Table I. Data on Molten Cu-Sn System at 1073 K

X_{Sn}	emf, mV	a_{Sn}	a_{Cu}*	ΔG^M (J/g mole)†	a_{Sn} (Calculated from Selected Values[6])	a_{Sn} (Ref. 8)
0.1	–	0.007	0.858	–5,602	0.004	–
0.2	66.90	0.055	0.600	–8,755	0.058	–
0.3	35.65	0.214	0.386	–10,011	0.202	0.137 (at X_{Sn} = 0.35)
0.4	24.04	0.353	0.296	–9,467	0.367	–
0.5	17.25	0.474 (±0.007)	0.240	–9,190	0.503	0.501
0.6	12.80	0.575	0.182	–8,491	0.613	–
0.7	8.80	0.683	0.133	–7,373	0.705	0.839
0.8	5.00	0.805	0.086	–5,669	0.799	–
0.9	2.35	0.903	0.040	–3,479	0.897	0.949

*Reported values of a_{Cu} are with respect to pure liquid copper as the standard state. The values should be multiplied by 1.34 if pure solid copper is taken as the standard state.

†ΔG^M is integral molal free energy of mixing with pure liquids as standard state.

the curve merges with the Raoult's Law line at $X_{Sn} > 0.8$. These establish the general reliability of the data. The system exhibits a strong negative deviation from the Raoult's Law line indicating strong interaction between copper and tin atoms. Values of a_{Sn} of this study were compared with those calculated from the selected values of H_{Sn}^{M} and S_{Sn}^{M}.[6] These are presented in Table I. It is seen that the disagreement is less than 5 pct. Figure 3 shows the plot of log γ_{Sn} *vs* $(1 - X_{Sn})^2$. From this figure it appears that the solution behaves in a simple manner in the two extremes but behaves in a complicated manner in the middle composition range and this is in accordance with Darken's formalism.[7] In passing yet another aspect of this study is worth mentioning. The activity values of this study when compared with those of Predel and Schallner[8] demonstrate that the latter values except for X_{Sn} = 0.5 did not match. This can be ascribed to the uncertainties of their binary values when extrapolated from ternary experimental data.

The authors wish to gratefully acknowledge the financial support given to one of the authors (A.K.S.) by the Department of Atomic Energy, India during the course of this investigation.

1. P. J. Roychowdhury and A. Ghosh: *Met. Trans.*, 1971, vol. 2, p. 2171.
2. T. N. Belford and C. B. Alcock: *Trans. Faraday Soc.*, 1965, vol. 61, p. 443.
3. R. J. Fruehan and F. D. Richardson: *Trans. TMS-AIME*, 1969, vol. 245, p. 1721.
4. S. K. Das and A. Ghosh: *Met. Trans.*, 1972, vol. 3, p. 803.
5. L. S. Darken: *J. Amer. Chem. Soc.*, 1950, vol. 72, p. 2909.
6. R. Hultgren and P. D. Desai: *Selected Thermodynamic Values and Phase Diagrams for Copper and Some of Its Binary Alloys*, p. 160, INCRA series on metallurgy of copper, Monograph I, 1971.
7. L. S. Darken: *Trans. TMS-AIME*, 1967, vol. 239, p. 80.
8. B. Predel and U. Schallner: *Z. Metallk.*, 1972, p. 122.

Solubility of Water in $CaO-Al_2O_3$ Melts at 1600°C

KLAUS SCHWERDTFEGER AND
HANS GEORG SCHUBERT

In the present study we have measured the water solubility in $CaO-Al_2O_3$ slags at 1600°C. This work was carried out in conjunction with other research projects aimed at improving our knowledge of the chemistry of electro slag remelting of steel. It is well known that hydrogen pick up of the steel is a severe problem in the ESR process. Slags used in electro slag remelting usually consist of $CaF_2-CaO-Al_2O_3$ mixtures. No reliable solubility data are available for such slags which is due to the experimental difficulties involved with measurements of water solubilities in fluoride containing slags. Some estimates of water solubility in $CaF_2-CaO-Al_2O_3$ slags would be possible, however, if corresponding data for the CaF_2 free bounding system $CaO-Al_2O_3$ were known.

Several laboratory investigations deal with the solubility of water in silicate melts.[1-10] Although there is some disagreement between the various investigators on the absolute quantities of water dissolved, the results of all these studies agree that the water content increases proportionally to the square root of water vapor pressure. Some structural models have been suggested. At high basicity the water is assumed to be present in the silicates as free hydroxyl ions OH^- whereas in acid slags the water may be bound to silicon forming $-Si-OH$ groups.

Whereas in the previous investigations the water contents of the samples were determined by chemical analysis of quenched samples, we measured the solubilities applying the thermogravimetric method. This has the advantage that the difficulties associated with the analyses are avoided.

A platinum crucible containing 6 g of $CaO-Al_2O_3$ slag was suspended on a sensitive scale (Cahn/Ventron R100) in the hot zone of a molybdenum wound tube furnace. The furnace atmosphere consisted of $Ar-H_2O$

KLAUS SCHWERDTFEGER and HANS GEORG SCHUBERT are with the Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1 4000 Düsseldorf, Germany.

Manuscript submitted August 31, 1977.

ISSN 0360-2141/78/0310-0143$00.75/0

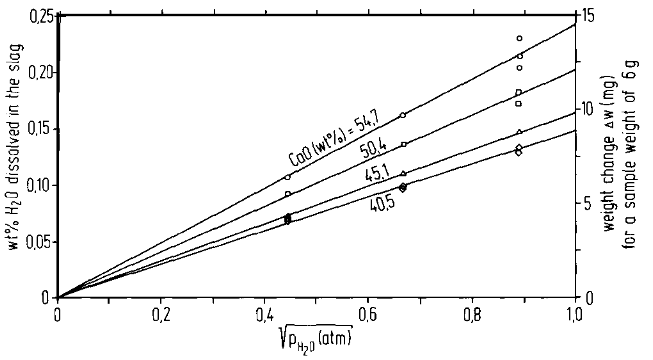

Fig. 1—Contents of water in the slag as a function of square root of water vapor pressure as measured in this work (1600°C).

gas mixtures and was prepared by bubbling 140 ml/min of argon through a water column held at constant temperature in a thermostat. Water vapor pressure of 150, 338 and 600 mm Hg were used. The slag samples were first held under dry argon till constant weight was attained. Then the moist gas was admitted and the pick up of water vapor was followed by continuously recording the weight change. Subsequently, dry argon was used and the water content was removed again from the slag. Afterwards, the similar cycles were performed with the other water vapor pressures. The weight changes were between 4 and 14 mg. Periodically between the actual experiments, we determined the blank values by carrying out the same cycles with the empty crucibles. The recorded weight changes depended on the water vapor pressure and were up to 1 mg. The weight changes observed with the slag samples were corrected correspondingly.

The master slags were prepared from reagent grade $CaCO_3$ and Al_2O_3. The furnace temperature (1600°C) was controlled electronically within ±2°C.

The chemical reaction occurring between gaseous H_2O and the slag can be written as

$$\tfrac{1}{2}O^{2-}(\text{slag}) + \tfrac{1}{2}H_2O(\text{gas}) = OH^-(\text{slag}). \quad [1]$$

Application of the law of mass action yields

$$K_{\text{hydrate}} = \frac{(H_2O)}{\sqrt{p_{H_2O}}} \quad [2]$$

where the equilibrium "constant" K_{hydrate} contains the activity coefficient of the OH^- ion and the activity of the oxygen ion. Hence, K_{hydrate} depends on slag composition. In Fig. 1 the measured H_2O contents of the slag are plotted against square root of water vapor pressure for different slags. The straight lines are obtained in accordance with Eq. [2]. The K_{hydrate} values were deduced from the experimental data and are listed in Table I. It is evident that K_{hydrate} increases with increasing CaO content of the slag, Fig. 2. This influence of slag composition is qualitatively similar as has been observed with respect to sulfide,[11,12] sulfate,[11,12] carbide[13] and cyanide[13] capacities of CaO-Al_2O_3 melts which also increase with increasing CaO/Al_2O_3 ratio. On comparing the water solubilities of CaO-Al_2O_3 melts with those of CaO-SiO_2 melts[6] it is evident that the aluminates pick up much more water by a factor of two to three than the silicates at 1600°C and at given water vapor pressure.

Table I. Experimental Results Obtained on Water Solubility in CaO-Al_2O_3 Melts at 1600 °C

wt pct CaO/wt pct Al_2O_3	$K_{\text{hydrate}} = (H_2O)/\sqrt{p_{H_2O}}$ wt pct atm$^{-1/2}$
0.681	0.149
0.822	0.164
1.016	0.202
1.208	0.243

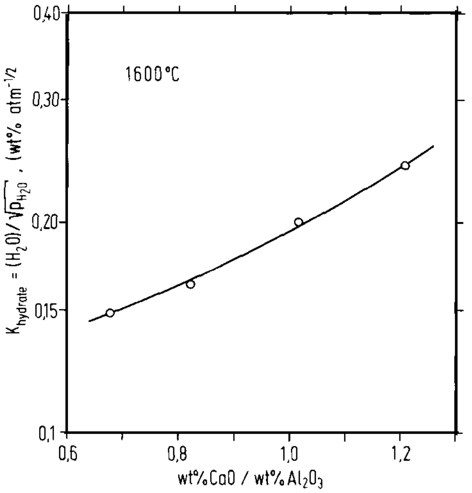

Fig. 2—Hydrate capacity of CaO-Al_2O_3 melts at 1600°C as measured in this work.

If water is dissolved in CaF_2-CaO-Al_2O_3 slags as the same ionic species as in CaO-Al_2O_3 melts, it should be expected that the influence of addition of some CaF_2 should not be very large. Due to the expected decrease of oxygen ion activity K_{hydrate} could decrease at given CaO/Al_2O ratio. On the other hand previous work on sulfide,[14] carbide[15] and cyanide[15] capacities has shown that these quantities increase somewhat on the addition of CaF_2 to CaO-Al_2O_3 melts.

1. J. H. Walsh, J. Chipman, T. B. King, and N. J. Grant: *Trans. AIME,* 1956, vol. 206, pp. 1568-76 (J. Metals, 1956, p. 1568).
2. I. A. Novokhatskii, O. A. Esin, and S. K. Chuckmarev: *Izvest. Vuz. Chern. Met.,* 1961, vol. 11, pp. 22-29.
3. M. Imai, H. Ooi, and T. Emi: *Tetsu to Hagané,* 1962, vol. 48, pp. 111-27.
4. J. M. Uys and T. B. Knig: *Trans. TMS-AIME,* 1963, vol. 227, pp. 492-500.
5. M. Imai, H. Ooi, and T. Emi: *Tetsu to Hagané,* 1964, vol. 50, pp. 878-87.
6. T. Fukushima, Y. Iguchi, S. Banya, and T. Fuwa: *Trans. Iron Steel Inst. Jap.,* 1966, vol. 6, pp. 225-32.
7. H. vom Ende, K. Hagen, and H. Trenkler: *Arch. Eisenhüttenwes.,* 1969, vol. 40, pp. 27-33.
8. M. Wahlster and H.-H. Reichel: *Arch. Eisenhüttenwes.,* 1969, vol. 40, pp. 19-25.
9. Y. Iguchi, S. Ban-ya, and T. Fuwa: *Trans. Iron Steel Inst. Jap.,* 1969, vol. 9, pp. 189-95.
10. Y. Iguchi and T. Fuwa: *Trans. Iron Steel Inst. Jap.,* 1970, vol. 10, pp. 29-35.
11. C. J. B. Fincham and F. D. Richardson: *Proc. Roy. Soc. A,* 1954, vol. 223, pp. 40-62.
12. F. D. Richardson and C. J. B. Fincham: *J. Iron Steel Inst.,* 1954, vol. 178, pp. 4-15.
13. K. Schwerdtfeger and H. G. Schubert: *Met. Trans. B,* 1977, vol. 8B, pp. 535-40.
14. G. J. W. Kor and F. D. Richardson: *Trans. TMS-AIME,* 1969, vol. 245, pp. 319-27.
15. K. Schwerdtfeger and H. G. Schubert: *Met. Trans. B,* 1977, vol. 8B, pp. 689-91.