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A SOLID STATE PROBE FOR SO_2/SO_3 BASED ON

Na_2SO_4 -I ELECTROLYTE

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ABSTRACT

Conductivity measurements as a function of temperature and partial pressures of SO_3 , SO_2 and O_2 , and transference experiments indicate that the transport number of Na^+ ions is unity in Na_2SO_4 -I. A concentration cell based on this electrolyte,

produces emfs that are in agreement with those calculated from the Nernst equation when equilibrium is assumed between the gas species at the electrodes. The cell can be used for monitoring the SO_2/SO_3 pollution in air, and in combination with an oxygen probe can be used for the determination of SO_2/SO_3 concentrations in coal combustion reactors, for the evaluation of the partial pressure of S_2 in coal gasification systems and for emission control in nonferrous smelters using sulfide ores. The probe is similar to that developed recently by Gauthier et al (4,5) using K_2SO_4 as the electrolyte, but can operate at higher pressures of SO_3 . Because of the greater polarizing power of the Na^+ ion compared to the K^+

ion, $\text{Na}_2\text{S}_2\text{O}_7$ is less stable and can be formed only at a considerably higher pressure of SO_3 than that required for $\text{K}_2\text{S}_2\text{O}_7$.

KEYWORDS: Sensor, Detector, Galvanic Cell, Pollution Control, Emission Control, Sulfur Probe, Sulfur Dioxide, Sulfur Trioxide.

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INTRODUCTION

The use of liquid sulfates in electrochemical cells was pioneered by Flood and Boye (1), who devised a SO_2 , O_2 electrode to study the thermodynamic properties of $\text{K}_2\text{SO}_4 - \text{K}_2\text{S}_2\text{O}_7 - \text{SO}_3$ and $\text{ZnO-ZnSO}_4\text{-SO}_3$ systems. Almost a decade later Boxall and Johnson (2) measured the emf between a SO_3, SO_2 , Pt electrode and an Ag, Ag^+ reference electrode in $(\text{Li,Na,K})_2\text{SO}_4$ melts. Salzano and Newman (3) developed a concentration cell using SO_3, SO_2 , Pt electrodes and $(\text{Li,Na,K})_2\text{SO}_4$ melts, separated by cation permeable glass, for monitoring SO_3 concentrations in gases in the parts per million range. Recently Gauthier et al (4,5) have shown that it is possible to detect sulfur oxides in the gas phase by a solid state cell based on K_2SO_4 . From an engineering point of view, such solid state sensors are preferable to devices that employ liquid electrolytes for a majority of applications.

At high partial pressures of SO_3 (eg. $P_{\text{SO}_3} > 10^{-1}$ atm at 973K), K_2SO_4 will transform to a liquid rich in $\text{K}_2\text{S}_2\text{O}_7$, as shown by the phase diagram in Figure 1, thus destroying the mechanical integrity of the solid electrolyte. In the pyrosulfate ion two SO_3 groups are connected by a single oxygen bridge;

Since the stability of the oxygen bridge decreases with increasing polarizing power of the cation, and the Na^+ ion is more polarizing than the K^+ ion, sodium pyrosulfate would be less stable than the corresponding potassium salt. The formation of sodium pyrosulfate can therefore

Figure 1. Phase diagram of the system K_2SO_4 - $K_2S_2O_7$, showing SO_3 isobars (reference 1).

occur only at a considerably higher partial pressure of SO_3 than required for potassium pyrosulfate. Although there are no accurate thermodynamic data in the literature for calculating the stability fields of the pyrosulfates, an indication of the relative stability of sodium and potassium pyrosulfate can be obtained from Flood and Förland (6), who measured the concentrations of sulfate and pyrosulfate ions in melts equilibrated with controlled streams of SO_3 . For the equilibrium,

they defined a pseudo equilibrium constant in terms of anionic fractions, X ,

$$K' = X_{\text{SO}_4^{2-}} P_{\text{SO}_3} / X_{\text{S}_2\text{O}_7^{2-}} \quad [2]$$

The variations of $\log K'$ with the reciprocal of the absolute temperature is shown in Figure 2 for sodium and potassium systems. For any specified temperature and ratio $X_{\text{SO}_4^{2-}} / X_{\text{S}_2\text{O}_7^{2-}}$ in the melt, the equilibrium SO_3 pressure is higher for the sodium system by approximately a factor of 50x compared to the potassium system.

High SO_3 partial pressures are encountered in some chemical industries and anticipated energy conversion systems. The object of this paper is to explore the possibility of using sodium sulfate as a solid electrolyte in a galvanic cell for the measurement of SO_2/SO_3 concentrations in the gas phase. Solid sodium sulfate undergoes phase changes at 450 K (V $\rightarrow$ III) and 515 K (III $\rightarrow$ I) (7). The high temperature form (I) has a modified $\alpha - \text{Ca}_2\text{SiO}_4$ structure (8) which can be visualized as

Figure 2. The variation of the 'equilibrium constant' for the reaction $M_2S_2O_7(l) \rightarrow M_2SO_4(l) + SO_3(g)$, with temperature. (M = Na, K)

layers parallel to the C-axis, some containing only Na^+ ions, and others containing a mixture of Na^+ and SO_4^{2-} ions. The details of the defect structure are not well understood. The conductivity and transport properties of Na_2SO_4 -I are not available in the literature. In the first phase of this research the electrical conductivity of this material was measured, using 2-terminal d.c. and 3-terminal guarded a.c. techniques, as functions of temperature and partial pressures of SO_3 , SO_2 and O_2 . Transference measurements were then performed to determine the relative cationic and anionic contributions to the conductivity. Finally emfs of concentration cells based on Na_2SO_4 -I were studied.

EXPERIMENTAL

MATERIALS:

Powdered, anhydrous, 99.99 percent pure Na_2SO_4 was used as the material for the electrolyte. Pellets 1.5 cm in diameter and thickness ranging from 0.3 to 0.6 cm were made by double end compression of the fine powder and subsequent sintering at 1090 K for 24 hours. By this procedure pellets with 98 (± 1) percent of the theoretical density were obtained.

Gas mixtures containing SO_2 , O_2 and Ar were prepared in two different ways depending on the concentration of SO_2 and O_2 . Test gas mixtures 1, 2 and 7 (see Table I) were made by mixing separate metered streams of dry, high purity SO_2 , O_2 and Ar in a tower packed with glass beads. Test gases 3 to 6 and 8 to 12 were made by passing analysed high

TABLE I

COMPOSITIONS OF THE TEST GASES AND THE EMFS OF THE CONCENTRATION CELL

Test Gas Number	Inlet Gas Composition vol.pct.			Temperature (K)	Gas Composition at Temperature vol.pct.				$P_{SO_3} \cdot P_{O_2}^{1/2}$	E_{expt} (mV)	E_{theor} (mV)
	SO ₂	O ₂	Ar		SO ₃	SO ₂	O ₂	Ar			
1	21.8	35.6	42.6	973	13.6	9.65	31.2	45.5	7.60×10^{-2}	248	252
2	6.30	17.8	75.9	973	3.24	3.16	16.5	77.1	1.32×10^{-2}	180	178
3	8.75×10^{-1}	5.15	94.0	973	3.16×10^{-1}	5.60×10^{-1}	5.00	94.1	7.07×10^{-4}	55	56
4 Ref. Gas	4.45×10^{-1}	2.36	97.2	973	1.23×10^{-1}	3.22×10^{-1}	2.30	97.3	1.87×10^{-4}	2	0
5	4.31×10^{-1}	8.87×10^{-3}	99.6	973	7.59×10^{-3}	4.23×10^{-1}	5.07×10^{-3}	99.6	5.40×10^{-7}	-240	-245
6	7.66×10^{-2}	5.13×10^{-3}	100.	973	1.35×10^{-4}	7.52×10^{-3}	5.07×10^{-3}	100.	9.61×10^{-9}	-394	-414
7	3.61	22.4	74.0	873	3.02	6.49×10^{-1}	21.2	75.1	1.39×10^{-2}		
8	2.56×10^{-1}	11.3	87.5	873	2.00×10^{-1}	5.67×10^{-2}	12.2	87.5	6.99×10^{-4}		
9	1.57×10^{-2}	5.41	94.6	873	1.10×10^{-2}	4.69×10^{-3}	5.40	94.6	2.56×10^{-5}		
10	2.73×10^{-2}	1.54×10^{-1}	99.8	873	7.67×10^{-3}	1.96×10^{-2}	1.50×10^{-1}	99.8	2.97×10^{-6}		
11	4.71×10^{-3}	5.23×10^{-3}	100.	873	3.16×10^{-4}	4.39×10^{-3}	5.07×10^{-3}	100.	2.52×10^{-8}		
12	1.27×10^{-3}	5.11×10^{-3}	100.	873	8.51×10^{-5}	1.18×10^{-3}	5.07×10^{-3}	100	6.06×10^{-9}		

purity O_2 +Ar mixtures from cylinders over SO_2 permeation tubes (9). These tubes are approximately 0.63 cm in diameter and range in length from 5 to 30 cm. The tubes containing liquid SO_2 are sealed at each end. The tubes leak SO_2 by diffusion at a fixed rate at a given temperature. They are calibrated by measuring the weight loss with time. This technique was used by Salzano and Newman (3) for preparing gas mixtures containing low SO_2 concentrations. The oxygen analysis of O_2 +Ar gas mixtures were checked by a solid state oxygen meter based on stabilized zirconia electrolyte.

APPARATUS AND PROCEDURE:

1) Conductivity Measurements

The electrical conductivity was measured using both 2-terminal d.c. and 3-terminal guarded a.c. techniques.

The 2-terminal d.c. technique was used primarily as a check of the a.c. results and to obtain an indication of the extent of electronic conduction within the samples (10). Gold contacts were evaporated onto the circular pellets of Na_2SO_4 approximately 1.5 cm in diameter and 0.3 cm in thickness. The sample was placed in a furnace and electrical measurements were made at 973K under SO_3 + SO_2 + O_2 +Ar gas mixtures corresponding to test gas compositions 1 and 3. Platinum catalysts were placed in the constant temperature zone of the furnace in the path of the gas mixtures so that equilibrium compositions are ensured before they contact the sample. A constant d.c. voltage of 0.5V was applied to the sample and the current was measured as a function of time by a digital electrometer operated in the fast current mode. When the circuit was closed,

the instantaneous current was used to measure the total (ionic plus electronic) current. The variation of the current with time gave an indication of the polarization that occurred at the electrodes. The final steady state current is related to the electronic contribution to the conductivity.

The 3-terminal measurements were made on samples which had a grounded guard electrode around the sample edge, as shown in Figure 3. This helped to minimize problems due to leakage currents across the surface of the samples and field fringing effects. The samples were prepared by cutting a circular groove through gold contacts. The grooves on the opposite surfaces are carefully aligned. The center circular electrodes were used for the conductivity measurements. The length to area ratio used in the measurements was approximately 0.47. The leads to the outer electrodes were connected to the grounded shields on the coaxial cables, which were also tied to a common system ground. The impedance of the sample was measured by a vector impedance meter at 973K under different gas atmospheres corresponding to test gases 1 to 6 and at 873K with test gases 7 to 12. The rms voltage across the samples varied from 3 to 250 mV. The conductivity was measured as a function of frequency in the range 50 to 10^4 Hz at each temperature and gas composition.

2) Transference Measurements

The assembly used for transference measurements is schematically depicted in Figure 4. A Na-Pb alloy containing 5 at pct Na was placed in two β -alumina crucibles, which were covered with alumina lids. Stainless steel electrical leads passed through holes drilled in the

Figure 3. A schematic diagram of the arrangement used for 3-terminal guarded a.c. measurements.

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Figure 4. Experimental arrangement for the measurement of the transport number in $\text{Na}_2\text{SO}_4\text{-I}$ at 700K.

center of the lids. The openings in the center and around the lids were closed with a high temperature cement. The crucible assemblies were weighed on a microbalance and placed one on each of the end blocks of a three-block Na_2SO_4 stack, which was held together by spring-loaded alumina slabs (not shown in the Figure). Each block of Na_2SO_4 was carefully weighed before the experiment.

β -alumina is a solid electrolyte in which the transport number of Na^+ ions is greater than 0.998 (11). When a d.c. current was passed from the left to the right through the entire assembly, β -alumina crucibles acted as electron blocking electrodes. The total quantity of current passed was measured by a coulometer. Because of the increased volatility of Na and the tendency of the β -alumina crucibles to stick to the Na_2SO_4 blocks at higher temperatures, the experiments were done at 700K and under an inert gas flowing at a rate of 150 ml min^{-1} . At the end of the experiment, the assembly was cooled and the β -alumina crucibles and Na_2SO_4 blocks were reweighed.

3) Studies on Concentration Cells

The emfs of the concentration cell,

were measured as a function of gas composition at 973K. A schematic diagram of the apparatus used is shown in Figure 5. A pellet of $\text{Na}_2\text{SO}_4\text{-I}$ was supported on a silica tube inside a reaction tube held in a vertical furnace. The space inside the reaction tube was separated into two

Figure 5. A schematic diagram of the apparatus used for emf measurements on the concentration cell,

gas-tight compartments by spring loading a silica tube against a gold O-ring placed on the Na_2SO_4 -I pellet. The reference gas was flown inside the spring loaded silica tube at a flow rate of 100ml min^{-1} , while the test gas was passed through the reaction tube around the Na_2SO_4 -I pellet at 200 ml min^{-1} . Preliminary experiments suggested the absence of thermal gradients across the electrolyte with these flow rates. Fine platinum mesh electrodes were placed on either side of the Na_2SO_4 -I pellet and connected to platinum leads. The emf developed between these leads was measured by a high impedance ($> 10^{12}$ ohms) digital voltmeter. The temperature of the cell was measured by a Pt-Pt (13%Rh) thermocouple. Platinum catalysts were hung on hooks on the supporting silica tubes in the constant temperature zone ($\pm 2\text{K}$) of the furnace in such a way as to contact the two gas streams before they impinge on the electrolyte surface. The presence of catalysts ensured equilibrium within the gas phase.

RESULTS AND DISCUSSION

1) High Temperature Gas Composition

At high temperatures SO_2 and O_2 in the inlet gases react to form SO_3 , thus changing the gas composition. The equilibrium high temperature composition can be calculated from the standard free energy change (12) for the reaction,

$$\Delta G_4^\circ = 97,780 - 92.78 T (\pm 300) \text{ J} \quad [5]$$

If the initial gas mixture contained 1 mole of SO_2 , η_{O_2} moles of oxygen and η_{Ar} moles of argon at a total pressure of one atmosphere, and if α moles of SO_3 are formed at equilibrium at any fixed temperature, then there remains $(1-\alpha)$ moles of SO_2 and $(\eta_{\text{O}_2} - \alpha/2)$ moles of O_2 . The total number of moles of gas at high temperature is given by $(1+\eta_{\text{O}_2}+\eta_{\text{Ar}}-\alpha/2)$. The equilibrium partial pressures are:

$$P_{\text{SO}_2} = (1-\alpha) / (1 + \eta_{\text{O}_2} + \eta_{\text{Ar}} - \alpha/2) \quad [6]$$

$$P_{\text{SO}_3} = \alpha / (1 + \eta_{\text{O}_2} + \eta_{\text{Ar}} - \alpha/2) \quad [7]$$

$$P_{\text{O}_2} = (\eta_{\text{O}_2} - \alpha/2) / (1 + \eta_{\text{O}_2} + \eta_{\text{Ar}} - \alpha/2) \quad [8]$$

The value of the equilibrium constant for reaction [4] can be calculated at any temperature and is related to the partial pressures:

$$\exp(-\Delta G_4^\circ/RT) = K_4 = P_{\text{SO}_2} P_{\text{O}_2}^{1/2} / P_{\text{SO}_3} \quad [9]$$

or

$$K_4 \propto (1 + \eta_{\text{O}_2} + \eta_{\text{Ar}} - \alpha/2)^{1/2} = (1-\alpha)(\eta_{\text{O}_2} - \alpha/2)^{1/2} \quad [10]$$

The value of α can be computed for a given input gas composition repre-

sented by η_{O_2} and η_{Ar} from a knowledge of K_4 at the specified temperature using a digital computer. The high temperature gas compositions calculated at 873K and 973K are summarized in Table I.

2) Conductivity Measurements

The total conductivity of Na_2SO_4 -I obtained from d.c. measurements is lower than that obtained from a.c. measurements by approximately 60 per cent. Since the d.c. results are obtained from instantaneous ($t=0$) current values when the circuit was closed, accurate values for conductivity cannot be obtained from this technique. The currents decreased rapidly with time, suggesting that most of the current was carried by ions. The final steady state current corresponds to an electronic conductivity of $2.6(\pm 2) \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 973K. This is approximately three orders of magnitude lower than the total conductivity. The electronic transport number, therefore, has an approximate value of 10^{-3} . Within the limits of experimental error the total and electronic conductivities remained constant under test gases 1 and 3. The absence of significant electronic conductivity in pure Na_2SO_4 -I is remarkable.

The 3-terminal guarded a.c. technique is superior for measuring the absolute conductivity. A steep increase in the imaginary part of the impedance with decreasing frequency is observed in the frequency range used in the measurements. Plots of imaginary versus real parts of the impedance are linear, and the true electrolyte resistance is obtained by extrapolation of the impedance curve to zero imaginary component. The increase in the imaginary part of the impedance with decreasing frequency

is a characteristic feature of such measurements and is associated with a double layer capacity in series with electrolyte resistance. The maximum frequencies used are not sufficient to delineate the high frequency semicircle on the complex impedance diagram due to geometrical capacity in parallel with the electrolyte (13).

The conductivity of Na_2SO_4 -I is plotted as a function of the partial pressure of SO_3 in the gas phase at 873K and 973K in Figure 6. The conductivity is independent of gas composition over several decades. The plot of $\log (\sigma T)$ against the reciprocal of absolute temperature is linear as shown in Figure 7. A least mean squares analysis of the data gives the following expression for conductivity:

$$\log (\sigma T) = - 4257/T + 4.695 \quad [11]$$

The activation energy for ionic conduction in Na_2SO_4 -I is 81.5(± 4) kJ. This value is lower than the activation energy for ionic conduction (105.5 kJ) in a solid solution between Na_2SO_4 -I and $\text{Y}_2(\text{SO}_4)_3$ having the composition $(\text{Na}_{0.835} \text{Y}_{0.055} \square_{0.110})_2 \text{SO}_4$ (14). Natarajan and Secco (15) have measured the electrical conductivity of pure and doped K_2SO_4 as a function of temperature using single crystal and polycrystalline samples. The conductivity perpendicular to the (100) face was always higher than that perpendicular to the (011) face. At temperatures above 856K K_2SO_4 is isostructural with Na_2SO_4 -I permitting a direct comparison of their conductivities. For polycrystalline samples the conductivity of Na_2SO_4 -I is higher by approximately an order of magnitude. The higher conductivity is probably related to the smaller ionic radius of the Na^+ ion.

Figure 6. Variation of the electrical conductivity of Na₂SO₄-I with the partial pressure of SO₃ in the gas phase.

Figure 7. Temperature dependence of the electrical conductivity of Na₂SO₄-I.

Transference Measurements

The results from a typical transference experiment are summarized in Table II. The comparatively small weight changes of the Na_2SO_4 -I blocks can be attributed to mechanical attachment of grains at the contact surfaces. The corrected weight changes of the β -alumina crucibles containing the Pb-Na alloy and Na_2SO_4 -I blocks correspond to an Na^+ ion transport number of 1.01 (± 0.023). Repeat experiments gave values of 0.99, 0.995 and 1.006 for t_{Na^+} at 700K. They differ from unity by about the usual experimental error in this type of measurement. Since Na^+ ions are the predominantly mobile species, it is reasonable to expect an increase in the conductivity by doping Na_2SO_4 -I with small amounts of di- and trivalent ions. Each divalent ion entering the Na_2SO_4 -I lattice would create one Na^+ ion vacancy, while each trivalent ion would create two vacancies. This reasoning is supported by a comparison of the conductivity data on $(\text{Na}_{0.835} \text{Y}_{0.055} \square_{0.11})_2 \text{SO}_4$ reported in the literature (14) with these obtained in this study for pure Na_2SO_4 -I. Introduction of 11% vacancies increases the ionic conductivity by approximately a factor of 50X. A simple model suggests that trivalent ions would be twice as effective as divalent ions in increasing ionic conduction in Na_2SO_4 at low concentrations of the dopant. As the concentration of the dopant is increased, defect clusters would become stable. The ionic conductivity will exhibit a maxima at an intermediate concentration of the dopant as in the case of calcia stabilized zirconia.

4) Studies on Concentration Cells

The measured reversible emfs of cell 3 corresponding to the various

TABLE II

TRANSFERENCE NUMBER MEASUREMENT ON Na_2SO_4 -I AT 700K

	Weight Change on Electrolysis	Corrected Weight Change
1) Pb-Na alloy in β -alumina Crucible (Anode)	- 0.0153 g	- 0.0151 g
2) Na_2SO_4 -I (A)	+ 0.0003 g	—
3) Na_2SO_4 -II (B)	- 0.0001 g	—
4) Na_2SO_4 -III (C)	+ 0.0002 g	—
5) Pb-Na Alloy in β -alumina Crucible (Cathode)	+ 0.0150 g	+ 0.0152 g

Charge passed = 63.17 coul.

 Na^+ equivalent = 0.01505 g O^{2-} equivalent = 0.00524 g S^{2-} equivalent = 0.0105 g SO_4^{2-} equivalent = 0.0314 g $t_{\text{Na}^+} = 1.01$

test gases are summarized in Table II. The reversibility of the emf was checked by passing small currents (5 μ A) through the cell in either direction for 2 minutes. It was found that the emf returned to the steady value before the titration in approximately 3 minutes. The emf was unaffected by 50 per cent change in the flow rate of the reference or test gas mixture.

Since Na₂SO₄-I is an ionic conductor in which Na⁺ ions are the mobile species, the emf developed across this material is given by,

$$E = \frac{1}{F} \int_{\mu'_{\text{Na}}}^{\mu''_{\text{Na}}} t_{\text{ion}} d\mu_{\text{Na}} \quad [12]$$

where E is the emf and μ'_{Na} and μ''_{Na} are the chemical potentials of sodium on each side of Na₂SO₄. Rewriting the chemical potential in terms of activities, one obtains,

$$E = \frac{RT}{F} \ln \frac{a''_{\text{Na}}}{a'_{\text{Na}}} \quad [13]$$

The activity of sodium at each electrolyte/electrode interface is fixed by the composition of the gas phase. For the reaction,

the equilibrium constant is given by,

$$K = a_{\text{Na}}^2 \cdot P_{\text{SO}_3} \cdot P_{\text{O}_2}^{1/2} \quad [15]$$

or

$$a_{\text{Na}} = K_{14}^{1/2} \cdot P_{\text{SO}_3}^{-1/2} \cdot P_{\text{O}_2}^{-1/4} \quad [16]$$

By combining Eq. [13] and [16], one obtains an expression,

$$E = \frac{RT}{2F} \ln \frac{P'_{\text{SO}_3} \cdot P'^{1/2}_{\text{O}_2}}{P''_{\text{SO}_3} \cdot P''^{1/2}_{\text{O}_2}} \quad [17]$$

that relates the emf to the ratio of the product of SO_3 pressure and square root of O_2 pressure on each side of the electrolyte. Eq. [17] is identical to that used by Salzano and Newman (3). The variation of the measured emf with the product of pressures, $(P_{\text{SO}_3} \cdot P_{\text{O}_2}^{1/2})$, in the test gas is shown in Figure 8 in comparison with that predicted by Eq. [17]. There is reasonable agreement ($\pm 3\text{mV}$) between theory and experiment, except when the concentration of one of the active gas species is below 10^{-3} vol. percent, as in the case of test gas 6. The experimental emf is then lower by 20 mV, probably due to polarization in the gas phase resulting from a small but finite electronic conductivity and consequent material transport across the electrolyte. Since the SO_3 concentration in the gas phase was calculated from the amounts of SO_2 and O_2 in the inlet gas on the basis of an equilibrium model, the close correspondence between theoretical and experimental emfs confirms the adequacy of platinum catalysts to ensure equilibrium in flowing gases containing SO_2 and O_2 . This result is in agreement with the findings of Gauthier et al (4), but differs from those obtained by Salzano and Newman (3) with

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Figure 8. Variation of the emf of the concentration cell [3] with gas composition.

molten sulfates.

The response of the cell to changes in gas composition is shown in Figure 9. Approximately 8 minutes are required for the emf to attain 98% of a step increase. About half this time is required to flush the reaction tube with a different test gas. For commercial application the response time can, therefore, be reduced by minimizing the volume of the test gas inside the probe.

Since the cell measures the product of two pressures, $(P_{SO_3} \cdot P_{O_2}^{1/2})$, the oxygen pressure must be independently measured, if absolute values for the partial pressure of SO_3 are required. For most general applications (i.e., SO_3/SO_2 determination in coal combustion reactors or emission control of nonferrous smelters using sulfide ores) a probe based on Na_2SO_4 -I must be coupled with an oxygen probe based on calcia-stabilized zirconia or yttria-doped thoria. An exception exists when the oxygen partial pressure of the test gas is the same as that of the reference gas. The emf is then simply related to the ratio of the partial pressures of SO_3 at the two electrodes, and the absolute value of the oxygen partial pressure is not required to compute the SO_3 concentration. This situation is encountered when the cell is used as a pollution monitor for SO_3/SO_2 in air, as discussed by Salzano and Newman (3).

An alternate formulation of the electrode reaction can be given as,

The activity of sodium is then related to the equilibrium constant for reaction [18] and the partial pressures of SO_2 and O_2 :

Figure 9. Typical emf response to changes in gas composition.

$$a_{\text{Na}} = K_{18}^{1/2} \cdot P_{\text{SO}_2}^{-1/2} \cdot P_{\text{O}_2}^{-1/2} \quad [19]$$

Combining Eq. [13] and [17] one obtains,

$$E = \frac{RT}{2F} \ln \frac{P_{\text{SO}_2}' \cdot P_{\text{O}_2}'}{P_{\text{SO}_2}'' \cdot P_{\text{O}_2}''} \quad [20]$$

Eq. [20] can also be derived from Eq. [17] by assuming equilibrium between SO_3 , SO_2 and O_2 species in the gas phase corresponding reaction [4]. With equilibrium gas mixtures both the Eq. [17] and [20] give identical emfs. The presence of platinum at the electrodes generally ensures equilibrium in the gas phase, at least in the region adjacent to the electrodes. However, at lower temperatures or high rates of flow of the gas mixture, non-equilibrium concentrations of gas species may be present. The emf developed with non-equilibrium gas mixtures will depend on the choice of electrode reaction. To determine the most significant electrode reaction, the test gas mixture 3 was flown at 600 m/min^{-1} through the cell, without the platinum catalysts in the path of the gas mixture. The flow rate of the reference gas had to be increased to 280 m/min^{-1} during this test at 973K to prevent differential cooling of the electrolyte/electrode interfaces. The platinum catalysts were maintained in the path of the reference gas. The emf generated was 35 mV lower than that obtained under equilibrium conditions, indicating that the concentration of SO_3 in the fast flowing test gas was below equilibrium levels and the reaction at the electrode is represented by [14]. If reaction [18] was more significant than [14], the measured emf under non-equilibrium conditions should have been higher than that obtained under equilibrium conditions

(i.e., low flow rate and in the presence of catalyst). It, therefore, appears that under non-equilibrium conditions the cell responds to SO_3 rather than SO_2 concentration in the gas phase. This finding is in general agreement with the observations of Salzano and Newman (3) for fused salt cells and Gauthier et al (4,5) for a cell using solid K_2SO_4 .

A cell based on Na_2SO_4 -I when coupled with a commercially available oxygen probe can, in principle, be used as a sulfur probe, provided equilibrium is established in the gas phase in the region adjacent to the electrodes. Under equilibrium conditions the following reaction can be formulated at the electrolyte interface:

The activity of sodium is then related to the sulfur and oxygen concentration in the gas:

$$a_{\text{Na}} = K_{21}^{1/2} \cdot P_{\text{S}_2}^{-1/4} \cdot P_{\text{O}_2}^{-1} \quad [22]$$

Combining Equations [13] and [22] one obtains,

$$E = \frac{RT}{4F} \ln \frac{P_{\text{S}_2}' \cdot P_{\text{O}_2}'^4}{P_{\text{S}_2}'' \cdot P_{\text{O}_2}''^4} \quad [23]$$

Eq. [23] forms the basis for the design of a sulfur probe. Continuous monitoring of the sulfur potential is important in coal gasification reactors for efficient gasifier operation and for accurate life prediction of corroding construction materials. A sulfur probe based on

Na_2SO_4 -I can be used for this purpose. Thermodynamic calculations based on available information (7, 12) suggest that Na_2SO_4 -I is stable under coal gasification environments. However, material compatibility tests and experiments to obtain proof of principle are required before commercial exploitation.

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