{(C)}$ to be 6.7 at 1,600°C.

Consequently, from the above mentioned equations, the equilibrium oxygen contents or the activities of oxygen at 1,600°C may be calculated when the equilibrium carbon and aluminium contents in the melts at the same temperature are known by analysis. When $f_C^{(Al)}$ is assumed to be independent of temperature in the wide steelmaking temperature range, the relationship between the equilibrium oxygen contents or the activities of oxygen and temperatures can also be determined.

The activity of aluminium in iron-carbon-aluminium-oxygen melts is expressed by the following formula:

$$a_{Al}=f_{Al}[\%\,Al]=f_{Al}^{(Al)}f_{Al}^{(O)}f_{Al}^{(C)}[\%\,Al] \quad \cdots\cdots\cdots(17)$$

where f_{Al} is the activity coefficient of aluminium in iron-carbon-aluminium-oxygen melts, $f_{Al}^{(Al)}$ is the activity coefficient of aluminium in iron-aluminium melts. Chipman and Floidis[20] expressed the relationship between the activity coefficient of aluminium and the atom fraction of aluminium N_{Al} in iron-aluminium melts by the following formula:

$$\log\gamma_{Al}^{(Al)}=-1.51+2.60N_{Al} \quad \text{when} \quad N_{Al}<0.2 \text{ (10.8 weight pct) at 1,600°C} \quad \cdots(18)$$

where $\gamma_{Al}^{(Al)}$ is the activity coefficient of aluminium in iron-aluminium melts, standard state being pure aluminium melt.

The recalculation of the works of Chipman and Floridis by the present authors, however, led to the following formula which is described later:

$$\log\gamma_{Al}^{(Al)}=-1.68+3.80N_{Al} \quad \text{when} \quad N_{Al}<0.1 \text{ (5.1 weight pct) at 1,600°C} \quad (19)$$

Althought their results are controvertible, Eq. (19) was adopted in the following calculation.

Generally speaking, from Eq. (19) the relationship between the activity coefficient $f_{\mathrm{Al}}^{(\mathrm{Al})}$ (standard state being one pct Henry solution of aluminium in iron-aluminium melts) and the weight pct of aluminium $[\%\mathrm{Al}]$ in iron-aluminium melts can be derived as expressed by the following formula:

$$\log f_{\mathrm{Al}}^{(\mathrm{Al})}=\frac{212.23[\%\mathrm{Al}]}{2{,}698+28.87[\%\mathrm{Al}]}+\log\frac{2{,}698}{2{,}698+28.87[\%\mathrm{Al}]}. \qquad \cdots\cdots\cdots(20)$$

As in the present case, however, the equilibrium aluminium contents in the melts is very low, $f_{\mathrm{Al}}^{(\mathrm{Al})}$ can be determined from the following equation:

$$\log f_{\mathrm{Al}}^{(\mathrm{Al})}=\frac{212.23[\%\mathrm{Al}]}{2{,}698} \qquad \cdots\cdots\cdots(21)$$

$f_{\mathrm{Al}}^{(\mathrm{O})}$ is the interaction coefficient in iron-aluminium-oxygen melts, and its value is obtainable from the relationship between the interaction parameter $e_{\mathrm{Al}}^{(\mathrm{O})}=\partial\log f_{\mathrm{Al}}^{(\mathrm{O})}/\partial[\%\mathrm{O}]$ and temperatures given by Gokcen and Chipman[21]. Because the following equation is valid in the very dilute solutions of oxygen which are the concern here:

$$\log f_{\mathrm{Al}}^{(\mathrm{O})}=e_{\mathrm{Al}}^{(\mathrm{O})}[\%\mathrm{O}] \qquad \cdots\cdots\cdots(22)$$

$f_{\mathrm{Al}}^{(\mathrm{C})}$ is the interaction coefficient in iron-aluminium-carbon melts and, as stated previously, $\varepsilon_{\mathrm{Al}}^{(\mathrm{C})}=6.7$ at 1,600°C according to Chipman and Floridis. Hence, $e_{\mathrm{Al}}^{(\mathrm{C})}=\partial\log f_{\mathrm{Al}}^{(\mathrm{C})}/\partial[\%\mathrm{O}]$ at the same temperature can be derived from Eq. (14) and, further, the following equation is also valid in the present case where the equilibrium carbon contents are in the range from about 0.4 to about 1.1 pct, as it was confirmed by Chipman and Floridis that $e_{\mathrm{Al}}^{(\mathrm{C})}$ is constant in the above range of carbon contents:

$$\log f_{\mathrm{Al}}^{(\mathrm{C})}=e_{\mathrm{Al}}^{(\mathrm{C})}[\%\mathrm{C}] \qquad \cdots\cdots\cdots(23)$$

Consequently, from Eqs. (17), (21), (22) and (23), the activites of aluminium in the equilibrated iron-carbon-aluminium-oxygen melts at 1,600°C can be determined which are the concern here, and also at various temperatures

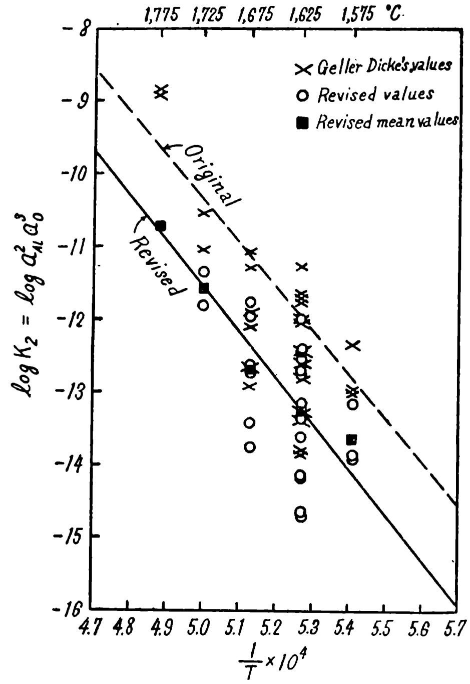

Fig. 3 Relationship between $\log K_2=\log a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3$ and temperature, revised result of Geller-Dicke

when $f_{\mathrm{Al}}^{(\mathrm{Al})}$ and $f_{\mathrm{Al}}^{(\mathrm{C})}$ are assumed to be independent of temperature.

The calculations regarding the equilibrium constant $K_2 = a_{\mathrm{Al}}^2\, a_{\mathrm{O}}^3$ of the reaction expressed by Eq. (1) were carried out in the procedure mentioned above using the experimental data given by Geller and Dicke and the result is shown in Figs. 3, 1 and 2. From the straight full line in Fig. 3, the following revised equation can be obtained:

$$\log K_2 = \log a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3 = -\frac{62{,}500}{T} + 19.70 \qquad \cdots\cdots\cdots(24)$$

It is worth noticing that the straight line representing Eq. (24) approximately agrees with the straight line representing Eq. (5) given by Gokcen and Chipman as shown in Fig. 1 and Fig. 2.

2. Thermodynamic Calculations

Among the thermodynamic calculation attempted to find the equilibrium constant K_1 or K_2 by many investigators, the result obtained by Chipman[22] is thought to be the most reliable one, because the thermodynamic data used in his calculation are new and reliable and, especially, the result of his calculation exactly agrees with the experimental result of Gokcen and Chipman as stated previously.

The procedure of calculation taken by Chipman was as follows:

$$2\mathrm{Al}(1) = 2\underline{\mathrm{Al}}(1\%), \qquad \Delta F_1^\circ = -23{,}400 - 15.4T \qquad \cdots\cdots\cdots(25)$$

$$\frac{3}{2}\mathrm{O}_2(\mathrm{gas}) = 3\underline{\mathrm{O}}(1\%), \qquad \Delta F_2^\circ = -83{,}790 - 1.71T \qquad \cdots\cdots\cdots(26)$$

$$\mathrm{Al_2O_3(s)} = 2\mathrm{Al}(1) + \frac{3}{2}\mathrm{O}_2(\mathrm{gas}), \qquad \Delta F_3^\circ = 400{,}000 - 76.6T \qquad \cdots\cdots\cdots(27)$$

$$\mathrm{Al_2O_3(s)} = 2\underline{\mathrm{Al}}(1\%) + 3\underline{\mathrm{O}}(1\%), \qquad \Delta F_4^\circ = \Delta F_1^\circ + \Delta F_2^\circ + \Delta F_3^\circ = 292{,}800 - 93.7T \qquad \cdots\cdots\cdots(28)$$

In the above equations, the notation (1%) means that one pct Henry solution is chosen as standard state.

Hence,

$$\log K_2{}^* = \log a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3 = -\frac{64{,}000}{T} + 20.48 \qquad \cdots\cdots\cdots(29)$$

The above equation is exactly the same as Eq. (5) experimentally determined by Gokcen and Chipman.

Last year, Hillert et al.[23] determined the activities of aluminium in solid silver-aluminium alloys at three temperature, e.g., 642°, 722° and 820°K by electromotive force measurements of the cell:

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* In the original paper of Chipman, the equilibrium constant in Eq. (29) is expressed by $K_1 = [\%\mathrm{Al}]^2 [\%\mathrm{O}]^3$ instead of $K_2 = a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3$.

$$\mathrm{Al(s)\,|\,AlCl_3\ in\ NaCl(l)\,|\,Ag\text{-}Al\ alloy(s)}\ .$$

Chipman and Floridis[24] extrapolated the values obtained by Hillert et al. up to 1,052° −1,183°K to determine the activities of aluminium in liquid silver-aluminium melts, and further determined the activity coeffients of aluminium, $\varepsilon_{\mathrm{Al}}^{(\mathrm{Al})}(=\partial \ln \gamma_{\mathrm{Al}}^{(\mathrm{Al})}/\partial N_{\mathrm{Al}})$ and $\varepsilon_{\mathrm{Al}}^{(\mathrm{C})}(=\partial \ln \gamma_{\mathrm{Al}}^{(\mathrm{C})}/\partial N_{\mathrm{C}})$ in iron-aluminium or iron-carbon-aluminium melts, after they obtained the data regarding the distribution of aluminum between silver and carbon-free iron or liquid iron containing carbon by experiments at 1,600°C.

Eq. (18) is the results of the above mentioned investigation. Consequently, Eq. (29) was revised utilizing this new thermodynamic data.

For this purpose, the results obtained by Chipman and Floridis were inspected by recalculation in the exactly same procedure as that these authors adopted.

The results of recalculation regarding extrapolation of the values obtained by Hillert et al. up to 1,052°-1,183°K are given in Table 1, in which the common logarithm of the activity of aluminium in silver-aluminium melts, e.g., $\log a(a_{\mathrm{Al(s)}}=1)$, was calculated under the assumption that the values dE/dT given in Table 1 in the paper of Chipman and Floridis can be applied up to 1,183°K. In order to convert $a(a_{\mathrm{Al(s)}}=1)$ into $a(a_{\mathrm{Al(l)}}=1)$, the activity of pure solid aluminium was determined taking pure liquid aluminium as standard state. For this purpose, the change in standard free energy of the following reaction was obtained:

$$\mathrm{Al(s)}=\mathrm{Al(l)},\quad \Delta F^0=F^0(\mathrm{l})-F^0(\mathrm{s})$$

ΔF^0 may be expressed by Eq. (30) when the values of the molecular heat of aluminium at liquid and solid states and molecular heat of fusion of aluminium are taken as follows:

$$C_p(\mathrm{l})=7.0^{25)},\quad C_p(\mathrm{s})=4.80+3.22\cdot10^{-3}T,^{25)}\quad \Delta H_f=2{,}550\ \mathrm{cal\ at\ }931.7^\circ\mathrm{K}^{25)}$$

$$\Delta F^0=1{,}898+11.5T-5.07T\log T+0.00161T^2 \qquad \cdots\cdots\cdots(30)$$

The values in the second column in Table 1 were determined from this equation. Hence, the values of $\log a(a_{\mathrm{Al(l)}}=1)$ can be obtained as given in the fifth column in Table 1.

Table 1. Recalculated values of $\log \gamma_{\mathrm{Al}}$ by the same method of calculation as Chipman et al. from Hillert's data.

Temp. °K	ΔF° cal	$\log a_{\mathrm{Al(s)}}$ $(a_{\mathrm{Al}(l)}=1)$	Liquidus in silver-aluminium melts				
			$\log a$ $(a_{\mathrm{Al(s)}}=1)$	$\log a$ $(a_{\mathrm{Al}(l)}=1)$	N_{Al}	$\log N_{\mathrm{Al}}$	$\log \gamma_{\mathrm{Al}}$ $(a_{\mathrm{Al}(l)}=1)$
1052	−340	0.0706	−1.9355	−1.8649	0.212	−0.6737	−1.19
1093	−448	0.0896	−2.2090	−2.1194	0.170	−0.7696	−1.35
1138	−563	0.1081	−2.5311	−2.4230	0.120	−0.9208	−1.50
1183	−686	0.1267	−3.1394	−3.0127	0.070	−1.1549	**−1.86**

Table 2. Values of log γ_{Al} in silver-aluminium melts at 1,873°K.

N_{Al}	log γ_{Al} recalculated	log γ_{Al} by Chipman et al.
0.212	-0.67	-0.67
0.170	-0.79	-0.79
0.120	-0.91	-0.93
0.070	**-1.17**	**-1.08**

Table 3. Recalculated values of log γ_{Al} in iron at 1,873°K.

Heat No.	Silver layer N_{Al}	Iron layer		N_{Al}(in Ag) / N_{Al}(in Fe)	log γ_{Al} (in Ag) (Fig. 4)	γ_{Al} (in Ag)	γ_{Al} (in Fe)	log γ_{Al} (in Fe)
		N_{Al}	N_C					
2	0.0047	0.0080	—	0.588	-1.43	0.0372	0.0219	**-1.66**
3	0.0241	0.0377	—	0.639	-1.34	0.0457	0.0292	**-1.53**
4	0.0994	0.1447	—	0.687	-1.02	0.0955	0.0656	**-1.18**
6	0.2435	0.3330	—	0.731	-0.58	0.263	0.192	-0.72
7	0.3033	0.3993	—	0.760	-0.41	0.389	0.296	-0.53
21	0.2690	0.3501	—	0.768	-0.50	0.316	0.243	-0.61
29	0.0673	0.0954	—	0.705	-1.15	0.0708	0.0499	**-1.30**
30	0.1400	0.1858	—	0.753	-0.88	0.132	0.0994	-1.00
8	0.0601	0.0488	0.1835	1.232	-1.18	0.0661	0.0814	**-1.09**
9	0.1625	0.1551	0.1408	1.048	-0.81	0.155	0.162	-0.79
11	0.2815	0.2969	0.0928	0.948	-0.47	0.339	0.321	-0.49
12	0.2775	0.2615	0.1313	1.061	-0.48	0.331	0.351	-0.45
13	0.3260	0.3611	0.0789	0.903	-0.34	0.457	0.413	-0.38
31	0.0235	0.0173	0.1944	1.358	-1.34	0.0457	0.0621	**-1.21**
32	0.2700	0.2700	0.1008	1.000	-0.50	0.316	0.316	-0.50
34	0.0731	0.0490	0.1880	1.492	-1.13	0.0741	0.111	**-0.95**
16	0.0294	0.0408	0.0388	0.721	-1.32	0.0479	0.0345	**-1.46**
18	0.1856	0.2375	0.0353	0.781	-0.74	0.182	0.142	-0.85
20	0.3034	0.3668	0.0372	0.827	-0.41	0.389	0.322	-0.49
22	0.0198	0.0224	0.0538	0.884	-1.36	0.0437	0.0386	**-1.41**
24	0.1004	0.1178	0.0474	0.852	-1.02	0.0955	0.0814	**-1.09**
25	0.1801	0.2169	0.0365	0.830	-0.76	0.174	0.144	-0.84
33	0.1044	0.1300	0.0415	0.803	-1.01	0.0977	0.0785	**-1.11**

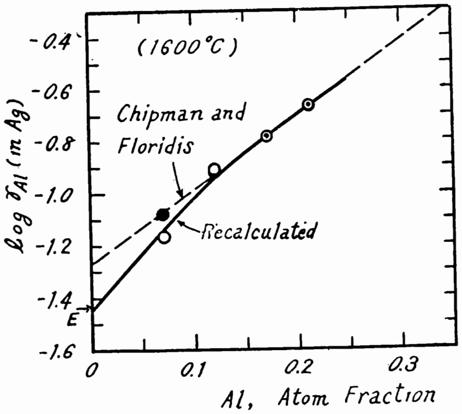

Fig. 4 Activity coefficient of aluminium in silver-aluminium alloys at 1,600°C.

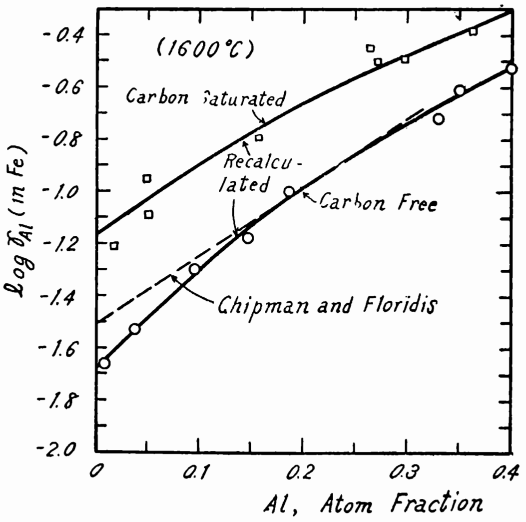

Fig. 5 Activity coefficient of aluminium in iron at 1,600°C.

Comparing the last column in Table 1 in the paper of Chipman and Floridis with the last column in Table 1 given above, we can see that there is a great discrepancy between the values determined at 1,183°K by Chipman and Floridis and the present authors.

Now, the results of recalculation regarding log $\gamma_{\mathrm{Al(in\ Ag)}}(a_{\mathrm{Al(l)}}=1)$ in silver-aluminium melts at 1,873°K (1,600°C) are given in Table 2 and shown in Fig. 4. This is conducted under the same assumption that $\log\gamma_{\mathrm{Al(in\ Ag)}}(a_{\mathrm{Al(l)}}=1)$ is inversely proportional to absolute temperature as assumed by Chipman and Floridis. Fig. 4 shows that the value of the common logarithm of the activity coefficient of aluminium in an infinitely dilute silver-aluminium solution, e.g., $\log\gamma^{0}_{\mathrm{Al(in\ Ag)}}(a_{\mathrm{Al(l)}}=1)$, to be determined by the extrapolation of the full line curve given by the present authors, somewhat deviates from that determined by Chipman and Floridis, however, our value approximately agrees with that estimated by Chou and Elliott75).

Recalculations were further continued to find the relationship between the activity coefficients of aluminium $\gamma^{(\mathrm{Al})}_{\mathrm{Al}}$ and γ_{Al} respectively in iron-aluminium and iron-carbon-aluminium melts at 1,600°C (standard state being pure liquid aluminium) and the atom fraction of aluminium, using the curve in Fig. 4 given by the present authors and the data obtained by Chipman and Floridis who carried out experiments regarding the distribution of aluminium between silver and carbon-free iron melts or iron melts containing carbon at 1,600°C. The results of this calculation are given in Table 3 and shown in Fig. 5.

As to $\gamma^{(\mathrm{Al})}_{\mathrm{Al}}$, Chipman and Floridis formulated Eq. (18) from a straight broken line given by these authors in Fig. 5. Eq. (19), however, can be obtained from the results of our recalculation instead of Eq. (18).

The interaction coefficient $\gamma^{(\mathrm{C})}_{\mathrm{Al}}$ in iron-carbon-aluminium melts is expressed by the following equation:

$$\log\gamma^{(\mathrm{C})}_{\mathrm{Al}}=\log\gamma_{\mathrm{Al}}-\log\gamma^{(\mathrm{Al})}_{\mathrm{Al}} \quad \cdots\cdots\cdots(31)$$

When $\log\gamma^{(\mathrm{Al})}_{\mathrm{Al}}$ and $\log\gamma_{\mathrm{Al}}$ are obtained respectively from Fig. 5 and Table 3 the relationship between $\log\gamma^{(\mathrm{C})}_{\mathrm{Al}}$ and the atom fraction of carbon N_{C} can be determined as shown in Fig. 6. The curve in this figure agrees exactly with that determined by Chipman and Floridis, and the value of interaction parameter $\varepsilon^{(\mathrm{C})}_{\mathrm{Al}}=\partial\ln\gamma^{(\mathrm{C})}_{\mathrm{Al}}/\partial N_{\mathrm{C}}$ can be determined as stated previously from this curve.

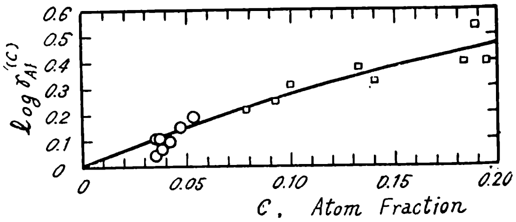

Fig. 6 Effect of carbon on activity coefficient of aluminium.

In order to revise Eq. (28) given by Chipman which is necessary for calculation of the equilibrium constant K_2 of the reaction expressed by Eq. (1), it is very important to obtain the value of ΔF_4^0 in Eq. (28) as accurately as possible. One of the means for this purpose is to have a reliable value of the activity coefficient of aluminium in an infinitely dilute iron-aluminium solution γ^0_{Al}.

The values of γ^0_{Ai} are as follows:

$$\log \gamma^0_{Al} = -1.51 \quad \text{from Eq. (18)}$$

$$\log \gamma^0_{Al} = -1.68 \quad \text{from Eq. (19).}$$

Strictly speaking, it is impossible to decide which is more reliable of the two values given above. Because in the electromotive force measurements of Hillert et al. mentioned previously, the accuracy of the values measured at 642° and 722°K for an silver-aluminium alloy containing aluminium of 0.053 atom fraction is pretty low, and consequently it is probable that the accuracy of the last value of dE/dT, e.g., 20.8 in Table 1 in the paper of Chipman and Floridis is likely unsatisfactory.

In the following calculations, however, the value determined by the present authors, e.g., $\log \gamma^0_{Al} = -1.68$ was adopted assuming $\log \gamma^0_{Al}$ to be independent of temperature.

Now, the change in the standard free energy ΔF_1^0 of the reaction Al(1) = Al(1%) is expressed by the following formula:

$$\Delta F_1^0 = RT \ln a_{Al}(1\%) \qquad \cdots\cdots\cdots(32)$$

where $a_{Al}(1\%)$ represents the activity of aluminium in iron-aluminium melts, standard state being one pct Henry solution of aluminium, and its value can be obtained from the following formula:

$$a_{Al}(1\%) = \gamma^0_{Al}\frac{0.5585}{M_{Al}} = 4.35\times10^{-4}$$

where M_{Al} is the atomic weight of aluminium.

Hence,

$$\Delta F_1^0 = -15.39T$$

$$2\text{Al}(1) = 2\text{Al}(1\%) \quad \Delta F_1^0 = -30.78T \qquad \cdots\cdots\cdots(33)$$

Therefore, the change in the standard free energy of the reaction expressed by Eq. (28), e.g., ΔF_4^0 can be found from Eqs. (33), (26) and (27) as given in the following formula:

$$\Delta F_4^0 = 316{,}210 - 109.09T$$

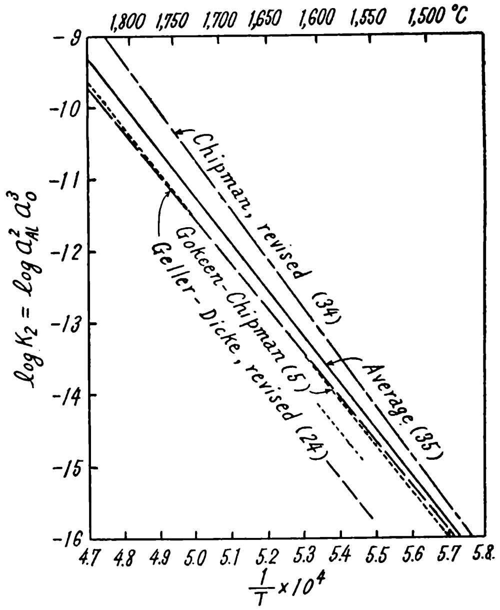

Fig. 7 Relationship between $\log K_2$ and temperature. Number in bracket indicates number of equation.

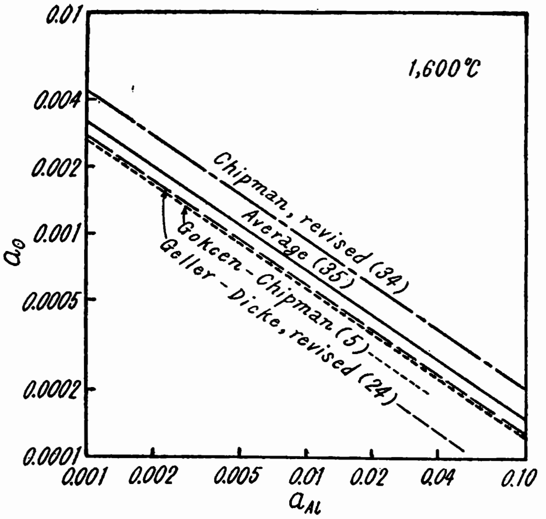

Fig. 8 Relationship between a_O and a_{Al} at 1,600°C. Number in bracket indicates number of equation.

Hence, the equilibrium constant of the reaction expressed by (1) is

$$\log K_2 = \log a_{Al}^2 a_O^3 = -\frac{69,117}{T} + 23.84 \qquad \cdots\cdots\cdots(34)$$

This result is graphically shown in Figs. 7 and 8, in which the result obtained by Gokcen and Chipman together with the results of Geller and Dicke, and of Chipman, revised by the present authors, are included. Although these results do not agree each other, the disparity observed among them is so small that we can consider the agreement to be very good. The equation representing the mean value of the equilibrium constant K_2, to be determined from Eqs. (5), (24), and (34), can be expressed as follows:

$$\log K_2 = \log a_{Al}^2 a_O^3 = -\frac{65,200}{T} + 21.33 \qquad \cdots\cdots\cdots(35)$$

By the method described by Gokcen and Chipman, the relationship between the actual concentrations of aluminium and oxygen in iron-aluminium-oxygen melts equilibrated at 1,600°C was obtained as shown in Fig. 9. In this calculation, it was assumed that Eq. 11 is valid even up to 0.1 pct of aluminium. It is worthy of note that the minimum point in the actual concentration of oxygen is at about 0.02 pct of aluminium. Addition of aluminium beyond this point, leads to the increase in the concentration of oxygen.

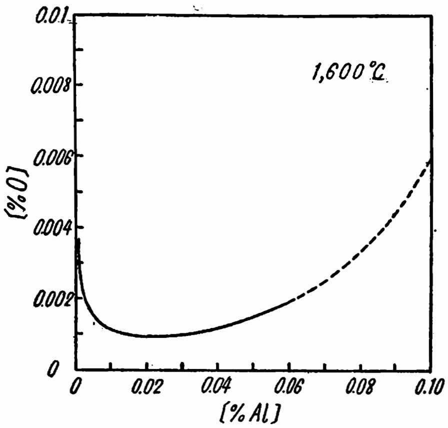

Fig. 9 Relationship between [%O] and [%Al] at 1,600°C.

Summary

The results of the present investigation may be summarized as follows:

1) The purpose of the present investigation is to determine the reliable formula

concerning the equilibrium constant of the deoxidation reaction with aluminium in liquid steel.

2) The result of experiments carried out by Geller and Dicke was revised, using the recent thermodynamic data regarding iron solutions.

3) Prior to the revision of the result of thermodynamic calculation of Chipman concerning the equilibrium constant in question, the result of investigation of Chipman and Floridis, who studied on the activity and the activity coefficient of aluminium in iron-carbon-aluminium melts, was recalculated.

4) Agreement among the results of the following investigations is very good:

i) The experimenatal result of Geller and Dicke, revised by the present authors.

ii) The experimental result of Gokcen and Chipman.

iii) The result of thermodynamic calculation of Chipman, revised by the present authors.

5) The average of these three results mentioned above is expressed by the following formula:

$$\log K_2 = a_{\mathrm{Al}}^2 a_{\mathrm{O}}^3 = -\frac{65{,}200}{T} + 21.33$$

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