The Slag-Metal Equilibrium in Tin Smelting

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An equilibrium study was undertaken to investigate the effect of the CaO/SiO_2 and Fe/SiO_2 ratios and the SnO and Al_2O_3 contents of slags on the distribution of Fe and Sn between slag and metal in tin smelting. The experiments were performed at 1200 °C by equilibrating Sn-Fe alloys with silicate slags under reducing conditions in closed crucibles. The slag and metal analyses were used to calculate the $\gamma_{SnO}/\gamma_{FeO}$ ratio in the slags and a multiple-linear regression on these values indicated that, in the range of slag compositions investigated, $\gamma_{SnO}/\gamma_{FeO}$ is a function only of the CaO/SiO_2 ratio. At 1200 °C, $\gamma_{SnO}/\gamma_{FeO}$ varies from about 1.1 for CaO-free slags to 3.6 for slags in which the CaO/SiO_2 ratio is 1.0. In practical applications, the slag-metal equilibrium in tin smelting is usually discussed in terms of the variation of the distribution coefficient, k, with the Fe content of the metal, where k is defined as k = [pct Sn]/[pct Fe] · (pct Fe)/(pct Sn). An equation for k was derived in terms of the atom fraction of iron in the metal, the $\gamma_{SnO}/\gamma_{FeO}$ in the slag, and the temperature. This equation was used to construct graphs of k as a function of the iron content over the slag compositions and at temperatures which cover the range of tin smelting practice.

I. INTRODUCTION

In the conventional smelting of tin, cassiterite (SnO_2) concentrate is reduced with coke or coal at between 1150 and 1300 °C to produce metal and slag. Iron oxides are invariably present in the concentrate and, as FeO and SnO_2 have standard free energies of formation of comparable magnitude, iron is reduced along with the tin. A two-stage reduction is necessary to produce tin with a low contamination of iron. In the first stage tin (with up to about 2 pct Fe) is produced by a mild reduction which leaves a high proportion of the charged tin unreduced in the slag. The slag is further reduced in a second stage under more severe conditions to produce a high iron alloy known as hardhead, which typically contains 20 to 60 pct Fe, and a low tin-containing slag (usually less than 1 pct SnO) which is discarded. Tin is recovered from the hardhead by incorporating it in the charge to the first stage. A more complete description of the process and its many variations has been given by Wright.[1]

In both stages of smelting, the relative distribution of Fe and Sn between slag and metal is governed by the equilibrium of the reaction

$$(SnO) + [Fe] = (FeO) + [Sn] \qquad [1]$$

where ( ) indicates solution in slag and [ ] indicates solution in metal. The equilibrium constant of Eq. [1] is given by

$$K_1 = \frac{a_{FeO}\,a_{Sn}}{a_{SnO}\,a_{Fe}} \qquad [2]$$

which on expanding and rearranging leads to

$$\frac{N_{FeO}}{N_{SnO}} = K_1 \cdot \frac{a_{Fe}}{a_{Sn}} \cdot \frac{\gamma_{SnO}}{\gamma_{FeO}} \qquad [3]$$

where N indicates mole fraction and γ indicates activity coefficient. For a specific alloy composition and temperature (*i.e.*, constant a_{Fe}, a_{Sn}, and K_1) the relative amount of Fe and Sn in the slag and alloy depends on the value of the ratio $\gamma_{SnO}/\gamma_{FeO}$. To improve the recovery of Sn relative to Fe a high value of $\gamma_{SnO}/\gamma_{FeO}$ is desired. The value of the activity coefficient of components of solutions depends on the composition of the solution, and hence slag composition is likely to be an important metallurgical parameter in tin smelting.

The aim of the present work was to determine the effect of slag composition on the value of the ratio $\gamma_{SnO}/\gamma_{FeO}$ in silicate slags. In particular, the effect of CaO/SiO_2 and Fe/SiO_2 ratios and the concentration of Al_2O_3 and SnO in slag were investigated. The technique used was to equilibrate Sn-Fe alloys with slags and determine the value of $\gamma_{SnO}/\gamma_{FeO}$ by means of Eq. [3].

Several investigators[2–5] have measured the absolute value of γ_{SnO} in silicate slags and their results are summarized in Table I. A value of around 1 to 1.5 applies to SnO-FeO-SiO_2 slags containing up to 10 pct Al_2O_3 while a value of 1.8 was found by Carbó Nóver and Richardson[2] for a commercial slag with a CaO/SiO_2 ratio of 0.22. Values of the ratio $\gamma_{SnO}/\gamma_{FeO}$ have been reported though there has been little work in this area.[6,7] It appears that a value of $\gamma_{SnO}/\gamma_{FeO}$ of about 1.4 may apply to CaO-free slags and that Al_2O_3 has little effect on the value.

II. EXPERIMENTAL

The alloy system Sn-Fe was selected for equilibration with silicate slags because it permitted determination of $\gamma_{SnO}/\gamma_{FeO}$ directly by means of Eq. [3] and because the variation of the activity of Sn and Fe are known with a fairly high degree of accuracy.[8] Equilibrations of the slag and alloy were conducted in such a way that equilibrium was approached from the high Sn in slag side since Harris and Hallett[9] have shown that equilibrium is approached quickly from this direction (about half hour in unstirred melts in their experiments) but only very slowly when tin oxide is required to diffuse into the slag *away* from the metal interface. According to some investigators[5,10] the results of some previous studies are suspect due to volatilization of SnO from slags and the possible prevention of attainment of

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Table I. Values of the Activity Coefficient of SnO in Slag Systems

Investigator	Slag Composition	γ_{SnO}	Temperature (°C)	Method of Measurement
CaO-free slags				
Carbó Nóver and Richardson[2]	$SnO-SiO_2$	~1.0	1000 1160 1250	Determination of oxygen content of Sn equilibrated with slag *via* the gas phase.
Grau and Flengas[3]	$SnO-SiO_2$	1.22 to 1.50	1100	Emf measurement using the cell $Sn,(SnO/SiO_2)/ZrO_2-CaO/NiO$, Ni.
Nagamori and Mackey[4]	$FeO-Fe_2O_3-SiO_2-Al_2O_3-CuO_{0.5}$			Equilibration of slags with Cu under a controlled $CO-CO_2$ atmosphere.
	$Fe/SiO_2 = 1.5$	2.4 ± 0.3	1200	
	$Fe/SiO_2 = 2.0$	1.5 ± 0.3	1200	
	$Fe/SiO_2 = 2.0$	0.8 ± 0.1	1300	
Grimsey and Dawson[5]	$FeO-Fe_2O_3-SiO_2(sat)-SnO$	1.0 ± 0.1	1300	Emf measurement using the cell Pt/Sn-Ag, SnO slag/ZrO_2-CaO/NiO, Ni/Pt.
Slag containing CaO				
Carbó Nóver and Richardson[2]	41.6 pct SiO_2, 9.1 pct CaO, 18.3 pct SnO, 18.0 pct FeO, 2.7 pct Al_2O_3, 5.0 pct NaO_2, 5.3 pct other oxides	1.8	1160	Determination of oxygen content of Sn equilibrated with slag *via* the gas phase.

equilibrium as a result. In this study, accordingly, the equilibrations were conducted in closed crucibles to minimize the loss of tin from the system.

A. *Materials*

The equilibrations were performed in fireclay crucibles containing initially a charge of 20 g pure tin in lump form and a mixture of 30 g of slag-forming materials. Reagent grade chemicals were used. The slag-forming mixtures were composed of CaO, SiO_2, Al_2O_3, SnO_2, Fe_2O_3, and Fe, all as fine powders, mixed in various proportions to give a range of slag compositions. The Fe_2O_3 and Fe were always present in the ratio 1:2.857 by mass which is the proportion required to form FeO on reaction:

$$Fe_2O_3 + Fe = 3FeO \qquad [4]$$

B. *Procedure*

Weighed amounts of the raw materials were placed in a crucible. A length of graphite rod was wedged across the inside of the opening of the crucible, above the raw materials, and the crucible was placed in a furnace set at a temperature to produce 1200 ± 5 °C inside the crucible. A piece of refractory brick was then placed on top of the crucible to close it.

The furnace was electrically heated by silicon carbide elements, and the function of the graphite was to maintain a low oxygen potential inside the crucible. This was necessary because the atmosphere in the furnace was air and a low oxygen potential was required to maintain the iron in the slag in the divalent state. The experimental results indicate that the graphite had a reducing effect on the system (*via* CO in the atmosphere of the crucible), but that equilibrium of the slag and metal with gas was not attained.

The crucibles were left in the furnace usually for 2 hours which was found to be sufficient to attain equilibrium of the slag and metal. After this the crucible was lifted out of the furnace, the refractory brick closure was removed by tapping it, and the contents were quenched by pouring into an inverted steel cone of the type used in fire-assaying. Usually the metal collected at the bottom of the cone and was easily separated from the slag. This technique was used to ensure rapid quenching of the slag and metal to prevent segregation within the samples and also to prevent reversal of reaction [1] during cooling. No oxidation of the metal in air occurred during this operation and there was negligible surface oxidation of the slag.

Though the bulk of the metal collected as a single piece, the slag usually contained numerous prills of metal which were clearly visible in polished samples under the microscope. A procedure was developed to clean the slag of metal prills prior to analysis. The slags were hand ground in a number of steps with sizing between the steps using a 250 μm screen. At each stage liberated prills were removed and the oversize material was further ground. This was continued until all prills were liberated and all the slag had passed the 250 μm screen. The procedure was effective because the liberated prills were flattened during grinding and were easily detected in the oversize slag and removed.

The bulk metal was sampled by drilling. The metal was analyzed for its Fe content using a wet chemical method and the slags for Sn, SiO_2, Fe, Al_2O_3, and CaO using X-ray fluorescence. The analyses were done by the South African Council for Mineral Technology (MINTEK). Measurement of the metallic content of the slags was not made, and in retrospect this is seen as a serious limitation of the data as it is not possible to ascertain how much of the scatter in the results is due to metallic entrainment. Determination of the Fe(III) content of the slag likewise was not made.

III. RESULTS

An initial series of runs was performed to examine the effect of time on the slag and metal compositions. The starting charge for these runs was:

Sn	20.0 g
CaO	4.5 g
SiO_2	10.5 g
Fe_2O_3	8.89 g
Fe	3.11 g
SnO_2	3.36 g

The results are shown in Table II, and the variations of the SnO content of the slag and Fe content of metal are shown in Figure 1. The SnO content of the slag decreased (after an initial increase) and the Fe content of the metal increased with time; *i.e.*, the reaction was in the desired direction for rapid attainment of equilibrium. The initial increase in the SnO content of the slag was due to oxidation of part of the Sn before the atmosphere in the crucible became reducing by reaction of the graphite with the air in the closed crucible.

The reducing nature of the atmosphere after the initial heating-up period is apparent in the continuous reduction of SnO and FeO over the 8-hour period. However, slag-metal equilibrium was attained within 2 hours though its position was continually changed thereafter by the reducing atmosphere. The attainment of slag-metal equilibrium within 2 hours is evident from the approximate constancy of the $\gamma_{SnO}/\gamma_{FeO}$ ratio (calculated as subsequently described) from 2 hours onward (Table II). Since the slag parameters did not change greatly during the equilibration trials (CaO/SiO_2 from 0.22 to 0.31, Fe/SiO_2 from 0.41 to 0.50, and pct Al_2O_3 from 4.0 to 10.6), approximate constancy of the ratio would be expected if the slag and metal were in equilibrium. The somewhat longer period to attain equilibrium than the 0.5 hour reported by Harris and Hallet for high SnO slags[9] is due probably to the need first to form a slag from the raw materials, particularly reaction [4] and the dissociation of SnO_2 into SnO, which from Figure 1 appear to have occurred within the first hour. Visual observation of crucibles randomly selected confirmed that the slag was fully melted after the first hour for those runs in which complete fusion of the charge occurred within 2 hours.

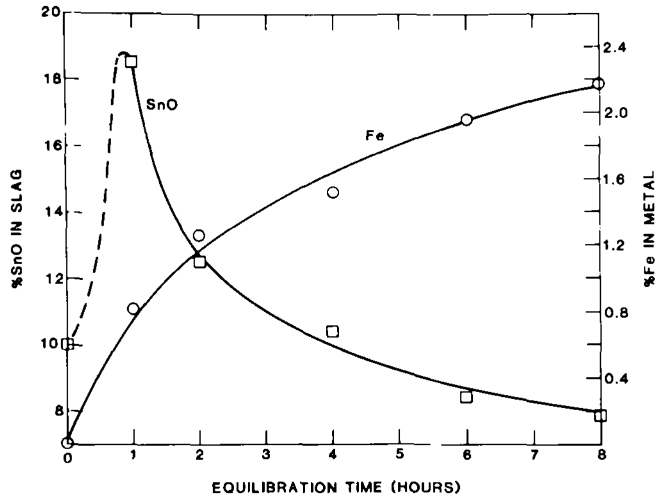

Fig. 1—The effect of time on the SnO content of slag and Fe content of metal in the equilibration experiments.

All remaining experiments were conducted for 2 hours and the complete set of analyses, for those runs in which complete fusion of the slag occurred, is shown in Table III; the runs from Table II are included. The sum of the slag components varies from 87 to 104 pct. Since the five components reported are the only ones present in significant amounts in the slags, the variation is attributed to the accumulated errors of the five separate analyses. The slag compositions are smoothed to 100 pct in the subsequent conversion to mole fractions. Table III also shows the CaO/SiO_2 and Fe/SiO_2 ratios of the slags based on their analyses and the $\gamma_{SnO}/\gamma_{FeO}$ ratios. The latter were calculated using Eq. [5], derived from Eq. [3].

$$\frac{\gamma_{SnO}}{\gamma_{FeO}} = \frac{1}{K_1} \cdot \frac{\gamma_{Sn}}{\gamma_{Fe}} \cdot \frac{N_{FeO}}{N_{SnO}} \cdot \frac{N_{Sn}}{N_{Fe}} \qquad [5]$$

Values of K_1, γ_{Sn}, and γ_{Fe} were determined using the relations

$$\log K_1 = 2.238 - \frac{1644}{T} \qquad [6]$$

$$\log \gamma_{Fe} = 0.91 N_{Sn}^2 - \frac{250}{T} + 0.101 \qquad [7]$$

$$\log \gamma_{Sn} = 0.91 N_{Fe}^2 \qquad [8]$$

where T is the temperature in Kelvin.

Equation [6] was derived by Grimsey and Dawson[5] from the ΔG°_{SnO} value of Grau and Flengas[3] and the ΔG°_{FeO} value of Michal and Schuhmann.[11] The standard states of the components in Eq. [1] are the pure liquids; *i.e.*, Eq. [6] applies to the reaction

$$SnO(l) + Fe(l) = FeO(l) + Sn(l)$$

Equations [7] and [8] were given by Davey and Turnbull[8] as the best available estimate of the activity coefficient of Fe and Sn, respectively, in Sn-Fe alloys up to the miscibility gap. The standard state of Sn and Fe in both cases is the pure liquid.

To assess the relative effects of the CaO/SiO_2 and Fe/SiO_2 ratios and the SnO and Al_2O_3 contents of the slag on the value of $\gamma_{SnO}/\gamma_{FeO}$, a multiple-linear regression was performed. In this approach it is assumed that the effects of

Table II. The Effect of Equilibration Time on the Slag and Metal Analyses

Time	Metal	Slag					$\frac{\gamma_{SnO}}{\gamma_{FeO}}$
(Hours)	Pct Fe	Pct SnO	Pct FeO	Pct CaO	Pct SiO_2	Pct Al_2O_3	
1	0.82	18.61	19.98	10.60	34.20	3.95	1.34
2	1.27	12.60	24.29	9.86	37.70	5.19	1.61
4	1.53	10.38	23.67	9.60	41.80	7.01	1.61
6	1.96	8.38	22.77	9.42	43.10	8.15	1.55
8	2.16	7.89	23.49	9.40	42.70	7.56	1.56

Table III. Results of the Slag-Metal Equilibration Tests (Includes the Results of Table II)

Metal	Slag					Pct CaO	Pct Fe (Slag)	γ_{SnO}
Pct Fe	Pct SnO	Pct FeO	Pct CaO	Pct SiO_2	Pct Al_2O_3	Pct SiO_2	Pct SiO_2	γ_{FeO}
0.12	34.72	8.56	16.09	41.93	1.62	0.38	0.16	1.99
0.19	22.47	9.01	20.85	50.27	0.79	0.41	0.14	2.06
0.26	16.27	12.91	22.60	35.15	3.90	0.28	0.23	1.47
0.30	25.17	11.30	10.80	38.20	1.71	0.28	0.23	1.47
0.32	14.20	12.24	20.90	23.90	19.80	0.87	0.40	2.65
0.38	22.04	15.87	12.74	32.53	17.39	0.39	0.36	2.38
0.41	17.14	16.85	14.27	26.80	17.95	0.39	0.36	2.38
0.43	11.42	13.81	23.10	32.70	12.10	0.71	0.33	2.79
0.44	19.87	12.01	17.00	35.05	6.18	0.49	0.27	1.37
0.44	21.22	17.24	16.79	46.21	2.53	0.36	0.29	1.84
0.46	13.28	18.27	20.29	49.63	1.06	0.41	0.29	2.98
0.48	18.27	17.50	16.37	41.93	8.69	0.39	0.32	1.99
0.56	19.97	22.64	12.38	42.36	5.46	0.29	0.42	2.03
0.57	6.68	14.76	31.80	37.70	1.56	0.84	0.30	3.89
0.68	16.45	24.44	13.22	38.72	9.39	0.34	0.49	2.21
0.82	18.61	19.98	10.60	34.20	3.95	0.31	0.45	1.34
0.83	8.34	25.91	18.50	21.10	20.20	0.88	0.95	3.82
0.88	9.86	21.24	16.30	44.60	2.62	0.37	0.37	2.52
1.08	14.13	29.03	11.48	30.39	17.58	0.38	0.74	1.99
1.13	8.67	19.62	22.40	37.00	5.95	0.61	0.41	2.11
1.16	11.21	25.86	17.07	46.42	2.55	0.37	0.43	2.09
1.17	11.74	24.65	11.90	39.70	4.06	0.30	0.48	1.89
1.27	12.60	24.29	9.86	37.70	5.19	0.26	0.50	1.61
1.33	8.96	25.87	14.35	36.60	7.12	0.39	0.55	2.31
1.41	12.48	31.90	12.80	41.93	5.25	0.31	0.59	1.94
1.51	7.91	24.34	17.25	36.50	8.17	0.47	0.52	2.20
1.53	10.38	23.67	9.60	41.80	7.01	0.23	0.44	1.61
1.64	6.29	23.31	15.20	40.20	9.18	0.38	0.45	2.46
1.68	7.13	25.01	17.80	31.20	14.00	0.57	0.62	2.28
1.71	6.75	23.67	17.20	41.00	4.19	0.42	0.45	2.25
1.89	7.08	24.65	14.05	37.35	10.60	0.38	0.51	2.05
1.96	8.38	22.77	9.42	43.10	8.15	0.22	0.41	1.55
2.16	7.89	23.49	9.40	42.70	7.56	0.22	0.43	1.56
2.47	3.80	22.51	18.89	46.21	10.39	0.41	0.38	2.78
2.49	3.32	20.25	26.20	34.00	11.30	0.77	0.46	2.84
2.54	8.21	20.35	11.20	39.30	5.50	0.28	0.40	1.14
2.60	5.23	30.23	15.25	39.79	10.68	0.38	0.59	2.60
3.31	3.53	27.53	14.55	34.66	20.41	0.42	0.62	2.91
3.44	3.06	24.38	24.30	38.10	6.35	0.64	0.50	2.89
3.63	4.74	33.19	16.65	44.93	2.49	0.37	0.57	2.44
3.71	4.68	30.32	17.50	35.40	7.17	0.49	0.67	2.22
3.90	2.92	25.87	23.35	38.65	6.15	0.60	0.52	2.92
4.17	4.90	36.66	12.45	41.29	5.03	0.30	0.69	2.35
4.23	3.28	25.65	22.00	33.00	12.80	0.67	0.58	2.34
4.25	4.56	29.96	17.90	35.90	8.24	0.50	0.65	2.04

each of the independent variables on $\gamma_{SnO}/\gamma_{FeO}$ can be represented by an equation of the form

$$\frac{\gamma_{SnO}}{\gamma_{FeO}} = A\frac{\text{pct CaO}}{\text{pct SiO}_2} + B\frac{\text{pct Fe}}{\text{pct SiO}_2} + C\text{ pct Al}_2\text{O}_3 + D\text{pct SnO} + E \qquad [9]$$

where A, B, C, D, and E are constants. This is a reasonable assumption over small ranges or when the dependent variable does not change rapidly as a result of changes in the independent variables. The calculated values of the constants are given in Table IV. Next, F-tests were performed to determine whether there were significant differences between the $\gamma_{SnO}/\gamma_{FeO}$ ratios calculated from the regression

Table IV. Results of the Multiple-Linear Regression on Data of Table III

	Coefficient (Equation [9])	Significance of the Correlation*
$\frac{CaO}{SiO_2}$	2.3758	>99.9 pct
$\frac{Fe}{SiO_2}$	0.1235	17.5 pct
Al_2O_3	-0.6298×10^{-2}	35.1 pct
SnO	-0.1701×10^{-1}	86.3 pct
Constant	1.3850	>99.9 pct

*According to the F test for significance.

using all five terms as opposed to regressions using only four of the terms. In this way a measure was obtained for the significance of each constant in the correlation; these values are shown in Table IV. Using the common criterion that 95 pct or greater indicates a significant correlation, it appears that only the CaO/SiO_2 ratio and the constant terms affect the value of $\gamma_{SnO}/\gamma_{FeO}$. Finally, and F-test was performed on the $\gamma_{SnO}/\gamma_{FeO}$ ratios obtained using all five terms and the ratios obtained from a regression using only the CaO/SiO_2 and constant terms. The significance was greater than 95 pct, thus confirming that the CaO/SiO_2 and constant terms only are necessary to explain the variation of $\gamma_{SnO}/\gamma_{FeO}$ in the experimental data. The variation of $\gamma_{SnO}/\gamma_{FeO}$ with CaO/SiO_2 is shown in Figure 2; the line of best fit is

$$\frac{\gamma_{SnO}}{\gamma_{FeO}} = 2.502\frac{\text{pct CaO}}{\text{pct SiO}_2} + 1.142 \qquad [10]$$

The data from Table II are indicated in Figure 2 and it is evident that they are consistent with the other data. It is reasonable to conclude that in all experiments in Table III slag-metal equilibrium was attained.

IV. DISCUSSION

It is worthwhile recalculating the earlier results of Rankin and Biswas[6,7] using the thermodynamic sources of this study. In the earlier study CaO-free slags were used and it was found that $\gamma_{SnO}/\gamma_{FeO}$ was a function of the SnO content of the slag. The experiments in that study were done in open crucibles with a flowing atmosphere, and this may have permitted loss of SnO from the slag at a rate such that it was not possible to attain slag-metal equilibrium.[5,10] If this were the case Eq. [5] indicates that the calculated $\gamma_{SnO}/\gamma_{FeO}$ values would be too high. The rate of volatilization of SnO would be greater the higher was the SnO concentration in the slag, and the observed increase in $\gamma_{SnO}/\gamma_{FeO}$ with increasing SnO is quite likely due to the changing rate of volatilization and the effect this has on the relative displacement of Eq. [1] from equilibrium.

The raw data of the earlier study and the recalculated values of $\gamma_{SnO}/\gamma_{FeO}$ are presented in Table V, and the results are shown graphically in Figure 3. The line of best fit is given by

$$\frac{\gamma_{SnO}}{\gamma_{FeO}} = 0.024 \text{ pct SnO} + 1.221 \qquad [11]$$

Since

$$\frac{p_{SnO}}{p^{\circ}_{SnO}} = a_{SnO} = \gamma_{SnO} N_{SnO}$$

therefore,

$$p_{SnO} = p^{\circ}_{SnO} \gamma_{SnO} N_{SnO}$$

where p°_{SnO} is the vapor pressure of pure SnO. As N_{SnO} approaches zero so does p_{SnO} because p°_{SnO} and γ°_{SnO} (the activity coefficient of SnO at infinite dilution) are constant and finite. If $\gamma_{SnO}/\gamma_{FeO}$ is independent of the SnO content of the slag, as Table IV indicates, then the true value of $\gamma_{SnO}/\gamma_{FeO}$ for slags in the earlier study is given by the value of $\gamma_{SnO}/\gamma_{FeO}$ at zero concentration of SnO. This is because at zero concentration of SnO, p_{SnO} is zero but γ°_{SnO} remains finite and the error introduced by volatilization of SnO is therefore absent. The value of 1.22 at 1250 °C for CaO-free slags with $Fe/SiO_2 = 1.25$ to 3.25 compares quite favorably with the value of 1.14 from the present study at 1200 °C for CaO-free slags with $Fe/SiO_2 = 0.14$ to 0.95, both slags containing alumina up to 20 pct or more. Grimsey and Dawson[5] estimated the value of $\gamma_{SnO}/\gamma_{FeO}$ to be 1.45 in CaO and Al_2O_3-free, silica-saturated iron silicate slags at 1300 °C.

For the slags of the study by Rankin and Biswas,[6] Mackey and Nagamori[12] suggested a value of γ_{FeO} of 0.83 at 1250 °C at infinite dilution of SnO. This means γ°_{SnO} equals 1.0 at 1250 °C for slags with $Fe/SiO_2 = 1.25$ to 3.25 containing up to 27 pct Al_2O_3, and this compares favorably with the value of 1.2 of Nagamori and Mackey[12] at 1250 °C for slags of comparable composition. It also compares favorably with the value of 1.0 ± 0.13 of Grimsey and Dawson[5] for silica-saturated CaO- and Al_2O_3-free slags at 1300 °C. These data together suggest that γ_{SnO} is fairly independent of the Fe/SiO_2 ratio and Al_2O_3 content over wide ranges. Carbó Nóver's result of 1.8 for γ_{SnO} at 1160 °C in slags of $Fe/SiO_2 = 0.34$ and $CaO/SiO_2 = 0.22$ suggests a raising of γ_{SnO} by the addition of CaO though the authors state the result may be on the high side because of the problem of volatilization. Nevertheless, the result is consistent with the basic nature of SnO and CaO.

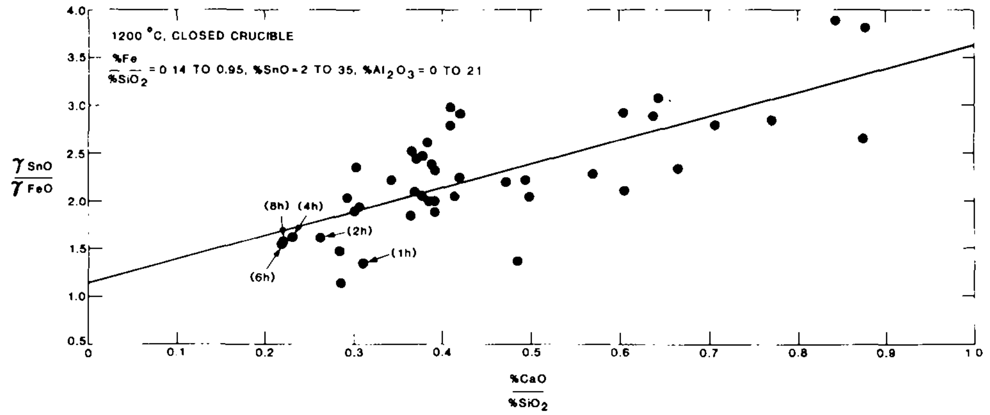

Fig. 2—Variation of $\gamma_{SnO}/\gamma_{FeO}$ with the CaO/SiO_2 ratio in slags at 1200 °C.

Table V. Raw Data of Rankin and Biswas[6] and Recalculated $\gamma_{SnO}/\gamma_{FeO}$ Values

Metal	Slag				Pct Fe (Slag)	γ_{SnO}	Time
Pct Fe	Pct SnO	Pct FeO	Pct SiO_2	Pct Al_2O_3	Pct SiO_2	γ_{FeO}	(Hours)
0.56	29.80	37.80	18.60	11.20	1.58	2.06	8
0.62	30.10	38.40	18.30	13.10	1.63	1.88	8
0.65	29.50	42.70	10.20	9.10	3.25	2.04	4
0.67	30.90	41.80	18.30	9.00	1.78	1.85	4
0.70	28.70	44.60	19.00	8.70	1.82	2.04	4
0.74	22.24	43.48	22.10	12.18	1.53	2.44	4
0.80	26.30	39.00	21.20	13.50	1.43	1.72	8
1.20	22.50	49.40	19.00	9.20	2.02	1.75	4
1.35	19.00	42.80	23.40	14.80	1.42	1.61	8
1.40	17.36	37.82	17.70	27.12	1.66	1.51	6
1.60	16.00	47.20	17.50	20.40	2.10	1.82	4
1.85	15.80	44.40	25.70	14.10	1.34	1.53	8
2.10	13.50	46.06	22.70	17.74	1.58	1.66	8
2.50	13.90	59.00	20.50	7.10	2.24	1.79	4
2.97	12.20	45.00	27.40	15.40	1.28	1.36	8
3.00	14.20	57.30	22.00	8.60	2.02	1.47	4
3.01	12.03	47.21	27.90	12.86	1.32	1.43	8
3.90	12.00	60.80	23.30	9.00	2.03	1.52	4
4.70	10.40	61.30	22.00	8.53	2.17	1.55	4
6.40	7.10	45.10	27.90	17.80	1.26	1.38	8

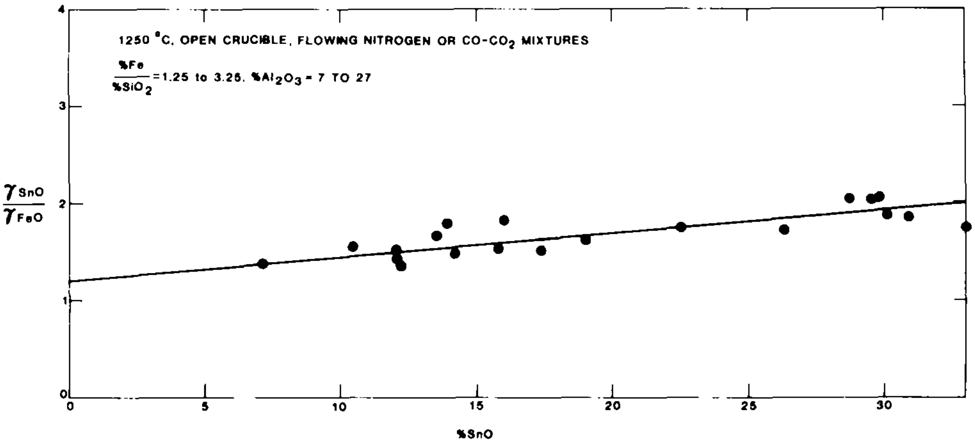

Fig. 3 — Apparent variation of $\gamma_{SnO}/\gamma_{FeO}$ with the SnO content of slags at 1250 °C (Rankin and Biswas[6] open crucible study).

V. PRACTICAL APPLICATIONS

In discussing practical aspects of Sn and Fe distribution between slag and metal in tin smelting, the use of a distribution coefficient, *k*, has been found to be useful:[1]

$$k = \frac{[\text{pct Sn}]}{[\text{pct Fe}]} \cdot \frac{(\text{pct Fe})}{(\text{pct Sn})} \qquad [12]$$

A number of experimental studies has been reported in which *k* was determined experimentally as a function of the iron content of the metal.[6,9,11,13,14] There are considerable discrepancies between some of these studies which appear to be due to the problem of attaining equilibrium either from the low tin in slag side of the equilibrium of Eq. [1] or in open crucibles. The present results appear not to suffer from either of these problems and, furthermore, they include the effect of CaO in slags and cover the range of slag compositions encountered in practice more realistically than some other studies.[5,6,13]

The $\gamma_{SnO}/\gamma_{FeO}$ values of this study can be used to calculate the variation of *k* for a range of conditions by utilizing the equality

$$\frac{[\text{pct Sn}]}{[\text{pct Fe}]} \cdot \frac{(\text{pct Fe})}{(\text{pct Sn})} \equiv \frac{[N_{Sn}]}{[N_{Fe}]} \cdot \frac{(N_{FeO})}{(N_{SnO})} \qquad [13]$$

Substitution in Eq. [5] yields

$$k = K_1 \cdot \frac{\gamma_{Fe}}{\gamma_{Sn}} \cdot \frac{\gamma_{SnO}}{\gamma_{FeO}} \qquad [14]$$

On substituting values from Eqs. [6], [7], and [8] in Eq. [14] the following expression for *k* is obtained:

$$\log k = 3.249 - \frac{1894}{T} - 1.820 N_{Fe} + \log \frac{\gamma_{SnO}}{\gamma_{FeO}} \qquad [15]$$

Equations [7] and [8] are valid strictly only up to the miscibility gap on the tin-rich side. Within the miscibility gap the calculated activities are not physically real, but they differ from the actual (constant) activities by a very small amount and for practical purposes Eqs. [7] and [8] can be used up to the miscibility gap at the iron-rich side. Accordingly, Eq. [15] applies strictly only up to the tin-rich miscibility gap, but values of k obtained using Eq. [15] are accurate to two significant figures when compared with the values calculated using the real, constant values of γ_{Sn} and γ_{Fe} within the miscibility gap and, for practical purposes, Eq. [15] may be applied for iron content in tin up to and across the miscibility gap. The miscibility gap data have been reviewed by Davey and Turnbull[8] who selected the "best estimate" values given in Table VI.

Table VI. Miscibility Gap Compositions According to Davey and Turnbull[8]

Temperature (°C)	Composition (Atom Fraction Fe)	
	Tin-Rich Boundary	Fe-Rich Boundary
1128	0.326	0.680
1200	0.340	0.661
1300	0.362	0.634
1400	0.385	0.606
1500	0.411	0.575
1600	0.450	0.533

Values of k calculated using Eq. [15] are presented in Figure 4 as a function of the Fe content of the metal. These values are independent of the experimental results of this work since the curves are drawn at constant $\gamma_{SnO}/\gamma_{FeO}$ ratios. The relevance of the present work is the indication it gives that in slags of practical interest $\gamma_{SnO}/\gamma_{FeO}$ will range from about 1 to 3 according to the CaO/SiO_2 ratio. $\gamma_{SnO}/\gamma_{FeO}$ values are characteristic of the slag only and though, in this study, they were obtained from equilibrations with Sn-Fe alloys in which the iron content did not exceed 4.25 pct,

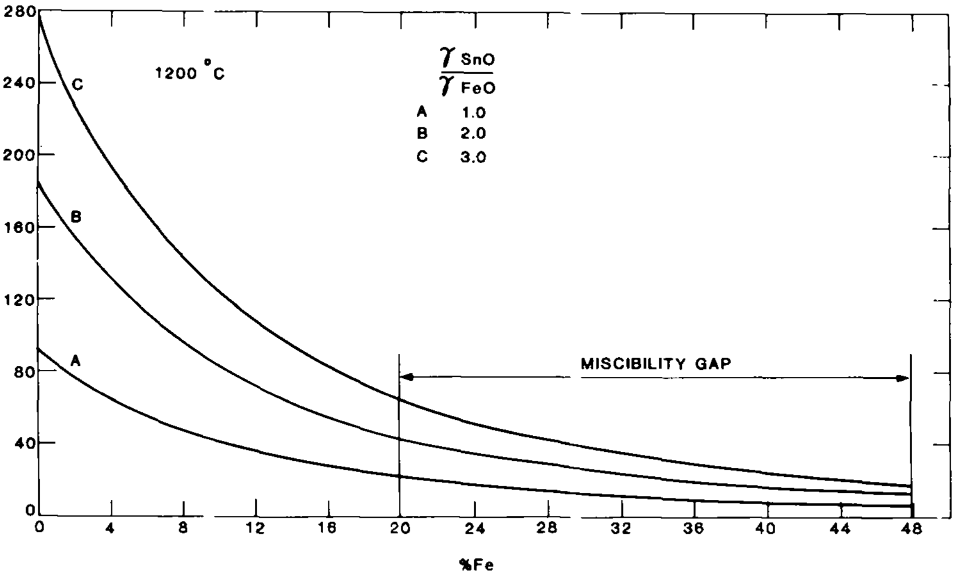

Fig. 4 — Variation of the distribution coefficient, k, as a function of the iron content of alloy at 1200 °C for $\gamma_{SnO}/\gamma_{FeO}$ ratios of 1, 2, and 3.

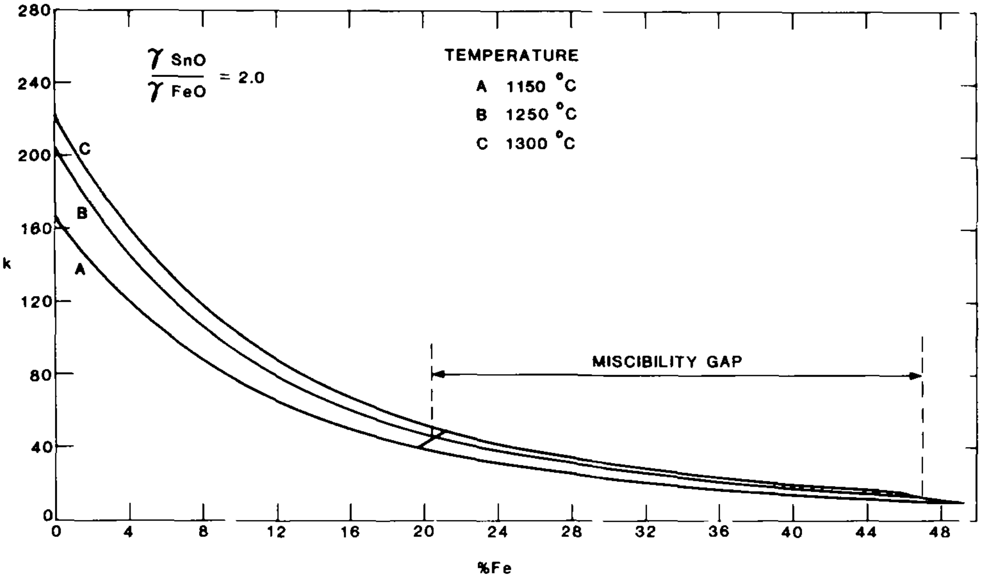

Fig. 5 — Variation of the distribution coefficient, k, as a function of the iron content of alloy at a $\gamma_{SnO}/\gamma_{FeO}$ ratio of 2 for temperatures of 1110, 1250, and 1300 °C.

they may be applied over a much wider range of alloy compositions using Eq. [15]. The problem of uncertain equilibration in high iron alloys is obviated by this approach.

The advantage of working with high CaO/SiO_2 slags in improving the recovery of Sn from slag in preference to Fe is clearly seen from Figure 4.

The effect of temperature on k, determined from Eq. [15], is shown in Figure 5 for a constant $\gamma_{SnO}/\gamma_{FeO}$ ratio of 2. The advantage to be gained by operating at high temperature is clear though, within the practical range of temperature, the variation of k is less than that obtainable by control of the CaO/SiO_2 ratio.

VI. CONCLUSIONS

1. In CaO-FeO-SiO_2-SnO-Al_2O_3 slags in which $CaO/SiO_2 = 0.2$ to 0.9, $Fe/SiO_2 = 0.1$ to 1.0, $Al_2O_3 = 0$ to 21 pct, and $SnO \leq 35$ pct, the ratio $\gamma_{SnO}/\gamma_{FeO}$ is a function only of the CaO/SiO_2 ratio. At 1200 °C the value of $\gamma_{SnO}/\gamma_{FeO}$ as a function of the CaO/SiO_2 ratio is given by Eq. [10].
2. The value of $\gamma_{SnO}/\gamma_{FeO}$ from the present study at $CaO/SiO_2 = 0$ is 1.14 and this is comparable to the values found in other studies of CaO-free slags.
3. The variation of the distribution coefficient k (defined by Eq. [12]) is given as a function of the Fe content of the metal, the $\gamma_{SnO}/\gamma_{FeO}$ ratio of the slag, and the temperature by Eq. [15]. Equation [15] indicates that an increase in $\gamma_{SnO}/\gamma_{FeO}$ (*i.e.*, an increase in the CaO/SiO_2 ratio) results in an improved Sn recovery and that an increase in temperature is also beneficial to the recovery of Sn.

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