

Solubility of Nitrogen and Carbon in CaO-Al₂O₃ Melts in the Presence of Graphite

KLAUS SCHWERDTFEGER AND HANS GEORG SCHUBERT

CaO-Al₂O₃ slags were melted in graphite crucibles under N₂-CO-Ar gas mixtures at 1600°C. The contents of total nitrogen, cyanide and total carbon of the slags were determined by chemical analyses of quenched samples taken by suction from the melt. The nitrogen is present in the melt as nitride N³⁻ ion and cyanide CN⁻ ion, and carbon as cyanide and carbide C₂²⁻ ion. The equilibrium constants for the respective reactions were evaluated. It is found that the nitride capacity of the melt decreases whereas the cyanide and carbide capacities increase with increasing CaO/Al₂O₃ ratio.

METALLURGICAL slags melted under reducing conditions often contain noticeable contents of nitrogen and carbon which may cause nitrogenation and carburization of the metal phase, or they may influence other reactions. Several laboratory investigations have been carried out on the thermodynamics and kinetics of solution of these elements. The results obtained by the different authors, however, are very conflicting, so that more research is desirable on this subject. The previous literature has been reviewed recently.¹⁻³

In the present study the solubility of nitrogen and carbon in CaO-Al₂O₃ slags of various compositions is investigated. This work is a continuation of a previous investigation conducted on the aluminate melt with 55 wt pct CaO-45 wt pct Al₂O₃,¹ in which nitrogen was found to be present as nitride N³⁻ and cyanide CN⁻, and carbon as CN⁻ and carbide C₂²⁻. The slags were melted in graphite crucibles under atmospheres of controlled partial pressures of N₂ and CO, and the equilibrium contents of nitrogen and carbon were determined as a function of gas composition for a temperature of 1600°C and a total pressure of 1 atm.

EXPERIMENTAL TECHNIQUE

The experiments were performed in a similar manner as described in previous publications from this laboratory.^{1,3,4} A Tammann furnace was used. The reaction tube of recrystallized alumina was inserted into the carbon tube of the furnace and closed gas tight at both ends. The gas phase was prepared by mixing nitrogen, carbon monoxide and argon with capillary flow meters. The major part (250 cc per min) of the gas was introduced into the reaction tube through a packing of graphite granules located under the crucible, a small part (15 cc per min) was bubbled through the melt (via a graphite tube) to ensure stirring. The starting slags were premelted from reagent grade CaCO₃ and Al₂O₃. The graphite crucibles were machined from high purity (99.98 pct) graphite.

An amount of 100 g of slag was used in the individual experiments. The slag was heated to 1600°C under

pure CO and held under the same gas for 1 h. Then the N₂-CO-Ar gas was admitted. Total reaction time was between 30 and 100 h, during which samples of about 3 g were taken from the melt by suction into 4 mm ID graphite tubes, in regular intervals. The samples were sand blasted (to remove adhering graphite) and analyzed for total carbon, total nitrogen, and cyanide contents. In some of the samples also the acid soluble carbon was determined which was practically identical to total carbon, in agreement with previous measurements.³ Hence, the amounts of graphite in the slag are negligibly small. The applied analytical procedures have been described in a preceding paper.¹ Further, the Ca and Al contents were analyzed in order to check whether changes of Ca/Al ratio occurred during the long reaction times.

EXPERIMENTAL RESULTS AND DISCUSSION

The typical concentration-time curves are shown in Figs. 1 and 2. The zero point of the time scale is at the time when the carbon monoxide atmosphere was changed to the N₂-CO-Ar gas mixture. In the upper diagrams the contents of total nitrogen (N)_{total}, of cyanide (CN) and of total carbon (C)_{total} are shown. Similar curves were obtained for all the other experiments. In the lower diagrams the analyzed Ca/Al ratios are plotted against time. Because of the relative unprecision of the individual Ca/Al values average values are given for all the experiments conducted with the same master slag. Error bars indicate the scatter of the individual points. With slags of nominal composition 40 wt pct CaO/60 wt pct Al₂O₃ constant (N)_{total}, (CN) and (C)_{total} contents are attained after some time (*e.g.* Fig. 1), and the Ca/Al ratio does not change within the experimental error. With the CaO-rich slag of 50 wt pct CaO/50 wt pct Al₂O₃, however, the curves for carbon and cyanide have maxima (*e.g.* Fig. 2). Further the Ca/Al ratios decrease with time which is apparently due to volatilization of some Ca containing species. The similar observations have been made in the previous experiments^{1,2} using slag of 55 wt pct CaO/45 wt pct Al₂O₃. With the slag of 45 wt pct CaO/55 wt pct Al₂O₃ there were very slight carbon and cyanide maxima visible only in the experiments conducted at low partial pressure of CO (*p*_{CO} = 0.2 atm). Presumably, the decarburization and the decrease of (CN) are related to the change of the Ca/Al ratio and the associated decrease of the carbide

KLAUS SCHWERDTFEGER and HANS GEORG SCHUBERT are with Max-Planck-Institut für Eisenforschung GmbH, Metallurgical Department, 4000 Düsseldorf, Germany.

Manuscript submitted October 26, 1976.

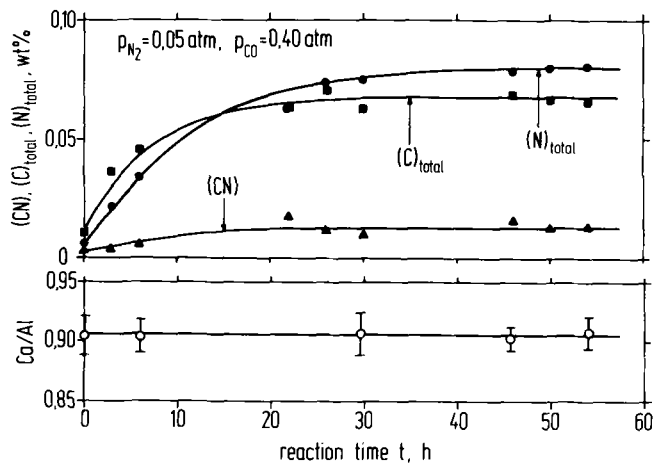


Fig. 1—Typical results on compositional changes occurring in slag of nominal 40 wt pct CaO/60 wt pct Al₂O₃ during equilibration with graphite and N₂-CO-Ar gas mixture (1600°C, 1 atm).

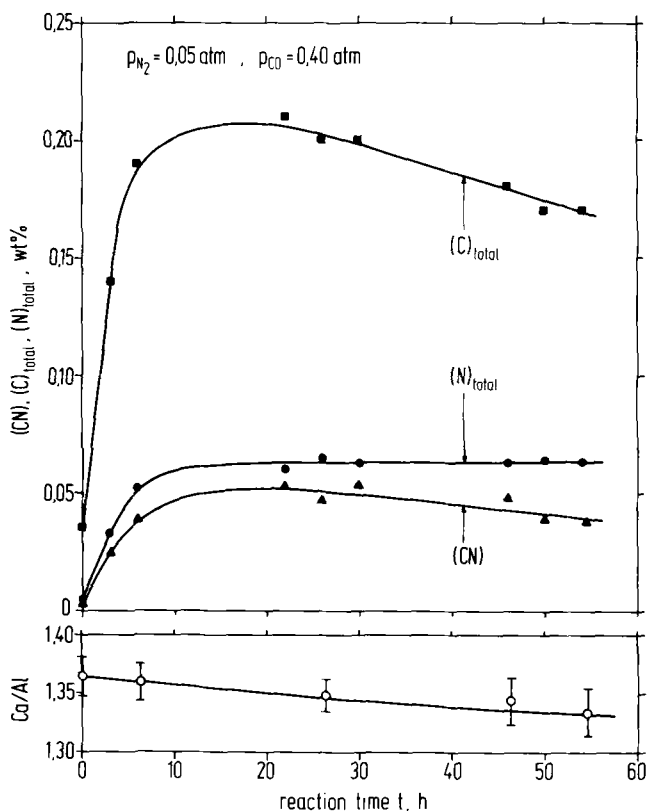
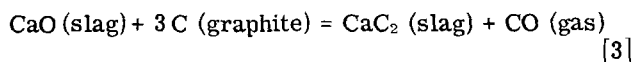
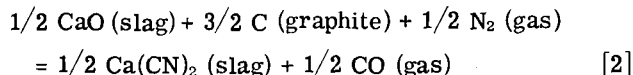
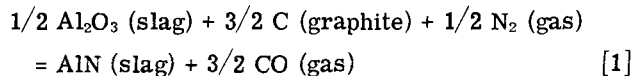


Fig. 2—Typical results on compositional changes occurring in slag of nominal 50 wt pct CaO/50 wt pct Al₂O₃ during equilibration with graphite and N₂-CO-Ar gas mixture (1600°C, 1 atm).

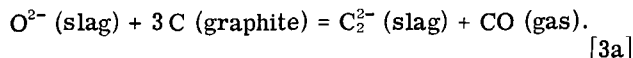
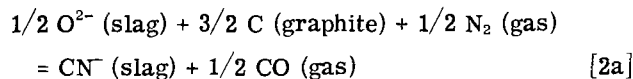
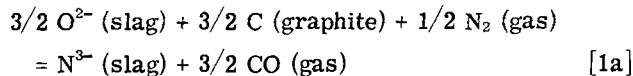
and cyanide solubilities. It is reasonable that the volatilization rate of Ca containing gaseous species and hence the associated change of Ca/Al ratio should increase with CaO content. These compositional changes cannot be avoided. Since they occur very slowly, however, it can be assumed that the system has enough time to respond so that, after passage through the maxima, the contents of carbide, cyanide and nitride are effectively close to the equilibrium values corresponding to the used gas phase and the particular Ca/Al ratio being present. The experimental

results are listed in Table I. For the 50 pct CaO/50 pct Al₂O₃ slag the data are given for two reaction times (30 h and 55 h) after the passage of the concentration maxima.

The chemical reactions for the formation of nitride, cyanide, and carbide can be written as



or in terms of ionic species as



In the sufficiently dilute solutions the activities of the nitride, cyanide, carbide can be set proportional to their mass fractions at constant CaO/Al₂O₃. Hence, by application of the law of mass action the equations

$$(\text{N})_{\text{nitride}} = K_{\text{nitride}} \sqrt{\frac{p_{\text{N}_2}}{p_{\text{CO}}^3}} \quad [1b]$$

$$(\text{CN}) = K_{\text{cyanide}} \sqrt{\frac{p_{\text{N}_2}}{p_{\text{CO}}}} \quad [2b]$$

$$(\text{C})_{\text{carbide}} = \frac{K_{\text{carbide}}}{p_{\text{CO}}} \quad [3b]$$

are obtained. The equilibrium "constants" K_{nitride} , K_{cyanide} , K_{carbide} contain the activity coefficients of the nitride, cyanide and carbide ions (or neutral species) respectively, and the activity of the oxygen ions (or neutral oxide components), and therefore depend on the slag composition. One may call these K 's "nitride capacity", "cyanide capacity", and so forth in accordance with the terms "sulfide capacity" or "sulfate capacity" introduced by Fincham and Richardson⁵ for the equilibrium constants describing the sulfur transfer between gas and slag phase.

According to Eqs. [1a] and [2a] the nitride and cyanide contents increase proportionally to $\sqrt{p_{\text{N}_2}}$ at constant p_{CO} . Hence, also $(\text{N})_{\text{total}}$ should increase with $\sqrt{p_{\text{N}_2}}$. For constant p_{N_2} the nitride content should vary proportionally to $p_{\text{CO}}^{-3/2}$ and the cyanide content proportionally to $p_{\text{CO}}^{-1/2}$. The carbide content should increase with p_{CO}^{-1} . The nitride content is computed from total nitrogen content $(\text{N})_{\text{total}}$ and cyanide content (CN) according to $(\text{N})_{\text{nitride}} = (\text{N})_{\text{total}} - \frac{1}{2}(\text{CN})$, and carbide content according to $(\text{C})_{\text{carbide}} = (\text{C})_{\text{total}} - \frac{12}{26}(\text{CN})$. The relationships are fulfilled, as shown in Fig. 3.

Two methods were used to evaluate the equilibrium constants. In the first method the $(\text{N})_{\text{nitride}}$ and $(\text{C})_{\text{carbide}}$ values were calculated from the analyti-

Table I. Equilibrium Contents of Total Nitrogen (N)_{total}, Cyanide (CN) and Total Carbon (C)_{total} in CaO-Al₂O₃ Melts Equilibrated with Graphite and N₂-CO-Ar Mixtures at 1600°C and 1 atm

P_{N_2} , atm	P_{CO} , atm	P_{AR} , atm	Reaction Time, h	(N) _{total} , Wt Pct	(CN), Wt Pct	(C) _{total} , Wt Pct	Wt Pct Ca/Wt Pct Al*	Wt Pct CaO ‡ Wt Pct Al ₂ O ₃
Nominal Initial Composition: 40 Wt Pct CaO/60 Wt Pct Al ₂ O ₃ †								
0.05	0.50	0.45	30	0.054	0.015	0.062	0.936	0.693
0.05	0.50	0.45	100	0.065	0.016	0.065	0.907	0.672
0.10	0.50	0.40	30	0.068	0.024	0.062	0.936	0.694
0.25	0.50	0.25	30	0.13	0.032	0.064	0.936	0.696
0.50	0.50	0	30	0.15	0.041	0.075	0.936	0.696
0.05	0.20	0.75	100	0.16	0.018	0.11	0.907	0.674
0.05	0.20	0.75	54	0.18	0.019	0.10	0.907	0.675
0.05	0.40	0.55	54	0.080	0.013	0.068	0.907	0.673
0.05	0.65	0.30	30	0.039	0.014	0.040	0.936	0.694
0.05	0.95	0	30	0.023	0.013	0.030	0.936	0.693
0.10	0.20	0.70	100	0.33	0.025	0.16	0.907	0.679
Nominal Initial Composition: 45 Wt Pct CaO/55 Wt Pct Al ₂ O ₃ †								
0.05	0.50	0.45	30	0.053	0.029	0.085	1.132	0.838
0.10	0.50	0.40	30	0.063	0.041	0.090	1.132	0.837
0.25	0.50	0.25	30	0.11	0.062	0.092	1.132	0.839
0.50	0.50	0	30	0.15	0.086	0.115	1.132	0.840
0.05	0.40	0.55	54	0.074	0.029	0.12	1.118	0.827
0.05	0.65	0.30	30	0.040	0.022	0.080	1.132	0.837
0.05	0.95	0	30	0.030	0.020	0.060	1.132	0.838
0.05	0.95	0	54	0.031	0.021	0.070	1.118	0.827
0.10	0.20	0.70	70	0.25	0.057	0.21	1.118	0.832
0.20	0.20	0.60	70	0.35	0.076	0.22	1.118	0.837
Nominal Initial Composition: 50 Wt Pct CaO/50 Wt Pct Al ₂ O ₃								
0.05	0.50	0.45	30	0.052	0.052	0.19	1.345	0.990
			55	0.052	0.044	0.18	1.333	0.982
0.10	0.50	0.40	30	0.074	0.055	0.18	1.345	0.992
			55	0.074	0.049	0.17	1.333	0.984
0.25	0.50	0.25	30	0.12	0.093	0.20	1.345	0.993
			55	0.11	0.093	0.20	1.333	0.983
0.50	0.50	0	30	0.17	0.15	0.21	1.345	0.994
			55	0.16	0.13	0.20	1.333	0.985
0.05	0.95	0	30	0.030	0.031	0.090	1.345	0.994
			55	0.028	0.026	0.090	1.333	0.985
0.05	0.65	0.30	30	0.043	0.036	0.14	1.345	0.992
			55	0.043	0.038	0.13	1.333	0.984
0.05	0.40	0.55	30	0.063	0.049	0.20	1.345	0.990
			55	0.063	0.039	0.17	1.333	0.983
0.05	0.29	0.75	30	0.14	0.085	0.33	1.345	0.988
			55	0.14	0.070	0.29	1.333	0.982

*The Ca/Al ratios are round values. They are read from the curves representing the chemically analysed Ca/Al ratios as a function of time. For each master slag one single curve was drawn to represent all the experimental points (see Figs. 1 and 2).

†Two batches of master slag were prepared in the investigation of the 40 pct CaO/60 pct Al₂O₃ and 45 pct CaO/55 pct Al₂O₃ slags which had slightly different compositions. Hence, two different numerical values appear in the column for Ca/Al.

‡Calculated according to the following procedure: () means contents in wt pct)

$$z = (Al_2O_3) + (CaO) = 100 - [(AlN) + (Ca(CN)_2) + (CaC_2)]$$

$$z = [(Al) - (Al)_{nitride}] \frac{102}{54} + \left[(Al) \frac{Ca}{Al}_{analysis} - (Ca)_{cyanide} - (Ca)_{carbide} \right] \frac{56}{40}$$

with

$$(AlN) = \left[(N)_{total} - \frac{14}{26}(CN) \right] \frac{41}{14}, (Ca(CN)_2) = (CN) \frac{92}{52},$$

$$(CaC_2) = \left[(C)_{total} - \frac{12}{26}(CN) \right] \frac{64}{24}, (Al)_{nitride} = \left[(N)_{total} - \frac{14}{26}(CN) \right] \frac{27}{14},$$

$$(Ca)_{cyanide} = (CN) \frac{40}{52}, (Ca)_{carbide} = \left[(C)_{total} - \frac{12}{26}(CN) \right] \frac{40}{24}.$$

These equations are solved for (Al)₂O₃ is then computed from

$$(Al_2O_3) = [(Al) - (Al)_{nitride}] \frac{102}{54} \text{ and } (CaO) \text{ from } (CaO) = z - (Al_2O_3).$$

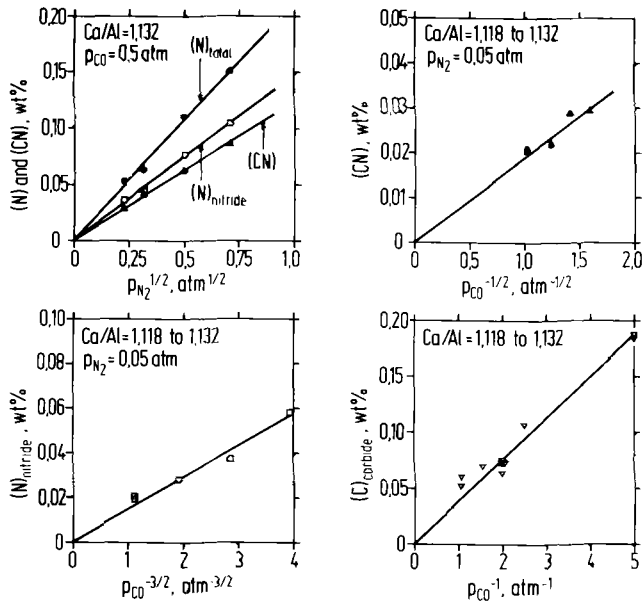


Fig. 3—Test of Eqs. [1a], [2a], [3a] on results obtained with slag of nominal initial composition 45 wt pct CaO/55 wt pct Al₂O₃ (1600°C).

cally determined (N)_{total}, (C)_{total} and (CN) values, and the *K*'s were calculated by application of Eqs. [1b], [2b], [3b]. The other method is graphical and serves to check the consistency of the *K* values derived with the first method. Only (N)_{total} and (C)_{total} are used in this evaluation. The total nitrogen content is given as

$$(N)_{\text{total}} = (N)_{\text{nitride}} + \frac{14}{28}(CN) = K_{\text{nitride}} \sqrt{\frac{p_{N_2}}{p_{CO}^3}} + \frac{14}{28} K_{\text{cyanide}} \sqrt{\frac{p_{N_2}}{p_{CO}}} \quad [4]$$

and total carbon as

$$(C)_{\text{total}} = (C)_{\text{carbide}} + \frac{12}{28}(CN) = \frac{K_{\text{carbide}}}{p_{CO}} + \frac{12}{28} K_{\text{cyanide}} \sqrt{\frac{p_{N_2}}{p_{CO}}} \quad [5]$$

Multiplying both sides of Eqs. [4] and [5] with $\sqrt{\frac{p_{CO}}{p_{N_2}}}$ the expressions

$$(N)_{\text{total}} \sqrt{\frac{p_{CO}}{p_{N_2}}} = \frac{K_{\text{nitride}}}{p_{CO}} + \frac{14}{28} K_{\text{cyanide}} \quad [6]$$

$$(C)_{\text{total}} \sqrt{\frac{p_{CO}}{p_{N_2}}} = \frac{K_{\text{carbide}}}{\sqrt{p_{N_2} p_{CO}}} + \frac{12}{28} K_{\text{cyanide}} \quad [7]$$

are derived. Hence, by plotting (N)_{total} $\sqrt{\frac{p_{CO}}{p_{N_2}}}$ against $1/p_{CO}$, or (C)_{total} $\sqrt{\frac{p_{CO}}{p_{N_2}}}$ against $1/\sqrt{p_{N_2} p_{CO}}$, straight lines should be obtained with the slopes being *K*_{nitride} or *K*_{carbide}, and the intersections on the ordinate being $\frac{14}{28} K_{\text{cyanide}}$ or $\frac{12}{28} K_{\text{cyanide}}$, respectively. These

plots are shown in Figs. 4 and 5. Alternatively it follows from Eqs. [4] and [5] that

$$(N)_{\text{total}} \sqrt{\frac{p_{CO}^3}{p_{N_2}}} = K_{\text{nitride}} + \frac{14}{28} K_{\text{cyanide}} p_{CO} \quad [8]$$

$$(C)_{\text{total}} p_{CO} = K_{\text{carbide}} + \frac{12}{28} K_{\text{cyanide}} \sqrt{p_{N_2} p_{CO}} \quad [9]$$

Hence, by plotting (N)_{total} $\sqrt{\frac{p_{CO}^3}{p_{N_2}}}$ against p_{CO} , or (C)_{total} p_{CO} against $\sqrt{p_{CO} p_{N_2}}$, again straight lines should be obtained with the slopes given by $\frac{14}{28} K_{\text{cyanide}}$

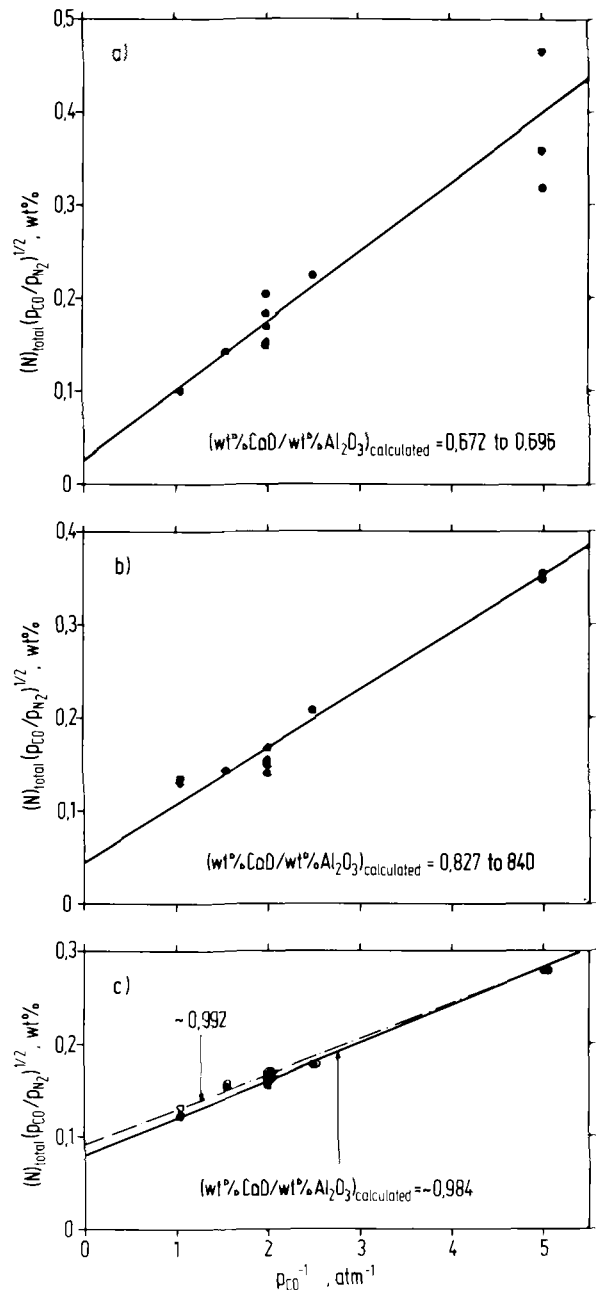


Fig. 4—Plot of experimental data in accordance with Eq. [6]. (a) Data for slags with nominal initial composition of 40 wt pct CaO/60 wt pct Al₂O₃, (b) data for slags with nominal initial composition of 45 wt pct CaO/55 wt pct Al₂O₃, (c) data for slags with nominal initial composition of 50 wt pct CaO/50 wt pct Al₂O₃.

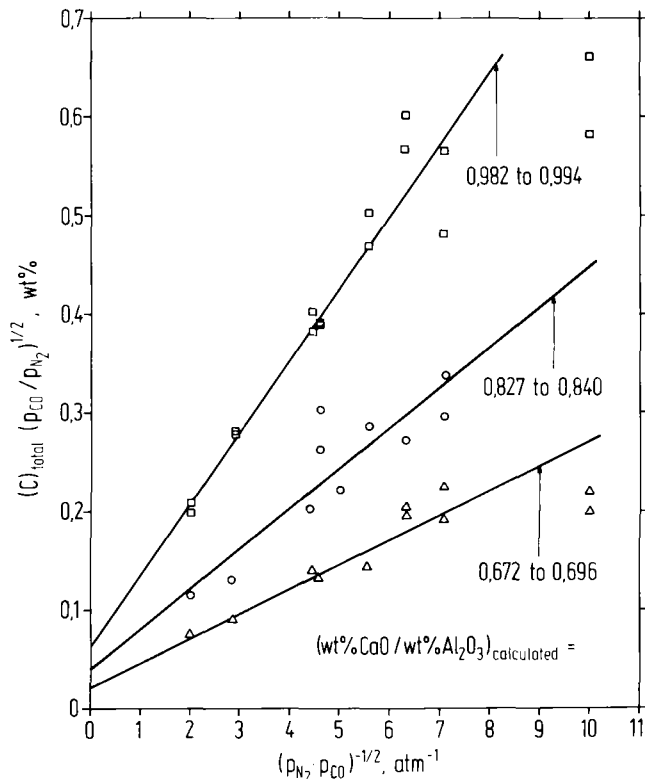


Fig. 5—Plot of experimental data in accordance with Eq. [7].

or $\frac{12}{26} K_{\text{cyanide}}$ and the intersections on the ordinate being K_{nitride} or K_{carbide} , respectively. These plots were also made.

It was found that K_{nitride} and K_{cyanide} could be determined, with sufficient precision (by using either Eq. [6] or Eq. [8]) for the slag with nominally 50 wt pct CaO/50 wt pct Al_2O_3 , Fig. 4(c). However, for the slags lower in CaO content only K_{nitride} could be evaluated. Since K_{cyanide} decreases with decreasing CaO content, the values for the intersection on the ordinate (Eq. [6], Figs. 4(a) and 4(b)) or for the slope (Eq. [8]) decrease and their precise numerical values could not be evaluated, due to the scatter of the experimental points. Hence, the analytically determined K_{cyanide} values were used and only the K_{nitride} values were obtained from the plots. On the other hand, K_{nitride} decreases with increasing CaO content. Consequently, for the CaO richer slag with 55 wt pct CaO/45 wt pct Al_2O_3 , which has been investigated previously,¹ only precise K_{cyanide} values can be evaluated from plots according to Eqs. [6] and [8]. Out of similar reasons the analytically determined K_{cyanide} values were used to obtain the K_{carbide} values from plots according to Eqs. [7] and [9].

The K values as obtained with the different methods are listed in Table II. There is a strong influence of slag composition. Although the K values can well be correlated with the Ca/Al ratios, it is more appropriate to choose a "basicity" $\text{CaO}/\text{Al}_2\text{O}_3$ for correlation, where CaO and Al_2O_3 comprise only the Ca and Al cations stoichiometrically attributable to the oxygen anions. The CaO and Al_2O_3 contents were computed from the chemically analyzed values for (Ca/Al), (N)_{nitride}, (CN), (C)_{carbide} taking AlN, $\text{Ca}(\text{CN})_2$ and CaC_2 as the neutral nitride, cyanide and carbide com-

ponents, in accordance with Eqs. [1] to [3]. The obtained (wt pct CaO/wt pct Al_2O_3) ratios are included in Table II, and the dependence of K_{nitride} , K_{cyanide} , K_{carbide} on (wt pct CaO/wt pct Al_2O_3) is shown in Fig. 6. Previous results on the solubility of carbon in nitrogen free aluminate melts³ have been used in drawing the curves in Fig. 6(c). The K_{carbide} values measured by Swisher⁶ are shown for comparison. Further, two points for K_{cyanide} as evaluated previously¹ from the data of Shimoo *et al*⁷ and Choh *et al*⁸ are included in Fig. 6(a).*

*Shimoo *et al*⁷ performed another series of experiments with $p_{\text{CO}} = 0.08$ atm, $p_{\text{N}_2} = 0.92$ atm (1550°C) and slag compositions ranging from 42 to 58 wt pct CaO. Although the dependence of nitride, cyanide and carbide solubilities on slag composition is qualitatively similar, the K_{cyanide} , K_{nitride} , K_{carbide} values evaluated from the results are smaller by a factor of 2 to 3 than the present values. The reason cannot be given with certainty for this severe disagreement. It is noted, however, that these experiments have been conducted in the range of partial pressures in which solid AlN is stable. This range is given by $p^3_{\text{CO}}/p_{\text{N}_2} \leq 0.073 a_{\text{Al}_2\text{O}_3}$, atm² (at 1600°C) as shown previously.¹ Inserting numerical values for $a_{\text{Al}_2\text{O}_3}$, it is seen that the used gas phase ($p_{\text{CO}} = 0.08$ atm and $p_{\text{N}_2} = 0.92$ atm) had a much too low ratio $p^3_{\text{CO}}/p_{\text{N}_2}$. Hence, the data are not included in Fig. 6 for comparison.

It is evident from Fig. 6 that K_{cyanide} and K_{carbide} increase with CaO/ Al_2O_3 ratio, whereas K_{nitride} decreases. Such a composition dependence is reasonable in view of Eqs. [1] to [3]. If the activity coefficients of AlN, $\text{Ca}_{0.5}\text{CN}$, CaC_2 change less with composi-

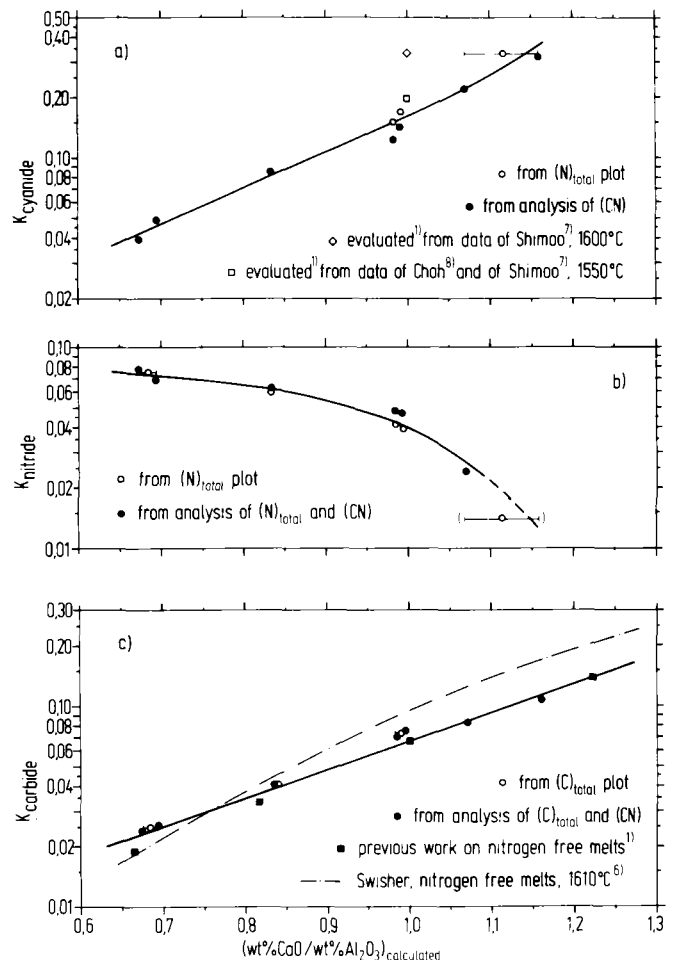


Fig. 6—Cyanide, nitride and carbide capacities as a function of CaO/ Al_2O_3 ratio for CaO- Al_2O_3 melts at 1600°C.

Table II. Numerical Values for K_{cyanide} , K_{nitride} and K_{carbide} in CaO-Al₂O₃ Melts at 1600°C

Nominal Initial Slag Composition, Wt Pct CaO	Basicity,* Wt Pct CaO Wt Pct Al ₂ O ₃	$K_{\text{cyanide}} = (\text{CN}) \sqrt{\frac{p_{\text{CO}}}{p_{\text{N}_2}}}$, Wt Pct			$K_{\text{nitride}} = (\text{N})_{\text{nitride}} \sqrt{\frac{p_{\text{CO}}}{p_{\text{N}_2}}}$, Wt Pct atm		$K_{\text{carbide}} = (\text{C})_{\text{carbide}} p_{\text{CO}}$, Wt Pct atm	
		From Chemical Analysis of (CN) [†]	From (N) _{total} [‡] Plot	From (C) _{total} [‡] Plot	From Chemical Analysis of (N) _{total} and (CN) [†]	From (N) _{total} Plot	From Chemical Analysis of (C) _{total} and (CN) [†]	From (C) _{total} Plot
40	0.675	0.0394	(0.044)	(0.044)	0.0779	0.075	0.0244	0.025
	0.694	0.0491	(0.044)	(0.044)	0.0697	0.075	0.0250	0.025
45	0.835	0.0854	(0.085)	(0.085)	0.0628	0.062	0.0408	0.041
	0.984	0.126	0.15	(0.135)	0.0481	0.041	0.0702	0.073
50	0.992	0.143	0.17	(0.135)	0.0464	0.039	0.0738	0.073
	1.07	0.222	0.33	n.d.	0.0240	0.014§	0.0825	n.d.
55¶	1.16	0.326	0.33	n.d.	n.d.	0.014§	0.107	n.d.

*Computed, see Table I.

† Average values for slags in same basicity group. (N)_{nitride} and (C)_{carbide} were computed from (N)_{total}, (CN) and (C)_{total} by (N)_{nitride} = (N)_{total} - $\frac{14}{26}$ (CN) and (C)_{carbide} = (C)_{total} - $\frac{12}{26}$ (CN).

‡ K_{cyanide} values in parenthesis are the average values of the analytically determined values (third column) for the slag with the same nominal initial composition. These values were used to locate the straight lines in plots according to Eqs. [6] to [9].

¶ Results from previous work (Ref. 1).

§ This value is unprecise due to the difficulties in the evaluation procedure as described in text.

tion than the activities of the oxide components, as might be anticipated, the nitride capacity should in fact increase with alumina activity, and cyanide as well as carbide capacities should increase with calcium oxide activity.

SUMMARY

The solubility of nitrogen and carbon in CaO-Al₂O₃ melts contained in graphite crucibles has been measured at 1600°C as a function of partial pressures of nitrogen and carbon monoxide. Nitrogen is dissolved as nitride N³⁻ and cyanide CN⁻, and carbon as carbide C₂²⁻ and cyanide CN⁻. The cyanide and carbide solubilities increase and the nitride solubility decreases with increasing CaO/Al₂O₃ ratio of the melt. Nitride, cyanide and carbide capacities have been computed from the experimental data and are given for slags with composition from 40 to 55 wt pct CaO.

ACKNOWLEDGMENTS

The authors wish to thank Messrs. I. R. Put and B. Seuren and Miss J. Rutten for their help in performing the experiments.

REFERENCES

1. K. Schwerdtfeger and H. G. Schubert: *Arch. Eisenhuettenw.*, 1974, vol. 45, pp. 649-55, 905.
2. K. Schwerdtfeger, H. G. Schubert, and W. Fix: Unpublished research, Max-Planck-Institut für Eisenforschung, 4000 Düsseldorf, Germany.
3. H. G. Schubert and K. Schwerdtfeger: *Arch. Eisenhuettenw.*, 1974, vol. 45, pp. 437-39.
4. K. Schwerdtfeger and H. G. Schubert: *Arch. Eisenhuettenw.*, 1974, vol. 45, pp. 499-507.
5. C. J. B. Fincham and F. D. Richardson: *Proc. Roy. Soc. A*, 1954, vol. 223, pp. 40-62.
6. J. H. Swisher: *Trans. TMS-AIME*, 1968, vol. 242, pp. 2033-37.
7. T. Shimoo, T. Iida, H. Kimura, and M. Kawai: *Nippon Kinzoku Gakkai-Shi*, 1972, vol. 36, pp. 723-27.
8. T. Choh, Y. Hanaki, T. Kato, and M. Inouye: *Trans. Iron Steel Inst. Jap.*, 1973, vol. 13, pp. 218-25.
9. R. H. Rein and J. Chipman: *Trans. TMS-AIME*, 1965, vol. 233, pp. 415-25.