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Chemical and electrochemical studies relevant to fused fly ash deposits

Leblanc, Patrick Philippe, Ph.D.

The Ohio State University, 1992
CHEMICAL AND ELECTROCHEMICAL STUDIES RELEVANT TO FUSED FLY ASH DEPOSITS

DISSERTATION
Presented in Partial Fulfillment of the Requirements for the degree of Doctor of Philosophy in the Graduate School of The Ohio State University

by
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*****

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To my parents, my wife Tatjana, and my son, Alexander
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CHAPTER I
INTRODUCTION

Materials used in high temperature industrial systems develop a resistance to corrosion by forming a dense, slow-growing oxide scale upon exposure to oxidizing environments. This oxide layer acts as a barrier against further attack by aggressive oxidizing gases containing inorganic impurities. However, these materials may experience accelerated oxidation when their surfaces are coated with a layer of fused salt in an oxidizing gas. The most commonly observed and dominant salt involved in this mode of corrosion is sodium sulfate because of its high thermodynamic stability. Hot corrosion induced by sodium sulfate (type I corrosion) is observed at temperatures above the 884°C melting temperature of pure Na$_2$SO$_4$. However, the presence of mixed alkali and sulfur impurities in the gaseous environment may result in condensates which are liquid well below 884°C. Such condensates are the precursors of a mode of attack called low-temperature hot corrosion. This type of corrosion (also named type II hot corrosion) is one of the main obstacles to long term operation in coal fired utility boilers. This work is concerned with the determination of the chemical and electrochemical characteristics of the inner layers of ash deposit forming on superheater tubes and particularly the sulfur trioxide pressure required for their formation.
The deposit layer immediately next to the tube metal (white layer), considered to be a factor in coal ash corrosion, has been qualitatively characterized by several investigators and shown to consist largely of complex alkali iron sulphates. The synthetic ash used in this study was composed of Na$_2$SO$_4$, K$_2$SO$_4$, and Fe$_2$(SO$_4$)$_3$ (Na$_2$SO$_4$/K$_2$SO$_4$ ratio: 4:1). The thermodynamic properties of the liquid ternary have not been reported in the literature, and during the course of this research, the determination of reasonable data for comparison with the experimental results was undertaken.

At the present time, the generally accepted mechanism for low-temperature hot corrosion is a fluxing/reprecipitation mechanism as in type I hot corrosion. This theory proposes that the protective oxide scale formed on the metal or alloy is dissolved by the fused salt at the oxide/salt interface and is reprecipitated somewhere in the liquid salt in a non-protective form. The dissolution may be either acidic or basic in nature depending on the local chemistry of the molten salt. The electrochemical monitoring of the chemistry of the fly ash deposits requires the use of a reference electrode. A silver/silver ion/mullite (or quartz) reference electrode commonly used as a Na$^+$ sensor in electrochemical studies of pure sodium sulfate or sodium sulfate-vanadate melts at temperatures around 900°C is not suitable for the study of low-melting multication sulfate melts for the following reasons. The first reason is that, at intermediate temperatures, the $x$Ag$_2$SO$_4$-$\quad$($1-x$)Na$_2$SO$_4$ reference melt solidifies and the ionic conductivity of the membrane of the
electrode drops to levels at which the stability is affected. Secondly, the migration of K⁺ (and maybe Fe³⁺) through the membrane results in erroneous values of the sodium activity. In this work, an electrode which indicates the partial pressure of sulfur trioxide for a low-melting multi-cation sulfate salts is described. In this way, the electrode can be used to identify the acidity for the Na₂SO₄-K₂SO₄-Fe₂(SO₄)₃ system at intermediate temperatures.

Melts comprised of one anion and different cations can be described in terms of acidity (defined as log(P₅O₃)), rather than basicity (-log(aNa₂O)), which is used for a melt containing only Na⁺ and multiple anions. The demonstration (calibration) of the acidity electrode was done by measuring the emf between a Pt wire (reference electrode) equilibrated with a Fe₂O₃-saturated ternary sulfate melt and a Pt wire (working electrode) contacting a melt of the same nominal composition but equilibrated to a known P₅O₃ by contact with a gas phase. The stability of this electrode was studied in three melts of different composition equilibrated with an oxidizing gas phase containing 100 to 10000 ppm SO₃. The partial pressure of SO₃ in the reference electrode was measured and compared to a calculated value.

The measured solubilities of oxides in fused salts are particularly useful in interpreting fluxing/reprecipitation mechanisms. The dependence on the acidity of the fly ash deposits of the solubility of Cr₂O₃ and SiO₂ has been measured.
CHAPTER II
OUTLINE OF THE PROBLEM—FIRESIDE CORROSION IN UTILITY BOILERS

A boiler facility at an electric utility is intended to produce steam which is expanded in turbines to produce electricity. A description of such units for steam generation and their operation can be found in the literature\(^1\).

A boiler is a large chamber of square or rectangular cross-section (Fig. 1). Coal is injected with preheated combustion air into the boiler as 200 mesh or smaller particles through burners. The walls of the furnace are comprised of vertical water tubes. Water passes through the tubes which are heated by convection and radiation. The coal ash and residues of the combustion reaction form large slag particles which are withdrawn through an opening at the tapered bottom of the furnace. The remainder of the mineral matter forms small particles (fly ash) which are carried up with the combustion gases. The hot gases lose heat by radiation as they rise through the furnace. The water entering the tubes at the bottom boils at some point above the level of the burners. There might or might not be a clear interface between water and steam depending on the configuration of the burner. At the critical point, the liquid and gas phases become undistinguishable. In subcritical conditions,
there is a clear interface between steam and water. In this case, water is separated and returns to the boiler. On the average, the water may pass several times through the water walls before it is evaporated. In a supercritical unit, there is no clear interface between water and steam.

The water-free steam is then heated further during the superheating stages. In the most common design of boiler, the combustion gases reach the top of the boiler and turn horizontally into a section where heat is transferred to the reentering steam by convection. The heat exchanger through which the steam first re-enters the boiler is the primary superheater. Steam then passes to a second heat exchanger hanging from the roof of the furnace above the radiant section. Fireside corrosion is the most likely to occur in the secondary superheater, where the temperature is higher.

The materials of the superheater are subject to requirements for strength and oxidation resistance. Austenitic steels such as Type 304 and Type 347 are commonly used. From a thermodynamic point of view, a higher temperature and pressure for the steam leaving the boiler result in increased efficiency. However, because of materials limitations, costs, and safety concerns, the temperature in current units does not exceed 538°C at pressures of 2400 psi for subcritical units and 3500 psi for supercritical units.

The superheated steam is expanded through a high pressure turbine, and then returned to the boiler and heated up again in the reheater. The reheat steam is then expanded through an
Figure 1  Schematic of a utility boiler.\(^{(1)}\)
Figure 2  Analysis of typical ash deposit from 18Cr-8Ni superheater tube.\(^{(1)}\)
intermediate pressure turbine before going to a low pressure turbine whose back end pressure is controlled to lower the condensation temperature to the minimum value possible. The gas temperature in the vicinity of the secondary superheater may be as high as 1427°C or as low as 1093°C. The metal temperature is of the order of 600°C.

Deposits build up on the superheater tube surfaces during operation. Some molten phase is present on the surface of the ash particles themselves and the fly ash particles stick as a condensate on the tubes. As the deposit thickens, the surface temperature rises because the steam within the tube is a less effective coolant. The deposit may then fuse or sinter. When the system is cooled, a white deposit is often observed beneath the ash in contact with the metal. This layer is rich in iron, sodium and potassium oxides (last column in Fig. 2).

The effect of temperature on the corrosion rate is shown in Fig. 3. The shape of the curve is much the same for austenitic steels (304, 347) and for alloys containing molybdenum (17-14 CuMo)\(^2\). Other alloys containing molybdenum such as Esshete 1250 (15Cr10Ni6Mn1MoVNb) are also severely corroded\(^3\). The onset of accelerated attack is associated with the appearance of the molten alkali sulfate phase. The attack increases to a maximum at 720°C. Above this temperature, the partial pressure of SO\(_3\) falls below the dissociation pressure of the salt so that the salt dissociates into products with higher melting points and solidifies. The corrosion attack is also dependent on the gas temperature as shown in Fig. 4.
The addition of iron, originating both from the ash and the oxide scale on the tubes produces a ternary sulfate system of great importance because its liquidus temperature can fall well within the range of metal temperatures for the superheater and reheater. For laboratory studies, melts based on the sodium, potassium, lithium sulfate system which are molten at 530ºC are often chosen for experimental convenience. But these were rejected here because lithium sulfate is not normally found in the deposits. In general, the corrosion attack associated with such heat exchanger tubes is known as low temperature hot corrosion.
Figure 3  Corrosion tests of specimens exposed for 50 hours in a simulated coal-fired boiler atmosphere.\(^{(2)}\)
Figure 4  Effect of gas and metal temperature on superheater corrosion.\(^{(4)}\)
CHAPTER III
LITERATURE REVIEW OF HOT CORROSION

1. Low Temperature Hot Corrosion

About fifteen years ago, an apparently new form of hot corrosion attack of gas turbine materials was identified during the operation of a marine turbine at temperatures between 600°C and 750°C (5). Gas turbine blades coated with a cobalt-chromium-aluminum-yttrium coating (CoCrAlY) had shown satisfactory hot corrosion resistance in the temperature range 800°C to 1000°C. Salts containing sodium sulfate deposited on the blades were expected to be solid at those temperatures because 884°C is the melting temperature of pure Na₂SO₄. But the corrosion rates on the coated blades were greater than anticipated for metal temperatures between 600°C and 730°C. Similar unexpected corrosion problems at lower temperatures surfaced at the same time period in rig testing and on airfoils from ground-based turbines (6). This form of corrosion was named low-temperature, or Type II, hot corrosion in contrast to high temperature (800°C-1000°C), or Type I, hot corrosion. The latter occurs at temperatures exceeding the melting point of pure Na₂SO₄.

Low-temperature hot corrosion (LTHC) causes degradation of most alloys but is particularly detrimental to CoCrAlY coatings. The attack is characterized primarily by pitting, with no internal
sulfidation and little depletion of the alloy below the pit\(^{(7)}\). In a study of Co-Cr-Al alloys, Luthra\(^{(8)}\) found that the resistance to corrosion of a Co-Cr (or Co-Al) alloy improved with increasing chromium (or aluminum content) of the coating. However, the addition of Cr to a Co-Al alloy or Al to a Co-Cr alloy was detrimental because they disrupted the formation of protective films.

The major characteristics of low-temperature hot corrosion can be briefly summarized as follows\(^{(5,6,9,10)}\):

- Under conditions where sodium salts ingested into high temperature systems cause the deposition of Na\(_2\)SO\(_4\), hot corrosion of coatings or alloys with chromium content of approximately 10-20% occurs at rates greater at about 700\(^{\circ}\)C than at 800\(^{\circ}\)C to 1000\(^{\circ}\)C. The phenomenon is not exclusive to sodium sulfate but can occur in potassium sulfate melts or binary and ternary salts involving Na\(_2\)SO\(_4\).
- An analysis of the products soluble in water leached from the corroded surface reveals the presence of water-soluble sulfate.
- The corroded microstructure exhibits pitting and there is no zone of alloy depletion or of chromium sulfides in contrast to structures observed at higher temperatures.

For both type I and type II hot corrosion, a surface coverage with a molten salt film is necessary. The condensate is based on Na\(_2\)SO\(_4\) in a gas turbine or on Na\(_2\)SO\(_4\)-K\(_2\)SO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\) in fireside corrosion. Since the formation of a liquid sulfate mixture is required for the occurrence of hot corrosion, the value of the partial pressure of SO\(_3\) in contact with the melt is of great importance. Very small
changes in $P_{SO_3}$ can cause large increases in corrosion, if they result in a transition from a solid to liquid sulfate. At a temperature below the melting point of $Na_2SO_4$ ($884^\circ C$), very little corrosion would be observed at $SO_3$ levels lower than the minimum required to stabilize the liquid. At higher $SO_3$, a liquid phase forms and initiates corrosion. The liquid is a low melting sulfate mixture involving $Na_2SO_4$ and acid solutes of the oxides of the base metal (e.g., NiSO$_4$, CoSO$_4$, Fe$_2$(SO$_4$)$_3$ or FeSO$_4$). The sulfate can also contain other impurities present in the environment ($K_2SO_4$). A comparison of the stability of different oxides relative to their acid sulfates can direct the choice of the alloy to be used. For instance, ferric and nickel sulfates are less stable than CoSO$_4$ and therefore require a higher $SO_3$ level to maintain a liquid phase. The $SO_3$ levels needed to stabilize the $Na_2SO_4$-NiSO$_4$ liquid are 10 times higher than those for $Na_2SO_4$-CoSO$_4$\(^8\). Even higher $SO_3$ partial pressures are required to stabilize a $Na_2SO_4$-Fe$_2$(SO$_4$)$_3$ melt. This implies that the use of nickel-base or preferably iron-base alloys or coatings instead of cobalt-base can prevent the formation of the liquid phase.

Sulfur trioxide and dioxide exist in the combustion product gases associated with the burning of an impure fossil fuel through the reaction

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

(1)
The reaction is temperature-dependent, with SO$_2$ increasingly favored at elevated temperatures, e.g., in air, the equilibrium SO$_3$/SO$_2$ ratio is 3.08 at 900 K but only 0.11 at 1200 K. In the absence of a catalyst, however, equilibrium does not appear to be achieved$^{(11)}$. Flue gases from industrial boilers show SO$_3$/SO$_2$ ratios of 0.01-0.05 even though the combustion product gas temperatures ($<650^\circ$C) are such that substantial SO$_3$ should be produced. A local catalytic conversion of SO$_2$ to SO$_3$ by local oxides$^{(11)}$ or other surfaces would explain how SO$_3$ produces corrosive mixed sulfates from combustion gases with P$_{SO_3}$ partial pressures well below those required for the sulfate formation.

A review of the literature reveals that some authors$^{(12,13)}$ had have some success applying the mechanistic concepts of type I hot corrosion to low-temperature hot corrosion. In the next paragraph, a summary of early mechanistic studies corrosion due to liquid salts is presented.

2. Early Studies of High Temperature (Type I) Hot Corrosion

Prior to the condensation or deposition of the salt on a surface covered with a protective oxide layer, there is only a slow reaction. In order for serious oxidation to occur, this protective oxide barrier has to be breached. An initiation period with very slow kinetics can result in oxide removal in three imaginable ways. The first is a mechanical disruption by erosion, thermal cycling or by elastic tensile straining of the substrate. The second is the diffusion (or
penetration) of sulfur through the oxide until sulfides (i.e. chromium sulfides) form internally, which impede the growth of a protective oxide. The third is the fluxing (dissolution) of the oxide by the salt film, and a reprecipitation of the oxide in the salt. In a subsequent stage, the corrosion rates increase dramatically, usually with fast linear kinetics.

It is now generally agreed that fluxing is responsible for the destruction of the protective oxide during hot corrosion. Bornstein and DeCrescente\(^{14,15}\) demonstrated that hot corrosion does not necessarily depend on sulfidation/oxidation of the alloy which was once a popular mechanism, but rather on a dissolution of the protective barrier by the action of Na\(_2\)O, the basic minority species of Na\(_2\)SO\(_4\). This dissolution mechanism in basic local environments was later termed basic fluxing. Their experiments showed that Ni-base alloys coated with sodium nitrate oxidized at rates comparable to those coated with sodium sulfate, which led to the conclusion that the acceleration of corrosion was not a consequence of the metal/sulfur interaction. For alloys/sulfate reactions, high activities of Na\(_2\)O are generated by the removal of sulfur from the salt by the formation of nickel sulfide through the reaction

\[\text{Na}_2\text{SO}_4 + 4 \text{Ni} = \text{Na}_2\text{O} + \text{NiS} + 3\text{NiO}\]  \hspace{1cm} (2)

whereby the Na\(_2\)O is fully dissociated as ions in the fused salt.
The oxidation is accelerated as the protective oxide is dissolved by $O^{2-}$ as\(^{(16)}\)

\[
\text{NiO} + O^{2-} = \text{NiO}_2^{2-} \quad (3a)
\]
or

\[
2 \text{NiO} + O^{2-} + \frac{1}{2} O_2 = 2 \text{NiO}_2^- \quad (3b)
\]

If $SO_3$ was not present or not absorbed from the gas phase, the corrosion would be non-sustaining once the sulfidation reaction stopped and the salt became saturated with basic oxide solutes.

Goebel et al.\(^{(16,17)}\) demonstrated that $Al_2O_3$-forming Ni-base alloys could suffer "acidic fluxing" if Mo, W or V were present in the alloy. The interaction of the oxides of these alloying elements with the sodium sulfate melt reduces the activity of $Na_2O$ by the formation of complexes, e.g. $MoO_3 + O^{2-} = MoO_4^{2-}$. This reaction drops the oxide ion activity to levels at which the protective oxide can dissolve in an acidic manner, e.g. $NiO = Ni^{2+} + O^{2-}$. In this case, acidic fluxing might be self-sustaining and might lead to a catastrophic degradation of the material.

3. Salt Chemistry

Oxyanion melts of alkali sulfates exhibit an acid-base character where the basic component can be chosen as either the oxide ion or the alkali oxide. The basicity can be defined as $-\log(a_{Na_2O})$, where
$a_{\text{Na}_2\text{O}}$ is the activity of Na$_2$O. For pure Na$_2$SO$_4$, the basicity and acidity 
$log(\text{P}_{\text{SO}_3})$ are related through the equation

$$log(a_{\text{Na}_2\text{O}})+log(\text{P}_{\text{SO}_3})=-\log K_0$$

(4)

where $K_0$ is the equilibrium constant for the reaction

$$\text{Na}_2\text{O}+\text{SO}_3=\text{Na}_2\text{SO}_4$$

(5)

At 1200 K, $\log K_0= -16.7$. This equilibrium constant is the analog to the dissociation constant of water. According to Eq. (4), a specification of $-\log(a_{\text{Na}_2\text{O}})$ or $\log(\text{P}_{\text{SO}_3})$ is redundant for pure sodium sulfate. For more complex systems, basicity or acidity concepts may take different expressions. For instance, $\text{P}_{\text{CO}_2}$ appears to be an unambiguous choice for acidity in a melt comprised of one anion, carbonate, and multiple cations.

The parameter $-\log(a_{\text{Na}_2\text{O}})$ is an unequivocal measure of salt basicity of a melt containing a single cation (Na$^+$) and multiple anions (sulfate, vanadate, chromate). But for a melt consisting of different cations and one anion (SO$_4^{2-}$), the acidity parameter $\log(\text{P}_{\text{SO}_3})$ must be chosen.

$$\text{SO}_4^{2-}, \quad \text{Na}^+ + \text{VO}_3^{2-}, \quad \text{CrO}_2^- \quad \Rightarrow -\log a_{\text{Na}_2\text{O}} \equiv \text{basicity}$$
4. Phase Stability and Oxide Solubilities

4.1. Phase Stability Diagrams

These diagrams have been used in the literature to describe the environmental regimes of stability for metals or oxides. As for the Pourbaix diagrams of E vs pH describing aqueous systems, the coordinates of a stability diagram correspond to an oxidizing potential (log(P_{O_2}) for instance) and the acidity (or basicity) of the solvent. Figure 5 presents the high temperature stability diagram of the Fe-S-O system superimposed on the Na-S-O diagram\(^{(18)}\). The construction of the diagram requires only the knowledge of the standard Gibbs energy of formation of the compounds considered. The solid lines separating two regions correspond to equilibrium coexistence and are calculated assuming equal activities for the condensed phases. The broken lines indicate the activities of the various solutes in Na\(_2\)SO\(_4\). The Fe-S-O stability diagram was calculated here for two low temperatures, 600°C and 700°C (Fig. 6). NaFeO\(_2\) does not appear on these diagrams because it is only stable at very low P_{SO_3}. The diagrams show that ferric sulfate is expected to
Figure 5  Superimposed Na-S-O and Fe-S-O phase stability diagrams at 1200K.(18)
Figure 6  Superimposed Na-S-O and Fe-S-O phase stability diagrams.
be the acidic solute of $\text{Fe}_2\text{O}_3$ at $P_{O_2}=1$ atm. In more reducing environments, ferric sulfate should transform to ferrous sulfate.

### 4.2. Oxide Solubilities

From a phase stability diagram, the stability of an oxide with respect to dissolution as either acidic solutes or as basic solutes can be inferred. The solubility of an oxide changes as the acid/base chemistry of the melt varies. This is fundamental in the dissolution-reprecipitation mechanism.

Figure 7 shows the measured solubilities of $\text{Co}_3\text{O}_4$, NiO, $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$ and $\text{SiO}_2$ in sodium sulfate against basicity at 1200 K$^{19}$. Experimentally, the melt basicities may be adjusted by adding $\text{Na}_2\text{O}$ to increase the basicity, by using different $\text{SO}_2$-$\text{O}_2$ gas mixtures as a means of acidification or by electrochemically pumping oxide ions into or out of the melt. Samples of the salt have been taken by quenching some melt onto a cool alumina rod. The samples have then been weighed, dissolved in water and analyzed using an atomic absorption spectrophotometer (Perkin-Elmer, Series 360)$^{20}$ or a colorimetric absorption spectrophotometer (Cary 2200)$^{21}$. The lines through the measured oxide solubilities have the theoretical slopes predicted by the reaction between the oxide and its predominant solute.

As an example, the dissolution of $\text{Fe}_2\text{O}_3$ in $\text{Na}_2\text{SO}_4$ is now considered. On the stability diagram (Fig. 5), $\text{FeO}_2^-$ is the predominant minority species at high activities of $\text{Na}_2\text{O}$ and $\text{Fe}^{3+}$ is the
predominant minority species at high activities of $\text{SO}_3$. The dissolution reaction of hematite at high $a_{\text{Na}_2\text{O}}$ is expected to be

$$\text{Fe}_2\text{O}_3 + \text{O}^2- \rightarrow 2\text{FeO}^2- \quad \text{or} \quad \text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} \rightarrow 2\text{NaFeO}_2$$ (6)

with

$$\frac{\partial (\log a_{\text{FeO}^2-})}{\partial (-\log a_{\text{Na}_2\text{O}})} = \frac{1}{2}$$ (7)

The dissolution reaction at high $P_{\text{SO}_3}$ depends on $P_{\text{O}_2}$. If $\text{Fe}_2\text{O}_3$ is in equilibrium with $\text{Fe}_2(\text{SO}_4)_3$, the reaction is

$$\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}^{3+} + 3\text{O}^2-$$

or

$$3\text{Na}_2\text{SO}_4 + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{O}$$ (8)

with

$$\frac{\partial (\log a_{\text{Fe}^{3+}})}{\partial (-\log a_{\text{Na}_2\text{O}})} = \frac{3}{2}$$ (9)

At lower $P_{\text{O}_2}$, if $\text{Fe}_2\text{O}_3$ is in equilibrium with $\text{FeSO}_4$, the reaction is

$$\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}^{2+} + 2\text{O}^2- + \frac{1}{2}\text{O}_2$$

or

$$\text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 \rightarrow 2\text{FeSO}_4 + 2\text{Na}_2\text{O} + \frac{1}{2}\text{O}_2$$ (10)
Figure 7  Measured oxide solubilities in fused Na$_2$SO$_4$ at 1200K and 1 atm O$_2$. (19)
Figure 8  Measured solubilities of Fe$_2$O$_3$ in fused Na$_2$SO$_4$ at 1200K and 1 atm O$_2$.\(^{(20)}\)
with

\[
\frac{\partial (\log a_{Fe^{2+}})}{\partial (-\log a_{Na_2O})} = 1
\]  

(11)

Zhang and Rapp\(^{(20)}\) have measured the solubility of \(\alpha\)-\(Fe_2O_3\) at 1200K against \(-\log(a_{Na_2O})\). The plot is a V-shaped curve with slopes of \(-\frac{1}{2}\) and \(\frac{3}{2}\) (or 1) (see Fig. 8). The good agreement also substantiates the fact that the activity coefficient of each solute in dilute solution is constant (Henry's law).

Silica stands apart from the other oxides in Fig. 7 because its solubility was independent of basicity in the range of basicity considered\(^{(21)}\). This was attributed to the fact that SiO\(_2\) did not form dominant ionic species and therefore dissolved only as molecular SiO\(_2\). For more basic melts, the solute SiO\(_3^{2-}\) is found.

Solubility studies in a mixed sulfate/vanadate salt system has been done by Zhang and Rapp\(^{(22)}\). They measured the solubility of CeO\(_2\), HfO\(_2\) and Y\(_2\)O\(_3\) as a function of melt basicity in 70 m/o sodium sulfate and 30 m/o sodium metavanadate (NaVO\(_3\)) and the solubility of CeO\(_2\) in pure sodium sulfate. They observed a large increase in the acidic solubility of CeO\(_2\) in the mixed salt as compared to that in pure Na\(_2\)SO\(_4\). In both solvents, the solubility plot on the basic side obeys the expected basicity dependency corresponding to the reaction:

\[
CeO_2 + Na_2O = Na_2CeO_3
\]  

(12)
with

$$\frac{\partial (\log a_{\text{CeO}_3^-})}{\partial (-\log a_{\text{Na}_2\text{O}})} = -1$$

(13)

Acidic dissolution of CeO₂ led to Ce₃(VO₄)₄ (slope: 2/3) in the presence of vanadate and to Ce(SO₄)₂ in Na₂SO₄ (slope=2). The solubility minimum and acidic solubilities in the sulfate-vanadate solvent were much higher than in pure Na₂SO₄. This experimental study provided one interpretation for the detrimental effect of vanadate in hot corrosion.

Hwang\(^{(23)}\) studied the synergistic dissolution kinetics of Cr₂O₃, Al₂O₃ and Fe₂O₃ in fused sodium sulfate at 1200 K. Some increase in the rate of dissolution of an oxide in the presence of a second one was observed for Cr₂O₃-Fe₂O₃ mixtures but not for Al₂O₃-Fe₂O₃ mixtures.

In the next section, the relevance of such solubility plots to interpret the fluxing mechanisms involved in type I and type II hot corrosion is presented.

5. Rapp-Goto Criterion. Fluxing Mechanisms

Rapp and Goto\(^{(24)}\) took the next step in understanding the mechanism of fluxing when they proposed that an accelerated degradation of the protective oxide could be sustained provided that
the gradient in solubility of the oxide with distance away from the oxide into the melt is negative, i.e.,

\[
\left( \frac{d[\text{oxide solubility}]}{dx} \right)_{x=0} < 0 \quad (14)
\]

This criterion explains how an oxide can dissolve at the oxide/salt interface and the solute ions migrate down their concentration gradient to a region of lower solubility where they precipitate as an oxide in a non-protective form (Fig. 9). The reaction product layer become or perhaps locally penetrated at flaws or grain boundaries. The process can be sustained as long as the solubility gradient remains. The solubility gradient for the oxide is a consequence of a gradient in activity of Na$_2$O. The applicability of this criterion to the solubility curve of an oxide is demonstrated in Fig. 10. In this Figure, I and I' represent certain salt basicities at the oxide/salt interface and II and II' are certain basicities at the salt/gas interface. These sets of conditions would set up and maintain continued basic hot corrosion (I and II) and continued acid hot corrosion (I' and II'). As the oxide solute diffuses down a concentration gradient away from the oxide/salt interface, it precipitates in a non-protective manner in the zone of lower solubility. The authors indicated that such a gradient can be established across a thin film as a result of local electrochemical reactions taking place at either the film/salt or salt/gas interface.
The model for the hot corrosion attack of a metal covered by an oxide film is shown in Fig. 11. Electrochemical reduction reactions generate $O^{2-}$ as reaction products and are expected to create a condition of locally high basicity. If the salt film contains a relatively low concentration of transition metal ions, the reduction reaction occurs at the oxide/salt interface where electrons are supplied from the oxidation reaction of the metal (Fig. 11a). If the electrons can be carried through the thin film by the counter-diffusion of two differently charged transition metals or by electron hopping, the site for the reduction reaction may be shifted to the salt/gas interface which becomes the most basic location in the fused salt (Fig. 11b). Thus, the gradient in basicity can be decided by the location of the reduction reaction. Whether or not this gradient set up and maintain hot corrosion is decided by the relative positions of the salt/gas and oxide/salt interfaces in Fig. 10.

A mechanism involving the counterdiffusion of $Fe^{2+}$ and $Fe^{3+}$ had been proposed for the oxidation of iron beneath a liquid slag in air as early as 1934\cite{25}. More recently, the accelerated corrosion of iron in molten sulfate was explained by a similar mechanism by Numata et al\cite{12} who studied the corrosion of steels in an alkali-sulfate melt containing ferric sulfate at 700°C. The rate of corrosion of iron increased as the concentration of $Fe_2(SO_4)_3$ increased and was found to be controlled by the diffusion limited reduction of $Fe^{3+}$. A counter-diffusion of $Fe^{3+}$ and $Fe^{2+}$ establishes an "autocatalytic" corrosion. The mechanism proposed is consistent with that of Fig. 11.
6. Mechanisms for Low-Temperature Hot Corrosion (LTHC)

Luthra\(^{13}\) applied some concepts of type I hot corrosion to type II hot corrosion of CoCr, CoAl and CoCrAl alloys. He proposed a variation of the dissolution-reprecipitation model of Rapp and Goto. In this case, the dissolution/reprecipitation of cobalt oxide disrupted the growth and coalescence of Cr\(_2\)O\(_3\) or Al\(_2\)O\(_3\) preventing the formation of these protective scales. The counter-transport of Co\(^{2+}\) and Co\(^{3+}\) was involved in this model; in order to conserve the electrical neutrality, two Co\(^{3+}\) migrated in through the melt and three Co\(^{2+}\) migrated out leading to the net outward diffusion of one cobalt ion. The locus of the precipitation depended on the P\(_{SO_3}\), the temperature, and the relative limiting transport rates of the reactants through the fused salt. The minimum P\(_{SO_3}\) needed to form a Na\(_2\)SO\(_4\)-CoSO\(_4\) liquid phase from CoO and Co\(_3\)O\(_4\) at different temperatures is shown in Fig. 12. The minimum P\(_{SO_3}\) levels required to stabilize the liquid at P\(_{O_2}\)=1 atm follow curve A. Above curve B, CoSO\(_4(s)\) is stable. At intermediate concentrations of SO\(_3\) where a liquid phase is stable but CoSO\(_4(s)\) is unstable, the cobalt migrating out will form Co\(_3\)O\(_4\) near the salt/gas interface because the inward
Rapp-Goto model. Reprecipitation of a porous MO oxide supported by the solubility gradient in a fused salt.\(^{(24)}\)
Basic dissolution:
$$2\text{NiO} + \text{Na}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{NaNiO}_2$$

Acidic dissolution:
$$\text{NiO} + \text{Na}_2\text{SO}_4 = \text{NiSO}_4 + \text{Na}_2\text{O}$$

Figure 10 Solubility of NiO in fused Na$_2$SO$_4$ at 1200K.\(^{(26)}\)
Figure 11 Cathodic reduction of $\text{SO}_3(g)$ or $\text{O}_2(g)$ for (a) a high permeability of the gases, (b) high concentrations and diffusivities of $\text{M}^{2+}$ and $\text{M}^{3+}$, or electronic conduction, in the salt film.\(^{(24)}\)
Figure 12 Effect of temperature on the stability of solid CoSO₄ and Na₂SO₄-CoSO₄ liquid. (27)
transport rate of oxygen is relatively slow. At higher $P_{SO_3}$ where $CoSO_4(s)$ is stable, cobalt diffusing out will precipitate as cobalt sulfate. The interface where this precipitation reaction occurs is decided by the relative transport rates of the oxidant ($SO_3$) and cobalt. If the rates are comparable, $CoSO_4(s)$ forms in the liquid salt. If the diffusion of $SO_3$ is faster, $CoSO_4(S)$ will form at the scale/salt interface. If cobalt diffuses out faster, the precipitation takes place at the salt/gas interface. This mechanism is described schematically in Fig. 13. However, Luthra could not account for the tendency for pits formation rather than general corrosion on a broad front.

Misra and Whittle\(^{(27)}\) studied the corrosion of Ni by $Na_2SO_4$ and demonstrated that the oxide layer was penetrated by the melt which then reacted with the metal to form sulfides. Lillerud and Kofstad\(^{(28)}\) also studied the behavior of Ni during $Na_2SO_4$-induced corrosion. They proposed the formation of an outer layer of liquid sulfates containing NiO particles through which the oxidants migrated in and an inner layer of NiO comprising a nickel sulfide network serving as a path for the outer diffusion of nickel.

A fluxing mechanism or the sulfide formation, both of which prevent protective oxide formation, can occur simultaneously, but a given alloy generally exhibits features of predominantly one type. For instance, Meier and coworkers\(^{(7)}\) have shown that Ni-Cr and Ni-Cr-Al and to some extent Co-Cr alloys have features indicative of a sulfidation mechanism, and that Co-Cr-Al alloys degraded by an acid fluxing mechanism.
The Bell-shape dependence of the corrosion rates on temperature (Fig. 3) can be explained by the competitive effects involving $P_{SO_3}$ and the temperature\(^{(29)}\). The rate of sulfation of a protective oxide is influenced by the rate of transport of $SO_3$ through the liquid phase. The flux should increase with increasing \((P_{SO_3} - P_{SO_3}^{i})\), where $P_{SO_3}^{i}$ denotes $P_{SO_3}$ at the salt/oxide interface. Thus, the reaction rate will tend to increase as $P_{SO_3}$ increases. However, the concentration levels above curve B in Fig. 12 lead to the precipitation of solid sulfate which may impede the diffusion of $SO_3$. The dependence on temperature is influenced by different factors, such as ability to grow a protective film and transport rate of sulfur trioxide through the salt. With increasing temperature, the diffusion coefficient of $SO_3$ increases but $P_{SO_3}$ decreases. At higher temperatures, the diffusion of the alloying elements responsible for the formation of the protective oxide layer is faster and the corrosion rates are reduced. Also at higher temperature, the $SO_3$ species is less stable. At lower temperature the transport rate of $SO_3$ may be inhibited by the presence of solid sulfates. Under these competing effects, the corrosion should take a maximum value at some intermediate temperature.
Figure 13 Schematic representation of the reaction products formed at different locations and the transport steps involved during the dissolution and reprecipitation of cobalt in LTHC. The dotted line is the initial alloy/salt interface. (13)
7. Electrochemical Studies

7.1 Electrochemical Aspects

Alkali-metal sulfates melts such as K$_2$SO$_4$, Na$_2$SO$_4$ and Li$_2$SO$_4$ and their solutions are good ionic conductors with negligible electronic conductivity ($\text{telectrons} = 10^{-4}$, $\text{telectron holes} = 10^{-6}$). They are analog to the electrolytes in aqueous electrochemistry. There is no doubt that the anodic reaction during hot corrosion is the oxidation of the metal. The cathodic reaction is usually transport-limited because the electron transfer step is extremely fast at high temperatures. The oxidant involved in the cathodic reaction can be either dissolved SO$_3$ (as S$_2$O$_7^{2-}$) or O$_2^-$ depending on the basicity of the melt. Shores and Fang$^{(30)}$ studied the cathodic limiting current density of a platinum electrode under a thin film of fused Na$_2$SO$_4$ in various O$_2$-SO$_2$-SO$_3$ gas mixtures and concluded that S$_2$O$_7^{2-}$ was the principal oxidant with only a small contribution from O$_2$ in an acidic melt. For either basic$^{(18,31)}$ or acidic conditions$^{(31)}$, studies confirmed that O$_2^-$ or else pyrosulfates ions were the predominant oxidants, respectively.

7.2 Reference Electrodes

The monitoring of electrochemical reactions requires the use of a reversible reference electrode which is stable with time. In high temperature hot corrosion studies, a set of two electrodes is frequently used for the determination of the activity of Na$_2$O. The
{Ag, Ag+/ Na+-conductive membrane/salt} reference electrode indicates the activity of Na in the electrolyte while a O$_2^-$ selective membrane indicates the activity of oxygen.

7.2.1 O$_2^-$ Sensor

The O$_2^-$ selective electrode usually consists of a (CaO or Y$_2$O$_3$)-stabilized zirconia tube enclosing a platinum wire in contact with a gas phase of known oxygen activity. The comparison of responses from Y$_2$O$_3$ and CaO-stabilized zirconia electrodes indicates that yttria is more stable in acidic sulfate melts than calcia, which is leached from the zirconia matrix. The leaching attack results in a locally high Na$_2$O activity at the ZrO$_2$/melt interface and provides an erroneously high indication of P$_{O2}$(32).

7.2.2 Na$^+$ Sensor

Several materials have been employed as a membrane for the Na$^+$-sensor: Pyrex (borosilicate)(33-36), fused silica or quartz(37), mullite(21,26,38,39), porcelain (Na$_2$O-SiO$_2$-Al$_2$O$_3$)(40), sodium-β-alumina(41,42) and Nasicon (Na$_3$Zr$_2$Si$_2$PO$_{12}$)(43). Conductivity measurements have also shown that Na$^+$ in NaSbO$_3$ has a very high mobility at low temperatures(43). However, this membrane has never been tested in an electrochemical cell in relation to hot corrosion. According to Schmalzried(44), a material can perform successfully as a solid electrolyte if the ionic conductivity, $\sigma_i$, of the species is greater than approximately 10$^{-6}$ Ω$^{-1}$cm$^{-1}$. This condition is necessary
to achieve a stable cell potential. In addition, to make good thermodynamic measurements, the transference number in the membrane of the species being measured must be essentially one.

When two solutions, each containing a cation $M^+$ and differing activities for the metal $M$, are separated by a membrane which conducts only $M^+$ cations ($t_{M^+} = 1$), a potential develops across the membrane. The magnitude of the potential is determined by the concentration gradient for $M^+$ corresponding to the metal activity gradient across the membrane. It is described as

$$E_{\text{emb}} = \frac{RT}{nF} \ln \left( \frac{a(M)_I}{a(M)_O} \right) \quad (15)$$

where $R$ is the gas constant, $T$ is temperature, $n$ the absolute value of the charge of the cation, $F$ is Faraday's constant, and $a(M)_I$ and $a(M)_O$ are the activities of the metal $M$ inside and outside the membrane. The cell responsible for this potential is

$$(+) \text{ lead wire, } a(M)_I / \text{membrane} / a(M)_O, \text{ lead wire } (-) \quad (16)$$

A membrane described by this equation is perfectly selective for $M^+$; it conducts only that cation. In general, however, solid electrolytes are not exclusive conductors of one cation. It is well known that $\beta$-alumina easily exchanges $Na^+$ with monovalent cations and silver ions. Whittingham and Huggins$^{(41)}$ have reported a
conductivity of Ag\(^+\) in \(\beta\)-alumina as high as half the conductivity of sodium ions at 25°C. Glassy electrolytes usually conduct the alkali metal cations and some other small monovalent cations such as Ag\(^+\). Doremus\(^{(46)}\) has shown that even if the value of \(t_{Na^+}\) in clear-fused silica is essentially unity, the transference numbers for the other impurities (Li\(^+\), Ag\(^+\), K\(^+\), Fe\(^{2+}\), O\(^{2-}\), Ca\(^{2+}\) and Al\(^{3+}\)) are not zero. There is a contribution from foreign cations to the ionic conductivity of a solid-state conductor. The potential generated across the membrane obeys then the more complicated equation

\[
E_{memb} = \frac{RT}{nF} \ln \left( \frac{a(M)_I + K_{MN}^{POT} a(N)_I}{a(M)_O + K_{MN}^{POT} a(N)_O} \right)
\]

(17)

\(N^+\) is the second ion conducted by the solid electrolyte and \(K_{MN}^{POT}\) is the potential selectivity coefficient which describes the relative conductivity of each ion. It is a measure of the preference of the membrane for \(N^+\) over \(M^+\) for passing ionic current. Obviously, if \(K_{MN}^{POT}=0\), the membrane is perfectly selective for \(M^+\).

Potentials across glasses in high melting salts cannot be measured because all except silica soften below the melting points of the salts or because other glasses are degraded by the harsh environment\(^{(39,47)}\). Rahmel reported a very short useful life at 1173 K for a Supremax (Vycor) glass\(^{(39)}\). As a result, most separators and solid electrolytes used today in molten salts are ceramics. Mullite and zirconia are the most common. Mullite has been shown to conduct
alkali metal cations via a glassy phase at the grain boundaries and has been found mostly successful as a sodium conductor in contact with pure Na$_2$SO$_4$\cite{22,26,38}, (Na$_2$, Ca, Mg)SO$_4$ and (Na, K)$_2$SO$_4$ fused salts\cite{47} around 900°C. Nevertheless some problems associated with its use have been reported\cite{26,38,48,49}. Degradation of the Ag/Ag$^+$/mullite electrode has been found as indicated by the drift in the measured potential\cite{26,48,49}. Discoloration of mullite tubes has also been observed and silver has been detected in the electrolyte as a consequence of the transport of Ag\cite{39}. Mullite, fused silica and β-alumina were tested by Hwang and Rapp\cite{23} in acidic Na$_2$SO$_4$ at 1200 K. Their results showed that fused silica was the most stable of the three membranes in acidic conditions. A significant transport of silver was detected which could decrease the activity of Ag$_2$SO$_4$ in the reference melt and cause potential drifts. However, the authors thought that the drifts resulted from diffusion potentials created by the incorporation of silver ions into the membrane.

The presence of cations other than Na$^+$ in a molten salt is a potential source of error when attempting measuring the activity of sodium. The molten salt relevant to this study is a multication (Na$^+$, Fe$^{3+}$, K$^+$) salt and one must be concerned that Fe$^{3+}$, but particularly K$^+$, may migrate through the membrane of the reference electrode.

The Ag/Ag$^+$/mullite electrode which is successful at higher temperatures is useless at 550°C, because the conductivity of mullite at this temperature is not high enough to establish a stable potential in a galvanic cell. Quartz, β-alumina, porcelain, and to a lesser extent
Pyrex, are better candidates because their ionic conductivities are greater than $10^{-6}\Omega^{-1}\text{cm}^{-1}$. Quartz and Pyrex have been often used instead of mullite at temperatures below their softening point in sodium sulfate at 900K$^{(50,51)}$ and in molten nitrates at 400°C$^{(52)}$. A satisfactory long term potential stability over a few hundred hours could be achieved at 900 K with Pyrex and up to 1073 K with a Supremax membrane even if a coloration of the glass seemed to indicate that a transport of silver ions occurred. The second reason is that the $\text{Ag}_2\text{SO}_4-(1-x)\text{Na}_2\text{SO}_4$ mixture is solid at 500°C.

For these two reasons, different reversible $\text{Ag}/\text{Ag}^+$ redox system must be considered. An 80% $\text{AgCl}$-20% $\text{NaCl}$ solution is liquid at 550°C and above, and its thermodynamic properties have been documented by Panish et al.$^{(53)}$. These authors have measured the variation of emf for galvanic cells of the type $\text{Ag}/\text{AgCl}-x\text{NaCl}/\text{Cl}_2$ in the temperature range 300°C to 900°C. The activities of $\text{AgCl}$ in the solid or liquid binary system were measured and the activities of sodium chloride were obtained by integration of the Gibbs Duhem relationship.

### 7.2.3 $\text{SO}_3$ Sensor

Because a multication melt such as $\text{Na}_2\text{SO}_4-\text{K}_2\text{SO}_4-\text{Fe}_2(\text{SO}_4)_3$ can be unequivocally described in terms of acidity, a reference electrode suitting this purpose should correctly determine $\text{SO}_3$ activities in the melt.
Some authors\(^{(52-59)}\) have studied reference electrodes which are SO\(_3\) sensors. Most of these works involve galvanic cells of the type

\[
\text{Pt, SO}_2, \text{O}_2/\text{electrolyte/ SO}_2', \text{O}_2', \text{Pt} \quad (18)
\]

where the emf takes the form

\[
E = \frac{RT}{2F} \ln \frac{P_{SO3}}{P_{SO3}'} + \frac{RT}{4F} \ln \frac{P_{O2}}{P_{O2}'} \quad (19)
\]

Boxall and Johnston\(^{(52)}\) have described a SO\(_3\), O\(_2\), Pt/glass reference electrode and tested it in (Li, K, Na)\(_2\)SO\(_4\) at 550\(^\circ\)C. They measured the emf of this electrode versus a silver, silver ion reference electrode when the SO\(_3\) and oxygen pressures were varied from 0.390 to 0.842 atm and, from 0.036 to 0.577 atm, respectively. At high P\(_{SO3}\), the emf was a linear function of log (P\(_{SO3}\).P\(^{1/2}\)O\(_2\)). The slope of this line indicated that two electrons are involved in the electrode reaction.

Flood and Boye\(^{(54)}\) have used a similar SO\(_2\), O\(_2\), Pt/Pyrex electrode to obtain thermodynamic information on the systems K\(_2\)SO\(_4\)-K\(_2\)S\(_2\)O\(_7\)-SO\(_3\) and ZnO-ZnSO\(_4\)-SO\(_3\). The performance of this electrode was again found to depend upon achieving the equilibrium between SO\(_2\), SO\(_3\) and O\(_2\) on Pt. Two electrons per mole of SO\(_2\) were involved.
Salzano and Newman\(^{(55)}\) studied a SO\(_3\), O\(_2\), SO\(_4^{2-}\), Pt/quartz electrode at SO\(_3\) concentrations in the ppm range. The cell consisted of two similar electrodes separated from each other by a quartz membrane. A schematic of the experimental cell is shown in Figure 14. One electrode is a reference electrode through which passes an air or oxygen stream containing a known concentration of SO\(_2\). Through the other electrode is passed a similar gas mixture containing a variable concentration of SO\(_2\). The emf vs SO\(_2\) concentration was recorded; the emf exhibited a behavior in agreement with Eq. (19) in the range of 80% SO\(_3\) to below 1 ppm.

Sequeira and Hocking\(^{(56)}\) demonstrated that a Pt (or Au), SO\(_2\), O\(_2\), SO\(_4^{2-}\) reference electrode served as an oxygen electrode which also responded to SO\(_2\) and SO\(_3\). They also reported that Pt suffered a more serious attack from the sulfate melt than did Au.
Figure 14 Schematic of an experimental cell used for the detection of SO₃.(55)
The bivariant phase equilibria in metal-sulfur-oxygen (M-S-O) systems can be investigated by high temperature galvanic cells. This technique is an alternative to gas equilibration or thermogravimetric methods. Jacob and Iyengar\(^{57}\) used a solid electrolyte (Na\(_2\)SO\(_4\)-I) for the determination of thermodynamic properties of the system Fe\(_2\)O\(_3\)-Fe\(_2\)(SO\(_4\))\(_3\). Sodium sulfate is a sodium ion conductor and can be used as the solid electrolyte in a galvanic cell for the measurement of SO\(_3\)/SO\(_2\) partial pressures\(^{58}\). Potassium sulfate can also be used as a solid electrolyte\(^{59}\). The emf of the concentration cell:

\[
\text{Pt, Ar+SO}_3+\text{SO}_2+\text{O}_2/\text{Na}_2\text{SO}_4-\text{I}/\text{Fe}_2\text{O}_3+\text{Fe}_2(\text{SO}_4)_3,\text{Pt} \quad (20)
\]

was measured in the temperature range 800 to 1000 K.

Gauthier et al.\(^{59}\) analyzed the performance of four different reference electrodes adapted for use in solid-state sulfate detectors for sulfur oxides. The first one was a thermal-decomposition type of reference electrode using a MgO-MgSO\(_4\) and Mn\(_2\)O\(_3\)-MnSO\(_4\) couple. The whole electrochemical cell involved could be described as

\[
\text{Pt, MO-MSO}_4, \text{O}_2(\text{air})/\text{K}_2\text{SO}_4(\text{s})/\text{SO}_3',\text{O}_2(\text{air}), \text{Pt.} \quad (21)
\]

The binary system was contained in an alumina crucible open to the atmospheric pressure through a small-diameter hole (0.05 mm). The second electrode studied was a recirculation type of electrode in a concentration cell of the type
where one of the two gases circulating was of known composition. This electrode was the most stable and the most reliable, although it is expensive and awkward to operate. The third electrode was the Ag/Ag\(^+\) type in the cell

\[
\text{Ag/Ag}_2\text{SO}_4 \text{ (0.01 mole fraction in K}_2\text{SO}_4) / \text{K}_2\text{SO}_4(\text{s})/\text{SO}_3', \text{O}_2 \text{ (air), Pt (23)}
\]

The emf of such a SO\(_2\) detector in air is expressed as follows

\[
E=\text{Const.} \frac{RT}{2F} \ln a_{\text{Ag}_2\text{SO}_4} + \frac{RT}{2F} \ln (P_{\text{SO}_2})_{\text{in}} \quad (24)
\]

Two distinct types of behavior were observed in the signal versus time. The first was a rapid increase in potential which may be traced to a decrease in the Ag\(^+\) activity at the silver electrode. According to the authors, this was due to a rapid diffusion of the silver ions through the entire solid electrolyte. The second type of behavior was observed when the emf began to steadily decrease. This was attributed to the formation of silver oxide at the silver electrode in contact with air.

The last cell investigated by these authors was
\( \text{Pt, O}_2(\text{air})/\text{ZrO}_2(\text{CaO})//\text{K}_2\text{SO}_4/\text{SO}_3, \text{O}_2(\text{air}), \text{Pt} \) (25)

whose emf expression can be expressed as

\[
E = \text{Const.} + \frac{RT}{2F} \ln(P_{\text{SO}_2})_{\text{in.}}
\]  

(26)

where the constant includes the oxygen pressure \(-\frac{RT}{4F} \ln(P_{\text{O}_2})_{\text{ref}}\) of the reference electrode and the sulfate-zirconia junction potential. This type of reference electrode had satisfactory results but was very difficult to build because of the need to control the atmosphere at the junction.
CHAPTER IV

Thermodynamics of Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$

1. Introduction

The fused salt electrolyte responsible for fly ash corrosion of boiler tubes is a ternary system consisting of Na$_2$SO$_4$-K$_2$SO$_4$ and Fe$_2$(SO$_4$)$_3$. This salt and iron oxide are the principal components of the so-called white layer that is commonly found on the outside surface of cooled heat exchange tubes. The ternary melt (Na, K, Li)$_2$SO$_4$ has been investigated but is of no interest here because Li$^+$ is not a major constituent of the flue gases in fossil-fired boilers.

Figure 15 shows the liquidus temperature for the multication sulfate Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ system for different concentrations of ferric sulfate$^{(3)}$. A minimum melting temperature of 530°C exists at approximately 30 w/o Fe$_2$(SO$_4$)$_3$ (14 m/o), and all compositions from 6 m/o to 30 m/o are molten below 550°C.

There is no phase diagram for Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ in the literature, and thermodynamic properties are not available. Therefore, the activities for the different components in the ternary melt need to be calculated using the thermodynamic properties of the binary systems Na$_2$SO$_4$-K$_2$SO$_4$, Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ and K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$.
The phase diagrams of these three binaries are shown in Fig. 16, Fig. 17 and Fig. 18. Hendry and Lees\textsuperscript{(3)} have estimated a section of the ternary phase diagram by a graphical projection of the three binary systems. This construction is presented in Fig. 19. The section abb'a' of Fig. 19 corresponds to Fig. 15.

2. Ideal Entropy of Mixing (Temkin Entropy of Mixing)

The activity of a component A (for a binary system A-B) in a phase $\alpha$ can be written as the sum of ideal and excess terms

$$RT \ln a_A = G_A^{E(\alpha)} - T S_A^{(id)(\alpha)}$$

(27)

where $G_A^{E(\alpha)}$ represents the partial molar excess Gibbs energy of component A in the phase $\alpha$ and $S_A^{(id)(\alpha)}$ is the partial ideal entropy of mixing of A.

The expression for the partial ideal entropy of mixing of an ionic solution was first proposed by Temkin\textsuperscript{(60)} and developed further by Forland\textsuperscript{(61)}. According to this model, the cations and anions are assumed to mix randomly on their respective sublattices, regardless of charge. The validity of this approach has been verified between 850$^\circ$C and 900$^\circ$C for the Na$_2$SO$_4$-NiSO$_4$ system\textsuperscript{(62)} up to a NiSO$_4$ molar fraction of $\approx 0.5$ and at 850$^\circ$C for the Na$_2$SO$_4$-ZnSO$_4$ system\textsuperscript{(63)} up to a ZnSO$_4$ molar fraction of $\approx 0.7$. In the Temkin
model, for a solution of the type $M_2SO_4$-$Fe_2(SO_4)_3$, where $M$=Na or K, the expressions of the partial ideal entropies of mixing are

$$S^{(id)}_{M_2SO_4} = -2R \ln N_{M_2SO_4} \quad (28a)$$

and

$$S^{(id)}_{Fe_2(SO_4)_3} = -2R \ln N_{Fe_2(SO_4)_3} \quad (28b)$$

where $N_{M_2SO_4}$ and $N_{Fe_2(SO_4)_3}$ are the cation fractions in the melt, and from mass balance consideration are given by

$$N_{M_2SO_4} = \frac{2X_{M_2SO_4}}{2X_{M_2SO_4} + 2X_{Fe_2(SO_4)_3}} = X_{M_2SO_4} \quad (29a)$$

and

$$N_{Fe_2(SO_4)_3} = \frac{2X_{Fe_2(SO_4)_3}}{2X_{Fe_2(SO_4)_3} + 2X_{M_2SO_4}} = X_{Fe_2(SO_4)_3} \quad (29b)$$

where $X_{M_2SO_4}$ and $X_{Fe_2(SO_4)_3}$ represent the mole fractions of $M_2SO_4$ and $Fe_2(SO_4)_3$, respectively. The factor 2 in Eq. (28a)-(28b) originates from the fact that each component of the binary system contributes two non-common ions ($2Fe^{3+}$ or $2M^+$).

As the ionic radius of $Fe(III)$ is about 10% less than that of $Ni(II)$, $Co(II)$, and $Zn(II)$, taking into account its additional positive charge, the validity of Eq. (28a)-(28b) is probably limited to a narrower range of $X$ values in comparison with the molten systems $Na_2SO_4$-$NiSO_4$, $Na_2SO_4$-$CoSO_4$ and $Na_2SO_4$-$ZnSO_4$. The stronger repulsive interactions between cations of different nature ($Na(I)$ and
Fe(III)) affect the validity of the hypothesis of random cations mixing, which is the basis for Forland's model. On the other hand, the eutectic compositions in Na₂SO₄-Fe₂(SO₄)₃ and K₂SO₄-Fe₂(SO₄)₃ are about 0.2 as compared with a value of ≈0.4 for the Na₂SO₄-NiSO₄ system and a value of ≈0.5 for the Na₂SO₄-ZnSO₄ system.

3. Excess Properties of the Solution

The integral molar excess Gibbs energy of a solution A-B is given by

\[ G^E = H^E - T S^E = X_A G_A^E + X_B G_B^E \]  

(30)

where \( H^E \) is the molar enthalpy of mixing and \( S^E \) is the excess molar entropy of mixing. For a binary system A-B, these two quantities may be conveniently expressed as polynomials in mole fractions as follows

\[ H^E = X_A X_B (h_0 + h_1 X_B + h_2 X_B^2 + \ldots) \]  

(31)

\[ S^E = X_A X_B (s_0 + s_1 X_B + s_2 X_B^2 + \ldots) \]  

(32)

where the coefficients \( h_i \) and \( s_i \) can be found empirically. Because the charge of the cations \( M^+ \) and Fe\(^{3+} \) is different, it is sometimes advantageous to replace the mole fractions by the equivalent ionic
Figure 15 Melting temperature of the Na₂SO₄-K₂SO₄-Fe₂(SO₄)₃ system for different Fe₂(SO₄)₃ concentrations. (3)
fractions in these equations. The equivalent ionic fractions for the components of $\text{M}_2\text{SO}_4$$\cdot$$\text{Fe}_2(\text{SO}_4)_3$ are defined as:

$$Y_{\text{M}_2\text{SO}_4} = \frac{X_{\text{M}_2\text{SO}_4}}{X_{\text{M}_2\text{SO}_4} + 3X_{\text{Fe}_2(\text{SO}_4)_3}} \quad (33a)$$

$$Y_{\text{Fe}_2(\text{SO}_4)_3} = \frac{3X_{\text{Fe}_2(\text{SO}_4)_3}}{X_{\text{M}_2\text{SO}_4} + 3X_{\text{Fe}_2(\text{SO}_4)_3}} \quad (33b)$$

If we let $S^E = 0$ and if all coefficients $h_i = 0$ for $i \geq 1$ then $G^E = H^E = h_0 Y_A Y_B$ which is the expression of a regular solution. The enthalpic term $H^E$ is generally larger in magnitude than the entropic term $T S^E$ for molten salt solutions (64). If available data are limited, it is a reasonable assumption to set $S^E = 0$ and to assume that $G^E$ is temperature-independent.

Differentiation of Eq.(31) and Eq.(32) yields the following expressions for the partial molar excess Gibbs energies of components A and B:

$$G^E_A = \sum (h_i - T s_i)(Y_B - i Y_A)Y_B^{i+1} \quad i \geq 0 \quad (34a)$$

$$G^E_B = \sum (h_i - T s_i)(i + 1)Y_A^2Y_B^i \quad i \geq 0 \quad (34b)$$

For a regular solution model (which assumes $S^E = 0$), Eqs.(34a)-(34b) become:
Figure 16 Na$_2$SO$_4$-K$_2$SO$_4$ phase diagram. (65)
Figure 17 Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ phase diagram.(66)
Figure 18  $\text{K}_2\text{SO}_4$-$\text{Fe}_2(\text{SO}_4)_3$ phase diagram. (67)
Figure 19  Phase diagram of Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ system constructed from the phase diagrams of the three binary systems. (3)
For equilibrium between a solid and a liquid phase in a binary system, we may write, for component A

\[
RT \ln a_A^l - RT \ln a_A^s = -\Delta_{\text{fus}} G^o_A
\]

(36)

where \( a_A^l \) and \( a_A^s \) are the activities of A on the liquidus (with respect to the liquid standard state) and on the solidus (with respect to the solid standard state) at temperature T. \( \Delta_{\text{fus}} G^o_A \) is the Gibbs energy of fusion of A at T. A similar equation may be written for component B or for any intermediate compound \( A_x B_y \).

Using Eq. (27), Eq. (36) can be written as

\[
G_A^{E(l)} - G_A^{E(s)} - T(S_A^{(id)(l)} - S_A^{(id)(s)}) = -\Delta G^0_{\text{fus(A)}}
\]

(37)

If the solubility of B in the terminal solid solution is sufficiently small that Raoult’s law may be assumed to hold for the solvent, \( G_A^{E(s)} = 0 \) and \( S_A^{(id)(s)} = 0 \). The experimental liquidus/solidus points can be used to calculate values of \( G_A^{E(l)} \) along the A-liquidus via Eq. (38)
\[ G_A^{E(l)} - T S_A^{(id)(l)} = G_A^{E(l)} + 2RT \ln X_A = -\Delta G_0^{\text{fus}(A)} \] (38)

4. Thermodynamics of the Na$_2$SO$_4$-K$_2$SO$_4$ system

The thermodynamics of the system Na$_2$SO$_4$-K$_2$SO$_4$ have been analyzed by Pelton et al.$^{(68)}$ who found that the liquid follows a regular behavior with a negative heat of mixing

\[ H_{\text{liq}}^M = -4393.X_{\text{Na}_2\text{SO}_4}X_{\text{K}_2\text{SO}_4} \text{ (J/mol)} \] (39)

The excess entropy of mixing was zero ($S^E = 0$).

The properties of the Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ and K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ systems are not available in the literature.

5. Thermodynamics of Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ system

The six rightmost liquidus points in the Fe$_2$(SO$_4$)$_3$-rich side of the phase diagram constructed by Sugiyama and Takahashi$^{(66)}$ have been extrapolated to $X_{\text{Fe}_2(\text{SO}_4)_3} = 1$ to determine the melting temperature of Fe$_2$(SO$_4$)$_3$. This extrapolation gives a value of 1418 K (Fig. 20). Even if the value of $\Delta S_0^{\text{fus}(\text{Fe}_2(\text{SO}_4)_3)}$ is unknown, a reasonable estimate can, however, be made. The mean value of $\Delta S_0^{\text{fus}}$ from thermochemical data on oxides, tellurides and sulphides of the A$_2$X$_3$ type is $\approx$ 2 cal g(ion)$^{-1}$K$^{-1}$, whereas for sulfates of monovalent and divalent cations, it is $\approx$ 2.5 cal g(ion)$^{-1}$K$^{-1}$$^{(69)}$. This latter value was used in the calculation ($\Delta S_0^{\text{fus}(\text{Fe}_2(\text{SO}_4)_3)} = 7.5$ cal g(ion)$^{-1}$K$^{-1}$).
The Gibbs energy of fusion of Fe$_2$(SO$_4$)$_3$ can then be expressed as a function of temperature in the form

$$\Delta G^o_{\text{fus}}(T)_{\text{Fe}_2(\text{SO}_4)_3} = 31.35 \times (1418 - T) \text{ (J/mol)}$$  \hspace{1cm} (41)

The phase diagram for compositions between X=0 and X=0.18 has been calculated with the assumptions that the liquid was regular (in terms of equivalent fractions) and that the solid solution was ideal. In this range of X$_{\text{Fe}_2(\text{SO}_4)_3}$, it was assumed that the hypothesis of random mixing still held. For a given temperature, the compositions on the liquidus and the solidus lines (2 unknowns) can be calculated by simultaneously solving the two non-linear equations

1. $$\Delta G^o_{\text{fus}}(\text{Na}_2\text{SO}_4) = 2RT\ln(1 - X_{\text{Fe(liq)}}) + h_0(Y_{\text{Fe(liq)}})^2 - 2RT\ln(1 - X_{\text{Fe(sol)}})$$

2. $$\Delta G^o_{\text{fus}}(\text{Fe}_2(\text{SO}_4)_3) = 2RT\ln X_{\text{Fe(liq)}} + h_0(1 - Y_{\text{Fe(liq)}})^2 - 2RT\ln X_{\text{Fe(sol)}}$$

Different trial values of $h_0$ were used until a good agreement was reached between calculated and experimental values. The calculated liquidus and solidus compositions appear as a solid line in Fig. 21. The experimental data points are the filled circles. The pairing energy $h_0$ corresponding to the calculated lines was -51,000 J/mol.
Figure 20 Fit to experimental data on the Fe$_2$(SO$_4$)$_3$-rich side of the Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ phase diagram.
Figure 21  Na₂SO₄-Fe₂(SO₄)₃ binary phase diagram for \( X_{\text{Fe}_2(\text{SO}_4)_3} < 0.18 \).
In this range of composition, the integral excess Gibbs energy of the Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ liquid takes the form

\[ G^E_{Na-Fe} = -51,000 \cdot Y_{Na_2SO_4} \cdot Y_{Fe_2(SO_4)_3} \ (J/mol) \quad (42) \]

6. Thermodynamics of K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ system

The phase diagram constructed by Rahmel and Jaeger\(^\text{67}\) for this system is shown in Fig. 18. There is no reported solubility for Fe$_2$(SO$_4$)$_3$ in solid solution and, consequently, the K$_2$SO$_4$-rich side of the phase diagram (X<0.12) has been used in combination with Eq. (38) to determine the partial excess Gibbs energy of K$_2$SO$_4$. However, there are only three experimental data points on this range of composition (X=0, X=0.11 and X=0.12) and there is a large experimental uncertainty on the temperature for X=0.11. The melting temperature of potassium sulfate is 1069°C (it is not 1096°C as indicated in Fig. 18). From the differentiation of Eq. (38), and the fact that, when X$_{K_2SO_4} \rightarrow 1$, the excess Gibbs energy of the liquid approaches zero, it may be deduced that

\[ \lim_{X_{K_2SO_4} \rightarrow 1} \left( \frac{dX_{K_2SO_4}}{dT} \right) = \frac{\Delta S^\circ_{fus(K_2SO_4)}}{2RT_{fus(K_2SO_4)}} \quad (43) \]

The standard Gibbs energy for the reaction of fusion

\[ K_2SO_4(s) = K_2SO_4(l) \quad (44) \]
is given by (64)

\[ \Delta G^0(44) = 36819 \times (1 - \frac{T}{1342}) \text{ (J/mole)} \]  \hspace{1cm} (45)

The limiting slope of the liquidus was calculated as \( \frac{dT}{dX} = -812 \). A liquidus line passing through the top of the error-bar at \( X=0.11 \) satisfied this condition better than a liquidus curve passing through the bottom of the error-bar at this same composition. Two liquidus lines were calculated using Eq. (38) and assuming that the liquid is regular (Fig. 22). They correspond to two different values of the pairing energies, \( h_0 \). The experimental uncertainty on the temperature at \( X=0.11 \) resulted in less than 10% error on the integral excess Gibbs energy of the liquid phase. The magnitude of \( h_0 \) has been tested in the vicinity of the point of congruent melting of the compound \( K_3Fe(SO_4)_3 \) (at \( X_{Fe2(SO4)_3}=0.25 \)). At the congruent melting point of a stoichiometric compound \( \alpha \) (at the composition \( X_\alpha \)), the first order derivative \( \frac{dT}{dX} \) is equal to zero. The second order derivative is given by (70)

\[ \left( \frac{d^2T}{d(Xl)^2} \right)_T = \frac{T^{(1\rightarrow\alpha)}}{\Delta H^{(1\rightarrow\alpha)}} \left( \frac{d^2G^{(1)}}{d(Xl)^2} \right)_{Xl=X_\alpha} \]  \hspace{1cm} (46)

where \( \Delta H^{(1\rightarrow\alpha)} \) is the enthalpy of transformation of liquid (of the same composition as \( \alpha \)) to \( \alpha \), \( T^{(1\rightarrow\alpha)} \) is the melting temperature of \( \alpha \),
and $G^1$ is the Gibbs free energy of the solution. $X^l$ and $X_\alpha$ are the compositions on the liquidus and at the congruent transformation point, respectively (see Fig. 23). In the vicinity of the congruent melting point (i.e., neglecting terms of the third order in $X^l - X_\alpha$),

$$ (X^l(T) - X_\alpha)^2 = -\frac{2(T(\rightarrow \alpha) - T)\Delta S(\rightarrow \alpha)}{[\partial^2 G^1/\partial (X^l)^2]_{X^l = X_\alpha}} $$

Here, $G^1 = -133,000 \cdot Y_{Na}Y_{Fe} + 2RT(X_{Na}lnX_{Na} + X_{Fe}lnX_{Fe})$ (relative to the pure liquids) and $X_\alpha = 0.25\ (Y_{Fe} = 0.5)$.

The first derivative with respect to $X_{Fe}$ of the integral excess Gibbs energy is

$$ \frac{\partial G^1}{\partial X_{Fe}} = -133,000 \cdot (1 - 2Y_{Fe}) \frac{\partial Y_{Fe}}{\partial X} + 2RT(lnX_{Na} - lnX_{Fe}) \qquad (48) $$

where $\frac{\partial Y_{Fe}}{\partial X_{Fe}} = \frac{3}{(1 + 2X_{Fe})^2}$

Then,

$$ [\partial^2 G^1/\partial (X^l)^2]_{X^l = 0.25} = 2 \cdot 133,000 \cdot \frac{(\frac{\partial Y_{Fe}}{\partial X})^2}{\partial X} + 2RT(1/X_{Na} + 1/X_{Fe}) - 133000 \cdot (1 - 2Y_{Fe}) \frac{\partial^2 Y_{Fe}}{\partial X^2} \qquad (49) $$

The second order derivative of $G^1$ at $X_{Fe} = 0.25\ (1 - 2Y_{Fe} = 0)$ is equal to

$$ \frac{3}{9} \cdot 133000 + 2 \cdot 8.314 \cdot T \left(\frac{1}{0.25} - \frac{1}{0.75}\right). $$

Using the experimental liquidus data points near the melting point of the compound and Eq. (47), the entropy of melting of $K_3Fe(SO_4)_3$ was estimated as 57.92 J.K$^{-1}$.mol$^{-1}$. The entropy of melting of $LiK(SO_4)$ is of the same order of magnitude (42 J.K$^{-1}$.mol$^{-1}$). Using Eq. (38), the liquidus line of $K_3Fe(SO_4)_3(s)$ can
be calculated, provided the compound is assumed stoichiometric. The activity of the compound $K_3Fe(SO_4)_3$ is given as

$$a_{K_3Fe(SO_4)_3} = \frac{a_{K_2SO_4}^{3/4}a_{Fe_2(SO_4)_3}^{1/4}}{[a_{K_2SO_4}^{3/4}a_{Fe_2(SO_4)_3}^{1/4}]_{X=0.25}} \quad (50)$$

$\Delta G^o_{fus}(K_3Fe(SO_4)_3)$ was taken as $57.92*(976-T)$. The calculated liquidus curve is compared with the measured liquidus line in Fig. 24. The calculated temperatures agree very well with the experimental temperatures except for the eutectic composition.

For $0<X_{Fe_2(SO_4)_3}<0.28$, the calculation suggests that the integral excess Gibbs energy of the $K_2SO_4-Fe_2(SO_4)_3$ liquid system can be represented by

$$G^E_{K-Fe} = -133,000*Y_{K_2SO_4}*Y_{Fe_2(SO_4)_3} \quad (51)$$

The value of the pairing energy $h_0$ in $K_2SO_4-Fe_2(SO_4)_3$ is much smaller than that found in the system $Na_2SO_4-Fe_2(SO_4)_3$. The parameter $h_0$ has a simple atomistic interpretation: it compares the energy $u_{12}$ of the bond between the dissimilar atoms 1 and 2 with the arithmetic mean of the bonds between like atoms:

$$h_0 = Z(u_{12}-\frac{1}{2}(u_{11}+u_{22}))$$
Figure 22  Comparison of the $K_2SO_4$-rich side of the $K_2SO_4$-$Fe_2(SO_4)_3$ phase diagram as measured by Rahmel$^{(66)}$, with that calculated assuming regular behavior in liquid solution and no solid solubility.
Figure 23 Phase boundaries in the vicinity of the congruent transformation point of a compound.
Figure 24  K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ phase diagram near the congruent melting of the compound K$_3$Fe(SO$_4$)$_3$. 
where $Z$ is the number of nearest neighbours to an atom (e.g. 12 in the case of an fcc lattice). $h_0$ is negative for a net attraction between the atoms 1 and 2 and positive for a net repulsion between the atoms 1 and 2.

Table 1 lists the ionic radii of different elements\(^{(71)}\). Figure 25 shows that the pairing energies for liquid mixtures of lithium sulfate with other alkali sulfates decrease as the difference in size increases\(^{(72)}\) as observed in the present study.

The conformal solution theory of Reiss, Katz and Kleppa\(^{(73)}\) has been fairly successful in rationalizing the solution behavior of simple mixed-cation/common-anion melts. According to the RKK theory, the enthalpies of mixing for a series of related mixed-cation/common-anion fused salt systems should be given by an expression of the type

$$\Delta H^M = \Omega \delta^2 X_1 X_2 \quad (52)$$

where $X_1$ and $X_2$ are the mole fractions of the two components and $\delta$ is a size parameter, $\delta = 1/d_2 - 1/d_1$ ($d_1$ and $d_2$ are interionic distances in the two salts being compared), while $\Omega$ is a negative constant which depends only on the coulombic interactions between the ions of the salt mixture. Østvold and Kleppa\(^{(74)}\) extended the RKK theory to account quantitatively for the Van der Waals interactions and the difference in polarizability between the two cations. From these studies, $h_0$ for regular sulfate mixtures decreased (or increased in absolute value) as the difference in size of the cations became larger.
Figure 25 Pairing energies for liquid mixtures of lithium sulfate with other alkali sulfates (72)
<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radius (Å)</th>
</tr>
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<tbody>
<tr>
<td>Na⁺</td>
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<td>Fe³⁺</td>
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<td>Fe²⁺</td>
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<td>Li⁺</td>
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<tr>
<td>Co²⁺</td>
<td>0.82</td>
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</table>

Table 1  Goldschmidt's ionic radii of elements.\(^{(71)}\)
Table 2  Thermodynamic properties of the binary systems.

<table>
<thead>
<tr>
<th>System</th>
<th>$H^E$ (J/mole)</th>
<th>$SE$ (J/moleK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na_2SO_4$-$K_2SO_4$</td>
<td>$-4393\times X_{Na_2SO_4} \times X_{K_2SO_4}$</td>
<td>0</td>
</tr>
<tr>
<td>$Na_2SO_4$-$Fe_2(SO_4)_3$</td>
<td>$-51,000\times Y_{Na_2SO_4} \times Y_{Fe_2(SO_4)_3}$</td>
<td>0</td>
</tr>
<tr>
<td>$K_2SO_4$-$Fe_2(SO_4)_3$</td>
<td>$-133,000\times Y_{K_2SO_4} \times Y_{Fe_2(SO_4)_3}$</td>
<td>0</td>
</tr>
</tbody>
</table>
7. Thermodynamics of Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ system

The composition of three melts studied are shown in the triangle depicted in Fig. 26. The three melts have the following compositions:

melt ①: 58.4 m/o Na$_2$SO$_4$, 14.6 m/o K$_2$SO$_4$, 27 m/o Fe$_2$(SO$_4$)$_3$

melt ②: 67 m/o Na$_2$SO$_4$, 17 m/o K$_2$SO$_4$, 16 m/o Fe$_2$(SO$_4$)$_3$

melt ③: 72 m/o Na$_2$SO$_4$, 18 m/o K$_2$SO$_4$, 10 m/o Fe$_2$(SO$_4$)$_3$

The thermodynamic properties at any point P in the ternary phase diagram can be determined by "geometrical" formulae proposed by Toop(75), Koehler(76) or Colinet(77) or by the Conformal Ionic Solution (CIS) equation(78). The diagrams in Fig. 27 show the relevant geometrical constructions used to derive these useful equations. The C.I.S. equation is based upon statistical mechanical perturbation theory.

The "geometrical" formulae (Toop, Kohler, Colinet) are much easier to apply than the CIS. These formulae are exact if the binary and ternary solutions are regular. The Kohler equation has the advantage over the Toop equation of being symmetrical with respect to the threee components. However, for ternary charge asymmetrical fused salt systems, such as K$_2$SO$_4$-Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$, Toop's equation is preferred over Kohler's equation, with the asymmetrical component (Fe$_2$(SO$_4$)$_3$) being component (2) in Fig. 26.
Figure 26 Ternary composition triangle (mole fractions) indicating experimental melts 1, 2 and 3.
Figure 27 Alternative geometries for the calculation of ternary thermodynamics properties from binary data.
From Darken's equation and the geometrical properties of the triangle, Toop derived an equation giving the integral excess molar Gibbs energy at any point P in Fig. 26 in a liquid or solid solution. For non regular solutions, the method provided fairly reliable ternary thermodynamic properties\(^{(68)}\). In this study, the Na\(_2\)SO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\) and K\(_2\)SO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\) systems are regular in terms of equivalent ionic fractions. They are not regular in terms of molar ionic fractions since the integral excess Gibbs energy, \(G^E\), cannot be simply expressed as \(h_0X_{Fe}(1-X_{Fe})\). Therefore, Toop's equation, which is based on molar ionic fractions, is not expected to be rigorously exact in this calculation.

The expression for the activity coefficient of component (2) in the ternary liquid can be expressed as

\[
\log \gamma_{2(\text{ternary})} = \frac{X_1}{1-X_2} \log \gamma_{2(1)} + \frac{X_3}{1-X_2} \log \gamma_{2(3)} - (1-X_2)^2 \frac{G^E_{13}}{2RT} \frac{X_1}{X_3} \tag{53}
\]

where \(\gamma_{i(j)}\) is the activity coefficient of \(j\) in the binary \(i-j\). \(G^E_{13}\) is the integral excess molar Gibbs energy of the binary system 1-3.

The integral excess Gibbs energy of the liquid systems Na\(_2\)SO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\) and K\(_2\)SO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\) is plotted against \(X_{Fe2(SO4)3}\) in Fig. 28. At a given \(X_{Fe2(SO4)3}\), the activity coefficients of Fe\(_2\)(SO\(_4\))\(_3\) in these two binary systems can easily be calculated through the following equation
\[
\text{RTln} \gamma_{\text{Fe}_2\text{(SO}_4)_3} = G^E + (1 - X_{\text{Fe}_2\text{(SO}_4)_3}) \frac{\partial G^E}{\partial X_{\text{Fe}_2\text{(SO}_4)_3}} \tag{54}
\]

The values of the integral excess molar Gibbs energy of the liquids and \( \frac{\partial G^E}{\partial X_{\text{Fe}_2\text{(SO}_4)_3}} \) are shown in Table 3 for \( 0 < X_{\text{Fe}_2\text{(SO}_4)_3} < 0.3 \).

At \( T = 690^\circ\text{C} \), the calculated results for the three melts are the following:

**melt\(^1\):**
\[
\begin{align*}
\log \gamma_{2(1)} &= -0.53 \\
\log \gamma_{2(3)} &= -1.38 \\
\frac{G^E_{13}}{2.3RT} &= -0.047 \\
\rightarrow \quad \log \gamma_{2(1-2-3)} &= -0.675 \\
\rightarrow \quad a_{2(1-2-3)} &= \gamma_{2(1-2-3)} X^2 = 0.0154
\end{align*}
\]

**melt\(^2\):**
\[
\begin{align*}
\log \gamma_{2(1)} &= -1.65 \\
\log \gamma_{2(3)} &= -4.30 \\
\frac{G^E_{13}}{2.3RT} &= -0.034 \\
\rightarrow \quad \log \gamma_{2(1)} &= -2.162 \\
\rightarrow \quad a_{2(1-2-3)} &= \gamma_{2(1-2-3)} X^2 = 1.76 \times 10^{-4}
\end{align*}
\]

**melt\(^3\):**
\[
\begin{align*}
\log \gamma_{2(1)} &= -2.97 \\
\log \gamma_{2(3)} &= -7.74
\end{align*}
\]
\[
\frac{G_{E13}}{2.3RT} = -0.021
\]
\[\rightarrow \log \gamma_{2(1)} = -3.91\]
\[\rightarrow a_{2(1-2-3)} = \gamma_{2(1-2-3)}X^2 = 1.23 \times 10^{-6}\]

The standard Gibbs energy for the reaction

\[
Fe_2O_3(s) + 3SO_3 = Fe_2(SO_4)_3(solid) \quad (55)
\]

is given by

\[
\Delta G^0(T)(55) = -576985 + 546.1T \text{ (J/mol)} \quad (56)
\]

By adding the standard Gibbs energy of fusion estimated (Eq. (41)) to \(\Delta G(T)(55)\), the standard Gibbs energy for the reaction

\[
Fe_2O_3(s) + 3SO_3 = Fe_2(SO_4)_3(liquid) \quad (57)
\]

is given by

\[
K_T(47) = \frac{a_{Fe_2(SO_4)_3(liq)}}{PSO_3^3} \quad (58)
\]

\[
\Delta G(T)(47) = -RT \ln K_T(47) = -532531 + 514.75T \text{ (J/mol)} \quad (59)
\]

At 690°C (963K), \(K_T(47) = 99.672\)
The $P_{SO_3}$ values expected at 690°C when excess Fe$_2$O$_3$ is equilibrated with the liquid ternary system are 0.054, 12*10$^{-3}$ and 2.31*10$^{-3}$ atm, respectively. The calculated activity of Fe$_2$(SO$_4$)$_3$ in the melt containing the lowest concentration of Fe(III) is expected to be closer to reality because the hypothesis of random cation mixing, which is the basis for Forland's model, is probably limited to a narrow range of $X_{Fe(III)}$. For high concentrations of Fe(III), this hypothesis is probably not valid anymore.
Figure 28 Integral excess Gibbs energy for the Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ and K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ liquids.
Table 3  Integral Excess molar Gibbs Energy ($G^E$) and $rac{\partial G^E}{\partial X_{Fe_2(SO_4)_3}}$ for the Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ and K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ binary liquids.

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<tr>
<th>$X_{Fe_2(SO_4)_3}$</th>
<th>$G^E_{Na-Fe}$</th>
<th>$\frac{\partial G^E_{Na-Fe}}{\partial X_{Fe}}$</th>
<th>$G^E_{K-Fe}$</th>
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CHAPTER V
EXPERIMENTAL PROCEDURE

In the early stage of this research aimed at developing a low temperature (600°C - 770°C) reference electrode for use in mechanisms studies of low temperature hot corrosion of boiler tubing, a study of a Ag/AgCl-20 m/o NaCl reference melt as a substitute for Ag/Ag₂SO₄-Na₂SO₄, which is solid at temperatures above 650°C, was undertaken. After this preliminary investigation, a completely new electrode was designed and tested.

1. Experimental Arrangement

The reaction chamber was a closed-end McDaniel MV30 high temperature mullite tube (Ø=55 mm). The reaction tube was sealed by epoxy to a water-cooled brass flange. The brass flange was separated from the upper flange by a rubber O-ring (70 Durometer Buna-N) to insure that the chamber was gas-tight. The upper flange, made of 304SS, had six bore-through Cajon fittings soldered in place. The Cajon fittings were used to house the reference electrode, the gas inlet tube, the working electrode, the gas outlet tubing and the alumina rod used to hold an alumina crucible. An additional hole permitted the insertion and removal of a sampling tube. The alumina crucible was attached to the rod with Aremco Ceramabond 552.
The reaction tube was positioned in a vertical tubular electric furnace. The temperature within the furnace was controlled by a solid-state controller (Barber-Colman) using a Type-S (Pt/Pt/10%Rh) thermocouple. The profile of temperature in the furnace showed that a hot zone was located in the bottom 15 cm of the chamber. The temperature in this zone was within 5°C of the set point on the controller. Another thermocouple was inserted in the alumina tube supporting the crucible; the tip of the thermocouple was positioned at 2 cm from the center of the crucible.

Once the experimental set-up was in place, the temperature of the furnace was brought to 400°C and maintained for 12 hours to drive water off all the chemicals. The controller was then reset to the desired temperature. The gas was introduced into the reaction chamber and was allowed to equilibrate with the melt for a day.

Pre-mixed gases of 8 ppm, 0.1% and 1% SO₂ (balance O₂) were purchased from the Matheson Company. Intermediate concentrations in SO₂ could be obtained by metering and mixing these gases into a regulated stream of pure oxygen. Two Matheson series 600 flowmeters were calibrated and then used to measure the flow rates. After the gas of known SO₂ composition was dried by passing it over drierite, it was injected into the reaction chamber through a quartz tube partially filled with platinum mesh. The platinum mesh was located in the hot zone of the furnace. A catalyzed reaction converting SO₂ to SO₃ is expected to approach equilibrium if the flow rate is low.
The end of the inlet tube was above the melt but not submerged in the melt. The gas outlet was positioned in the upper part of the reaction chamber. The gas was evacuated to a hood after bubbling through a flask of dibutyl phtalate.

2. \{Ag/80 \text{ m/o} \ AgCl-20 \text{ m/o} \ NaCl/glass\} Reference Electrode

The electrochemical cells used for testing the performance of this electrode were the following:

\[
\text{Ag/AgCl-0.2NaCl/glass/Na}_2\text{SO}_4-0.5\text{NaCl, SO}_2, \text{O}_2, \text{Pt} \quad (1)
\]

and

\[
\text{Ag/AgCl-0.2 NaCl/glass/Na}_2\text{SO}_4-0.5\text{NaCl/l} \text{glass/AgCl-x NaCl/Ag} \quad (II)
\]

where the glass was either Vycor or quartz.

The experimental set-up for cell (I) and cell (II) is shown in Fig. 29 and Fig. 30. Reagent-grade Na\(_2\)SO\(_4\), NaCl and AgCl were used without further purification. The mixing of silver chloride and sodium chloride was done in a dark room to prevent the reduction of silver chloride by light. The chemicals were weighed out in the desired proportions and mixed thoroughly. The mixture was charged into a one-end-closed tube made of Vycor (or quartz). The electrode was stored in a closed box until it was placed into the furnace. The
Figure 29 Experimental set-up for cell (I)
Figure 30 Experimental set-up for cell (II)
silver wire was fused to a Pt wire which served as the lead wire. The electrolyte was an intimate mixture of sodium sulfate and sodium chloride, which was charged into a quartz crucible. The working electrode was a platinum sheet of 1 cm² spot-welded to a platinum wire of 0.5 mm diameter. The SO₂ content of the gas was 8 ppm.

3. SO₃ Sensor

In this second effort to design a reference electrode, the molten Na₂SO₄-K₂SO₄-Fe₂(SO₄)₃ system was brought in contact with known pressures of SO₃/SO₂/O₂ which had been brought to equilibrium over a Pt catalyst ("working melt"). Reagent-grade Na₂SO₄, K₂SO₄ and Fe₂(SO₄)₃ were weighed out in the desired proportion, thoroughly mixed and dried for a day at 200°C. The mixture was then charged into a quartz crucible and put into the furnace (Fig. 31).

The reference melt for the reference electrode was contained in a fused silica tube (OD=3 mm) with a small hole at the bottom. The size and location of the hole was subject to study. Initially (Fig. 32a), a platinum wire of 0.5 mm diameter extended the length of the tube and out through the hole and only particles of Fe₂O₃ were present in the fused silica tube. After the ternary working salt had melted, the silica tube was dipped into the melt and a small portion of the melt which wetted the Pt wire was drawn into the silica tube through the small hole (Fig. 32b). In this way, the ternary melt had the same nominal composition as the working melt and any diffusion potential arising from a concentration gradient was eliminated. The reference
melt established a known partial pressure of SO$_3$ through the equilibrium

$$\text{Fe}_2\text{O}_3 + 3\text{SO}_3 = \text{Fe}_2(\text{SO}_4)_3$$

(54)

The electrochemical cell(III) consisted of the fused ternary salt electrolyte, a half-immersed platinum foil acting as a working electrode (WE) and the Pt reference electrode (RE) within the silica tube:

$$(\text{RE})\text{Pt, Fe}_2\text{O}_3, \text{ternary melt/melt/ternary melt, PSO}_3, \text{Pt(WE)} \quad (\text{III})$$

The emf between the two Pt wires was recorded using an interface board with a personal computer. All potentials were measured at 30 second intervals.

4. Solubility Measurements

Five grams of reagent-grade Cr$_2$O$_3$ or SiO$_2$ powders were initially mixed with 20 grams of the ternary salt. Because the density of the oxides is higher than that of the fused salt, the oxides fall to the bottom of the crucible (see Table 4). The visual examination of the solidified melt after each experiment showed that the undissolved oxides were uniformly distributed in a 1 to 2 mm thick layer on the bottom of the crucible. The depth of the melt was about 2.5 cm. Salt samples were obtained by lowering thin quartz rods into
Figure 31 Experimental set-up for cell (III).
Figure 32 Reference electrode: (A) upon immersion; (B) during use.
the melt which had been allowed to equilibrate for approximately 50 hours. The samples froze onto the rods. Care was taken that the alumina sampling rod did not touch either the electrodes or the crucible, and avoided contact with the solid oxide powder.

Each sample of quenched salt consisted of about 0.05 g of material weighed to 0.1 mg accuracy. Such samples were then dissolved in a known quantity of demineralized double-distilled water and analyzed using atomic absorption spectroscopy (A. A. S.). Ten microliters of the solution containing Cr solute ions were taken with an Eppendorf micropipette and injected into the graphite furnace (model HGA 2100) of an Atomic Absorption Spectroscopy apparatus (Perkin-Elmer, model 360). For samples containing Si, 25 microliters of the solution containing Si were used in order to increase the magnitude of the absorption signal. The maximum volume which the HGA could accommodate at one time was 100 µl.

Non-coated graphite furnaces were used in the A. A. S. analyses. They were changed after 50 measurements. Chromium- and silicon-hollow lamps were operated at 25 mA and 40 mA, respectively. In each case, the most sensitive wavelength was selected. A slit opening of 0.2 nm was chosen. Argon was passed through the furnace at a flow rate of 8 l/min. The interruption option was selected. The temperature cycle run for both Cr and Si was the following:
Table 4  Density of oxides and fused salts

<table>
<thead>
<tr>
<th></th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}_2\text{O}_3(s)$</td>
<td>5.21 (25°C)</td>
<td>8 6</td>
</tr>
<tr>
<td>$\text{SiO}_2(s)$</td>
<td>2.63 (25°C)</td>
<td>8 6</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_4-\text{K}_2\text{SO}_4$</td>
<td>2.06 (900°C)</td>
<td>7 9</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_4-\text{ZnSO}_4$</td>
<td>2.6 (900°C)</td>
<td>7 9</td>
</tr>
</tbody>
</table>
Drying: 2 min at 120°C
Charring: 2 min at 1250°C
Atomizing: 12 sec at 2600°C

The relationship between the signal height and the concentration of the element under study was given by the standard calibration plot.

Calibration curves were obtained by measuring the absorbance of standard solutions prepared by volumetric dilution of a 1000 ppm standard (Fisher Scientific) in double distilled water.

The relationship between concentration and absorbance is generally linear only up to a certain signal height, depending upon the selected resonance, line, slit width, light source, graphite tube, etc. The reason for non-linearity of calibration plots is the presence of non-absorbable lines (apart from the resonance line, a further non-absorbable line passes through the exit slit). A deviation from linearity is seldom observed for signals lower than 40% absorbance.

As explained in the next chapter, the measurement of Si concentrations in quenched melt samples was perturbed by the presence of the large quantity of ferric iron in solution. A more intense absorption line for Fe is at 248.3 nm, 3 nm away from the absorption line for Si, making it impossible to separate the contribution of each element in the observed signal. To circumvent this problem, iron was removed from the solution by an extraction method prior to A. A. S. analysis (76). The extraction is possible
because ferric chloride is more soluble in ether than it is in aqueous solutions. A quenched salt sample of known weight was dissolved in a known quantity of 11% HCl. A few milliliters of hydrogen peroxide were added to this solution on a warm plate. The oxidizing power of hydrogen peroxide insure that iron was only present as trivalent iron. Hydrogen peroxide oxidized traces of Fe$^{2+}$ to Fe$^{3+}$. After the liquid had been cooled, it was placed in a funnel with ether. The solution was vigorously mixed under cold water and allowed to rest for twenty minutes. A clear separation appeared between the top organic phase and the bottom hydrochloric aqueous solution. The bottom layer was extracted and kept in a beaker. The ether phase containing the iron was discarded. After each extraction, 10 µl of the aqueous solution were analyzed by atomic absorption. The shape of the absorption signal and absorbance were recorded. The extraction was repeated until the absorption signal appeared as a single peak and the absorbance did not vary anymore. Five consecutive extractions were necessary to remove all iron from the solution.
CHAPTER VI
RESULTS AND DISCUSSION

1. The Ag/AgCl-0.2 NaCl/glass Reference Electrode

This electrode was chosen because a silver chloride-sodium chloride mixture is liquid above 550°C.

The emf of two electrochemical cells of the type (I) (see below) and four cells of the type (II) (see below) were measured. Vycor and quartz were chosen as solid-state membranes. The chemical compositions of Vycor, Pyrex and quartz are shown in Table 5. Figure 33 presents the values of the ionic conductivities of Vycor, quartz and Pyrex found in the literature\(^{81,82}\) for temperatures between 28°C and 500°C. The conductivities for 700°C were extrapolated from these data.

\[ \text{Ag,AgCl-0.2 NaCl/Vycor (or quartz)/ Na}_2\text{SO}_4\text{-0.5 NaCl,SO}_2\text{O}_2\text{,O}_2\text{,Pt} \]

(I)

\begin{align*}
\text{anodic reaction (left side): } & \quad \text{Ag+NaCl=AgCl+Na}^+\text{+e}^- \quad (55a) \\
\text{cathodic reaction (right side): } & \quad 2\text{Na}^+\text{+SO}_2\text{+O}_2\text{+2e}^-\text{=Na}_2\text{SO}_4 \quad (55b) \\
\text{overall reaction: } & \quad \text{Ag+NaCl+Na+SO}_2\text{+O}_2\text{=AgCl+Na}_2\text{SO}_4 \quad (55c)
\end{align*}
Table 5  Glass composition, in Wt.% Oxide

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<th>CaO</th>
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<td>0.1</td>
<td>0.05</td>
<td>2.2</td>
<td>12.6</td>
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Figure 33 Ionic conductivities of Vycor, Pyrex and quartz in the temperature range 28°C-500°C. (81,82)
Ag, AgCl-0.2 NaCl/Vycor/Na₂SO₄-0.5 NaCl, 8 ppm SO₂, O₂, Pt
Ag, AgCl-0.2 NaCl/Quartz/Na₂SO₄-0.5 NaCl, 8 ppm SO₂, O₂, Pt

- Ag, AgCl-0.2 NaCl /Vycor or quartz/ AgCl- x NaCl  (II)

  anodic reaction (left side):  Ag+NaCl=AgCl+Na⁺+e⁻  (56a)
  cathodic reaction (right side): AgCl+Na⁺+e⁻=Ag+NaCl  (56b)
  overall reaction: AgCl(right)+NaCl(left)=AgCl(left)+NaCl(right)  (56c)

The thermodynamic properties of silver chloride-sodium chloride solutions have been studied by Panish et al. (53). They measured the variation of emf with temperature for cells of the type

Ag/AgCl-x NaCl/Cl₂.  (57)

Their emf data were extrapolated to 650°C and 700°C (Table 6). Using these data, the activities of AgCl corresponding to different mole fractions of AgCl in the binary system at these two temperatures could be determined (Table 6). The plots of activity of AgCl against XₐgCl at 650°C and 700°C are shown in Fig. 34 and Fig. 35.
Table 6  Activities of AgCl at 650°C and 700°C calculated from extrapolated emf measurements\(^{53}\).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>X(AgCl)</th>
<th>Emf(V)</th>
<th>(\Delta G) (cal)</th>
<th>(a(AgCl))</th>
<th>(\gamma(AgCl))</th>
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<tr>
<td>923</td>
<td>1.0000</td>
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<td>-19752</td>
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<td>0.86608</td>
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<td>0.75500</td>
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<td>-20161</td>
<td>0.80016</td>
<td>1.0598</td>
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<td>0.64600</td>
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<tr>
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<td>0.88801</td>
<td>-20501</td>
<td>0.57416</td>
<td>1.1370</td>
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</tbody>
</table>
Figure 34  Activity of AgCl in the binary NaCl-AgCl at 650°C.
Figure 35 Activity of AgCl in the binary NaCl-AgCl at 700°C.
They exhibit a slight deviation from ideality. The activity of the second component (NaCl) can be calculated by an integration of the Gibbs-Duhem equation:

\[
\log \frac{a_1}{X_1} = -\int_0^{X_2} \frac{X_2}{X_1} \, d \log \frac{a_2}{X_2} 
\]

However, since emf values for compositions of AgCl less than 0.5 were not available, the integration could not be rigorously performed. In first approximation, the solution was considered to be ideal and the activity of NaCl was equated to its concentration in the binary mixture. This approximation introduced an error less than 10%.

The activity of sodium in the AgCl-x NaCl salt solution is fixed by the reaction

\[
\text{Ag}(s) + \text{NaCl}(l) = \text{AgCl}(l) + \text{Na}(l)
\]

whose standard Gibbs energy change can be calculated from \(\Delta G^{o}_{\text{AgCl}(l)}\) and \(\Delta G^{o}_{\text{NaCl}(l)}\). Pure solid silver and pure liquid sodium were taken as reference states. The activities for sodium in AgCl-0.2NaCl and AgCl-0.4 NaCl were calculated at 700°C and are reported in Table 7.
In the literature, the molten Na$_2$SO$_4$-NaCl solution has been reported as an ideal solution with a eutectic composition of 0.48 Na$_2$SO$_4$-0.52 NaCl at 613°C (83).

For fixed SO$_2$ and O$_2$ partial pressures, the activity of sodium in the Na$_2$SO$_4$-0.5NaCl liquid could be estimated using the standard Gibbs energy change of the reaction

$$2\text{Na}(l) + \text{SO}_2 + \text{O}_2 = \text{Na}_2\text{SO}_4(l) \quad (60)$$

$$\Delta G^\circ(60) = \Delta G^\circ_{\text{Na}_2\text{SO}_4} - \Delta G^\circ_{\text{SO}_2} = -RT\ln\left(\frac{X_{\text{Na}_2\text{SO}_4}}{P_{\text{SO}_2}P_{\text{O}_2}a_{\text{Na}}^2}\right) \quad (61)$$

Pure liquid sodium was chosen as the reference state. The result of this calculation is reported in Table 7.

Figure 36 presents the results of the tests performed on cells of type (I) at 650°C for a 8 ppm SO$_2$-O$_2$ gas mixture. Quartz and Vycor had similar responses and the emf stabilized at 360 mV. The difference in emf at a given time at the early stage was not expected because the electrodes only differed in the solid electrolyte materials used to contain the reference salt. The observed final potential was very different from the theoretical value of 578 mV. This theoretical value was calculated using data extrapolated from the literature and assuming that the mixture was ideal (which was a reasonable assumption according to Fig. 34 and 35). However, the small errors involved in this calculation cannot explain the large difference in emf.
in Fig. 36. A disadvantage of cell (I) is that equilibrating the sodium sulfate-sodium chloride melt with the gases may be hard to ensure resulting in erroneous emfs. This could be the reason for the difference in emf. Figure 37 presents the results for cells of type (II) at 700°C. The four cells of type (II) tested were these:

#1, Ag,AgCl-0.2 NaCl/Vycor/AgCl-0.2 NaCl, Ag
#2, Ag,AgCl-0.2 NaCl/Quartz/AgCl-0.2 NaCl, Ag
#3, Ag,AgCl-0.2 NaCl/Vycor/AgCl-0.4 NaCl, Ag
#4, Ag,AgCl-0.2 NaCl/Quartz/AgCl-0.4 NaCl, Ag

Cells of this type are easier to construct and test than cell (I) but they lack a calibrating ability because the data for both compartments of the cell are calculated using the same method and the same source. The emf of these cells did not reach a stable value until after approximately 20 hours. The expected emf at equilibrium were 0.0, 0.0, 81 mV and 81 mV, respectively. All the electrodes showed some "aging", which accounted for a drop in potential. This "aging" has been reported by Rahmel(50). The potential drop is particularly large on line#2 which represents the response for the quartz electrode. For Vycor, the decrease in potential seems to be

Table 7. Calculated activities of sodium in the binary system AgCl-x m/0 NaCl.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta G^0_{(59)}$ (kJ/mol)</th>
<th>$\Delta G^0_{(60)}$ (kJ/mol)</th>
<th>$a_{Na}$ (AgCl-0.2NaCl)</th>
<th>$a_{Na}$ (AgCl-0.4NaCl)</th>
<th>$a_{Na}$ (Na$_2$SO$_4$-0.5NaCl)</th>
</tr>
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<tbody>
<tr>
<td>923</td>
<td>242.787</td>
<td>-703.220</td>
<td>$4.5 \times 10^{-15}$</td>
<td>$1.2 \times 10^{-14}$</td>
<td>$3.15 \times 10^{-18}$</td>
</tr>
<tr>
<td>973</td>
<td>239.476</td>
<td>-</td>
<td>$3.5 \times 10^{-14}$</td>
<td>$9.3 \times 10^{-14}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 36 Emf of cells of the Type (I) at 650°C
#1, Ag,AgCl-0.2 NaCl/Vycor/AgCl-0.2 NaCl, Ag
#2, Ag,AgCl-0.2 NaCl/Quartz/AgCl-0.2 NaCl, Ag
#3, Ag,AgCl-0.2 NaCl/Vycor/AgCl-0.4 NaCl, Ag
#4, Ag,AgCl-0.2 NaCl/Quartz/AgCl-0.4 NaCl, Ag

Figure 37 Emf of cells of the Type (II) at 700°C.
more gradual (lines #1 and #3). The observed values of the emf were 15 to 25 mV lower than the expected values. There is yet no definitive explanation for the difference between the experimental and theoretical values. Two important factors should be noted. Silver chloride is easily reduced to atomic silver by light and, as a consequence, the composition of the reference melt may have changed. The reduction of Ag\(^+\) by light would most likely happen during the grinding of the AgCl particles. Secondly, the magnitudes of the conductivities of the glasses was borderline to the recommended value of 10\(^{-6}\) ohm\(^{-1}\)cm\(^{-1}\) and this could very well affect the stability of the reference electrode. The conductivity of quartz is about 10\(^{-6}\) ohm\(^{-1}\)cm\(^{-1}\) at 700\(^\circ\)C\(^{81}\). No ionic conductivity data for Vycor are available at 700\(^\circ\)C but they can be extrapolated from data collected between 500\(^\circ\)C and room temperature\(^{82}\). The conductivity of Vycor is slightly higher than quartz due to a higher amount of impurities. Moreover, the incorrect potential could be either explained by a silver ion exchange with the alkalis of the glasses, or by a diffusion gradient within the glass, or by a change in concentration of Ag\(^+\) in the compartments of the cell. The latter could result from the diffusion of silver through the membrane or the corrosion of the silver wire.

The emf of the cell

\[
\text{Ag/ AgCl, 0.6 NaCl/porcelain/AgCl} \\
\text{-NaCl-KCl/porcelain/AgCl, 0.22 NaCl/ Ag}
\]
has been measured by Labrie and Lamb. The emf at 750°C (111 mV) agreed with the value 97 mV calculated on the assumption that porcelain is reversible to both Na+ and K+ ions. Assuming that porcelain was reversible to Na+ only, the authors calculated the emf as 61 mV. The authors concluded that the porcelain membrane does not act solely as a Na+ electrode. Nevertheless, in view of its stability and reproducibility, it is still acceptable as a reference electrode in certain systems.

The discrepancy between the observed and calculated values in the current study could be in part a consequence the transport of silver ion through the glass. A correction factor for the transport of Ag+ could be assessed. But, the poor stability of the electrodes and the emf irreproducibility render them inadequate as reference electrodes.

2. Description of the Second Electrochemical Cell

The experimental cell arrangement was

\[(\text{RE})\text{Pt}, \text{Fe}_2\text{O}_3, \text{ternary melt/melt/ternary melt}, \text{PSO}_3, \text{Pt(WE)} \] \hspace{1cm} (III)

By assuming that equilibrium is maintained for reaction (62) at both the reference and working electrodes
\[
\text{SO}_3 + \frac{1}{2}\text{O}_2 + 2e^- = \text{SO}_4^{2-}
\] (62)

the following expression for the emf is obtained

\[
\text{Emf} = \frac{RT}{2F} \ln \left( \frac{(\text{P}_{\text{SO}_3})_{\text{WE}}}{(\text{P}_{\text{SO}_3})_{\text{RE}}} \right) + \frac{RT}{4F} \ln \left( \frac{(\text{P}_{\text{O}_2})_{\text{WE}}}{(\text{P}_{\text{O}_2})_{\text{RE}}} \right) \tag{63}
\]

with \((\text{P}_{\text{O}_2})_{\text{WE}}=1 \text{ atm and } (\text{P}_{\text{O}_2})_{\text{RE}}=0.2 \text{ atm}\) \((\frac{RT}{4F} \ln \left( \frac{(\text{P}_{\text{O}_2})_{\text{WE}}}{(\text{P}_{\text{O}_2})_{\text{RE}}} \right) =30 \text{ mV at } 690^\circ \text{C})\).

The partial pressure of \text{SO}_3 in the reference electrode is fixed by establishing the equilibrium between solid \text{Fe}_2\text{O}_3 and \text{Fe}_2(\text{SO}_4)_3 in liquid solution. This partial pressure increases as the activity of ferric sulfate in the ternary melt increases. For a melt of known composition, \((\text{P}_{\text{SO}_3})_{\text{RE}}\) was measured by calibrating the reference electrode in the following way. Different known values for \text{P}_{\text{SO}_3} were admitted into the reaction chamber at the same slow flow rate and came to equilibrium with the melt at the working electrode. A plot of the measured emf against \ln(\text{P}_{\text{SO}_3}) is linear as expected from Eq.(63). The \text{P}_{\text{SO}_3} at which emf=30 mV corresponds to the partial pressure of sulfur trioxide encapsulated in the reference electrode. Once \((\text{P}_{\text{SO}_3})_{\text{RE}}\) is known, any unknown \((\text{P}_{\text{SO}_3})_{\text{WE}}\) in contact with the working electrode can be estimated according to Eq.(63).
3. Design of the Reference Electrode

The following equilibrium fixes the partial pressure of sulfur trioxide in the reference electrode

\[ \text{Fe}_2\text{O}_3(s) + 3\text{SO}_3(g) = \text{Fe}_2(\text{SO}_4)_3(\text{in liq.}) \]  \hspace{1cm} (64)

This equilibrium is established when Fe\(_2\)O\(_3\) initially present in the quartz tube contacts the melt which entered the tube through a hole. In this way, the ternary melt in the reference electrode has the same nominal composition as the working melt.

A preliminary investigation was aimed at determining the best design for the electrode in order to answer the following questions:

- Should the top of the reference electrode be closed or open?
- Should the tube be inserted before or after the ternary mixture has melted?
- What is the influence of the size and location of the hole?

3.1 Size and Location of the Hole

Holes of diameters \( \emptyset = 0.5 \text{ mm} \) or \( 0.7 \text{ mm} \) were made at the bottom of quartz tubes during glass blowing. The platinum wire had a diameter of 0.5 mm. In one case, the fit was tight between the platinum wire and the hole, and in the other case the platinum wire was loose. The Fe\(_2\)O\(_3\) powder was charged into the quartz tube and the electrode was positioned in the solid ternary mixture. Figure 38 shows the responses of two electrodes to a sudden change in P\(_{\text{SO}_3}\).
Figure 38  Effect of the size of the hole on the response of the electrode to a sudden change in $P_{SO_3}$ in the working melt
over the working melt. Little difference (2 mV) was observed in the average emf obtained at the plateau. However, some moderate fluctuations about the average value (+/- 5 mV) were observed in the case of the bigger hole. A hole diameter of 0.5 mm was chosen to insure that no solid Fe$_2$O$_3$ dropped past the hole into the ternary mixture.

Next, the location of the hole was investigated. One electrode had a hole at the bottom of the closed-end quartz tube and one had a hole on the side, 1 cm from the bottom of the closed-end tube; these were dipped into the same fused salt. The later was positioned so that the hole stayed two millimeters above the surface of the melt. Some of the melt was expected to enter the quartz tube by capillarity. Initially, air was present in the chamber. It was replaced at t=4400 minutes by a mixture of SO$_2$ and O$_2$ corresponding to P$_{SO_3}$ = 10$^{-3}$ atm. The gas flow was stopped after 3 hours and introduced again at t=5400 minutes. The reaction chamber was finally exposed to air. The behavior of the electrodes is shown in Fig. 39 and Fig. 40. The electrode having the hole at the bottom responded quickly (within a few minutes) to the change in SO$_3$, and maintained a constant value while SO$_2$/O$_2$ was passed, and returned to the original potential in an equally fast time once the gas flow was stopped. The plateau of Fig. 40 is at the calculated value of 38 mV. A more detailed and quantitative description of the response is given later.
Figure 39  Response to sudden changes in $P_{SO_3}$ of the RE with hole on its side.
Figure 40  Response to sudden changes in $P_{SO3}$ of the RE with hole at the bottom of the tube.
The response for the electrode with the hole on the side is chaotic. Considerable noise was present and the average emf value did not correspond to any predictable value. Spikes can be observed at \( t = 4400 \text{ min} \) and \( t = 5400 \text{ minutes} \) and acknowledge the change in \( \text{P}_{\text{SO}3} \). Numerous tests were performed with this type of electrode without any satisfactory responses. The failure of this electrode probably stems from the fact that the melt, which is very viscous, encountered difficulty to enter the hole. A look at the tube after completion of the experiment showed that some liquid had at some time reached the hole and even above it. However, the level of the salt in the central region of the crucible near the RE had dropped while the level near the walls had increased. Therefore, the recess of the liquid could have prevented it from accessing the lateral hole above the surface. The melt entry to the reference electrode through the bottom hole is aided initially by the slow upward withdrawal of the platinum wire. All the subsequent tests were done using the reference electrode with a hole at the bottom of the quartz tube.

3.2 Immersion Time

Whether the electrode should be immersed into the fused salt or already be in position prior to the melting of the solid mixture did not make any difference. Figure 41 compares the behavior of one reference electrode positioned before melting and one dipped into the fused salt. A mixture of \( 1\% \text{SO}_2 - \text{O}_2 \) was introduced into the
Figure 41  Response of the RE to a sudden change in $P_{SO_3}$ in the working melt when it is positioned after or before melting of the ternary salt.
reaction chamber for approximately 5 hours. The responses were identical.

3.3 Influence of the Pressure Inside the Electrode

According to Eq. (63), the emf is dependent on the partial pressure of oxygen. To maintain a constant partial pressure of oxygen in the reference compartment, the tube was open to atmospheric pressure throughout the experiment via a capillary. The response of such an electrode was compared to the response of another electrode which was closed by some silicon sealant.

The counter diffusion of SO₃ and SO₂ through the orifice could result in lower partial pressures of these species at the electrode. Since the orifice must be large enough to transmit the external oxygen partial pressure to the electrode, the outward flux of SO₃ and SO₂ cannot in theory be neglected when there are significant gradients in the concentrations of these species across the orifice. Gauthier and Bale(84) tested a galvanic cell based on the same idea for the thermodynamic study of Fe₂O₃(s)-Fe₂(SO₄)₃(s). A mixture of these species with unit activities was encapsulated in a tube open to atmospheric pressure. In the reference compartment, a known partial pressure of sulfur trioxide was maintained. The potential measured across the reference and working compartments was a direct determination of the decomposition pressure of the oxide-sulfate system. The authors were unable to obtain reproducible emfs
Figure 42 Response of the RE to a sudden change in $P_{SO_3}$ in the working melt when its top is sealed or open to atmospheric pressure.
above 150 mV, which may in part be due to some SO₃ and SO₂ leaving through the orifice.

At a given temperature, the chemical potentials of the gaseous species SO₃, SO₂ and O₂ in the encapsulated oxide-sulfate electrode are uniquely fixed by the reactions

$$\text{SO}_3 = \text{SO}_2 + \frac{1}{2} \text{O}_2$$  \hspace{1cm} (65)

$$\Delta G^\circ_{(65)} = 97,780 - 92.78 \ T \ (\text{J/mole})$$  \hspace{1cm} (66)

$$K_{(65)} = P_{\text{SO}_2}P_{\text{O}_2}^{1/2}/P_{\text{SO}_3}$$  \hspace{1cm} (67)

and

$$\text{Fe}_2\text{O}_3 + 3\text{SO}_3 = \text{Fe}_2(\text{SO}_4)_3 (\text{in liq.})$$  \hspace{1cm} (68)

When the reference mixture is kept in a closed system, from stoichiometry it follows that

$$P_{\text{SO}_2} = 2P_{\text{O}_2}$$  \hspace{1cm} (69)

Therefore Eq.(67) becomes

$$K_{(65)} = \frac{2(P_{\text{O}_2})^{3/2}}{P_{\text{SO}_3}} \quad \text{or} \quad P_{\text{O}_2} = \left\{ \frac{K_{(65)}P_{\text{SO}_3}}{2} \right\}^{2/3} \text{atm}$$  \hspace{1cm} (70)

At T=690°C, $K_{(65)} = 0.349$. If $P_{\text{SO}_3} = 10^{-3}$ atm, $P_{\text{O}_2}$ equals 0.003 atm. If $P_{\text{SO}_3} = 10^{-2}$ atm, $P_{\text{O}_2}$ equals 0.014 atm. The use of these values in Eq.
would add 80 and 50 mV to the emf calculated assuming that 
\((P_{O_2})_{ref}=0.2\) atm (in air).

The responses of the two electrodes are compared in Fig. 42. A 
\(SO_2/O_2\) gas mixture was introduced in the reaction chamber at 
t=1300 min. A drop of 10 mV in emf immediately ensued. This drop 
could be explained by an initially faster oxygen entry into the 
reaction chamber than \(SO_3\). Then, the emf increased rapidly to 
stabilize at a fixed potential. The trough observed at 1500 min is 
probably due to a fluctuation in the gas flow. The equilibrium value 
observed for the reference electrode with the capillary agrees with 
the expected value of 58 mV (using \(P_{O_2}=0.2\) atm (in air)). However, 
the difference in emf between the two curves is much smaller than 
the 50 mV difference estimated above. The change in \(P_{O_2}\) could be 
offset by a simultaneous change in \(P_{SO_3}\) because of leakage. This is 
not substantiated by any of the numerous experiments done using an 
open-to-air reference electrode. Both type of electrode have always 
been reproducible and stable with time.

4. Stability of the Electrode

As could be seen in the previous figures, the response to a 
sudden change in partial pressure of sulfur trioxide in the working 
melt is almost immediate (a few minutes). Once the plateau is 
reached, the emf fluctuates only slightly and the average value 
always agrees with that predicted by Eq. (63) (to within 2 mV). After 
the \(P_{SO_3}\) is instantly changed to another value, the electrode responds
rapidly again and the emf reaches a new value. The responses which have been previously presented correspond to one single injection of gas starting and finishing with air. Figure 43 shows the response of the reference electrode to successive changes in $P_{SO_3}$ in the working melt. The gas initially in contact with the working melt is air containing some ppm of sulfur trioxide. A different gas mixture is then injected into the cell, one after another. On this graph, the numbers refer to the values of $P_{SO_3}$ corresponding to the gas mixture of $SO_2/O_2$ injected into the reaction chamber. A step and a plateau indicate the equilibrium with the new environment. The steady-state values can then be plotted as a function of the gas composition on a calibration graph.

The stability of the electrode was demonstrated in a test where a gas mixture corresponding to $P_{SO_3}=2.5 \cdot 10^{-3}$ atm was passed over the melt for a period of 48 hours. The results of this test are presented in Fig. 44. The emf remained equal to 56 mV (+/- 2 mV) for the duration of the experiment. The theoretical value is 57 mV. This graph also shows that the flow rate control over a long period of time is good.

Figure 45 shows the calibration curve of the RE in a melt of composition 72 m/o Na$_2$SO$_4$, 18 m/o K$_2$SO$_4$ and 10 m/o Fe$_2$(SO$_4$)$_3$. All gases were $SO_2/O_2$ mixtures passed over Pt mesh contained in the hot zone of the inlet tube. The flow rate was maintained at 60 cm$^3$/min. The influence of the flow rate on the emf will be discussed
later. The plot is linear according to Eq. (63) and confirms that reaction (62) is occurring at each electrode.

The constant \( \frac{RT}{4F} \ln \frac{(P_{O2})_{RE}}{(P_{O2})_{WE}} \) equals 30 mV at 690°C. The value of \( P_{SO_3} \) in the reference electrode is read from the plot at \( E=30 \) mV \( (P_{SO_3})_{RE}=(P_{SO_3})_{WE} \) and equals 1.3.10\(^{-3}\) atm. The same calibration procedure as been applied to the electrode for melt n°1 (58.4 m/o Na\(_2\)SO\(_4\), 14.6 m/o K\(_2\)SO\(_4\), 27 m/o Fe\(_2\)(SO\(_4\))\(_3\)) and n°2 (67 m/o Na\(_2\)SO\(_4\), 17 m/o K\(_2\)SO\(_4\), 16 m/o Fe\(_2\)(SO\(_4\))\(_3\)) at 690°C. Figure 46 shows an example of the responses of the reference electrode obtained in melt n°1, n°2 and n°3 in equilibrium with the same gas mixture \( (P_{SO_3}=1.4.10^{-3}\text{ atm}) \).

As the concentration of ferric sulfate increased, the \( P_{SO_3} \) in the reference electrode increased and the emf decreased. The values of \( (P_{SO_3})_{RE} \) are 3.75.10\(^{-3}\) atm, 2.4.10\(^{-3}\) atm and 1.3.10\(^{-3}\) atm, respectively. All calibration curves were linear. The agreement is better for the melt having the lowest content of ferric sulfate (10 m/o), in which the hypothesis of random mixing is probably more justified.
Figure 43 Response of the RE to consecutive changes in $P_{SO_3}$. 
Figure 44 Stability of the RE for 48 hours.
Figure 45  EMF vs log (PSO$_3$)$_{WE}$ at 690°C in a melt of composition 72 m/o Na$_2$SO$_4$, 18 m/o K$_2$SO$_4$ and 10 m/o Fe$_2$(SO$_4$)$_3$. 
a) 58.4 m/o Na$_2$SO$_4$, 14.6 m/o K$_2$SO$_4$, 21 m/o Fe$_2$(SO$_4$)$_3$

b) 67 m/o Na$_2$SO$_4$, 17 m/o K$_2$SO$_4$, 16 m/o Fe$_2$(SO$_4$)$_3$

Figure 46 Emf of cell comprised of WE and RE for the three melt at 690°C in equilibrium with $P_{SO_3}=1.4\times10^{-3}$ atm.
c) $72\% \text{ Na}_2\text{SO}_4$, $18\% \text{ K}_2\text{SO}_4$, $10\% \text{ Fe}_2(\text{SO}_4)_3$
5. Gas Equilibration and Influence of the Flow Rate

At high temperatures, \( \text{SO}_2 \) and \( \text{O}_2 \) in the inlet gases react to form \( \text{SO}_3 \). The equilibrium composition can be calculated from the free energy change for the reaction:

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 = \text{SO}_3 \tag{71}
\]

The corresponding equilibrium constant is,

\[
K_{(71)} = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}} \tag{72}
\]

The free energy change for reaction (71) at 963 K is -8433 J/mole. If the composition of the ingoing gas is given by

\[
\text{SO}_2: \text{O}_2 \leftrightarrow n: 1
\]

then the gas composition after the attainment of equilibrium at 1253K can be represented as

\[
\text{SO}_3: \text{SO}_2: \text{O}_2 \leftrightarrow 2x: n-2x: 1-x
\]

For a total pressure of one atmosphere, the equilibrium partial pressures are
\[ (\text{P}S\text{O}_3)_{\text{eq}} = \frac{2x}{1+n-x}; \quad (\text{P}S\text{O}_2)_{\text{eq}} = \frac{n-2x}{1+n-x}; \quad (\text{P}O_2)_{\text{eq}} = \frac{1-x}{1+n-x} \]  

(73)

and

\[ K^2_{(71)} = 8.22 = \frac{4x^2(1+n-x)}{(n-2x)^2(1-x)} \]  

(74)

The values of \( x \) can be calculated using a computer from known values of \( n \) corresponding to the input gas analysis. Because we used concentrations of \( \text{SO}_2 \) less than 1\%, \( 1+n=1 \) and Eq. (74) reduces to

\[ K_{(71)} = \frac{2x}{n-2x} = \frac{\text{(P}S\text{O}_3)_{\text{eq}}}{\text{(P}S\text{O}_2)_{\text{eq}}} = 2.867. \text{SO}_2 \text{ and SO}_3 \text{ are the predominant sulfur bearing species, so that} \]

\[ (\text{P}S\text{O}_2)_{\text{in}} = (\text{P}S\text{O}_3)_{\text{eq}} + (\text{P}S\text{O}_2)_{\text{eq}} \]

The partial pressure of sulfur trioxide at equilibrium is then given by

\[ (\text{P}S\text{O}_3)_{\text{eq}} = \frac{K_{(71)}}{(1+K_{(71)})} (\text{P}S\text{O}_2)_{\text{in}} = 0.7414 (\text{P}S\text{O}_2)_{\text{in}}. \]  

(75)

High temperatures favor the formation of lower partial pressures of \( \text{SO}_3 \). When the concentration of \( \text{SO}_2 \) injected into the oxygen is low we expect the rate of conversion to sulfur trioxide to be first order with respect to the inlet concentration of \( \text{SO}_2 \), i.e., for a small degree of conversion. This reaction is slow and in the commercial manufacture of \( \text{SO}_3 \) a platinum or metal oxide catalyst is employed to increase the rate of reaction. Gauthier et al.\(^{(59)}\) have reported a conversion of 99\% at 809\(^{\circ}\)C on platinum and palladium for a flow rate of 100 cm\(^3\)/min.
The same authors demonstrated that gold and rhodium have on the contrary a low catalytic activity. At a high fixed flow rate the fraction of SO\textsubscript{2} converted is expected to be small and approximately independent of the inlet concentration. An interesting question is whether the conversion of SO\textsubscript{2} to SO\textsubscript{3} took place at the platinum mesh or at the gas/salt interface. Salzano and Newman\textsuperscript{55} in a similar setup determined that the SO\textsubscript{2} conversion was independent of the surface area or volume of the salt, therefore suggesting that the catalysis took place on the platinum in the inlet tube. A slow flow rate is expected to bring the degree of conversion close to 100%. The minimum flow rate used in this study was 60 cm\textsuperscript{3}/min. Figure 47 shows the variation in potential with velocity at a fixed concentration of SO\textsubscript{2}. The relationship between P\textsubscript{SO\textsubscript{3}} and the flow rate appears on a log-log plot (Fig. 48). As the flow rate increases, the conversion of SO\textsubscript{2} to SO\textsubscript{3} decreases. The plot in Fig. 48 is linear with a slope close to -1/2. This inverse proportionality between the partial pressure of sulfur trioxide and the square root of the flow rate is expected under laminar flow conditions where the rate of reaction is controlled by diffusion through a gas film at the platinum surface.

The time-dependence of the equilibration of a sodium sulfate melt with the gas phase above it has been studied by Hwang\textsuperscript{30}. In his study, the gas phase above pure Na\textsubscript{2}SO\textsubscript{4} melt was changed from pure O\textsubscript{2} to He-1%O\textsubscript{2} and then from He-1%O\textsubscript{2} to 1%SO\textsubscript{2}-O\textsubscript{2}. The measurements were made at two locations in the melt: one close to the melt/gas interface and another in the middle of the salt.
Figure 47 Influence of the flow rate on emf at 690°C.
Figure 48 Influence of the flow rate on the conversion of SO\textsubscript{2} to SO\textsubscript{3}. 

![Graph showing the relationship between log of flow rate and log of SO\textsubscript{3} partial pressure.]

Log (flow rate, cm\textsuperscript{3}/min) vs. Log (P\textsubscript{SO\textsubscript{3}, atm})
A value corresponding to 86% of the final stable emf was reached within five hours. There was no difference in emf observed for the two locations. In our case, the change in emf takes place in three minutes. In one experiment, the emf immediately reached a value more positive than the final stable value. This is illustrated in Fig. 49 which shows the immediate response of the RE to a sudden change in PSO₃ in the working melt, followed by a sharp drop in emf. The emf reaches a stable value corresponding to the expected emf after 6 hours. A fast SO₃ entry then slower O₂ entry could explain this behavior or the temperature in the reaction chamber did not reach its final value when the gas was injected.
Figure 49 Abnormal behavior in the response of the RE to a sudden change in $P_{SO3}$ in the working melt starting and finishing with air.
6. Measurement of Oxide Dissolution Kinetics

The measurement of the dissolution kinetics in the melt of composition 72\%/ Na$_2$SO$_4$, 18\%/ K$_2$SO$_4$, 10\%/ Fe$_2$(SO$_4$)$_3$ for Cr$_2$O$_3$ is shown in Fig. 50. Normalized concentrations are used as ordinates. [Cr]$_s$ represents the measured final concentration of the dissolved chromium sesquioxide. Each datum point was obtained from the average value of the measured concentrations of soluble Cr$_2$O$_3$ for a separate salt sample, compared to a certified standard solution of the oxide. $P_{SO_3}$ measured with the reference electrode was 1.25.10$^{-3}$ atm. The temperature was 690°C. The acidity of the melt was monitored during the course of the experiment. No change in emf was observed upon sampling, showing that the system was not disturbed. The concentration of Cr$_2$O$_3$ solute increased steadily with time and reached a stable value after approximately 41 hours. In the following solubility measurements, the melt was allowed to equilibrate for 52 to 55 hours before a sample was taken.

7. Solubility of Chromium Sesquioxide in a Ternary Salt Melt

The calibration curve (Fig. 51) was obtained using 10 μl aliquotes prepared from a 1000 ppm standard solution. Each datum point shown is the average value from a set of at least five separate measurements from a given standard concentration. When evaluating a method utilizing the HGA, it is useful to observe the atomization signals on a strip chart recorder. Under optimum furnace
conditions, the signal produced should be a "clear" sharp peak-shaped tracing. Under certain conditions, non-ideal peaks will be obtained (Fig. 52). Broad peaks were observed in this study. They can be caused by using too low gas flow, too low atomization temperature or by analyzing elements with a tendency to form carbides. In their analysis of Si by atomic absorption, Christian and Lo\(^{(85)}\) observed some increase in sensitivity by soaking the furnace with a solution of lanthanum (or other carbide formers) and drying it before the injection of the solution to be analyzed. This treatment reduced the formation of silicon carbides. In our case a systematic change of the operating parameters and pre-soaking of the furnace with a solution of lanthanum did not alter the shape of the absorbance signal. However, the absorption signal was a single peak and the calibration plot was linear in the range 0.02-0.2 ppm.

Both acidic and basic dissolution of Cr\(_2\)O\(_3\) in pure Na\(_2\)SO\(_4\) at 1200K were studied by Zhang\(^{(38)}\) and his results are shown in Fig. 53. The basicity defined there as 

\[
-\log a_{\text{Na}_2\text{O}} (\log p_{\text{SO}_3} + \log a_{\text{Na}_2\text{O}} = -16.7)
\]

was measured using a zirconia electrode and a Na\(^+\)-sensor. The left side of the solubility curve represents the domain of basic dissolution where

\[
\text{Cr}_2\text{O}_3 + 2\text{O}^{2-} + \frac{3}{2} \text{O}_2 = 2 \text{CrO}_4^{2-}
\]

(76)

and

\[
\frac{\partial \log a_{\text{CrO}_4^{2-}}}{\partial (-\log a_{\text{Na}_2\text{O}})} = -1
\]

(77)
or
\[ \text{Cr}_2\text{O}_3 + \text{O}^{2-} = 2\text{CrO}_2^- \] (78)

and
\[ \frac{\partial \log a\text{CrO}_2^-}{\partial \log a\text{Na}_2\text{O}} = -\frac{1}{2} \] (79)

The slope of the branch corresponding to the basic dissolution is either -1 or -1/2. The right side of the curve corresponds to the acidic dissolution where

\[ \text{Cr}_2\text{O}_3 = 2 \text{Cr}^{3+} + 3\text{O}^{2-} \] (80)

and
\[ \frac{\partial \log a\text{Cr}^{3+}}{\partial \log a\text{Na}_2\text{O}} = \frac{3}{2} \] (81)

The predicted and experimental slope of the branch corresponding to acidic dissolution is \( \frac{3}{2} \).

Figure 54 shows the solubility curve obtained at 690°C in the melt 72\text{m} / 0 \text{ Na}_2\text{SO}_4, 18\text{m} / 0 \text{ K}_2\text{SO}_4, 10\text{m} / 0 \text{ Fe}_2(\text{SO}_4)_3. The partial pressure of SO3 over the melt was progressively increased using...
Figure 50  Time dependence of the normalized concentration of dissolved Cr$_2$O$_3$ in $72 \text{m/o }$ Na$_2$SO$_4$, $18 \text{m/o }$ K$_2$SO$_4$, $10 \text{m/o }$ Fe$_2$(SO$_4$)$_3$ at 690°C. $P_{SO_3}=1.25 \times 10^{-3}$ atm.
Figure 51 A.A.S. calibration curve for chromium
Figure 52 Possible types of Atomic Absorption signals

- Sharp peak
- Broad peak
- Multiple peaks
Figure 53 Solubility of Cr$_2$O$_3$ in fused Na$_2$SO$_4$ at 1200 K and 1 atm O$_2$.\(^{(38)}\)
Figure 54 Solubility of Cr$_2$O$_3$ in 72\text{m/o} Na$_2$SO$_4$, 18\text{m/o} K$_2$SO$_4$, 10\text{m/o} Fe$_2$(SO$_4$)$_3$ at 690°C.
a O₂/SO₂ mixture richer in sulfur dioxide. Samples were taken 50 hours after the injection of a different gas mixture. The plot is a straight line with a slope close to -1. The acidic dissolution regime was not observed in the range of SO₃ considered. Higher values of PSO₃ are not typical of industrial environments. According to these results, we expect the dominant solute to be CrO₄²⁻ at 690°C. The concentration of soluble Cr was found to be six times higher than in pure sodium sulfate at 1200 K.

8. Solubility of Silica in a Ternary Salt Melt

The solubility of SiO₂ was measured in fused sodium sulfate at 1200 K and the solubility dependence on the basicity is shown in Fig. 55.

The calibration curve for silicon obtained in our study is presented in Fig. 56. Aliquots of 25 μl (instead of 10 μl) were injected into the graphite furnace in order to increase the signal amplitude on the vu-meter. The signal appeared as a narrow single peak and no interference was detected as in Fig. 49a. The plot is a straight line.

The absorption signal for a sample of the solidified melt appeared as in Fig. 50b. Two peaks were clearly present and the magnitude of the absorbance was very high. The measured solubilities were of the order of thousands of ppm in the ternary salt compared to only a few ppm in pure sodium sulfate at 1200K. This difference suggested that there was a strong interference of the iron "matrix". The most sensitive line for Fe is 248.3 nm, which is
Figure 55  Solubility of SiO$_2$ in fused sodium sulfate at 1200K.$^{(21)}$
Figure 56  A.A.S. calibration curve for silicon
very close to the line used for the determination of silicon concentrations (251.6 nm). Two less sensitive absorption lines for Si are at 221.7 nm and 221.1 nm. In theory, these should be far enough to eliminate the interference caused by Fe. Measurements using these two lines were unsuccessful because of the lack of sensitivity (no signal was observed on the vu-meter). Neither iron nor silicon could be detected. A method of measurement by addition was then considered. Procedures for using this method are given now. Three aliquots of the sample were taken. The first was diluted to a known volume with water. The second and third aliquots were made up to the same volume with suitable quantities of known standards added so that the final solutions contain different additions of the metal to be determined. The absorbance for each solution was measured and plotted against the added concentration. The resulting straight line must then be extrapolated through zero absorbance. The intercept on the concentration axis should give the concentration of the metal in the diluted sample solution (see Fig. 55). In this study, the absorbance measurements resulted in a straight horizontal and no intercept could be found. The response to the additions of Si must have been masked by the large signal generated by the absorption of Fe. We decided to extract the iron from the sample by a separation technique. The extraction procedure is described in the chapter "Experimental procedures". After each extraction, the solution was analyzed by AAS. After five consecutive extractions, the value of the
absorbance did not change anymore. The results are presented in Fig. 56.

Each datum point in this plot is an average of a set of separate measurements. The acidity of the melt was changed from -3.1 to -2.1 atm in the measurements but the solubility of SiO₂ in the melt varied only within 7.92 and 10.5 ppm by weight, mean value 8.6 ppm, standard deviation 1.08 ppm. No trend in the dependence of the solubility on the melt acidity is revealed by the data. This suggests that SiO₂ dissolves as SiO₂ molecules without the formation of silicate. The formation of a silicate via the reaction Na₂O+SiO₂=Na₂Si₂O₅ would result in a dependence of the solubility on Na₂O. According to the criterion of Rapp and Goto for hot corrosion fluxing, the absence of a SiO₂-solubility dependence on the acidity is favorable for low-temperature hot corrosion resistance in the ternary salt because any gradient in solubility could lead to a dissolution-reprecipitation mechanism.
Figure 57 Method of additions.
Figure 58 Solubility of SiO$_2$ in 72m/o Na$_2$SO$_4$-18m/o K$_2$SO$_4$-10m/o Fe$_2$(SO$_4$)$_3$ at 690°C.
CHAPTER VII
CONCLUSIONS

The activity of ferric sulfate in Na$_2$SO$_4$-K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ melts has been calculated using the geometrical approach proposed by Toop. This thermodynamic approach is well suited for asymmetrical ionic ternary solutions with a common anion. The equations derived are considered to be rigorous only in cases where the binary systems behave as regular solutions and combine to form a regular ternary solution. The binary systems K$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ and Na$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ were found to be regular when the integral excess Gibbs energy was expressed in terms of equivalent ionic fractions. The pairing energies were negative and took the values of -133,000 J/mole and -51,000 J/mole, respectively. In terms of molar ionic fractions, the integral excess Gibbs energies could be written as polynomials of the form $XAXB(h_0+h_1XB+h_2X^2B)$. The binary systems considered by Toop were regular when the thermodynamic quantities were expressed in molar ionic fractions. It is expected that Toop's equation is not rigorously exact in this study. On the other hand, Toop also showed that the method gives results that are not grossly erroneous in the case of non regular systems.

The partial pressure of sulfur trioxide encapsulated in the reference electrode could be measured and was compared to
calculated values. Only in the case of the melt containing 10\textsubscript{m/o} \(\text{Fe}_2(\text{SO}_4)_3\) were the experimental and theoretical values of the same order of magnitude. The calculated activity of \(\text{Fe}_2(\text{SO}_4)_3\) in the melt containing the lowest concentration of Fe(III) were expected to be closer to reality because the hypothesis of random cation mixing, which is the basis for Forland's model, is probably limited to a narrow composition range of \(X_{\text{Fe(III)}}\). For high concentrations of Fe(III), this hypothesis of random mixing is probably not valid anymore.

A reference electrode consisting of a AgCl-0.8\% NaCl reference electrolyte enclosed in quartz or Vycor did not give satisfactory results. The measured steady-state emf of two different electrochemical cells did not correspond to any theoretical values and drifts in the potentials were also observed. The preparation of the reference melt was done in a dark room to avoid the reduction of silver chloride by light. The accuracy on the initial composition of the reference melt, possible fluctuations in this composition with time and a low ionic conductivity of the solid-state membrane are plausible explanations for the observed differences.

The experimental results show that the \(\text{SO}_3\) sensor can be used as a reliable reference electrode in the low-melting multi-cation salt. Its design is relatively simple and has been optimized with regard to stability and reproducibility. The emf between the working electrode and the reference electrode exhibits a linear dependence on the logarithm of \(P_{\text{SO}_3}\) according to the equation
\[
\text{Emf} = \frac{RT}{2F} \ln \left( \frac{P_{SO_3}}{P_{SO_3}^{WE}} \right) + \frac{RT}{4F} \ln \left( \frac{P_{O_2}}{P_{O_2}^{WE}} \right)
\]

which can be derived on the assumption that an equilibrium between \(O_2\), \(SO_3\) and \(SO_4^{2-}\) is maintained at each electrode. The response of the electrode to sudden changes in composition of the gas phase in equilibrium with the working melt was very rapid as \(SO_3\) was instantaneously available at the liquid/solid/gas interface. A longer time (=1 hour) elapsed before the emf returned to its initial value (obtained in air) after the \(SO_2/O_2\) gas flow was stopped. This relaxation time is controlled by the rate at which \(SO_3\) diffuses out of the reaction chamber. Furthermore, the electrochemical cell always reached a stable steady-state emf and maintained it for very long periods of time. The results showed that the catalytic conversion of \(O_2/SO_2\) at low flow rates gives \(P_{SO_3}\) close to the equilibrium values.

The solubility of chromia in \(Na_2SO_4-K_2SO_4-Fe_2(SO_4)_3\) at 973 K was six times higher than in pure sodium sulfate at 1200 K. The solubility plot obeys an acidity dependency which corresponds exactly to a basic dissolution of \(Cr_2O_3\) with formation of chromate. No acidic dissolution was observed in the range of acidity considered. The solubility of \(SiO_2\) in \(Na_2SO_4-K_2SO_4-Fe_2(SO_4)_3\) was \(8.55^{+}/-1.08\) ppm and it was not a function of \(P_{SO_3}\) in the experimental range of \(SO_3\) considered. The solubility of \(SiO_2\) was very low compared to that of \(Cr_2O_3\) and it was only two times higher than it was at 1200 K in pure
sodium sulfate. According to the criterion of Rapp and Goto for hot corrosion fluxing, the absence of a SiO\textsubscript{2}-solubility dependence on the acidity is favorable for low-temperature hot corrosion in the ternary salt. Any gradient in solubility could lead to a dissolution-reprecipitation mechanism.

The previous equation also shows that the reference electrode should respond to changes in the partial pressure of oxygen. In this study, the partial pressure of oxygen the reaction chamber was maintained at \( \approx 1 \) atm. In a future work, the behavior of this reference electrode in a more reducing atmosphere could be assessed. This future study would investigate the reactions taking place at the RE and WE and the dependence of the emf on \( P_{\text{SO}_3} \) and \( P_{\text{O}_2} \).
REFERENCES


(15) N.S. Bornstein and M.A. DeCrescente, Met. Trans., 2, 2875 (1971)


(33) A. Rahmel, Corrosion Sci., 13, 833 (1973)


(51) A. Rahmel and E. Tatar-Moisescu, Werkstoffe Korros., 26, 513 (1975)


(54) H. Flood and N.C. Boye, Z. Elektrochem., 66, 184 (1962)


(60) M. Temkin, Acta Physiochem. USSR, 20, 411 (1945)


(65) C. Perrier and A. Bellanca, Per. Mineral., 11, 163 (1940)


(72) P. Anderson, unpublished results (1968)


(75) G.W. Toop, Trans. Met. Soc. AIME, 233, 850 (1965)

(76) F. Koehler, Mh. Chem., 91, 738 (1960)

(77) C. Colinet, D.E.S., University of Grenoble, France (1967)


