Interactions of Gases in Molten Salts: Carbon Dioxide and Oxygen in Cryolite Alumina Melts

H. NUMATA and J. O'M. BOCKRIS

A radiotracer method has been developed to measure the solubility of CO_2 in cryolite-based systems at temperatures above 1273 K and also a method to measure the solubility of oxygen. The high solubility of CO_2 in cryolite (0.34 pct Al_2O_3, 1.68 pct CaF_2), and the highly negative ΔH of solution, suggest complex formation. In the presence of 5.33 pct excess Al_2O_3, the solubility of CO_2 is several times greater than in cryolite. In contrast, oxygen shows a solubility about a thousandth that of CO_2. The entropy of CO_2 in cryolite indicates a loss of translational degrees of freedom in a manner consistent with complexing. However, in the presence of increased Al_2O_3 (in spite of the increase of solubility) the entropy change upon solution appears to indicate little loss of translational freedom. It is suggested that CO_2 is complexed in both systems, but more strongly in the cryolite system. Complexing in cryolite produces the small carbonate ($CO_3^=$)ion, and this compensates the loss of translational freedom arising from the CO_2 complexing with aluminofluorides. Measured solubilities for CO_2 were 1.0×10^{-3} moles liter^{-1} atm^{-1} in cryolite at 1273 K, 4.6×10^{-3} moles liter^{-1} atm^{-1} in $(NaF)_{2:3}$ AlF_3 + 5.33 wt pct Al_2O_3 at 1233 K. At 1230 K, oxygen showed a solubility of only 3.0×10^{-6} moles liter^{-1} atm^{-1} in the latter melt.

I. INTRODUCTION

THE solubility of CO_2 and O_2 in cryolite and in cryolite-alumina has technological importance because of the possible reactions between these entities and aluminum in the Hall-Heroult Process. Thus,

$$\frac{2}{3}\,Al + CO_2 \rightarrow \frac{1}{3}\,Al_2O_3 + CO$$

Dissolved O_2 may react similarly:

$$\frac{2}{3}\,Al + \frac{1}{2}\,O_2 \rightarrow \frac{1}{3}\,Al_2O_3$$

Either process would reduce Faradaic efficiency. Because the solubility of these gases is not well known, the situation cannot be quantitatively assessed.

Remarkably, the solubility of oxygen in cryolite seems not to have been measured. As to CO_2, an estimate was made by Forland *et al.*[1] on the basis of specific gravity determinations, but the first measurements were by Haupin[2] who measured CO_2 solubility in cryolite.

Bratland *et al.*[3] carried out the same measurements in cryolite and cryolite-alumina. However, the data of Haupin and Bratland *et al.* do not agree in systems which are able to be compared. For example, in pure cryolite at 1303 K Haupin determined the solubility of CO_2 to be 0.10×10^{-3} moles liter^{-1} atm^{-1}, but according to the corresponding measurements of Bratland *et al.* it was 1.17 10^{-3} moles liter^{-1} atm^{-1}.

The theory of the solubility of gases has little predictive power. Thus, if ideality ($\Delta H_{soln} = 0$) is assumed, values for CO_2 at 1273 K of around 10^{-9} moles liter^{-1} atm^{-1} result. If the theory of regular solutions[4] is assumed, the values come to around the same value, if the volume of CO_2 used is that given by interatomic radii. The hole theory of molten salts gives realistic results,[5] but the predictive power is not better than an order of magnitude and[6] an adjustable parameter has to be used to obtain values agreeing with those of the experiment.

More information comes from surveys of the solubilities of gases in molten salts, *e.g.*, that made by Field.[7] Here, the solubility at 1000 K (moles liter^{-1} atm^{-1}) varies from 10^{-6} for noninteracting gases through 10^{-4} to occasional highs of 10^{-3} for reacting gases. This is, therefore, the range of orders we may expect for the solubility of CO_2 in cryolite, but it is clear that the precise information needed, *e.g.*, to distinguish modes of current-efficiency loss, can come only from accurate experiments.

II. VARIETIES OF EXPERIMENTAL APPROACH

Haupin absorbed CO_2 in cryolite, using a nickel crucible to withdraw a sample from the melt. After quick freezing, he heated the sample to 773 K, and observed the amount of CO_2 evolved in a mass spectrometer.

Bratland *et al.* used a volumetric method. The system was evacuated and the volume of gas measured. The system was then filled with CO_2 and, after absorption of CO_2 in the melt had occurred, again evacuated. The difference in volume was due to the dissolution of the CO_2.

Both methods have drawbacks. In Haupin's method, it is likely that not all the CO_2 is desorbed on heating to 773 K. In Bratland's method, the evaporation of the melt during evacuation may cause problems. Further, consideration of the apparatus indicates that a change in volume of about 0.1 cm^3 had to be measured in a total system volume of about 100 cm^3.

In these circumstances, it seemed wise to develop a radiotracer method. Gaseous CO_2 can be introduced into the melt and equilibrium attained. Then, the gas can be expelled by means of an inert gas and the attendant $C^{14}O_2$ measured by means of a scintillation counter.

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Manuscript submitted March 1, 1983.

In the measurements with O_2, no previous method has been reported. The method chosen depended upon the setting up of a concentration cell between O_2 in equilibrium with the melt and O_2 in equilibrium with Ni-NiO. The electrolyte was ZrO_2 (CaO stabilized).[8]

III. EXPERIMENTAL

A. *General*

The furnace used was from Lindberg (6 kW) with a temperature range of 1473 K. A section of the furnace, about 7 cm in length, could be maintained at ± 1 K. Arcing took place between the heating element and the stainless steel container of the crucible unless an alumina liner was used.

The temperature was measured by means of a chromel-alumel thermocouple, using the standard calibration. The thermocouple, sheathed in Inconel, was inserted in the melt for a short time, immediately after each measurement.

The crucible for the CO_2 measurements was made of graphite, ATJ grade, having dimensions 3.56 cm in diameter and 12.24 cm in length. For the O_2 measurements, the crucible was made out of BN (donated by ALCOA), and had dimensions of 3.05 cm in diameter and 8.89 cm in length.

The analysis of the cryolite along with liquidus and solidus temperature is shown in Table I (data supplied by ALCOA). The moisture was removed by conventional drying. Al_2O_3 was AR grade and not further treated. Oxygen was purified through a molecular sieve. Argon was deoxygenated while passing through a Ti column at 1173 K.

The oxygen sensor was made using ZrO_2 tube (Nippon Kagaku Tokyo Ltd.). NiO and Ni powder of 325 mesh were ground for four hours, making a paste which was pressed into contact with a Ni wire. This electrode was placed against the inside of the ZrO_2 tube, and a Pt wire was wound around the outside of the ZrO_2 tubing. Electrical contact was made to the Ni and Pt wires. The potential measured was in the region of -10 to 700 mV.

Table I. Analysis of Cryolite

Total F	54.03	pct
Total Al	12.8	pct
Na	32.06	pct
Ca	0.86	pct
Mg	0.08	pct
Li	0.00	pct
Sr	0.07	pct
$CO_3^{=}$	0.08	pct
SiO_2	0.024	pct
Fe_2O_3	0.034	pct
Loss on ignition	0.32	pct
Calculated comp. of cryolite	97.2	pct
Na_2CO_3	0.19	pct
Excess AlF_3	0.12	pct
MgF_2	0.22	pct
CaF_2	1.68	pct
SrF_2	0.10	pct
Al_2O_3	0.34	pct
M.P.	1273.2	K
Solidus	1234.2	K

B. *Carbon Dioxide*

At the beginning of a measurement, $C^{14}O_2$ was produced by dropping H_2SO_4 onto $BaC^{14}O_3$ (New England Nuclear, NEC-009A). The resulting Ar-$C^{14}O_2$ mixture was stored in a rubber balloon, and when a known quantity was needed for the melt, it was measured out with a syringe and introduced into the melt (Figure 1). A flow meter was used to monitor the amount of Ar being mixed with the CO_2, and this allowed an approximate control to be made upon the relative amounts of Ar and CO_2 being mixed. The precise amount and hence knowledge of the CO_2 in the mixture with Ar was found by removing a known volume from the sampling system A and introducing it into the scintillation cocktail.

The CO_2-Ar mixture was fed into the melting system and cycled around the circuit indicated by arrows (Figure 1). A peristaltic pump (Fischer Co., flow rate 3 to 6500 cm^3 per minute), usually run at 20 cm^3 per minute, was used to maintain the circulation for about 15 minutes. Two more additions of CO_2-Ar mixtures were necessary to saturate the melt with CO_2 at a given partial pressure (Figure 2).

The time needed to saturate the melt was about 90 minutes. The saturation was indicated by a constant partial pressure of CO_2 in the gas (as indicated by the sampling system). The circulating system had a volume of 30 cm^3 and the vial of about 5 cm^3.

To compensate for changes of pressure when the sampling system removed some gas, a syringe was used to replace the amount removed until pressure was restored to its former value.

After the condition of equilibrium had been thus established, pure Ar was gently bubbled through the melt for a period of about one hour. The Ar escaping from the melt containing $C^{14}O_2$ was trapped into vials that contained the appropriate scintillation liquid. Measurements continued until the CO_2 was reduced to the background level. At this condition, the procedure was terminated.

One of the difficulties of the present method involved the dead space which is shown in Figure 1. This space amounts to about 30 cm^3, and the volume of the melt was of the order of 100 cm^3. After the melt had been saturated with CO_2-Ar at each partial pressure, Ar was introduced through a tube in the bottom of the container (Figure 1). The Ar thus introduced was allowed to flow around the system until the dead space was filled with the gas. The time of contact of Ar with the melt was short, and soon after filling, the Ar was introduced for the bubbling procedure to force the dissolved CO_2 out of the melt.

A possibility which had to be examined was the exchange of $C^{14}O_2$ with the C^{12} of the crucible. This fact will be discussed in detail later.

C. *Oxygen*

The melt was first saturated with oxygen for 90 minutes using the head shown in Figure 3. Then Ar gas was flushed over the dead space in the crucible for several minutes. At this point, the head assembly was exchanged for the second head under N_2 atmosphere contained in the furnace. The second head, thus introduced (main section, Figure 3), consisted of a bubbling tube and the ZrO_2 oxygen sensor. This

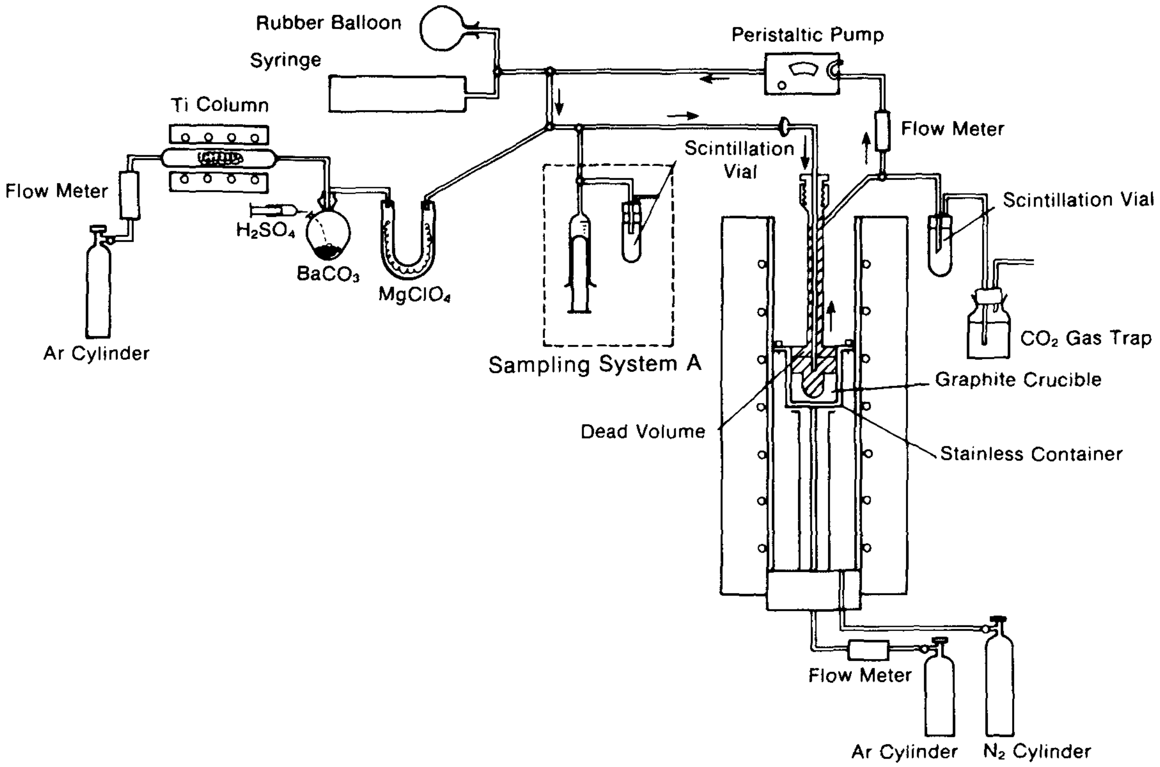


Fig. 1 — Apparatus for the measurement of solubility of gases in molten salt.

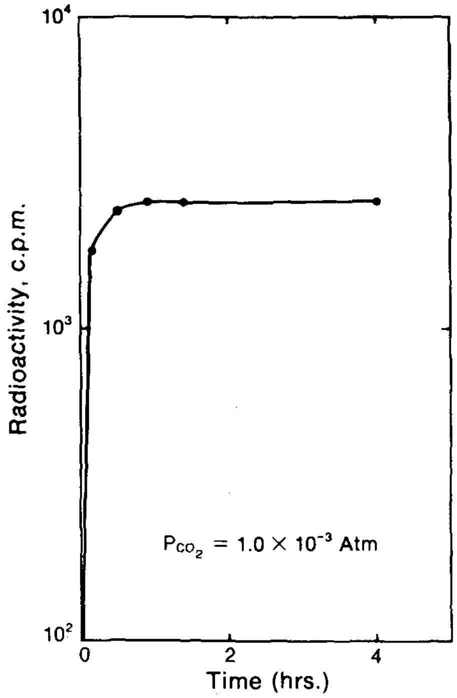
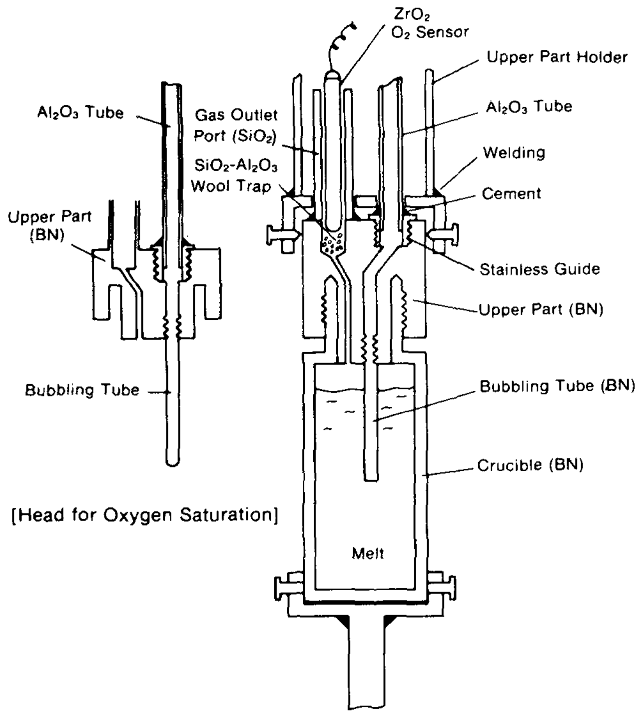


Fig. 2 — Change of radioactivity of the circulating gas due to the saturation equilibrium between CO_2 gas and melt.



[The Second Head and Crucible]

Fig. 3 — Apparatus for measurement of partial pressure of oxygen.

was first positioned over the melt. Then, Ar was allowed to flow into the dead space removing any oxygen in the free space above the melt. Thereafter, this head was lowered and screwed tightly into the BN crucible, allowing Ar to bubble directly into the melt. The amount of oxygen being out of the melt was followed by recording the potential at the ZrO_2 oxygen sensor.

There were two experimental difficulties. After each experiment, the outlet SiO_2 tube, which contained the

ZrO_2 sensor, broke, due to differences of thermal expansion between SiO_2 and ZrO_2, and had to be cemented to the lid. The other difficulty was the contamination of the surface of the ZrO_2 by the volatile[11] cryolite melt. This difficulty was reduced by putting an alumina-silica wool trap before the ZrO_2-oxygen sensor (Figure 3).

The ZrO_2 oxygen sensor was composed of ZrO_2-CaO solid electrolyte and Ni and NiO mixture which was used as a reference (Figure 4). The potential between the reference Ni-NiO electrode and the test electrode wound outside the ZrO_2 oxygen sensor is:

$$E = \frac{RT}{4F}\ln(P_{O_2}/P'_{O_2})$$

Here P'_{O_2} is the reference partial pressure of Ni-NiO determined by thermodynamic data[12] (See Appendix B). P_{O_2} is the oxygen partial pressure at the surface of the test electrode.

The device was tested by using known concentrations of oxygen and Ar in which P_{O_2} was varied over the range 1.5×10^{-3} to 1.0 atm, obtaining good agreement with the expected values.

IV. RESULTS

A. *Test of the Tracer Determination of* CO_2 *Solubility*

The radio-tracer method described above for the measurement of the solubility of CO_2 was first tested using water at room temperature. A glass cell replaced the crucible. The rest of the apparatus was as above.

After absorption equilibrium between $C^{14}O_2$ and water was reached, the dissolved $C^{14}O_2$ was forced out using Ar. This was then absorbed in a scintillation cocktail. The activity of each vial was determined in a Liquid Scintillation Counter (Model APL Packard Co.).

The number of counts in the vials decreased exponentially with the bubbling time down to the background level. The total number of counts (J cpm) was obtained by adding the individual activities in every vial. The calculation is shown in Appendix A. Thus, a satisfactory agreement was found for this test.

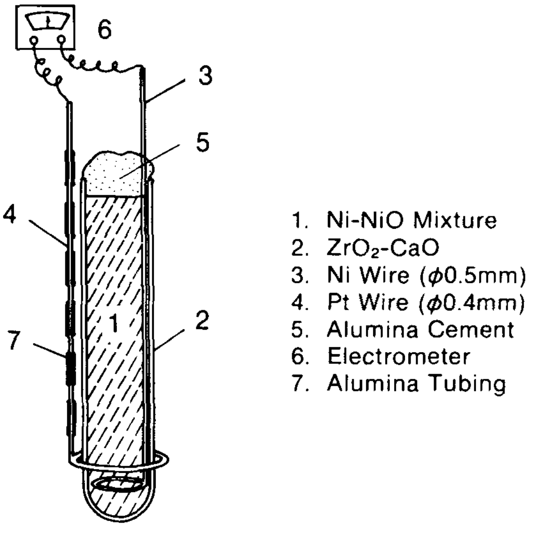


Fig. 4—The structure of the ZrO_2 oxygen sensor.

D. CO_2 *in Molten Salts*

1. *Cryolite*

Results for cryolite and cryolite-alumina are shown in Table II.

The results for cryolite are plotted as a function of temperature in Figure 5. The comparison with Haupin's data is made at 1303 K, where Haupin obtained 1×10^{-4} mole liter^{-1} atm^{-1}.

2. *Results in* $(NaF)_{2.3}$ AlF_3 + *5.33 wt pct* Al_2O_3

This system was selected for study because it is greatly used in the Hall-Heroult process for Al production. The results are shown in Table II and Figure 6.

It is possible to compare the results obtained by Bratland *et al.* in Na_3AlF_6 + 12.1 wt pct Al_2O_3 with the present

Table II. Solubility of CO_2 in Cryolite-Alumina Mixture

Molten Salt System	Temp. K	Solubility Moles Liter^{-1} atm^{-1}	Partial Pressure (atm) of CO_2
Na_3AlF_6 + 0.34 wt pct Al_2O_3	1273	1.06×19^{-3}	9.85×10^{-4}
		0.98×10^{-3}	2.20×10^{-3}
		1.09×10^{-3}	8.68×10^{-4}
	1285	7.73×10^{-4}	1.04×10^{-3}
	1326	5.91×10^{-4}	7.12×10^{-4}
	1348	4.30×10^{-4}	8.74×10^{-4}
$(NaF)_{2.3}$ AlF_3 + 5.33 wt pct Al_2O_3	1253	4.54×10^{-3}	0.774×10^{-3}
	1285	3.98×10^{-3}	0.774×10^{-3}
	1317	3.24×10^{-3}	1.77×10^{-3}
	1366	2.84×10^{-3}	1.75×10^{-3}

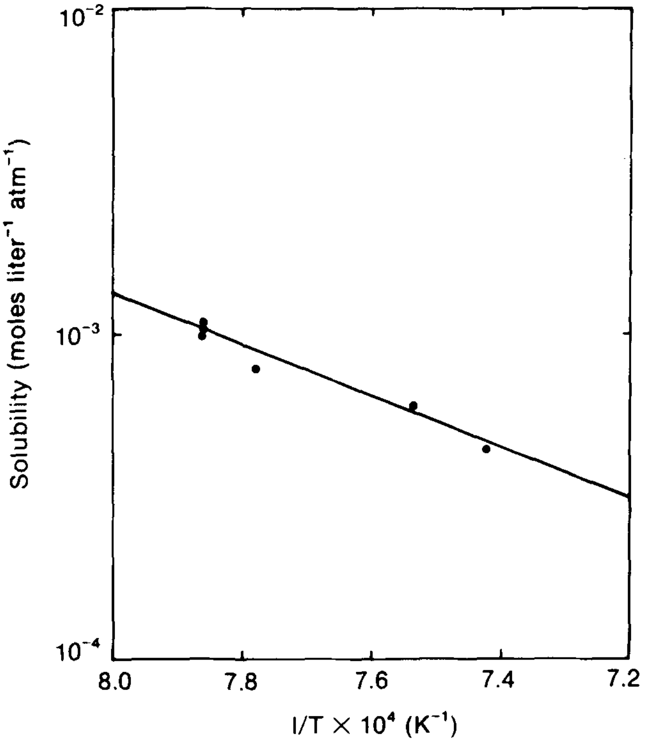


Fig. 5—CO_2 solubility in Na_3AlF_6 + 0.34 wt pct Al_2O_3.

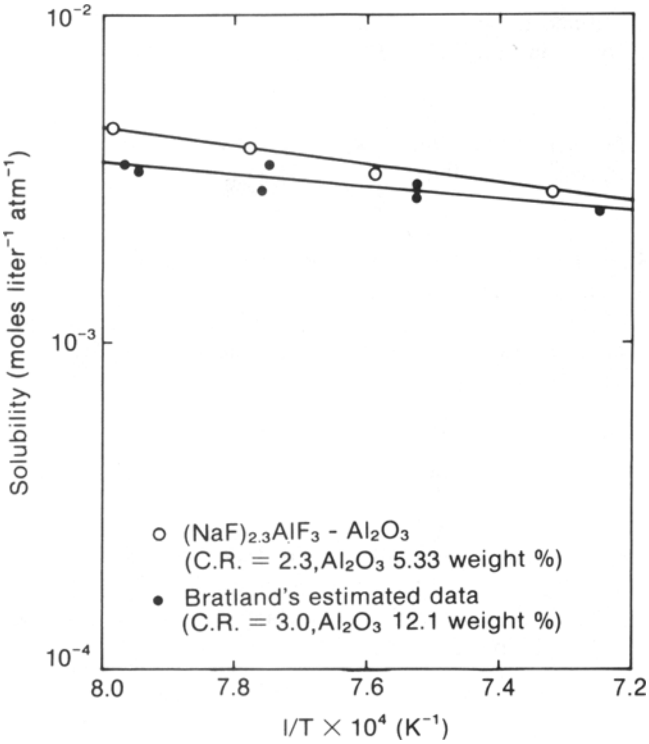


Fig. 6—CO_2 solubility in $(NaF)_{2.3}$ AlF_3 + 5.33 wt pct Al_2O_3; Bratland's data (C.R. = 3.0 Al_2O_3, 12.1 wt pct), estimated.

Table III. The Standard Entropy and the Enthalpy of Solution of CO_2 in Cryolite and Cryolite-Alumina Melts at 1273 K

	H_s	H_s/T	$R \ln (K_pR'T)$	S_{II}
Molten Salt	K_{cal} mol^{-1}	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}
Na_3AlF_6 + 0.34 wt pct Al_2O_3	−35.2	−27.7	−4.41	−32.15
$(NaF)_{2.3}AlF_3$ + 5.33 wt pct Al_2O_3	−13.3	−10.4	−1.72	−12.1
Na_3AlF_6 + 12.1 wt pct Al_2O_3	− 8.5	− 6.5	−2.2	− 8.7

results (Figure 6), finding a good agreement. The solubility of CO_2 in the Al_2O_3 containing system is 4 to 8 times higher than in cryolite +0.34 pct Al_2O_3.

3. *Heat of solution*

This was calculated conventionally, and the results are shown in Table III. The calculations of the entropy of solution are discussed below.

C. *Oxygen*

The calculation of the moles liter^{-1} of O_2 in contact with the sensor during the flushing out of the melt is given in Appendix B. A typical run pattern is shown in Figure 7 where the amount of oxygen is shown as a function of time during purging of the molten salt with argon.

Accounting for the 30 cm^3 of the melt, the solubility of oxygen is 3 × 10^{-6} moles liter^{-1} atm^{-1} at 1230 K in $(NaF)_{2.3}$ AlF_6 + 5.33 wt pct Al_2O_3. This compares with 4.6 × 10^{-3} moles liter^{-1} atm^{-1} for CO_2 under similar conditions.

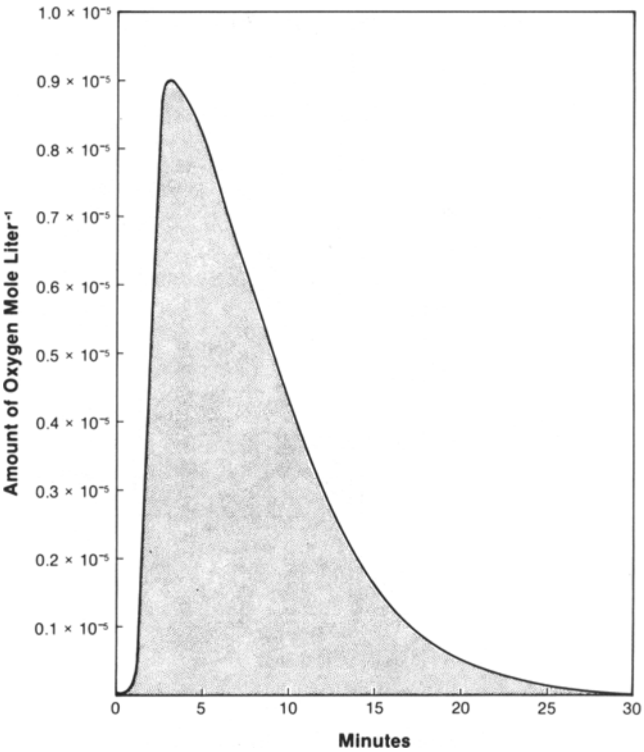


Fig. 7—Change of oxygen concentration in gas escaping out of the melt: $(NaF)_{2.3}$ AlF_3 + 5.33 wt pct Al_2O_3 at 1230 K.

V. TEST OF EXCHANGE REACTION IN SYSTEM

An experiment was carried out to ascertain whether there was any exchange reaction of finite velocity between $C^{14}O_2$ and carbon of the crucible. The apparatus is shown in Figure 8.

A flow of $C^{14}O_2$ was arranged to circulate around the crucible for about 90 minutes, while the crucible was maintained at 1200 K. After the saturation was reached, Ar was introduced from the tube at the bottom of the container and allowed to flow around the crucible, to flush out $C^{14}O_2$. Thereafter, oxygen was passed in from the bottom tube and allowed to flow around the container. The CO_2 from this experiment was passed into the scintillation system, but no radioactive carbon was detected. This proves that no significant exchange reaction such as $C^{14}O_2 + C^{12}$ (graphite) $\rightarrow$ $C^{14}O + C^{12}O$ occurs. Were it to occur significantly, it would decrease the apparent solubility of the CO_2.

VI. DISCUSSION

A. *Entropy*

In considering the solubility of a gas in a liquid, one has:

$$\mu^g_{CO_2} = \mu^l_{CO_2}$$

From this, it is obvious that:

$$S^{\circ,l}_{CO_2} - S^{\circ,g}_{CO_2} = \frac{\Delta H_s}{T} + R \ln (a^l_{CO_2}/a^g_{CO_2})$$

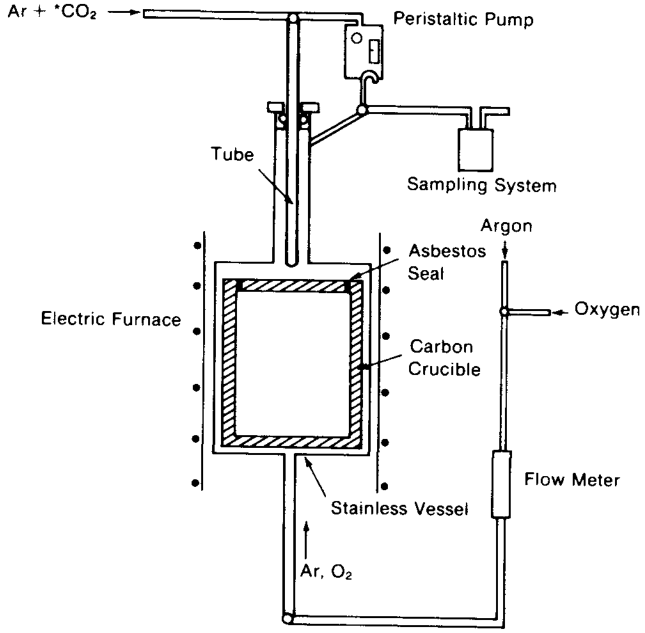


Fig. 8—Apparatus for C (carbon) exchange.

According to Grimes,[5] the standard entropy of solution of noble gases in molten fluoride mixtures is near zero, and thus the noble gases must have a full translational entropy when dissolved in molten salts.

In the case of CO_2, we can calculate the entropy in the gas phase by standard statistical mechanical equations[13] obtaining:

$$S_{1273\,K} = 42.66 + 15.93 + S\ \text{vibr.}$$

Now,

$$(S_{1273\,K})\,{}^{\text{gas}}_{CO_2} = 64.15\ \text{cal K}^{-1}\ \text{mol}^{-1}\ {}^{14}$$

Hence:

$$S_{\text{vib}} = 5.56\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

Here, CO_2 in the gaseous phase and the CO_2 dissolved in the liquid are in equilibrium. $S^{o,l}_{CO_2}$ is the entropy of CO_2 gas in the liquid and the activity $a^{l}_{CO_2}$ is unity due to the saturated condition; $S^{o,g}_{CO_2}$ is the entropy of CO_2 gas in the gaseous phase mixture with Ar, and $a^{g}_{CO_2}$ is the corresponding activity. The solubility measurement is referred to the standard state of $P_{CO_2} = 1$ atm, which is equal to $a^{g}_{CO_2}$. Hence, the entropy change upon solution, $\Delta S^{o}_{CO_2}$, is equal to the heat of solution divided by temperature:

$$\Delta S^{o}_{CO_2} = S^{o,l}_{CO_2} - S^{o,g}_{CO_2} = \Delta H_s/T$$

The standard entropy of solution includes also the entropy of mixing between the gas phase and the liquid, but it is easy to show that, per mole of liquid, the entropy of mixing in the present system is negligible.

Thermodynamically, the solution process of the gas in the liquid is divided into two steps:

$$CO_2(P = g) \xrightarrow{I} CO_2(P' = SR'T, g) \xrightarrow{II} CO_2(S, \text{soln})$$

where step I involves the isothermal gas expansion from the pressure of the vapor P to P', where P' is the partial pressure where there is equal concentration of the CO_2 in the liquid and the gaseous phase. From the value of the solubility, S, in mol liter^{-1}, P' is calculated as follows:

$$P'V = nRT$$

$M = S$ moles · liter^{-1} $V = 1$ liter $R' = 0.08206$ liter atm · K^{-1} mol^{-1}; thus,

$$P' = SR'T$$

Step II involves the solution process of the gas into the solvent at equal concentration.

The Gibbs free energy change, ΔG_T, is expressed as the sum of the Gibbs free energy change due to step I, ΔG_I, and to step II, G_{II}. Thus,

$$\Delta G_T = \Delta G_I + \Delta G_{II}$$

$$\Delta G_I = \Delta H_l - T\Delta S_I$$

$$\Delta G_{II} = \Delta H_{II} - T\Delta S_{II}$$

where ΔS_I is expressed as $-R\ \ln(P'/P_{\text{equil}}) = -R\ \ln(SR'T/P_{\text{equil}}) = -R\ \ln(K_P R'T)$ with $Kp = S/P_{\text{equil}}$, ΔS_{II} is the standard entropy of solution, and ΔH_{II} is equal to the heat of solution, ΔH_S. Now:

$$\Delta G_T = (\Delta H_I + \Delta H_{II}) - T(\Delta S_I + \Delta S_{II}) = 0$$

Since

$$\Delta H_I = 0$$

Hence,

$$\Delta H_s - T(-R\ \ln(KpR'T + \Delta S_{II}) = 0$$

or

$$\Delta S_{II} = \Delta H_s/T + R\ \ln(KpR'T)$$

In Table III the entropies of solution in cryolite-alumina mixture (C.R. = 2.3), calculated from the present data, and that of Bratland, exhibit high negative values.

Thus, in cryolite,

$$S^{\text{sol}}_{CO_2} = -32.15\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

B. *Interaction in Solution*

The value of the solubility of O_2 in $(NaF)_{2.3}\,AlF_6$ + 5.33 wt pct Al_2O_3 of 3×10^{-6} moles liter^{-1} atm^{-1} is the range expected for noninteracting gases.

Perusal of Table III shows that the largest negative heat of solution is for CO_2 in cryolite +0.34 pct Al_2O_3. Thus, the interaction of CO_2 in cryolite is more than that in the presence of Al_2O_3.

Correspondingly, for CO_2 in cryolite +0.34 pct Al_2O_3 the entropy of solution is highly negative, more so than for the solution containing 5.3 pct alumina and aluminum fluoride. This suggests that complexing is greater in the CO_2-cryolite system than in the system CO_2-Al_2O_3-cryolite -AlF_3.

The work of Grimes *et al.*[5] established that noble gases showed an entropy of solution of around −1.0 cal K^{-1} mol^{-1}. This means that, for noble gases, the molecular movements, and in particular translation (30 to 100 cal K^{-1} mol^{-1} for many systems), remain essentially unchanged.

The entropies of CO_2 in solution are given in Table IV.

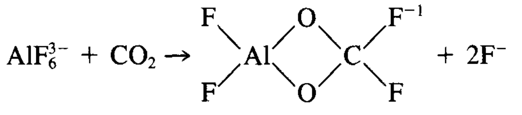
Let it be assumed that CO_2 is sufficiently complexed in cryolite so that it no longer has its own degrees of translational freedom in solution. If we subtract the translational

Table IV. Entropy of CO_2 in Solution

System	Value of Entropy $S^{\circ,l}_{CO_2}$ (cal K^{-1} mol^{-1})
CO_2 in cryolite + 0.34 pct Al_2O_3 at 1273 K	32.15
CO_2 in $(NaF)_{2.3}$ AlF_3 + 5.3 pct Al_2O_3 at 1273 K	52.05
CO_2 gas	64.15

entropy, 42.66 cal K^{-1} mol^{-1}, from the totally unimpeded value, 64.15 cal K^{-1} mol^{-1}, we get 21.49, and if it is assumed that the vibrational entropy passes from about 5 cal K^{-1} mol^{-1} in the gas to about 10 cal K^{-1} mol^{-1} (1273 K) on solution, one can account for the 32 cal K^{-1} mol^{-1} observed for the entropy of CO_2 in solution.

A complex which would be consistent with this reasoning (*i.e.*, the total removal of translational freedom) would be:



Less loss of entropy occurs in the Al_2O_3-containing system upon dissolution of CO_2 than in cryolite with low alumina. The complexing which occurs here removes less translational entropy than does that in pure cryolite. Nevertheless, something must occur to reduce the entropy by about 9 cal K^{-1} mol^{-1} from that in the gas phase.

Let is be supposed[5] that the complexing reaction is now:

$$AlOF_x^{1-x} + CO_2 = AlF_x^{3-x} + CO_3^{2-}$$

In this system, the CO_3^{2-} is a relatively small ion. On the basis of Grimes' result for the entropy of noble gases, it should have much translational entropy. On this model the translational entropy would be maintained. One might expect the vibrational entropy in the products to be less than that of the more complexed molecule, say 7 ± 1 cal K^{-1} mol^{-1}, and the rotation to be extinguished. The resulting entropy would be around 64.1-15.9 cal K^{-1} mol^{-1} (the rotational entropy) + 2.5 cal K^{-1} mol^{-1} (the assumed increase in the vibrational entropy) = 50.7 cal K^{-1} mol^{-1}, a reasonable approach to the observed values for CO_2 in Al_2O_3-containing liquids.

The model gives a qualitative and speculative account of the greater loss of entropy of CO_2 in cryolite on the basis that there is a loss of translation in the complexing there which is compensated by means of the translation of the CO_3^- ion, resulting from the preferred complexing of CO_2 with alumino fluoride anions.

C. *Significance of Results for Aluminum Technology*

The solubility range determined for CO_2 in all the mixtures was of the same order (10^{-3} moles $liter^{-1}$ atm^{-1}) as determined earlier by Bratland,[3] but in contrast to the results of Haupin.[2] Hence, the possible efficiency loss by the reaction of dissolved Al with CO_2 can indeed be estimated.

The O_2 solubility in cryolite-alumina melts is much (c. 1000 times) less than that of CO_2. Hence, were the aluminum industry to go over to oxygen evolving dimensionally stable anodes, the presence of O_2 in the melt would be unlikely to cause a reduction of efficiency.

APPENDIX A

The total measured $C^{14}O_2$ activity in the solution is J c.p.m.

In terms of disintegration per second, this is $J/(0.82 \times 60)$ where 0.82 is the efficiency of the scintillation counting employed in this measurement.* 1 Ci corresponds to 3.7×10^{10} (d.p.s.). Hence,

$$C^{14}O_2 \text{ activity} = \frac{\dfrac{J}{0.82 \times 60}}{3.7 \times 10^{10}} \text{ Ci}$$

The moles of $C^{14}O_2$ displaced from the water are calculated by dividing the above value by the specific activity. The amount of

$$CO_2 \text{ displaced from the water (moles)} = \frac{\dfrac{J}{0.82 \times 60}}{3.7 \times 10^{10} \times S}$$

The specific activity S was obtained from the New England Nuclear Co. and was 4.45 Ci/mole, the result being 2.00×10^{-2} mole $liter^{-1}$ with $P_{CO_2} = 1$ atm.

T. J. Morrison and F. Billett[15] obtained 2.0×10^{-2} mole $liter^{-1}$ 25 °C.

APPENDIX B

The number of moles of oxygen was calculated from the potential difference ΔE of a ZrO_2 sensor. ΔE is defined as:

$$\Delta E = \frac{RT}{4F} \ln P_{O_2}/P'_{O_2}$$

Here P_{O_2} is given by the equilibrium oxygen partial pressure due to Ni and NiO as follows:

$$Ni + \frac{1}{2}O_2 \rightarrow NiO$$

ΔG_T° is:[9]

$$\Delta G_T^\circ = 56{,}101 - 20.31{*}(1273)$$
$$= 30{,}079 \text{ cal mol}^{-1}$$

$$\Delta G_T^\circ = -RT2.3 \log \frac{a_{NiO}}{a_{Ni} - {P'_{O_2}}^{1/2}}$$

Hence,

$$P'_{O_2} = 10^{-10.3269 \text{ atm}}$$

$$E = \frac{RT}{4F} 2.3 \log \frac{P_{O_2}}{10^{-10.3269}}$$

Hence,

$$P_{O_2} = \frac{4F}{10^{2.303\ RT}} - 10.3269$$

The P_{O_2} value thus calculated is that of the O_2 in the Ar-O_2 flow from the melt during purging. The number of moles passing the sensor in a given time interval can be

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*This figure results from measurements of the efficiency of counting with ethanolomine carried out by S. L. Lee.

obtained from:

$$n_{O_2} = P_{O_2} \frac{\text{(flow rate) (time interval of observation)}}{1.987 \text{ (absolute temperature)}}$$

A plot of this quantity against time (Figure 7) shows the period of rise and exhaustion. Its integral gives the total O_2 in the melt.

ACKNOWLEDGMENTS

The authors are grateful to the Aluminum Company of America for financial support. Many thanks, in particular, are due to Mr. Warren E. Haupin for his supportive interaction and for knowledgeable discussion and advice. Also many thanks to Dr. S. L. Lee of Texas A&M University for his help with the scintillation counting.

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