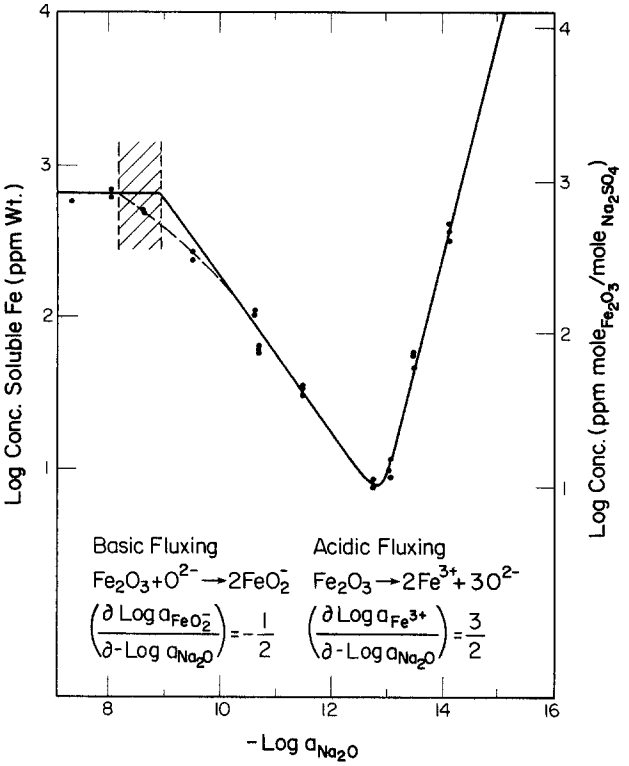

Fig. 2. Solubility of α-Fe_2O_3 in fused Na_2SO_4 at 1200 K and P_{O_2} = 1 atm.

the succeeding note (4). The dual designations for the abscissa are valid only in the regime where Na_2SO_4 is stable. Additionally, for 1200 K, $\Delta G°_{Fe_2O_3}$ = −512.2 kJ/mol (6), $\Delta G°_{Fe_3O_4}$ = −731.9 kJ/mol (6), $\Delta G°_{FeS}$ = −85.8 kJ/mol (6), $\Delta G°_{Fe_2(SO_4)_3}$ = −1216.9 kJ/mol (6), $\Delta G°_{FeSO_4}$ = −488.7 kJ/mol (6), $\Delta G°_{NaFeO_2}$ = −474.1 kJ/mol (7), and $\Delta G°_{Na_2FeO_2}$ = −527.2 kJ/mol (7). The data points in Fig. 2 are the measured solubilities of α-Fe_2O_3 in molten Na_2SO_4 at 1200 K and 1 atm oxygen. Each data point in Fig. 2 represents the average analysis for a separate salt sample compared against a certified standard solution. The high precision of the solubility values is indicated by the reproducibility of the data. In basic dissolution, the Na_2O dependence of the solubility indicates that the solute species of Fe_2O_3 is FeO_2^-. The dependence of the FeO_2^- concentration upon the melt basicity is consistent with the following dissolution reaction

$$Fe_2O_3 + O^{2-} = 2FeO_2^- \qquad [2]$$

$$\left\{\frac{\partial (\log a_{FeO_2^-})}{\partial (-\log a_{Na_2O})}\right\} = -\frac{1}{2} \qquad [2a]$$

The solubility plateau to the left of about $-\log a_{Na_2O}$ = 9 is expected because the dissolution of the equilibrium $NaFeO_2$ phase to form FeO_2^- ions does not involve O^{2-} ions in the reaction. The cross-hatched transition indicates the thermodynamic uncertainty in the location of the phase stability boundary.

For acidic dissolution of Fe_2O_3, the solute correlates to Fe^{3+}. The dependence of the Fe^{3+} concentration on the melt basicity is consistent with the reaction

$$Fe_2O_3 = 2Fe^{3+} + 3\,O^{2-} \qquad [3]$$

$$\left\{\frac{\partial (\log a_{Fe^{3+}})}{\partial (-\log a_{Na_2O})}\right\} = \frac{3}{2} \qquad [3a]$$

Close to 1 atm O_2, both the basic and acidic solutes of Fe_2O_3 involve trivalent iron. Because no oxidation step is involved in such dissolution reactions, no dependence of solute concentrations upon P_{O_2} is expected near P_{O_2} = 1 atm.

Figure 2 shows that the solubility minimum lies at $-\log a_{Na_2O}$ = 12.9. Thus, α-Fe_2O_3 is an oxide considerably more acidic than Co_3O_4 and NiO (2) but more basic than α-Al_2O_3 (4). The activity coefficients of the soluble species $NaFeO_2$ and $Fe(SO_4)_{1.5}$ were calculated by methods used previously (2, 4) to be 250 and 3.6×10^{-3}, respectively. But these values possess considerable uncertainties arising from the uncertainties in the thermodynamic data (6, 7) for $\Delta G°_{NaFeO_2}$ and $\Delta G°_{Fe_2(SO_4)_3}$.

In order to evaluate and test the P_{O_2} dependence of the solubilities of iron oxides, and to relate the data to the hot corrosion of iron-base alloys, the solubilities of iron oxides are being measured at lower oxygen pressures in a continuing study.

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Solubility of α-Al_2O_3 in Fused Na_2SO_4 at 1200 K

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Many alloys and coatings owe their resistance to high temperature oxidation to the slow growth of adherent Al_2O_3 scales. However, the dissolution of this protective oxide scale could represent an important step in the accelerated corrosion of engineering alloys in contact with a thin layer of fused salt. A number of salt films are known to cause such "hot corrosion." Because of its high stability in oxidizing sulfur-bearing gases, sodium sulfate is particularly aggressive toward protective coatings in aircraft and marine gas turbines and in other engineering systems. A knowledge of the solubility of the protective oxide and its dependence on the fused salt chemistry may aid the interpretation of hot corrosion mechanisms and in the development of new protective materials.

Liang and Elliott (1) have reported a few values for the solubilities of Cr_2O_3, Al_2O_3, and NiO in Na_2SO_4 over a lim-

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ited range of salt compositions. Stroud and Rapp (2) reported solubilities for α-Al_2O_3 and Cr_2O_3 in Na_2SO_4 at 1200 K as a function of P_{O_2} and log a_{Na_2O}. However, their results were inconsistent with thermodynamic expectation, because the observed minimum in the oxide solubility occurred at too high a value for a_{Na_2O}. It now appears that because of a reaction of Na_2SO_4 with their platinum electrode in the Na_2SO_4 melts, a faulty potential was indicated for the Pt/melt electrode. The present study reports measurements for Al_2O_3 solubility using improved methods. Two solid electrolyte probes were used to infer the basicity of Na_2SO_4 melts as suggested by Watt *et al.* (3), and used by Gupta and Rapp (4) in a determination of the solubilities of NiO and Co_3O_4 in Na_2SO_4 at 1200 K. Deanhardt and Stern (5) have employed two pairs of such probes to determine the solubility products for NiO in Na_2SO_4 at 1200 K. Misra *et al.* (6) calculated the solubilities and the interaction energy parameters for the acidic solutes of NiO and Co_3O_4 by use of existing phase diagrams and a regular solution model. They found good agreement with experimental solubility results.

The acid-base character of Na_2SO_4 can be described by the equilibrium

$$Na_2SO_4 = Na_2O + SO_3 \qquad [1]$$

in which Na_2O can be considered as the basic component and SO_3 the acidic component. The thermodynamic data listed in Table I were used to construct the Na-Al-S-O phase stability diagram of Fig. 1, which is analogous to the Pourbaix diagram of *E vs.* pH for aqueous solutions. The oxidation potential is plotted as the ordinate against the negative of salt basicity (defined as log a_{Na_2O}) as the abscissa. The dashed lines show that liquid Na_2SO_4 is stable over a large area in this diagram. Alternate abscissa variables of $-$ log a_{Na_2O}, or else log P_{SO_3}, can be used within the range of Na_2SO_4 stability at essentially unit activity. The diagram could provide quantitative values for the solubility of the metal oxide in the fused salt if the identity and the activity coefficients of the solute species were known. Conversely, if the solubility were known, the activity coefficients of the respective solutes in solution could be calculated. The reliability of activity coefficients obtained in this way depends greatly on the accuracy of the Gibbs energy of formation data for the soluble metal salts and the metal oxide and also on the accuracy of the experimental measurements. In the present study, the solubility of α-alumina in fused Na_2SO_4 at 1200 K was measured as a function of the thermodynamic activity of Na_2O for a fixed oxygen pressure of 1 atm. The results are related to the phase stability diagram and are used to infer the ionic solute species as well as the activity coefficients for the solute species of alumina.

Experimental Procedure

As in the preceding study by Gupta and Rapp (4), the voltage between two solid-state electrochemical probes was used to measure the basicity of the Na_2SO_4 melt. A closed-end mullite ($3Al_2O_3 \cdot 2SiO_2$) tube (McDanel MV30) with glassy grain boundaries is known to be an exclusive conductor of sodium ions at high temperatures. Within this tube, a small amount of liquid salt with composition 90 mole percent (m/o) Na_2SO_4, 10 m/o Ag_2SO_4 contacted a Ag wire which was welded within the hot zone to a Pt lead wire. The working electrode for this cell was either a

Table I. Thermodynamic data relevant to Na-Al-S-O system

Compound	ΔG_f° (1200 K) (kJ/mol)	Ref.
Na_2O (s)	−250	(8)
Na_2S (s)	−282	(8)
Na_2SO_4 (l)	−893	(8)
SO_2 (v)	−273.7	(8)
SO_3 (v)	−260.3	(8)
α-Al_2O_3 (s)	−1294	(8)
$NaAlO_2$ (s)	−862	(8)
$Al_2(SO_4)_3$ (s)	−1980	(9)
Al_2S_3 (s)	−657	(10)

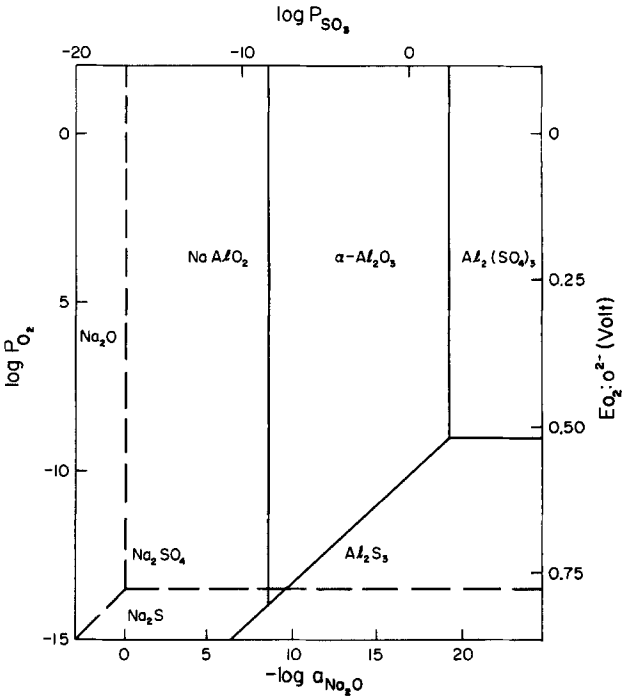

Fig. 1. Thermodynamic phase stabilities in the Na-Al-S-O system at 1200 K

Au or Pt wire contacting the Na_2SO_4 melt external to the mullite tube and remote from the gaseous environment; again, a Pt lead wire was attached. A closed-end 3.5 weight percent (w/o) CaO partially stabilized zirconia tube contacted the Na_2SO_4 melt. This zirconia tube was platinized on its aerated inside surface and provided with an internal Pt lead wire. The voltage between the zirconia electrode and the Au or Pt working electrode in the melt indicated the P_{O_2} of the melt (4). At 1200 K, the open-circuit voltage between the mullite and the zirconia electrodes is given by (4)

$$E(V) = 1.4943 + 0.119 \log a_{Na_2O} \qquad [2]$$

Strictly speaking, the a_{Na_2O} is measured at the ZrO_2/fused Na_2SO_4 interface (7), but this Na_2O value is valid for the entire melt under equilibrium conditions.

Excess amounts (30-40g) of α-Al_2O_3 powder were added to 100g of sodium sulfate in an alumina crucible placed within the mullite reaction tube. After drying the salt for a few days at 200°C, the temperature was raised to 1200 K. Salt samples were taken after various times by freezing salt onto a cold alumina tube after the electrochemical probes indicated equilibrium for oxygen between the fused salt and the gas, and after the salt basicity became constant. The salt samples were weighed, dissolved in distilled water, and analyzed by atomic absorption spectroscopy (Perkin-Elmer, Series 360) using a graphite furnace. For neutral water at pH = 7, the solubility of $Al(OH)_3$ is a factor of at least 150 times higher than the highest Al solute concentration from the dissolved salt.

Results and Discussion

Figure 2 presents the results of solubility measurements for α-Al_2O_3 in fused Na_2SO_4 at 1200 K in P_{O_2} = 1 atm. Although only a few points were obtained for the acidic segment of the solubility curve, the plot is well described by lines for one basic solute, AlO_2^-, and one acidic solute Al^{3+}. The minimum solubility occurs at about log a_{Na_2O} = −15.4 and 13 wt ppm dissolved Al. A single datum point from Liang and Elliott (1) is in good agreement after conversion of their measurement to a common value for $\Delta G^\circ_{Na_2SO_4}$ (reported in Table I).

For the dissolution of α-Al_2O_3 as a basic solute

$$Al_2O_3 + O^{2-} = 2AlO_2^- \qquad [3]$$

so that

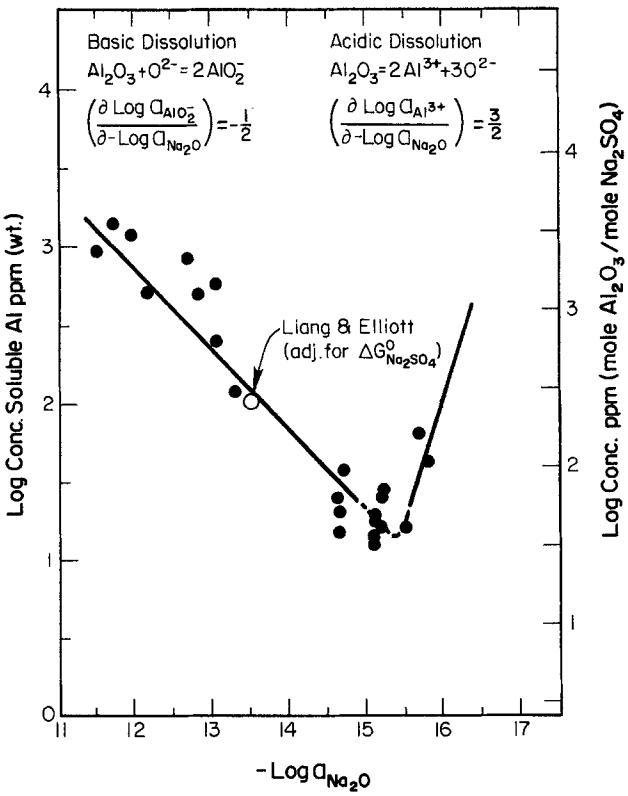

Fig. 2. Solubility of α-Al_2O_3 in fused Na_2SO_4 at 1200 K and P_{O_2} = 1 atm

$$\left(\frac{\partial \log a_{AlO_2^-}}{\partial - \log a_{Na_2O}}\right) = -\frac{1}{2} \quad [4]$$

With the assumption of a constant activity coefficient for the dissolved $NaAlO_2$ in these dilute solutions, the same dependence is expected for the plot of log concentration *vs.* $-\log a_{Na_2O}$, as shown in Fig. 2. Correlation of the data with the theoretical slope is good, implying that only the AlO_2^- ion is formed in basic dissolution. Any pair of values of salt basicity and oxide solubility can be used to calculate the activity coefficient for the dissolved $NaAlO_2$ component through the equilibrium

$$Na_2O + Al_2O_3 = 2NaAlO_2 \quad [5]$$

For the presence of Al_2O_3 at unit activity

$$2 \log a_{NaAlO_2} - \log a_{Na_2O} = 8.10 \quad [6]$$

From Fig. 2, for $\log a_{Na_2O} = -13$ and therefore $a_{NaAlO_2} = 3.55 \times 10^{-3}$, the soluble mole fraction of $NaAlO_2$ (equal to twice the soluble Al_2O_3) equals 10^{-3}. Then, the activity coefficient for $NaAlO_2$ in dilute solution in Na_2SO_4 is given by

$$\gamma^{Na_2SO_4}_{NaAlO_2} = a_{NaAlO_2}/N_{NaAlO_2} = 3.6 \quad [7]$$

Except for the indicated single solubility measurement from Liang and Elliott (1), previous measurements are not available for comparison.

For the dissolution of α-Al_2O_3 as an acidic solute

$$Al_2O_3 = 2Al^{3+} + 3\,O^{2-} \quad [8]$$

and

$$\left(\frac{\partial \log a_{Al^{3+}}}{\partial - \log a_{Na_2O}}\right) = +\frac{3}{2} \quad [9]$$

Only a few data for acidic dissolution are shown in Fig. 2, but they are consistent with the presence of a single Al^{3+} acidic solute. Acidic dissolution of Al_2O_3 in Na_2SO_4 can also be described in terms of an $Al(SO_4)_{1.5}$ solute

$$(3/2)\ Na_2SO_4 + (1/2)\ Al_2O_3 = (3/2)\ Na_2O + Al(SO_4)_{1.5} \quad [10]$$

For the presence of Al_2O_3 and Na_2SO_4 at unit activities

$$(3/2) \log a_{Na_2O} + \log a_{Al(SO_4)_{1.5}} = -27.05 \quad [11]$$

For $\log a_{Na_2O} = -16$, $a_{Al_2(SO_4)_3} = 8.91 \times 10^{-4}$, and the measured solubility (equal to twice the molar Al_2O_3 solubility) is about $N_{Al(SO_4)_{1.5}} = 2.5 \times 10^{-4}$, so that

$$\gamma^{Na_2SO_4}_{Al_2(SO_4)_3} = a_{Al(SO_4)_{1.5}}/N_{Al(SO_4)_{1.5}} = 2.3 \quad [12]$$

No previous values have been reported in the literature. Indeed, the uncertainty in each activity coefficient is large, as previously mentioned.

In this study, it has been shown that at 1200 K and P_{O_2} = 1 atm α-Al_2O_3 dissolves in fused Na_2SO_4 as one acidic and one basic solute species, with the minimum solubility occurring at $\log a_{Na_2O} = -15.4$. Because neither dissolution reaction involves a change in aluminum valence, the solubility plot of Fig. 2 should not depend upon P_{O_2}.

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