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S.D. Thompson
(M.S. Thesis)

September 1985

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Mass Transport in Sodium Polysulfide Melts

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M.S. Thesis

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September 1985
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Susan D. Thompson

Abstract

Mass transport plays an important role in the operation of the positive electrode in a sodium/sulfur cell. Diffusion of reactants and products to and from the electrode surface is especially important. The rate of diffusion in sodium polysulfide melts is the focus of this research. The method of restricted diffusion was used to determine differential diffusion coefficients as a function of melt composition and temperature.

The sodium polysulfide melt has been described by both microscopic and macroscopic models. The microscopic model considers the melt to be composed of sodium cations and seven different polysulfide anions, whereas the macroscopic model considers sodium cations, monosulfide anions, and neutral sulfur solvent. In this work, the macroscopic model of the melt is used. The transport equations of concentrated-solution theory are used to derive the governing equations for this binary-electrolyte melt model.

The method of restricted diffusion is inherently accurate, and each measured diffusion coefficient corresponds to a single, unique composition. The theory of restricted diffusion is presented for both dilute and concentrated solutions. The concentration profile relaxation is modeled for the dilute-solution case to show the effect of the shape of the initial profile. The effect of the position of the electrodes, which are used to monitor the concentration profile relaxation in the present high temperature work, is also
investigated.

Diffusion coefficients were measured as a function of melt composition (range: Na$_2$S$_3$ to Na$_2$S$_5$) and temperature (range: 300 to 350°C). The results are in good agreement with predictions based on the microscopic model and fall in the middle of the large range of results of other investigators ($2 \times 10^{-7}$ to $2 \times 10^{-5}$ cm$^2$/s). The following expression summarizes the experimental data:

$$D = 0.0153 \exp(-5.89 \times 10^3/T) \exp(5.30 \chi_a) \text{ cm}^2/\text{s}. \quad (A-1)$$

This correlation agrees with all but one data point within 6.7%; the largest variation is 17.5%.

Values of the diffusion coefficients based on a thermodynamic driving force, and of the binary interaction coefficients, are calculated from the experimental diffusion coefficients.
To my father
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Chapter 1. The Sodium/Sulfur System

1.1. Introduction

The sodium/sulfur secondary cell is probably the closest to commercial viability of all the molten-salt, high-temperature systems. It is one of the leading candidate batteries for both electric vehicle and load leveling applications. The specific-energy goal for the year 2000 is 130 Wh/kg, more than twice the capability of the near term lead/acid and nickel/iron systems. A specific energy of 160 Wh/kg is conceivable for load leveling applications.¹

The sodium/sulfur system has been under serious development for over ten years in the United States. The major technical problems concern safety, durability of the electrolyte and seals, and corrosion of the container materials. However, diffusion of reactants and products to and from the electrode surface plays a critical role in the operation of the sulfur electrode. Knowledge of the transport parameters of sodium polysulfides is necessary for accurate design and scale up of the sodium/sulfur battery.

The design and operation of the sodium/sulfur cell will be discussed in this chapter. This background information is being presented so that the reader can better understand the role of transport processes in the sodium/sulfur system.

1.2. Cell Designs

The sodium/sulfur cell consists of a sodium negative electrode and a sulfur positive electrode separated by a solid electrolyte. Both electrodes are molten since the cell typically operates between 300 and 375°C. There are several cell designs presently being developed; however, the primary difference between the various cell designs is the type of electrolyte. The Dow
Chemical cell uses a glass electrolyte, whereas Ford, and some foreign companies, are developing cells with ceramic electrolytes.

In the Dow Chemical cell, a borate glass is used as the electrolyte. The glass is drawn into hollow fibers, typically 70 µm id, 90 µm od, and 10 cm long, which are then bundled together with alternating layers of aluminum foil. The glass tubes are sealed on the bottom, filled with sodium, and then immersed in a sulfur reservoir. The open tube ends, which extend above the sulfur reservoir, communicate through a "tubesheet" with a common sodium reservoir. The aluminum foil acts as a current collector for the sulfur electrode. Levine\(^2\) provides a good discussion of the design and performance of sodium/sulfur cells with glass electrolytes.

The majority of the sodium/sulfur cell designs use a \(\beta\)-alumina \((Na_2O\cdot11Al_2O_3)\) ceramic electrolyte. Both \(\beta\) - and \(\beta'\)-alumina have been tested, with the latter providing a higher conductivity. The ceramic cells have only a single electrolyte tube of diameter 1 to 5 cm, and a wall thickness of 1.5 to 2 mm, since the \(\beta\)-alumina conductivity is much higher than that of the borate glass.\(^3\) This design requires that a graphite mat be used as the current collector in the sulfur electrode. A comprehensive review of sodium/sulfur cells using \(\beta\)-alumina electrolyte was recently completed by Sudworth and Tilley.\(^4\)

### 1.3. Phase Diagram

During discharge of the sodium/sulfur cell, sodium is oxidized at the negative electrode

\[
Na - Na^+ + e^-.
\]

(1-1)

and the sodium ions pass through the solid electrolyte into the sulfur electrode forming sodium polysulfides

\[
2Na^+ + xS + 2e^- \rightarrow Na_2S_x.
\]

(1-2)

The polysulfide composition in the sulfur electrode ranges between pure S
and \( \text{Na}_2\text{S}_3 \), depending on the state of charge. This range corresponds to 100 to 60 atom\% S on the sodium/sulfur phase diagram shown in figure 1–1. Tracing the discharge of a sodium/sulfur cell at 300°C on the phase diagram, we see that initially sodium and sulfur combine to form a single phase with a composition of nearly pure sulfur. The size of this single-phase region is exaggerated on the diagram; in reality it does not extend past 99\% S. When the cell is discharged further, a second liquid phase with a composition around \( \text{Na}_2\text{S}_{5.2} \) appears. Until the overall polysulfide melt composition reaches \( \text{Na}_2\text{S}_{5.2} \), these two liquid phases are present. The relative amount of the nearly pure sulfur phase and the \( \text{Na}_2\text{S}_{5.2} \) phase can be found using the lever rule. If the sulfur content of the positive electrode drops below 72.2 atom\%, corresponding to a cell which is 60\% discharged, the polysulfide becomes a single phase. The composition of this phase varies directly with the overall melt composition. Sodium-sulfur cells are considered fully discharged around 60 atom\% S, since a solid \( \text{Na}_2\text{S}_2 \) phase starts to form at 58.5 atom\% S. At polysulfide compositions at or below \( \text{Na}_2\text{S}_{2} \), the two solid phases \( \text{Na}_2\text{S} \) and \( \text{Na}_2\text{S}_2 \) coexist. The second single-phase region, between the approximate overall melt compositions \( \text{Na}_2\text{S}_3 \) and \( \text{Na}_2\text{S}_{5.2} \), is the focus of the present diffusion research.

1.4. Operation of the Sulfur Electrode

In order to appreciate the importance of transport processes in the sodium/sulfur cell, it is necessary to understand the processes which occur in the sulfur electrode during discharge. In a β-alumina cell, the sulfur electrode is bounded on one side by a solid electrolyte, and on the other side by an electronically conducting casing. The electrode is filled with an electronically conducting graphite matrix, at the surface of which the electrochemical reaction occurs. Initially the electrode is filled with sulfur, which has a very high resistivity. Consequently, the initial reduction of sulfur
Figure 1-1. Sodium-sulfur phase diagram according to Gupta and Tischer.⁵
5S + 2e\(^-\) → S\(_5^e\) (1-3)

can occur only at the carbon/electrolyte boundary. Once sodium pentasulfide, which is a good electrolyte, is formed, the reaction area is increased. Sulfur can then be reduced anywhere on the carbon matrix where there is an ionically conducting path of sodium polysulfide to the solid electrolyte. At this carbon-Na\(_2\)S\(_5\)-sulfur boundary, the reaction rate is limited by the transport rate of sodium ions through the melt. In addition, the sodium pentasulfide can be further reduced to lower polysulfides:

\[ xS_5^e + (10-2x)e^- \rightarrow 5S_x^e. \] (1-4)

As the reaction front moves away from the solid electrolyte, the reduction of pentasulfide, which is known to be diffusion controlled, becomes the dominant reaction.

1.5. Open-Circuit Cell Potential

The open-circuit potential of the sodium/sulfur cell is a function of the polysulfide composition in the sulfur electrode. If we think of the sulfur electrode as consisting of sodium sulfide electrolyte in neutral sulfur solvent, the polysulfide composition can be represented in terms of the mole fraction of Na\(_2\)S electrolyte (\(x_e\)). Using this notation, we can trace the equilibrium discharge of the cell at 360°C on the open-circuit potential diagram shown in figure 1-2. Initially, the potential drops very rapidly corresponding to the region of the nearly pure sulfur phase. When the Na\(_2\)S\(_5\)-sulfur phase starts to form, the existence of two phases forces the potential to level out and become independent of the state of charge of the sodium/sulfur cell. The potential in this two-phase region is approximately 2.1 V, although it varies slightly with temperature. When the overall polysulfide composition reaches Na\(_2\)S\(_{3.2}\), the melt again becomes a single phase, and the potential drops nearly linearly with the mole fraction of sulfur in the melt. At 360°C, the cell can be discharged up to 57.5 mole% S (\(x_e = 0.370\)), before the solid Na\(_2\)S\(_2\) phase
Figure 1-2. Cell potential versus sulfur electrode melt composition for an equilibrium cell discharge. Melt composition is defined by the mole fraction of sodium sulfide $x_e$. 
begins to form. If the cell could be discharged into this region, the existence of two phases would again force the potential to become independent of the state of charge. The cell potential in this region would be about 1.75 V.
Chapter 2. Macroscopic and Microscopic Models of the Sodium Polysulfide Melt

2.1. Introduction

The macroscopic model, emphasized in this thesis, considers the polysulfide melt as sodium cations and monovalent sulfur anions in neutral sulfur solvent. In contrast, the microscopic model developed by Tegman\(^7\) represents the melt as sodium cations and seven different polysulfide anions. This latter approach is in agreement with the work of Cleaver and Davies\(^8\) which indicates that no neutral sulfur is present in the melt.

Risch\(^9\) used the microscopic melt model to predict diffusion coefficients for sodium polysulfides in the single-phase composition region between Na\(_2\)S\(_3\) and Na\(_2\)S\(_5\). Later in this chapter, we will discuss the microscopic model in more detail, and show how it can be used to predict diffusion rates in sodium polysulfides. First, however, we will discuss mass transport in concentrated solutions, and develop binary-electrolyte flux expressions which are consistent with the macroscopic model.

2.2. Mass Transport in Concentrated Solutions

Concentrated solution theory was developed by Newman, Bennion, and Tobias,\(^10\) and has been more recently discussed by Newman.\(^11\) The multicomponent diffusion equations provided by concentrated solution theory will be used to obtain flux expressions for the case of a binary electrolyte. These expressions will be used in chapter 4, to solve the restricted-diffusion problem. In section 3 of this chapter, we will discuss how similar expressions could be solved for a multicomponent system, and used in conjunction with species concentrations calculated from the microscopic model, to determine
binary diffusion coefficients for the sodium/sulfur system.

2.2.1. Transport Equations

The multicomponent diffusion equation:

$$c_i \nabla \mu_i = \sum_j K_{ij} (\mathbf{v}_j - \mathbf{v}_i) = RT \sum_j \frac{c_i c_j}{c_i \beta_{ij}} (\mathbf{v}_j - \mathbf{v}_i).$$

(2-1)

is general and can be used for either dilute or concentrated solutions, although it is limited to isothermal, isobaric systems. The $K_{ij}$'s are friction coefficients, $\mu_i$ is the electrochemical potential of species $i$, the $\beta_{ij}$'s are transport properties defined by this equation, and $\mathbf{v}_i$ is the velocity of species $i$ as compared to some reference velocity. The total concentration is

$$c_T = \sum_i c_i,$$

(2-2)

where the sum includes the solvent. Equation 2-1 can be regarded as a force balance, where the term $-c_i \nabla \mu_i$ is the driving force for movement per unit volume acting on species $i$, and $\sum_j K_{ij} (\mathbf{v}_j - \mathbf{v}_i)$ is the sum of the opposing frictional forces exerted on species $i$ by the other species in solution. The $K_{ij}$ drag coefficients are dependent on temperature, pressure, and composition, and are related to the $\beta_{ij}$ binary interaction coefficients by the following expression:

$$K_{ij} = RT \frac{c_i c_j}{c_i \beta_{ij}}.$$  

(2-3)

Newton's third law of motion requires that $\beta_{ij} = \beta_{ji}$. Therefore equation 2-1 defines $\frac{1}{2} n(n-1)$ binary interaction coefficients where $n$ is the number of species present. The $\beta_{ii}$ are not defined.

2.2.2. Macroscopic Model Flux Expressions

To obtain explicit expressions for the solvent and electrolyte fluxes, the velocities must be expressed relative to some reference velocity. Then equation 2-1, together with a species conservation equation, can be inverted. The
three most common choices for the reference velocity are the solvent velocity, the mass average velocity, and the molar average velocity. The solvent reference velocity will be used for the present problem; however, the expressions for the fluxes, transference numbers, and the diffusion coefficient with respect to each of the reference velocities, have been previously derived.\cite{12,13}

Equations 2-4 through 2-6 are the flux expressions, based on a solvent reference velocity, for a binary electrolytic solution:

\[
N_+ = c_r v_r = -\frac{\nu c_T/c_0}{\nu RT} \partial c \frac{\nabla \mu_e}{F^2} + c_r v_0, \quad (2-4)
\]

\[
N_- = c_r v_r = -\frac{\nu c_T/c_0}{\nu RT} \partial c \frac{\nabla \mu_e}{F^2} + c_r v_0, \quad (2-5)
\]

\[
N_0 = c_0 v_0, \quad (2-6)
\]

where \(\mu_e\) is the electrochemical potential of the electrolyte, \(\nu\) is a stoichiometric coefficient, \(c_T\) is the total solution concentration, and \(i\) is the current density:

\[
\mu_e = \nu_+ \mu_+ + \nu_- \mu_-, \quad (2-7)
\]

\[
\nu = \nu_+ + \nu_-, \quad (2-8)
\]

\[
i = \sum_i c_i z_i v_i. \quad (2-9)
\]

The corresponding diffusion coefficient, transference numbers, and conductivity are defined in terms of the multicomponent transport properties in the following three equations:

\[
\mathcal{D} = \frac{D_+ D_- (z_+-z_-)}{z_+ D_+ - z_- D_-}, \quad (2-10)
\]

\[
t_+^0 = \frac{z_+ D_+}{z_+ D_+ - z_- D_-}, \quad (2-11)
\]

\[
\kappa = \frac{-RT}{c_T z_+ z_- F^2} \left( \frac{1}{D_+} + \frac{c_0 t_+^0}{c_r D_0} \right). \quad (2-12)
\]

In the absence of current, an electrolyte flux expression can be obtained by dividing the present ion flux expressions by the appropriate stoichiometric coefficients:
\[ N_+ \frac{\partial N_+}{\partial y} = N_- \frac{\partial N_-}{\partial y} = -\frac{c_T}{c_0} \sum c \frac{\partial \mu_\ast}{\partial c} + c \nu_0. \] (2-13)

The flux expression for the solvent remains the same. At constant temperature and pressure, the gradient of the electrochemical potential of the electrolyte can be defined as follows:

\[ \nabla \mu_\ast = \nu RT \ln (m \gamma_s), \] (2-14)

where \( \gamma_s \) is the mean molal activity coefficient and \( m \) is the molality. The diffusion coefficient based on a gradient of electrochemical potential can be related to the more common diffusion coefficient based on a concentration driving force by the following expression:

\[ D = \sum c_T r (1 + \frac{d \ln \gamma_s}{d \ln m}). \] (2-15)

This relationship can also be expressed in terms of the mean activity coefficient on a concentration basis (\( y \)):

\[ D = \sum c_T V_0 (1 + \frac{d \ln y}{d \ln c}), \] (2-16)

or in terms of the activity of sulfur (\( a_s \)):

\[ D = \sum c_T \frac{1}{c_0 \nu} \frac{d \ln a_s}{d \ln x_s}, \] (2-17)

where \( x_s \) is the mole fraction of sulfur. At infinite dilution the two diffusion coefficients \( D \) and \( \sum \) are equivalent.

2.3. Microscopic Model

2.3.1. Introduction

In Tegman's model, the polysulfide melt consists of sodium cations and polysulfide anions. However, the microscopic composition of sodium polysulfides has not been conclusively determined, therefore the melt species had to be assumed. The sulfide ions which may exist in the melt can be represented as \( \text{S}_i^\omega \), where \( i \) ranges between 1 and \( \omega \). The microscopic melt model considers all of these sulfide ions except \( \text{S}_\omega^\omega \). This particular ion was
only required in very small amounts when the model was used to fit thermodynamic data, and therefore it was excluded from further model predictions.

The microscopic melt model predicts the equilibrium composition of a polysulfide melt by considering the reactions between the polysulfide ions and diatomic sulfur vapor. The reactions are of the form

\[
\frac{i-1}{2} S_2(g) + S^a = S^e_i;
\]  

(2-18)

therefore, the equilibrium polysulfide ion concentrations \(c_i\) are related to the vapor pressure of ideal diatomic sulfur, and the concentration of \(S^e\), by the expression

\[
c_i = K_i c_i P_{S_2}^{\frac{i-1}{2}}. \tag{2-19}
\]

It should be mentioned that this analysis assumes an ideal solution, and therefore species concentrations have been used in the equilibrium expression. The equilibrium constants \(K_i\)’s can be expressed in terms of changes in enthalpy and entropy:

\[
\Delta G_i^0 = -RT \ln K_i = \Delta H_i^0 - T \Delta S_i^0, \tag{2-20}
\]

assuming that the \(\Delta H_i^0\) and \(\Delta S_i^0\) terms are independent of temperature. A polysulfide melt with \(N-1\) polysulfide species, species \(N\) being sodium, requires \(N-2\) enthalpy and \(N-2\) entropy terms.

An expression relating the overall melt composition \(x_a\) to the equilibrium vapor pressure of sulfur:

\[
x_a = \frac{\sum_{i=2}^{N-1} K_i p_{S_2}^{\frac{i-1}{2}}}{1 + \sum_{i=2}^{N-1} i K_i p_{S_2}^{\frac{i-1}{2}}}. \tag{2-21}
\]

was derived from material balances over all components, and on sulfur alone. For any given overall melt composition, the equilibrium vapor pressure of diatomic sulfur can be determined from this expression. The individual polysulfide ion concentrations can not be calculated directly using equation
2-19 since the concentration of $S^n$, ($c_1$), is not known. However, the species concentrations can be calculated as the particle fraction of sulfide ions. The particle fraction of species $i$ is defined as

$$ n_i = \frac{c_i}{\sum_{i=1}^{N-1} c_i} \quad (2-22) $$

Therefore the particle fraction of the species $S_2^n$ can be represented as

$$ n_i = \frac{K_i ps_2^{(\frac{i-1}{2})}}{1 + \sum_{i=2}^{N-1} K_i ps_2^{(\frac{i-1}{2})}} \quad (2-23) $$

Finally, the ionic concentrations can be determined from the particle fractions using the expressions

$$ c_N = c_{Na^+} = c_+ = \nu_+ c $$ \quad (2-24)$$

and

$$ c_i = c_{S_2^n} = n_i c_+ = n_i \nu_+ c $$ \quad (2-25)$$

Besides predicting the distribution of polysulfide ions in a melt as a function of overall melt composition and temperature, the microscopic model has been used to calculate both the open-circuit potential of sodium/sulfur cells with either single-phase or two-phase sulfur electrodes, and the diffusion coefficients in sodium polysulfide melts as a function of temperature and composition.

### 2.3.2. Prediction of Diffusion Coefficients

The microscopic melt model can be used to predict the thermodynamic factor in equation 2-15. Determination of this factor is a necessary precursor to the prediction of concentration based diffusion coefficients. The chemical potential of sodium sulfide can be represented as

$$ \mu_s = \mu_s^0 + \nu RT \ln (\gamma_m) = \mu_{Na^+S}^0 + RT \ln n_1 \quad (2-26) $$

where the new expression on the right is derived from the microscopic model.
Using the definition of molality:

\[ m = \frac{1}{M_S} \frac{x_a}{(1-x_a)}, \quad (2-27) \]
equation 2-26 can be differentiated with respect to the mole fraction of sodium sulfide to obtain the expression

\[ 1 + \frac{d \ln y_a}{d \ln m} = \frac{x_a(1-x_a)}{\nu n_1} \frac{d n_1}{d x_a}. \quad (2-28) \]

Using the chain rule, the derivative of the particle fraction of \( S^a \), with respect to the mole fraction of sodium sulfide, can be expressed as

\[ \frac{d n_1}{d x_a} = \frac{d n_1}{d p_{S^2}} \frac{d p_{S^2}}{d x_a}. \quad (2-29) \]

Using equations 2-23 and 2-21 to evaluate the derivative of the particle fraction of \( S^a \) with respect to the vapor pressure of ideal diatomic sulfur, and the derivative of the vapor pressure of ideal diatomic sulfur with respect to the mole fraction of sodium sulfide, respectively, we obtain a microscopic expression for the factor relating the thermodynamic diffusion coefficient to the one based on a concentration driving force:

\[ 1 + \frac{d \ln y_a}{d \ln m} = \frac{(1-x_a)}{\nu} \frac{1}{x_a \sum_{i=2}^{N-1} K_i (i-1) p_{S^2}^{i-2} - 1} \quad (2-30) \]

Values of this thermodynamic factor at 300 and 360°C have been plotted as a function of overall melt composition, and compared to experimental data, in figures 2-1 and 2-2 respectively. The microscopic model predicts considerably larger variations of the thermodynamic factor with composition and temperature than the experimental data suggest. Unfortunately, these errors will be carried through to the estimation of \( D \).

The final step in predicting the concentration based diffusion coefficient is to evaluate the thermodynamic diffusion coefficient \( B \), which is a function of the \( \mathcal{Y}_j \) transport properties. Considering \( N-1 \) species in the polysulfide
Figure 2-1. Predicted values of the thermodynamic activity coefficient factor versus melt composition at 573.15 K. Solid line is calculated from the microscopic model. Dashed curves are obtained from experimental data.
Figure 2-2. Predicted values of the thermodynamic activity coefficient factor versus melt composition at 633.15 K. Solid line is calculated from the microscopic model. Dashed curve is obtained from experimental data.
melt, there are N-1 independent diffusion equations of the form of equation 2-1. In a similar manner as the flux expressions were obtained for a binary system, these equations can be inverted numerically to obtain flux expressions for the multicomponent melt. The resulting flux expressions are functions of the gradients of electrochemical potential, current density, and the choice of reference velocity.

Risch assumed the following form for the $\mathcal{D}_{ij}$ transport parameters:

$$\mu \mathcal{D}_{ij} = \epsilon_1 \frac{1}{(r_i + r_j)^3} \quad \text{for } i,j \neq N, \quad (2-31)$$

and

$$\mu \mathcal{D}_{iN} = \epsilon_2 \frac{1}{(r_i + r_N)^3} \quad \text{for } i \neq N, \quad (2-32)$$

where the parameters $\epsilon_1$ and $\epsilon_2$ are independent of melt composition, although they are functions of temperature and pressure. The ionic radii ($r_i$) are defined as

$$r_i = \left[ \frac{\bar{V}_i}{\frac{3}{N_A} \frac{4}{3}} \right]^{\frac{1}{3}}, \quad (2-33)$$

where $N_A$ represents Avagadro's number, and the partial molar volumes are derived from density data. Published viscosity data were fit with a continuous interpolation so that it could be used for all melt compositions in equations 2-31 and 2-32.

To determine values for $\epsilon_1$ and $\epsilon_2$, the $\mathcal{D}_{ij}$ transport properties were related to transport parameters for which experimental data are available. By equating flux expressions for sodium ions and sulfur from the microscopic model, to those obtained from the binary electrolyte representation, Risch obtained expressions for $\mathcal{D}$, melt conductivity, and transference numbers, in terms of the $\mathcal{D}_{ij}$ parameters. Fitting the conductivity and transference number expressions to actual data resulted in values for $\epsilon_1$ and $\epsilon_2$ as a function of temperature. The original fitting resulted in values which were also
composition dependent. However, average values were chosen which fit the data reasonably well across the entire composition region of interest. The results are summarized in table 2-1.

Table 2-1. Fitted $e_1$ and $e_2$ Parameter Values

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$e_1/\mu x 10^{28}$ cm$^2$/s</th>
<th>$e_2/\mu x 10^{28}$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>573.15</td>
<td>5.12</td>
<td>2.21</td>
</tr>
<tr>
<td>633.15</td>
<td>6.32</td>
<td>4.68</td>
</tr>
</tbody>
</table>

Although the model reproduces the approximate range of the conductivity and transference data reasonably well, it predicts a greater dependence on the overall melt composition than was experimentally observed. This is the same result as was found for the thermodynamic factor discussed previously. The $D$ values which were calculated at 300 and 360°C using these parameter values are plotted in figure 2-3. Finally, the corresponding $D$ values can be calculated, using the microscopic model predictions for the thermodynamic factor. The results are plotted in figure 2-4.

In an attempt to assess the effect of the poor model prediction of the thermodynamic factor on the resulting diffusion coefficients, a better prediction of $D$ will be obtained by using the values of the thermodynamic factor calculated from experimental open-circuit potential data for a sodium/sulfur cell. Going back to equation 2-26, and differentiating the left two terms of the equation with respect to the mole fraction of sodium sulfide we obtain the following expression:

$$1 + \frac{d\ln y_s}{d\ln m} = \frac{x_o(1-x_o) d\mu}{\nuRT dx_o}$$

(2-34)

With the Gibbs-Duhem equation:

$$x_o d\mu_o + x_3 d\mu_3 = 0,$$

(2-35)

equation 2-34 can be rewritten as
Figure 2-3. Predicted values of the diffusion coefficient for a thermodynamic driving force versus melt composition. Solid lines are for variable values of $\epsilon_1$ and $\epsilon_2$ which fit the conductivity and transference data at all compositions. Dashed line is for constant values of $\epsilon_1/\mu$ and $\epsilon_2/\mu$. 
Figure 2-4. Predicted values for the concentration based diffusion coefficient from the microscopic model.
The definition of the chemical potential of sulfur can be written in terms of the activity of sulfur:

\[ \mu_S = \mu_S^0 + RT \ln \alpha_S. \]  

(2-37)

Upon substitution we obtain

\[ 1 + \frac{d \ln \gamma}{d \ln \alpha} = -\frac{(1-x)_S}{\nu RT} \frac{d \ln \alpha_S}{dx}. \]

(2-38)

The activity of sulfur can be related to the potential of a sodium/sulfur cell:

\[ C | Na(l) || Na_2S_x(l) | C, \]  

as derived in appendix A. The final expression relating the thermodynamic factor to the sodium/sulfur cell potential is

\[ 1 + \frac{d \ln \gamma}{d \ln \alpha} = -\frac{2Fx(1-x)_S}{\nu RT} \frac{d U}{dx}. \]

(2-39)

Cleaver and Davies\(^9\) have measured this cell potential at two temperatures. Their data at 300 and 360°C are plotted in figures 2-5 and 2-6 respectively. The data can be approximated quite accurately using linear correlations:

at 300°C, \( U = 2.084 + 1.9728(0.193-x)_S. \)

(2-40)

and

at 360°C, \( U = 2.072 + 2.0299(0.1936-x)_S. \)

(2-41)

Substitution of these correlations into equation 2-39 results in values for the thermodynamic coefficient as a function of composition, at the two temperatures 300 and 360°C.

The experimental thermodynamic factors shown in figures 2-1 and 2-2 were calculated from equation 2-39 by Risch, using the open-circuit potential data of Gupta and Tischer, and Cleaver and Davies. Equations 2-40 and 2-41 are slightly different than the correlations Risch used to represent Cleaver and Davies's data. The resulting difference in the calculated thermodynamic
Figure 2-5. Sodium-sulfur cell potential versus sulfur electrode melt composition at 573.15 K. Comparison of experimental data and linear approximation.
Figure 2-6. Sodium-sulfur cell potential versus sulfur electrode melt composition at 633.15 K. Comparison of experimental data and linear approximation.
coefficients is shown in figure 2-7. The difference is small, and the thermodynamic coefficients calculated using equations 2-40 and 2-41 were used in the calculation of modified diffusion coefficients from Risch's $\Phi$ values. The results, plotted in figure 2-8, do not differ greatly from Risch's original predictions, which were based on thermodynamic coefficients calculated from equation 2-30. The modified diffusion coefficients vary more strongly with temperature and melt composition than the original predictions. The calculated activation energies are 30.6 and 27.8 kJ/mol for the modified and original predictions, respectively.
Figure 2-7. Predicted values of the thermodynamic activity coefficient factor versus melt composition at 573.15 K. Solid line is calculated using the linear approximation of Cleaver and Davies's data given in equation 2-40. Dashed curves were obtained from experimental data by Risch.
Figure 2-8. Comparison of predicted values for the concentration based diffusion coefficient from the microscopic model. Solid line uses values for the thermodynamic coefficient predicted from experimental data. Dashed line uses thermodynamic coefficients predicted from the microscopic model.
Chapter 3. Review of the Diffusion Coefficients Available for Sodium Polysulfides from Experimental Results

The diffusion data presently available for sodium polysulfides are rather limited. The diffusion coefficients which are available have been obtained using a variety of experimental methods, many of which are difficult to apply accurately to sodium polysulfides. Consequently the data of different investigators differ by as much as two orders of magnitude. In the following two sections, the various methods which can be used to measure diffusion coefficients will be briefly discussed, and the published diffusion data will be compared to one another and to the predictions of Tegman's model.

3.1. The Measurement of Diffusion Coefficients

Many experimental methods have been used to determine diffusion coefficients in concentrated solutions: self-diffusion in a capillary tube, optical methods,\textsuperscript{14} rotating-disk measurements,\textsuperscript{15} and restricted diffusion.\textsuperscript{14,16,17} The different methods will be briefly discussed, in order to understand the difficulties of applying each method to the sodium/sulfur system.

3.1.1. Capillary-Tube Method

The capillary-tube method has been used extensively to determine self- and tracer-diffusion coefficients of electrolytes, although it is strictly valid only for dilute solutions. A capillary tube of known length ($a$) is filled with a radioactively tagged solution. The tube is then immersed in a larger, stirred vessel. To measure self-diffusion strictly, the untagged solution in the larger vessel should be the same concentration as the tagged solution in the capillary. However, a solution of a different concentration is commonly placed in the larger vessel. After some time $t$, the tagged material inside the tube is
measured and compared to the initial amount. This measurement, and the cell height are all that is needed to determine the diffusion coefficient.

The governing equation for this problem is Fick's second law in one dimension:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2},
\]  

(3-1)

where \( y \) is the distance from the bottom of the capillary tube, and \( c \) is the concentration of the tagged species. The boundary conditions are as follows

at \( t=0 \), \( c = c_0 \) for \( 0 < y < a \)  
\( c = 0 \) for \( y > a \),  
\( \frac{\partial c}{\partial y} = 0 \) at \( y = 0 \),  
and at \( t > 0 \), \( c = 0 \) at \( y = a \)  
\( \frac{\partial c}{\partial y} = 0 \) at \( y = 0 \),

(3-2)  
(3-3)

where \( c_0 \) is the initial concentration of the tagged species inside the tube.

The solution to this problem is the series

\[
c = \sum_{n=0}^{\infty} B_n \exp\left[ -\frac{\pi^2(2n+1)^2Dt}{4a^2} \right] \cos \frac{\pi(2n+1)y}{2a}
\]  

(3-4)

where

\[
B_n = (-1)^n \frac{4c_0}{\pi(2n+1)}.
\]  

(3-5)

The average concentration in the tube at time \( t \) is

\[
c_{av} = \frac{1}{a} \int_0^a c \, dy
\]  

(3-6)

or more explicitly

\[
\frac{c_{av}}{c_0} = \sum_{n=0}^{\infty} \frac{8}{\pi^2(2n+1)^2} \exp\left[ -\frac{\pi^2(2n+1)^2Dt}{4a^2} \right].
\]  

(3-7)

Knowing \( c_{av} \), \( D \) can be determined from a prepared graph of the right side of equation 3-7 versus \( Dt/a^2 \).

Unfortunately serious errors, up to 10%, have been found to occur from improper stirring. If turbulent flow occurs near the open end of the capillary, the transport process is enhanced by a "scooping out" of tagged solution from
the tube. Insufficient stirring can also be a problem, because the boundary condition of \( c = 0 \) for \( y > a \) will not be maintained.

3.1.2. Optical Methods

The optical methods are also based on a solution of Fick’s second law. This procedure uses an effectively infinite column of liquid with a sharp concentration boundary in the middle. Therefore, the boundary conditions are that a constant concentration is maintained at both ends of the column. The concentration changes with time are monitored by measuring the gradient of the index of refraction as a function of time. The diffusion coefficient is usually considered to be a constant in this method, therefore the initial concentration difference must be minimized. This technique has been applied with considerable accuracy to concentrated solutions. However it can not be applied to the sodium/sulfur system since the polysulfides are nearly opaque.

3.1.3. Rotating-Disk Measurements

Diffusion coefficients can be determined from limiting-current, chronopotentiometric, or alternating-current measurements on a rotating-disk electrode. However, a diffusion coefficient measured at a rotating-disk electrode is a weighted average value, since the transport properties vary across the diffusion layer. This type of diffusion coefficient is referred to as an integral diffusion coefficient, and can only be strictly applied to systems with similar hydrodynamic conditions.

The rotating-disk system has been used to determine diffusion coefficients in sodium polysulfide melts; however, there are problems which arise when large potentials are applied to the electrode. Polarizing the polysulfide to high anodic potentials causes a second phase of nearly pure sulfur to form near the electrode. The effect of this second phase on the
hydrodynamics of the system is not well understood. Alternatively, at high cathodic potentials a sodium disulfide film forms on the electrode surface.

Both of these effects have been reported by Armstrong et al.\textsuperscript{19} and South et al.\textsuperscript{20} Armstrong et al. used a rotating vitreous carbon disk electrode to study steady-state current-voltage curves in molten polysulfides at 305-350°C. They reported that the electrode reaction is a diffusion controlled redox process near the equilibrium potential of the melt. At higher cathodic potentials, the current reaches a plateau and becomes diffusion limited. At the onset of the cathodic limiting current, they also observe the formation of a film on the electrode. On the other hand, Divisek et al.\textsuperscript{21} do not report sodium disulfide film formation during their cathodic chronopotentiometric diffusion measurements. They observe rotating disk electrode currents which vary linearly with the square root of rotation speed, and therefore suggest that system is diffusion controlled. In addition, Tischer and Ludwig\textsuperscript{22} claim that the precipitation effects of sodium disulfide are small and should not have a significant effect on the results. In their linear sweep studies, they found that most of the film formation in Na\textsubscript{2}S\textsubscript{4} occurs immediately after the cathodic diffusion peak, and that no film formation occurs during the cathodic peak of the second cycle in Na\textsubscript{2}S\textsubscript{5.2}. These results were based on cell resistance measurements. For example, in Na\textsubscript{2}S\textsubscript{4} the resistance at the current peak was only slightly higher than at the rest potential; however it increased sharply after the current peak.

3.1.4. Restricted Diffusion

Restricted diffusion refers to stagnant diffusion in a closed cell of finite height. The differential diffusion coefficient measured using this method, corresponds to a single, unique composition. It is determined by measuring the rate of decay of an initial concentration profile in the diffusion cell. The
method used to monitor the concentration profile decay varies with the system under investigation. This method has been previously applied to both dilute and concentrated solutions, and now it will be used to measure diffusion coefficients in sodium polysulfides. The theory of restricted diffusion is discussed in the next chapter.

3.2. A Survey of the Experimental Diffusion Data Available

Tischer and Ludwig\textsuperscript{22} combined experimental data of several investigators to determine a few diffusion coefficients which are internally self consistent. Rotating-disk data have the functional form $cD^{2/3}$, where $c$ is the concentration of the diffusing species involved in the electrode reaction. However, the concentration of the individual ions in the melt can not be measured; therefore the rotating-disk data were combined with chronopotentiometric data of the form $cD^{1/2}$. Ludwig combined the rotating-disk data of Armstrong, Dickenson, and Reid\textsuperscript{19} with the stationary electrode chronopotentiometric data of South \textit{et al.}\textsuperscript{20} to obtain diffusion coefficients for Na$_2$S$_5$ of 2.4 x 10$^{-7}$ cm$^2$/s at 300°C, and 6.3 x 10$^{-7}$ cm$^2$/s at 350°C. The activation energy obtained from these results, 13.7 kcal/mole, is larger than the value of 11.2 kcal/mole obtained from viscosity data. Tischer and Ludwig also combine linear sweep and chronopotentiometric data at 350°C of South \textit{et al.} with their own linear sweep and rotating-disk data at 300°C to obtain a value of $D = 2 \times 10^{-7}$ cm$^2$/s for Na$_2$S$_4$ at 300°C.

Divisek \textit{et al.}\textsuperscript{21} determined diffusion coefficients for sodium polysulfides using chronopotentiometry at a rotating-disk electrode. To prevent sodium disulfide film formation during the cathodic polarizations, a transient pulsing technique was used. This method requires no knowledge of the concentration of the electroactive species and no assumptions regarding the reactions at the electrode surface. The results obtained from cathodic limiting-current
measurements are listed in table 3-1. The activation energy calculated from these results is approximately 12 kcal/mole.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$D \times 10^6$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.7</td>
</tr>
<tr>
<td>320</td>
<td>1.0</td>
</tr>
<tr>
<td>330</td>
<td>1.2</td>
</tr>
<tr>
<td>340</td>
<td>1.4</td>
</tr>
<tr>
<td>350</td>
<td>1.6</td>
</tr>
<tr>
<td>370</td>
<td>2.1</td>
</tr>
</tbody>
</table>

These results are in reasonable agreement with those of Ludwig and Tischer. Divisek et al. also determined, by the stirred-capillary method, self-diffusion coefficients for sulfur in Na$_2$S$_4$ and Na$_2$S$_{5.2}$, using labeled S-35 as a tracer. The results at 300°C were $D = 2.3 \times 10^{-5}$ cm$^2$/s for Na$_2$S$_4$ and $1.5 \times 10^{-5}$ cm$^2$/s for Na$_2$S$_{5.2}$. They propose that the order of magnitude difference between their two sets of results is due to different transport mechanisms. The diffusing species in the two cases are different; a sulfide ion, and simultaneously a sodium ion, are diffusing in the first case, whereas an uncharged sulfur species is moving in the second case. They suggest that the transport of sulfur takes place by a rapid exchange of sulfur between the polysulfide ions. The sulfur essentially "hops" from one polysulfide molecule to the next, without being part of any one molecule's rigid structure. They argue that the transport of the sulfide ions would therefore be slower since it requires the movement of entire polysulfide ions. This hypothesis can not be valid however, since there should be only one value of the diffusion coefficient for each overall melt composition.

Armstrong, Dickenson, and Reid determined diffusion coefficients at 350°C, from alternating-current impedance measurements made on a rotating-disk electrode. Their results, $D = 9.9 \times 10^{-6}$ cm$^2$/s for Na$_2$S$_{3.08}$ and $D = 1.4 \times 10^{-5}$ cm$^2$/s for Na$_2$S$_{4.68}$, are 20 times greater than those of Ludwig and
Tischer. It has been suggested that the discrepancy is due to the assumptions upon which Armstrong et al. based their calculations. For both melt compositions investigated, a single reversible diffusion controlled redox reaction was assumed, with a single electron transfer. This is not in agreement with the voltammetric curves of Divisek et al., which show that there are two redox systems present in a sodium tetrasulfide melt.

The diffusion data available at 300 and 350°C are compared in figures 3-1 and 3-2, respectively. The data fall into two distinct groups, which disagree by at least an order of magnitude. The self-diffusion data of Divisek et al. fall into the same group as the ac impedance results of Armstrong et al. However, Divisek's chronopotentiometric data, which agree well with Tischer and Ludwig results, seem more reasonable since they also agree with results predicted from conductivity data. Tischer and Ludwig estimated a diffusion coefficient of \(7-9 \times 10^{-7} \text{ cm}^2/\text{s}\) for \(\text{Na}_2\text{S}_4\) at 300°C, from the equivalent conductance of the melt using the Nernst-Einstein relation. It should be mentioned, that all of these results assume that the polysulfide melt is a dilute solution, and that Fick's law can be used to govern the diffusion process. All of the experimental results are compared to the microscopic model predictions for \(D\) in figure 3-3. The model results fall in between the two groups of experimental results. However, the activation energy calculated from the model results is approximately 8.85 kcal/mole, noticeably less than that measured by either Divisek et al. or Tischer and Ludwig.
Figure 3-1. Comparison of the experimental diffusion coefficients available at 573 K.
Figure 3-2. Comparison of the experimental diffusion coefficients available at 623 K.
Figure 3-3. Comparison of the experimental diffusion coefficients and the microscopic model predictions.
Chapter 4. Theory of Restricted Diffusion

4.1. Introduction

Restricted diffusion refers to diffusion in a vertical cell closed at both ends. Accurate binary diffusion coefficients can be measured by observing isothermal diffusion in such a cell, at long times. The measured differential diffusion coefficient corresponds to the final, or average, cell composition. Onsager originally devised the method of restricted diffusion, and Harned and French\textsuperscript{16} further developed the method in 1945. More recently, the theory was extended by Newman and Chapman,\textsuperscript{17,18} who performed a rigorous analysis for concentrated solutions.

Now restricted diffusion will be used to determine diffusion coefficients in sodium polysulfide melts. In this work, the polysulfide is considered as a binary melt consisting of sodium sulfide electrolyte ($\text{Na}_2\text{S}$) and neutral sulfur solvent; therefore the binary-electrolyte flux expressions derived in chapter 2 are applicable. Only the species sodium cations, divalent monosulfide anions, and neutral sulfur solvent are considered, although the melt is known to contain the ions $S_2^\pm$, $S_2^-$, $S_2^+$, $S_2^0$, and $S_2^{2-}$\textsuperscript{22,7} and to be free of elemental sulfur.\textsuperscript{8} However, assuming there is rapid equilibration among the components of the melt, the species used in this analysis will not affect the final result.

The governing equations for restricted diffusion in dilute solutions will be presented first. The solution to this problem is straightforward, and the first term of the resulting series for the electrolyte concentration is identical to that of the concentrated-solution expression. Taking advantage of this similarity, the dilute-solution result has been used to model the relaxation of several different initial concentration profiles. This modeling work is presented in the last section of this chapter.
4.2. Restricted Diffusion in Dilute Solutions

Figure 4-1 is a schematic of the restricted diffusion problem. The vertical cell is filled with a binary solution of varying composition. The cell height \(a\) is a constant for a dilute, constant-property solution. The electrolyte flux is zero at both ends of the cell, and the concentration at infinite time is everywhere \(c^m\). The conservation equation for each species is of the following form:

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i \tag{4-1}
\]

where the homogeneous reaction term \(R_i\) is zero. The electrolyte flux expression for a dilute solution is

\[
\mathbf{N}_e = -D \nabla c + c \mathbf{v}, \tag{4-2}
\]

c refers to the electrolyte concentration and is defined in the usual manner:

\[
c = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-}. \tag{4-3}
\]

The subscripts +, -, 0, and e refer to the cation, anion, solvent, and electrolyte, respectively. The diffusion coefficient of the salt \(D\) is a function of the individual anion and cation diffusion coefficients and valencies:

\[
D = \frac{D_+D_- (z_+z_-)}{(z_+D_+ - z_-D_-)}. \tag{4-4}
\]

In this problem the fluid velocity \(\mathbf{v}\) is zero, and the governing equation is simply Fick's second law in one dimension:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2}. \tag{4-5}
\]

where \(y\) is the distance from the bottom of the cell. The boundary conditions can be expressed as

at \(y = 0\), \(\frac{\partial c}{\partial y} = 0, \tag{4-6}\)

and
Figure 4-1. Schematic of the restricted-diffusion problem. Electrolyte concentration is plotted as a function of vertical position in the cell. Dashed line represents a greater time than the solid line.
at \( y=a \), \( \frac{\partial c}{\partial y}=0 \). \hfill (4-7)

The solution to this problem\(^\text{16,17}\) is simply the Fourier series

\[
c = \sum_{n=0}^{\infty} A_n \exp\left(-\frac{n^2 \pi^2 Dt}{a^2}\right) \cos \frac{n \pi y}{a}.
\] \hfill (4-8)

Applying the condition at infinite time

\[
as t \to \infty, \ c = c^\infty,
\] \hfill (4-9)

we can obtain a value for \( A_0 \), and equation 4-8 can be rewritten as

\[
c = c^\infty + \sum_{n=1}^{\infty} A_n \exp\left(-\frac{n^2 \pi^2 Dt}{a^2}\right) \cos \frac{n \pi y}{a}.
\] \hfill (4-10)

The values of the \( A_n \) coefficients in equation 4-10 depend on the initial concentration profile in the diffusion cell.

In the experimental system, we are interested in the concentration difference between two points in the diffusion cell. Harned and French\(^\text{16}\) used the two points \( y=a/6 \) and \( y=5a/6 \) to take advantage of the symmetry of the cosine function in the expression for concentration. However, the concentration difference can be monitored between any two convenient points in the diffusion cell. The expressions for the concentration difference between the points \( y=a/6 \) and \( y=5a/6 \), and between the points \( y=0 \) and \( y=a \), are as follows:

\[
\Delta c = c\left(\frac{a}{6}\right) - c\left(\frac{5a}{6}\right) \hfill (4-11)
\]

\[
= 2A_1 \exp\left(-\frac{\pi^2 Dt}{a^2}\right) \cos \frac{\pi}{6} + 2A_5 \exp\left(-\frac{25\pi^2 Dt}{a^2}\right) \cos \frac{5\pi}{6} + \ldots
\]

\[
\Delta c = c(0) - c(a) \hfill (4-12)
\]

\[
= 2A_1 \exp\left(-\frac{\pi^2 Dt}{a^2}\right) + 2A_5 \exp\left(-\frac{9\pi^2 Dt}{a^2}\right) + \ldots
\]

At long times the higher order terms rapidly become negligible compared to the first term in either expression, and a plot of \( \ln \Delta c \) versus time will be a straight line of slope \( \frac{-\pi^2 D}{a^2} \). Thus the diffusion coefficient can be determined from the time dependence of concentration, or any property which is linear
in concentration.

Harned and French placed a pair of electrodes at each of the two points, \( y = a/6 \) and \( y = 5a/6 \), and determined diffusion coefficients by measuring the conductivity difference between the pairs of electrodes as a function of time. This method works well for dilute solutions; however, in concentrated solutions the higher conductivities necessitate larger cell dimensions, and free convection can become a problem.

Harned's method is limited to dilute solutions by several other factors. The theory assumes that the physical properties of the solution and the diffusion coefficient are not functions of composition, and that the solvent velocity is zero. Fick's law assumes that the driving force for diffusion is simply the concentration gradient, instead of a gradient of electrochemical potential. Finally, the assumption that the cell height is a constant may break down due to the volume changes of mixing in a concentrated solution.

4.3. Restricted Diffusion in Concentrated Solutions

Newman and Chapman\textsuperscript{17} present a rigorous analysis of restricted diffusion based on concentrated-solution-theory flux equations; it includes the effects of solvent flux and variable solution properties. The multicomponent diffusion equations provided by concentrated solution theory were used to obtain flux expressions for the case of a binary electrolyte in chapter 2. These flux expressions will be used, in conjunction with the conservation equations and the boundary conditions, to solve the restricted diffusion problem for concentrated solutions.

The binary electrolyte flux expressions derived in chapter 2 are:

\[
N_0 = c_0v_0, \quad (4-13)
\]

and
\[ N_i = -\frac{c_i}{\nu RT} \frac{\partial c_i}{\partial t} \nabla \mu_i + c_i \nabla \rho. \]  

(4-14)

By substituting these flux expressions into the conservation equations, and replacing the gradient of chemical potential by a gradient of concentration:

\[ \frac{\partial c_i}{\partial t} = -c_i \nabla \rho_i - \nabla V_i. \]  

(4-15)

the governing equations for isothermal, isobaric diffusion in a concentrated solution are obtained:

\[ \frac{\partial c_0}{\partial t} = -c_0 \nabla \rho_0 - \nabla \rho_0, \]  

(4-18)

and

\[ \frac{\partial c}{\partial t} = \nabla \left[ D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - c \nabla \rho_0 - \nabla \rho_0. \]  

(4-17)

Using the definition of the partial molar volume of the solvent \((V_0)\),

\[ c_0 V_0 = \frac{1}{1 - \frac{c c_0}{dc}}, \]  

(4-18)

the governing equations can be rewritten as

\[ \frac{\partial c_0}{\partial t} = -c_0 \nabla \rho_0 - \nabla \rho_0. \]  

(4-19)

and

\[ \frac{\partial c}{\partial t} = \nabla \left\{ D \frac{\rho_0}{c_0 V_0} \nabla c - c \nabla \rho_0 - \nabla \rho_0 \right\}. \]  

(4-20)

These equations can be rearranged to give

\[ \frac{\partial c}{\partial t} = c_0 \nabla \rho_0 - \frac{D}{c_0 V_0} \nabla c - \nabla \rho_0 \nabla c \]  

(4-21)

and

\[ \nabla \rho_0 + \frac{d c_0}{d c} V_0 \frac{D}{c_0 V_c} \nabla c = 0. \]  

(4-22)

Equations 4-21 and 4-22 have been solved, using the appropriate boundary conditions, for a long-time solution of the restricted-diffusion problem.\(^\text{19}\) As time approaches infinity, the concentration, density, and height of the liquid column approach the steady-state values \(c^*, \rho^*, \) and \(a^*.\)
respectively. Two boundary conditions result from the zero flux at the bottom of the cell:

\[ \mathbf{v}_0 |_{y=0} = 0 \]  

(4-23)

and

\[ \frac{\partial c}{\partial y} |_{y=0} = 0. \]  

(4-24)

The zero flux at the top of the cell requires

\[ \frac{\partial c}{\partial y} |_{y=a} = 0. \]  

(4-25)

The final condition is that the total mass in the system remain constant:

\[ \int_0^a \rho \, dy = \int_0^a \rho^* \, dy = a^* \rho^*. \]  

(4-26)

At large times the variables can be expanded in singular perturbation expansions:

\[ c = c^* + \varepsilon c^{(1)} + \varepsilon^2 c^{(2)} + \ldots, \]  

(4-27)

\[ a = a^* + \varepsilon a^{(1)} + \varepsilon^2 a^{(2)} + \ldots, \]  

(4-28)

and

\[ \mathbf{v}_0 = \varepsilon \mathbf{v}_0^{(1)} + \varepsilon^2 \mathbf{v}_0^{(2)} + \ldots, \]  

(4-29)

where \( \varepsilon \) is an inverse function of time. The coefficients in these expansions are independent of time, and the \( c^{(i)} \) and \( \mathbf{v}_0^{(i)} \) are functions of \( y \). The diffusion coefficient is approximated by a Taylor series expansion around \( c^* \):

\[ D = D^* + \frac{dD}{dc} |_{c^*} (c - c^*) + \frac{1}{2} \frac{d^2D}{dc^2} |_{c^*} (c - c^*)^2 + \ldots \]  

(4-30)

The expansions for \( c, a, \mathbf{v}_0 \), and \( D \) are substituted into equations 4-21 and 4-22. A series of differential equations is then obtained by equating terms of equal order of \( \varepsilon \). The form of \( \varepsilon \) and the coefficients \( c^{(i)} \), \( a^{(i)} \), and \( \mathbf{v}_0^{(i)} \) are obtained by solving these differential equations and applying the appropriate boundary conditions. The manipulations are quite complicated, and therefore only the final results will be discussed here; the details have been presented by Chapman. The form of \( \varepsilon \) is
\[ \varepsilon = \exp \left[ -\frac{D^\infty t \pi^2}{(a^\infty)^2} \right] \]  

where \( D^\infty = D(c_\infty) \). The resulting concentration difference between the two points \( y = a/6 \) and \( y = 5a/6 \) is

\[ \Delta c = c \left( \frac{a}{6} \right) - c \left( \frac{5a}{6} \right) = A_1 \sqrt{3} \exp \left( \frac{-D^\infty t \pi^2}{a^2} \right) 
+ [K^\sqrt{3} + L(3^\sqrt{3/4}) - \frac{a}{3} M] \exp \left( -\frac{3D^\infty t \pi^2}{a^2} \right) + \ldots \]  

where \( A_1 \) is a function of the initial concentration profile, and \( K, L, \) and \( M \) are complicated functions of the concentration derivatives of the solution properties. In this equation, no distinction was made between the cell height and the height of the liquid column since the results show that \( a^{(1)} = 0 \) and \( a^{(2)} \) is very small. A similar equation can be written for the concentration difference between the top and the bottom of the cell:

\[ \Delta c = c(0) - c(a) = 2A_1 \exp \left( \frac{-D^\infty t \pi^2}{a^2} \right) + 2(K + L) \exp \left( -\frac{3D^\infty t \pi^2}{a^2} \right) + \ldots \]  

It will take longer for the higher order terms in equations 4-32 and 4-33 to become negligible, than it did for dilute solutions, since the second term in the series is of order \( \varepsilon^3 \) instead of \( \varepsilon^2 \) or \( \varepsilon^0 \) as found in equations 4-11 and 4-12. However at sufficiently long times, the differential diffusion coefficient \( D \), corresponding to the final cell concentration \( c^\infty \), can be determined from a plot of \( \ln \Delta c \) versus time.

4.4. Model of Concentration Profile Relaxation

It has been shown that the method of restricted diffusion can be used in either dilute or concentrated binary solutions, to measure the differential diffusion coefficient corresponding to the final cell concentration. The diffusion coefficient is determined from the slope of a semi-log plot of the concentration difference across the diffusion cell versus time, at long times. However, the time scale has not been discussed, nor has the effect of the initial concentration profile on the diffusion data. To predict the shape of the
lnΔc versus time plot, the concentration profile relaxation was modeled using the concentration expression developed for dilute solutions (equation 4-10).

Three initial concentration profiles were considered: a cosine profile, as shown in figure 4-1, a sharp boundary or step-change profile, and a linear profile. In all three cases the initial concentration difference across the diffusion cell, from \( y=0 \) to \( y=a \), is represented as \((Δc)_0\). As discussed earlier, the concentration difference across the diffusion cell can be represented by a Fourier series:

\[
Δc = c(0) - c(a) = \sum_{n=1}^{\infty} 2A_n \exp(-\frac{n^2\pi^2Dt}{a^2}).
\]  

(4-34)

The \( A_n \) coefficients for the various concentration profiles are listed in table 4-1.

<table>
<thead>
<tr>
<th>Table 4-1. Coefficients of the Fourier Series for Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosine Profile</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>( A_1 = -\frac{1}{2}(Δc)_0 )</td>
</tr>
<tr>
<td>( A_n = 0 ) for ( n \neq 1 )</td>
</tr>
</tbody>
</table>

The first fifteen terms of equation 4-34 were used to calculate the concentration difference, \( Δc \), for the three initial concentration profiles, as a function of dimensionless time. The results are shown in figure 4-2. The semi-log plot is linear over the entire time scale for the cosine profile. The other two profiles relax to a cosine profile in the time period \( Dt/a^2 < 0.05 \). Assuming a cell height of 1 cm and a diffusion coefficient of \( 10^{-6}\text{ cm}^2/\text{s} \), we can estimate long times, or times after which straight-line behavior is obeyed, to be \( t > 13.9 \) hours. It should also be noted that the initial sharp boundary and linear profile curves have initial slopes of zero and infinity respectively.

The location of the reference electrodes in the diffusion cell also effects the shape of the \( \lnΔc \) versus time plot. If the reference electrodes are placed
Figure 4-2. Concentration difference between the top and the bottom of the cell plotted versus dimensionless time. $[\Delta c]_0$ is the initial concentration difference between the top and the bottom of the cell.
at \( y = \frac{a}{6} \) and \( y = \frac{5a}{6} \), the concentration difference between the electrodes becomes

\[
\Delta c = c\left(\frac{a}{6}\right) - c\left(\frac{5a}{6}\right) = \sum_{n=1}^{6} 2A_n \exp\left(-\frac{n^2 \pi^2 Dt}{a^2}\right) \cos \frac{n\pi}{6},
\]

(4-35)

where the \( A_n \) coefficients are the same as in table 4-1 except that \( A_{3i} = 0 \), for every integer \( i \), in all three cases. Figure 4-3 shows the results for reference electrodes placed at \( \frac{a}{6} \) and \( \frac{5a}{6} \). The electrodes are exposed to the entire applied concentration difference only for the case of the step-change profile, since \( (\Delta c)_0 \) represents the initial concentration difference between the top and the bottom of the cell. For the initial cosine and step change profiles, the general shape of the plot is the same as for the previous case. However, the linear concentration profile has an initial slope of zero instead of infinity. As mentioned earlier, straight-line behavior occurs considerably faster for this electrode arrangement due to the symmetry of the cosine function. However, it is not always possible to design cells with electrodes at these locations. More interesting results are found when the electrodes are placed at \( \frac{a}{4} \) and \( \frac{3a}{4} \). The concentration difference for this case is

\[
\Delta c = c\left(\frac{a}{4}\right) - c\left(\frac{3a}{4}\right) = \sum_{n=1}^{4} 2A_n \exp\left(-\frac{n^2 \pi^2 Dt}{a^2}\right) \cos \frac{n\pi}{4},
\]

(4-36)

where the \( A_n \) coefficients are again the same as in table 4-1. In figure 4-4 we see that although the linear and cosine profiles behave as expected, the step change profile actually shows an inflection point. This electrode arrangement is not practical however, since the deviations from straight line behavior become negligible more slowly than in the previous two cases.
Figure 4-3. Concentration difference between the two points \( y = a/6 \) and \( y = 5a/6 \) plotted versus dimensionless time. \([\Delta c]_0\) is the initial concentration difference between the top and the bottom of the cell.
Figure 4-4. Concentration difference between the two points \( y = a/4 \) and \( y = 3a/4 \) plotted versus dimensionless time. \([\Delta c]_0\) is the initial concentration difference between the top and the bottom of the cell.
Chapter 5. Experimental Equipment and Procedure

5.1. Introduction

The method of restricted diffusion was applied to sodium polysulfide melts in order to determine differential diffusion coefficients spanning the composition range of the single-phase liquid region, at temperatures between 300 and 350°C. In this method, an initial concentration profile, like the one shown in figure 4-1, is allowed to relax with time. At sufficiently long times, as described in the previous chapter, the concentration profile reduces to a simple exponential function of time. The time dependence of the concentration difference across the diffusion cell can then simply be described by the equation

\[ \Delta c = c_{\text{top}} - c_{\text{bottom}} = A \exp \left( \frac{-\pi^2 D t}{a^2} \right). \] (5-1)

If the height of the diffusion cell \(a\) is known, the diffusion coefficient can be determined from the slope of a semi-log plot of the concentration difference across the diffusion cell versus time. The initial concentration profile in the cell determines the coefficient \(A\) in equation 5-1; however it has no effect on the diffusion coefficient being measured.

The concentration difference across the diffusion cell can not be measured directly. However, any property of the sodium polysulfide melt which varies linearly with concentration will have a time dependence of the form of equation 5-1. The only difference will be the value of the coefficient \(A\). Refractive index\(^{24,17}\) and conductance\(^{16}\) are two properties which have been used in conjunction with restricted diffusion to determine diffusion coefficients in other systems. Unfortunately sodium polysulfides are opaque, and the melt conductivity does not vary greatly with composition. Consequently neither of these methods is readily applicable to the sodium
polysulfide system.

It has been proposed\textsuperscript{25} that the potential difference between two reference electrodes, one at each end of the cell, could be related to the concentration difference across the cell. Cleaver and Davies\textsuperscript{8} have measured the \textit{emf} of the following concentration cell with transference:

\[
C \mid Na_2S_x(l) \ || \ Na_2S_y(l) + S(l) \ | \ C
\]

for a large range of sodium polysulfide compositions. The data at 300°C are shown in figure 5-1. The \textit{emf} between the polysulfide melt (\(Na_2S_x\)) and the two-phase constant potential melt is a strong and nearly linear function of composition. Therefore the potential measured across the diffusion cell can be related linearly to the concentration difference and can be used to measure diffusion coefficients in the sodium polysulfide melt.

5.2. Experimental System

5.2.1. Cell Design

A sketch of the diffusion cell is shown in figure 5-2. The cell is simply a 1 cm tall pyrex disk, with a 3.5 mm hole bored through the center, sandwiched between two 0.635 cm thick molybdenum electrodes. The cell size was chosen to limit the run time of each diffusion measurement to 2 days. The touching pyrex and molybdenum surfaces are highly polished to ensure a tight seal. The molybdenum electrodes were polished on a Buehler Ecomet III polisher with 400 grit sandpaper, and the disks were cut from polished pyrex sheets.

Molybdenum electrodes were chosen due to the corrosive nature of the sodium polysulfides. All metal sulfides have a negative free energy of formation at 350°C, and only metals that form a stable, conductive coating of sulfide can be considered for use in the cell. Molybdenum, chromium, hafnium, zirconium, aluminum, and stainless steel all form sulfide layers which provide some corrosion resistance.\textsuperscript{26}\textsuperscript{,}4\textsuperscript{.}27 Unfortunately, the aluminum sulfide
Figure 5-1. Potential data versus melt composition for a sodium-sulfur cell with transference. The composition of the sodium polysulfide $\text{Na}_2S_x$ is defined by the mole fraction of sodium sulfide.
Figure 5-2. Sketch of the diffusion cell.
formed has a high electrical resistivity. Chromium and molybdenum are both rather expensive and difficult to fabricate. However, stainless steel is considerably less corrosion resistant than molybdenum, and hafnium and zirconium have never been tested in cells. Molybdenum electrodes were chosen since its sulfide coating is electronically conducting, and the cost of the electrodes was negligible for this application.

The body of the diffusion cell had to be electrically insulating, and inert in molten sodium polysulfides, in the temperature range 300 to 350°C. Pyrex was chosen since it satisfies these requirements (ionic conductivity is $4 \times 10^{-4}$ (ohm-cm)$^{-1}$), and has the added advantage that its thermal expansion coefficient is similar to that of molybdenum.

During operation, the diffusion cell had to remain completely sealed for periods of several weeks at operating temperatures around 325°C. The seal at the bottom of the diffusion cell between the pyrex disk and the bottom electrode was the most critical. Many cements were tested for their resistance to sodium polysulfides at these elevated temperatures. Ultra-temp cement, made by Electronic Space Products, Inc., withstood the corrosive conditions for the required time period. However this zirconia based cement required a drying period of at least 24 hours at 150°F and made cell reuse impossible. In the final cell design the zirconia cement, between the pyrex cell and the bottom molybdenum electrode, was replaced by an aluminum gasket. The gasket removed the possibility of introducing impurities from sealants into the system and shortened the preparation time between runs.

Another consideration in the cell design was the importance of a uniform temperature profile. There are two main reasons for requiring the cell be isothermal: the possibility of natural convection, and thermocouple effects. Natural convection would clearly be a problem since it is not accounted for in the theory of restricted diffusion and would enhance the concentration
profile relaxation. The thermocouple effects are a little more subtle. If the two molybdenum electrodes are at slightly different temperatures, a potential offset occurs across the diffusion cell due to the thermocouple effect of the electrical connections.

Serious thermal effects were experienced in the first diffusion experiments. The apparatus placed the diffusion cell in the center of the furnace to obtain a relatively flat temperature profile. However, only an air space separated the cell from the furnace wall. The temperature variations produced potential offsets up to 20 mV. In the present apparatus the diffusion cell is operated inside a brass block. This design improvement reduced the equilibrium potential offset from 20 mV to 1 mV.

Figure 5-3 shows a schematic of two pyrex diffusion cells and their respective molybdenum reference electrodes inside a common brass block. The top of the block is held in place by two brass bolts not shown in the diagram. The upper electrodes are machined to extend approximately 2 mm into the top of the diffusion cells to account for the reduction in polysulfide density upon melting. The cells are electrically isolated on top and bottom from the brass block by transite insulators. Rockbestos-Micatemp high temperature copper wire, made by Cereske Electric Cable Company, runs through the top of the brass block and connects the molybdenum electrodes to the external electronic equipment. The bolts shown in the diagram are used to squeeze the diffusion cells closed. After heating the block up to the operating temperature, these bolts can be further tightened to account for thermal expansion and polysulfide density changes upon melting. A type K thermocouple, and a corresponding cold junction, in connection with a Keithly 173A multimeter were used for temperature measurement. The thermocouple well is shown in the schematic. The temperature was controlled using a series 3210 split furnace and a series SCR 2935 temperature controller.
Figure 5-3. Sketch of two diffusion cells enclosed in a brass block.
Figure 5-4. Photograph of the two diffusion cells and the common brass block.
manufactured by Applied Test Systems, Inc. Overall the temperature in the diffusion cell was controlled to about one degree centigrade, and no effect of natural convection was noticed. A photograph of the diffusion cell and block is shown in figure 5-4. The photograph shows cement holding the pyrex cells in place. As mentioned earlier this cement was replaced by an aluminum gasket in the final cell design.

5.2.2. Glove Box

Sodium polysulfides are very hygroscopic. It was therefore necessary to do all materials handling and experiments within an inert-atmosphere glove box. The glove box used for the diffusion experiments is a Dri-Lab model DL 002-D-P four-station, He-atmosphere box, with a single vacuum/transfer chamber, manufactured by Vacuum Atmospheres Corporation (VAC). VAC Pedatrol and Safe-Trol pressure control systems maintain a positive 435 Pa pressure inside the glove box. The glove box is equipped with two furnace wells, a VAC Ni-20 Ni-Train nitrogen removal system, a VAC MO40-2 Dri-Train for water and oxygen removal, and a VAC DK-3E Dri-Kool refrigeration unit. An on-line Hewlett-Packard 5880A gas chromatograph, with a 10 ft x 1/8 in. molecular sieve (13x) column, was used to monitor oxygen and nitrogen concentrations down to 5 ppm. Periodically, the molecular sieve column was replaced with a 6 ft x 1/8 in. Poropak Q column to measure the water content inside the glove box. The water concentration was never greater than 1 ppm. A model AO 316-H oxygen analyzer, with a model A A-1 audio alarm, was added to the system as a safety precaution. Figure 5-5 is a photograph of the glove box and purifying equipment.

The dimensions of the furnace and the glove-box furnace well are given in figure 5-6. The diffusion cell was placed in the center of the furnace to obtain the flattest temperature profile possible. The upper one third of the furnace well was water cooled to help maintain the glove box at a comfortable
Figure 5-5. Photograph of the glove box and purifying equipment.
Figure 5-6. Schematic showing the dimensions of the furnace and the glove-box furnace well.
working temperature and to protect the gasket. Heat shields were placed above the diffusion cell to reduce convection in the furnace well. The heat shields are simply aluminum plates, the same diameter as the well, separated vertically by 2.5 cm. The heat shields have 1.91 cm diameter holes cut through them, so ratchet wrenches can be used to tighten the bolts down on the diffusion cells without removing the brass block from the furnace well. If sulfur leaked from the diffusion cell, it would cool and condense in the upper third of the furnace well, instead of escaping into the glove box and poisoning the purification system. As an additional precaution, copper coils were placed between some of the heat shields to trap sulfur in the event of a large leak.

Figure 5-7 is a photograph showing the assembled diffusion apparatus: the brass block, the heat shields, the thermocouple, and the electrical connections. During operation the heat shields are suspended from the top of the furnace well, rather than resting on the top of the brass block. The brass rods shown in the photograph are used to lower the apparatus down into the furnace well. The rods are unscrewed and removed once the diffusion cell is in place.

5.2.3. Electronic Equipment

The potential across the diffusion cell was measured with two AIS, Floyd Bell Associates, Inc. BA-1 buffer amplifiers operated in differential mode, in series with a Keithly 173A multimeter. The potential was recorded every 10 minutes using a Keithly 750 printer which was connected to the multimeter with a digital interface. The buffer amplifiers are unity-gain devices with input impedances greater than $10^{12}$ ohms. In differential mode, the signal from the upper electrode is input to one buffer amplifier, and the signal from the lower electrode is input to the second buffer amplifier. Since both amplifiers exhibit unity gain, the difference of the potentials appearing at
Figure 5-7. Photograph showing the assembled diffusion apparatus, and the heat shields.
their outputs is the exact difference in the potentials of the two sources. The buffer amplifier input is a BNC connector. The center pin of this connector makes the connection to the diffusion cell, and the outer conductor is a guard. The guard is driven to the same potential as the input, by the buffer amplifier, to prevent leakage. A Keithly 602 electrometer with an input impedance of $10^{14}$ ohms was used periodically to check the potential measurements.

A schematic of all the electronic equipment is shown in figure 5-8. The buffer amplifiers were placed inside the glove box to be close to the cell. There is only one pair of coaxial cables connectors inside the glove box. Therefore two switching boxes were used to direct the signal through the buffer amplifiers for potential measurement. When two diffusion cells were operated simultaneously, a third switching box was used to alternate between them. At least once a day, the cell resistance was measured with a Wayne Kerr B642 autobalance universal bridge, to check for sulfur leaks. The oscillator frequency was set at 1591.5 Hz. A 6101A Hewlett-Packard power supply was used to establish the initial polysulfide concentration profiles. The potential could be adjusted to 0.01 mV.

5.3. Experimental Procedure

5.3.1. Raw Materials

Sodium sulfide and sulfur were used for sodium polysulfide preparation, and sodium was used to make sodium reference electrodes for polysulfide analysis. Anhydrous sodium sulfide was purchased from the Noah Chemical Div. of Noah Industrial Corp. The sodium sulfide grade was 4N and was analyzed to have a water concentration of 51 ppm when new. Grade 6N sulfur powder was purchased from Electronic Space Products Inc., and lump sodium metal was obtained from J. T. Baker Company. The lot analyses for the
Figure 5-B. Schematic of the electronic equipment. Dashed line represents the glove box boundary.
sodium and sodium sulfide are given in appendix B.

5.3.2. Filling the Diffusion Cell

Two primary methods of filling the diffusion cell were tested: powder filling, and using a prepared slug of polysulfides. Several of the early diffusion cells were powder filled. The polysulfide powder could be packed to only about 70% solid density, and the cell had to be filled with powder and heated and cooled back down several times before it was completely filled. Most of the cells, however, were filled using a prepared slug of polysulfides. The slug was placed into the diffusion cell, the upper electrode was placed onto the cell, and a bolt was used to tighten down on the cell as it was heated to account for the density change upon melting. This technique was more efficient than the first since it requires only one cell filling.

5.3.3. Polysulfide Preparation

There is a variety of methods used to prepare sodium polysulfides. In a recent review Cleaver\textsuperscript{29} describes five of these methods: reaction of alkali metal with sulfur under boiling toluene, reaction of sulfur with alkali metal hydrosulfide in ethanol, preparation of polysulfide in liquid ammonia, electrochemical preparation using $\beta$- or $\beta'$-alumina, and preparation from monosulfide and sulfur. For several of these methods, Brauer\textsuperscript{30} provides more detail. However, for the more recent methods, electrochemical preparation and preparation from monosulfide and sulfur, the best references are Cleaver and Davies\textsuperscript{31} and Rosén and Tegman,\textsuperscript{32} respectively.

The simplest technique is probably preparation from monosulfide and sulfur. However, polysulfide of a very exact composition, and 99.5 to 100% purity, can be prepared using the electrochemical method. For the restricted-diffusion experiments, the polysulfide composition is most accurately determined at the end of the diffusion-coefficient measurement.
Therefore the polysulfides were prepared from monosulfide and sulfur, and the melt was analyzed after the diffusion measurement.

The sodium polysulfides were prepared from sulfur and anhydrous sodium sulfide (Na₂S) by the procedure suggested by Rosén and Tegman.³² Stoichiometric amounts of sulfur and sodium sulfide are ground together, then the mixture is reacted in an evacuated sealed tube. To avoid excessive sulfur vapor pressures, the mixture is first reacted as a solid at 200 to 230°C for 12 hours, then the temperature is increased to 300 to 350°C for 1/2 hour to form a homogeneous liquid mixture. Usually the polysulfide forms a glass upon cooling. Rosén and Tegman suggest grinding the polysulfide and tempering at 200 to 220°C for 1 to 10 hours to form a crystalline material.

This procedure worked well for making the sodium polysulfide slugs. Stoichiometric amounts of sodium sulfide and sulfur were weighed on a Satorius Digital Balance to within 0.001 g, ground together using a mortar and pestle, and placed into the reaction tube. The pyrex reaction tube used had two sections. The upper section was 9 mm o.d. to fit the vacuum line, and the lower section was 3.5 mm i.d. so the polysulfide slug would fit into the diffusion cell. The cells were sealed inside the glove box, under 5.08 x 10⁴ Pa (15 in. Hg) vacuum, using a tungsten conduction coil. If there is sulfur on the pyrex when it is heated, the sulfur will react with the pyrex and cause it to crack instead of soften and seal. Therefore a pyrex funnel was used to fill the reaction tubes with polysulfides. To obtain a completely homogeneous polysulfide, the liquid reaction time was increased to 24 hours at 375°C. A crystalline product was obtained by cooling the polysulfide down slowly, eliminating the regrinding and tempering reaction steps. A crystalline product was preferred because a glass slug would crack and shatter while being removed from the reaction tube.
5.3.4. Measurement of Diffusion Coefficients

Once the molybdenum electrodes were polished, and the polysulfide slug was prepared, the diffusion cell is assembled inside the brass block. The bolt which presses on the top electrode to close the diffusion cell is tightened. The brass block and the heat shields are then lowered into the furnace well. When the block reaches the operating temperature, the cell is retightened to account for thermal expansion. To ensure that the cell is completely filled, the cell resistance is measured using an ac bridge. A potential of 30 to 100 mV is applied across the cell for at least 8 hours to establish the initial concentration profile. The diffusion coefficient measured was not affected by the potential applied nor the charging time. The top electrode is made positive with respect to the bottom electrode to produce the lower density polysulfide at the top of the cell and avoid natural convection. The power supply is then turned off, and the potential across the cell is monitored with time using two buffer amplifiers, a multimeter, and a printer. When the potential decays to zero, typically after two days, the diffusion coefficient corresponding to the average, or final, cell concentration can be obtained from the potential versus time data as described in the introduction to this chapter. Generally the potential levels out around 0.5 or 1 mV instead of zero, due to the temperature variation across the diffusion cell. As mentioned earlier, this offset was reduced from 20 mV by surrounding the cell with a brass block. The remaining small potential deviation is subtracted from the data before the diffusion coefficient is calculated. The temperature can then be increased, the cell retightened if necessary, a new concentration profile established, and a second diffusion coefficient measured without delay. The sodium polysulfide concentration is determined at the end of the series of measurements.
5.4. Analysis of Sodium Polysulfides

The sodium polysulfide analysis was primarily done by the UC Berkeley microanalytical laboratory. Sodium concentrations were detected using atomic adsorption, and the sulfur was oxidized to sulfate and then precipitated as barium sulfate. Both Scott\textsuperscript{38} and Fehér and Berthold\textsuperscript{34} describe in detail this analytical method for sulfur.

An alternative, electrochemical method of analysis was investigated. In this method the potential of the polysulfide melt was measured against a reference sodium electrode. Then the composition of the melt could be determined using Cleaver and Davies's\textsuperscript{5} potential-versus-composition data for the following cell:

\[
\begin{array}{c|c|c|c|c}
\text{C} & \text{Na(l)} & \text{Na}_2\text{S}_x(1) & \text{C} \\
\end{array}
\]

A simple cell was assembled to measure the potential between the polysulfide melt and the sodium reference electrode. A glass tube was drawn down to a fine capillary tip, filled with sodium polysulfide, and sealed with a stopper made from Loctite Superflex 596 silicone adhesive sealant. This polysulfide electrode was then placed into a pyrex tube filled with sodium and heated to 300°C. Tungsten wires were used as electrodes. The cell was discharged galvanostatically at a current of 1 mA, to obtain potential data as a function of composition. Periodically the cell discharge was interrupted, and after approximately two hours the steady-state, open-circuit potential was recorded. The potential data at 300°C are plotted against Cleaver and Davies's data in figure 5-9. In this figure the initial polysulfide concentration prior to galvanostatic discharge was assumed to be the one given by the initial potential measurement. Therefore the first point was made to coincide exactly with Cleaver and Davies's data. The rest of the data agree within 1.5% and demonstrate the possible accuracy of an electrochemical method of analysis.
Figure 5-9. Comparison of the potential data from a galvanostatic discharge of a simple sodium-sulfur cell and Cleaver and Davies's experimental results at 573.15 K.
Chapter 6. Experimental Results and Conclusions

6.1. Introduction

The restricted-diffusion apparatus has been used to measure diffusion coefficients in sodium polysulfide melts. As expected, no dependence on the initial concentration profile is observed, as long as the polysulfide at the top of the diffusion cell has a lower density than that at the bottom. However, natural convection due to an applied positive density gradient, greatly increases the measured diffusion coefficients. The shape of the potential-versus-time plots agrees with the modeling results presented in chapter 4.

The cell height, \( \alpha \), is the only parameter needed to determine the value of the diffusion coefficient from the potential data. The method of restricted diffusion is inherently accurate; however, any uncertainty in the cell height will result in twice as large an uncertainty in the diffusion coefficient. Therefore, the method of determining the cell height, and the possible sources of error, will be discussed.

The diffusion coefficients were measured as a function of composition and temperature. The results will be compared to the data of other researchers and the predictions of the microscopic model. A general correlation will be derived to summarize the restricted-diffusion data. Values of the diffusion coefficient based on a thermodynamic driving force, and of the multicomponent transport parameters, will be calculated from the experimental data.

6.2. Effect of the Initial Concentration Profile

Three types of initial concentration profiles were discussed in chapter 4. The choice of initial profile did not affect the value of the diffusion coefficient, but it did affect the nonlinear region of the potential data. Experimental
potential data for linear and step-change initial concentration profiles are shown in figure 6-1. The linear profile was established using an applied potential across the cell, whereas the step-change profile was established by placing two polysulfide pellets of different compositions one on top of the other in the diffusion cell. The results for the linear profile are in excellent agreement with the modeling work, both in the shape of the curve and in the time required to reach the linear region. The step-change profile looks like the modeling results for dimensionless times greater than about 0.04. The sharp potential drop at small times resulted from a direct-current resistance measurement, which briefly applied a potential across the cell. Later resistance measurements were made using an autobalance universal bridge, with an oscillator frequency of 1591.5 Hz.

Generally the initial concentration profiles were established by applying a potential of 30 to 100 mV across the cell for at least 8 hours. The resulting linear profiles were well behaved and reasonably reproducible. In general, a positive potential was applied to the upper electrode, with respect to the lower electrode to produce lower density polysulfide at the top of the cell and avoid natural convection. The potential used to charge the cell, and the amount of time it was applied, are two factors which could affect the accuracy of the experiments.

Values of $D/a^2$ measured for $\text{Na}_2\text{S}_{3.48}$ at 299°C are compared in table 6-1 for typical values of applied potential and charging time. The diffusion coefficients are not affected by either the potential or the amount of time it is applied. The discrepancies between the results are of the same magnitude as the standard variation between runs. From the data in table 6-1, we can calculate the standard error to be around 3%. It should be mentioned that there are both maximum and minimum limits to the potential which can be used. A very small applied potential will not produce a long enough linear region in
Figure 6-1. Potential decay of two initial concentration profiles. The potential between the top and the bottom of the diffusion cell has been plotted versus dimensionless time.
the potential-versus-time data to measure the diffusion coefficient accurately. Potentials greater than 300 mV can not be used because a second phase will form near one or both of the electrodes.

### Table 6-1. Diffusion Results for Na₂S₃₄₈ at 299°C

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>Time (hrs)</th>
<th>D/α² x 10⁵ (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>4</td>
<td>1.28</td>
</tr>
<tr>
<td>80</td>
<td>4</td>
<td>1.20</td>
</tr>
<tr>
<td>80</td>
<td>16</td>
<td>1.27</td>
</tr>
<tr>
<td>100</td>
<td>4</td>
<td>1.21</td>
</tr>
</tbody>
</table>

### 6.3. Determination of the Cell Height

A diffusion coefficient can only be measured as accurately as the cell height is known. The parameter measured from the experimental data is $D\pi²/α²$. Therefore, any error in the cell height will be doubled during the calculation of $D$. Looking at figure 6-2 we can see that the cell height ($α$) is the height of the pyrex cell, plus the thickness of an aluminum gasket, minus the length of the extension on the upper electrode. However, we cannot assume that measuring the size of the cell parts individually at room temperature is sufficient. We must also account for the effects of thermal expansion. Another error arises from the annular space between the extension on the upper electrode and the pyrex diffusion cell. The polysulfide in this region adds to the cell height; and this error must also be evaluated.

The coefficients of linear expansion for aluminum, molybdenum, and pyrex are listed in table 6-2. The values for molybdenum and pyrex are quite similar. Using a height of 0.102 mm for the aluminum gasket, and the values for the pyrex cell and molybdenum electrode extension given in table 6-3, we can calculate the cell heights at 25 and 325°C. The resulting cell heights are 0.7201 and 0.7209 cm at 25 and 325°C respectively. Raising the temperature by 300°C, increases the cell height by 0.11%.
Figure 6-2. Schematic showing how the cell height (a) is measured.
Table 6-2. Linear Thermal Expansion Coefficients

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature °C</th>
<th>Coefficient x 10^6 °C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum³⁵</td>
<td>25 - 350</td>
<td>25.3</td>
</tr>
<tr>
<td>molybdenum³⁵</td>
<td>25 - 350</td>
<td>5.4</td>
</tr>
<tr>
<td>pyrex³⁵</td>
<td>25 - 325</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The annular space between the extension on the upper electrode and the pyrex cell produces the other uncertainty in the calculation of the cell height. This source of error was unavoidable however, since the electrode extension proved necessary to fill the diffusion cell completely. The volume of the annular space was minimized by machining the electrode extension to approximately the same diameter as the pyrex cell. The uncertainty in the diffusion coefficient is twice that in the cell height. If we think of the annular space as an additional volume sitting above the closed cell volume, then a lower limit for this uncertainty is simply the volume of the annular space, divided by the closed cell volume, and multiplied by 100. Using this analysis and the dimensions given in table 6-3, we calculate that the diffusion coefficients could be up to 4.09% greater than reported.

Table 6-3. Dimensions of a Typical Cell and Electrode Extension

<table>
<thead>
<tr>
<th></th>
<th>Height (mm)</th>
<th>Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>9.182</td>
<td>3.581</td>
</tr>
<tr>
<td>Electrode Extension</td>
<td>2.083</td>
<td>3.454</td>
</tr>
</tbody>
</table>

The cell height listed in table 6-3 is not (a), but rather the empty pyrex cell height. However, the words "closed cell volume" refer to the cell height a multiplied by the cell cross sectional area.

Clearly the primary uncertainty in the cell height, and consequently the diffusion measurements, is due to the electrode extension. The effects of thermal expansion are negligible by comparison. Consequently, the cell
height used in the calculations was that measured at room temperature.

6.4. Results

Using the method of restricted diffusion, differential diffusion coefficients were measured as a function of sodium polysulfide melt composition and temperature. Two different lots of sodium sulfide were used to prepare the polysulfide melts. Lot 22719 was stored in the He-atmosphere glove box for two years prior to the experiments, whereas lot 38022 was new. The results, listed in table 6-4, show no dependence on the lot of sodium sulfide used.

<table>
<thead>
<tr>
<th>composition</th>
<th>Na₂S lot #</th>
<th>temperature (K)</th>
<th>$D \times 10^6$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S₃.₄₃</td>
<td>38022</td>
<td>573.15</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>598.15</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>597.15</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>624.15</td>
<td>2.96</td>
</tr>
<tr>
<td>Na₂S₃.₅₉</td>
<td>38022</td>
<td>573.95</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>598.25</td>
<td>3.65</td>
</tr>
<tr>
<td>~Na₂S₄</td>
<td>22719</td>
<td>572.95</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>576.55</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600.35</td>
<td>3.36</td>
</tr>
<tr>
<td>Na₂S₄.₀₂</td>
<td>22719</td>
<td>573.95</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>598.15</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>623.15</td>
<td>3.83</td>
</tr>
</tbody>
</table>

In this section, the activation energy calculated from the experimental results will be compared to that calculated from other sources, and the effect of natural convection on the measured diffusion coefficients will be discussed. In addition, values of the diffusion coefficient based on a thermodynamic driv-
ing force, and of the multicomponent transport parameters, will be calculated from the experimental results.

6.4.1. Temperature and Composition Dependence

The experimental diffusion coefficients are plotted in figure 6-3 as a function of temperature. The diffusion coefficients appear to have an Arrhenius form temperature dependence:

\[ D = C \exp(-E_A/RT), \]  

(6–1)

where \( E_A \) is an activation energy and \( C \) is a constant. All of the results have nearly the same temperature dependence. The average activation energy calculated from all of the experiments is 49.5 kJ/mol. In table 6-5, this value is compared to the results of Tischer and Ludwig, and Divisek et al., the microscopic model predictions, and values calculated from viscosity and conductivity data.

<table>
<thead>
<tr>
<th>Source</th>
<th>( E_A ) kJ/mol</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>restricted diffusion</td>
<td>49.5</td>
<td>( \text{Na}_2\text{S}_3 - \text{Na}_2\text{S}_5 )</td>
</tr>
<tr>
<td>Tischer and Ludwig\textsuperscript{22}</td>
<td>57.3</td>
<td>( \text{Na}_2\text{S}_5 )</td>
</tr>
<tr>
<td>Divisek et al.\textsuperscript{21}</td>
<td>48.1</td>
<td>( \text{Na}_2\text{S}_4 )</td>
</tr>
<tr>
<td>microscopic model\textsuperscript{9}</td>
<td>27.8</td>
<td>( \text{Na}_2\text{S}_3 - \text{Na}_2\text{S}_5 )</td>
</tr>
<tr>
<td>modified microscopic model</td>
<td>30.6</td>
<td>( \text{Na}_2\text{S}_3 - \text{Na}_2\text{S}_5 )</td>
</tr>
<tr>
<td>viscosity\textsuperscript{27}</td>
<td>-46.9</td>
<td>( \text{Na}_2\text{S}_3 - \text{Na}_2\text{S}_5 )</td>
</tr>
<tr>
<td>conductivity\textsuperscript{31}</td>
<td>32.2</td>
<td>( \text{Na}_2\text{S}_3 - \text{Na}_2\text{S}_5 )</td>
</tr>
</tbody>
</table>

The activation energy determined from the restricted diffusion experiments agrees with the results of Tischer and Ludwig, and Divisek et al., and the viscosity data, rather than the microscopic model prediction and the conductivity data. Since the microscopic model was based on the conductivity data, their agreement is expected. However, the discrepancy between the viscosity and the conductivity data is disturbing.
Figure 6-3. Diffusion coefficients determined experimentally, using the restricted diffusion method, plotted as a function of temperature.
The results obtained at 300°C are plotted as a function of melt composition and compared to the results of other researchers, and the microscopic model predictions, in figure 6-4. All of the restricted diffusion results for the temperature 300°C are in the region 1 to 4 x 10^6 cm^2/s. They fall between the two groups of experimental data obtained by other researchers. Most of the restricted diffusion results are in excellent agreement with the microscopic model predictions, both in value and composition dependence. However, the data from one cell (z = 0.292) lie in between Divisek et al.’s data and the microscopic model predictions. The variation between runs is considerably larger in this cell than in the others. This is an indication that the cell was not behaving properly, and thus these data should be neglected.

Faulty cell handling might be the cause of the smaller diffusion coefficients measured with this one cell. The polysulfide slug placed in the diffusion cell is made by melting powders and may be porous. If the top of the cell is pushed down very tightly immediately after the polysulfide pellet melts, it is possible that the gas bubbles will not have time to rise to the surface and escape from the melt. The rate of diffusion through the resulting "porous melt" would be slower, as was observed in the discrepant cell.

The composition dependence of the experimental diffusion coefficients can be added to the Arrhenius type temperature dependence to obtain a correlation of the form:

\[ D = C_1 e^{-E_A/RT} e^{C_2 x}. \]

Values for \( C_1, C_2, \) and \( E_A \) which were determined from the data are listed in table 6-6. The discrepant data obtained for \( \text{Na}_2\text{S}_{3.43} \) were not considered since they vary by almost 3 standard deviations from this fit.

The value of the activation energy given in table 6-6, 48.95 kJ/mol, is in better agreement with the viscosity data than the value of 49.5 kJ/mol calculated using all of the data. Therefore, the discrepant data will not be
Figure 6-4. Comparison of the experimental diffusion coefficients to the results of other researchers, and the predictions of the microscopic model, at a temperature of 573 K.
considered further. The correlation

\[ D = 0.0153 \exp(-5.89 \times 10^3 / T) \exp(5.30x_0) \text{ cm}^2 / \text{s}, \]  

(6-3)
is compared to the experimental data in figure 6-5.

| Table 6-6. Values of the Coefficients in Equation 6-2 |
|-----------------|-----------------|-------|
| \( C_1 \) cm\(^2\)/sec | \( C_2 \) | \( E \) kJ/mol |
| 0.0153          | 5.30           | 48.95 |

6.4.2. Effect of Natural Convection

Larger values for the diffusion coefficients are obtained when the initial linear concentration profile is established by applying a negative potential to the top electrode, with respect to the bottom electrode. In such cases, the polysulfide formed near the top electrode will have a relatively high mole fraction of sodium sulfide. We can see from figure 6-6 that the density of the sodium polysulfide melt generally increases with increasing sodium sulfide mole fraction, over the composition region of interest. Therefore, the density of the polysulfide is higher at the top of the diffusion cell, and the relaxation of the concentration profile is enhanced by natural convection. The diffusion coefficient measured in such an experiment is an effective diffusion coefficient because it includes the movement of species due to the positive density gradient.

Figure 6-7 shows the effect of natural convection on the measured diffusion coefficients. Natural convection due to the positive density gradient increased the rate of diffusion by at least 15% across the entire composition range. The resulting effective diffusion coefficients depend much more strongly on the melt composition. The values of \( C_2 \) in equation 6-2 are 7.54 and 5.30 for the effective and actual diffusion coefficients, respectively. Since the viscosity does not depend strongly on the melt composition, this observed increased dependence on composition implies that the density of sodium
Figure 6-5. Comparison of the experimental data to the derived correlation. Solid line represents the correlation $D = 0.0153 \exp(-5.89 \times 10^3 / T) \exp(5.30z_s) \text{cm}^2/\text{s}$. 
Figure 6-6. Sodium polysulfide density versus composition at 573 K. Data obtained by Cleaver and Davies.\textsuperscript{37}
Figure 6-7. Effect of natural convection on the experimental diffusion coefficients at 573 K.
polysulfides must vary more strongly with composition as the mole fraction of sodium sulfide increases. Unfortunately, the available density data, shown in figure 6-6, do not provide any conclusive information. A straight line could be drawn through the data just as easily as a curve whose slope increases in proportion to the mole fraction of sodium sulfide.

Individual data points are not plotted in figure 6-7. Rather, the data obtained for a specific melt composition and temperature are averaged and represented by one point. The variation between runs is less than 5%, and therefore individual data points would overlap, as in figure 6-5, and add very little information to the figure. Similarly, averaged data values will be used to calculate the diffusion coefficients based on a thermodynamic driving force and the binary interaction coefficients.

6.4.3. Calculation of the Thermodynamic Based Diffusion Coefficients

6.4.3.1. Introduction

Values of the diffusion coefficient \( D \), for a thermodynamic driving force, can be calculated as a function of composition from the experimental diffusion coefficients. Considering the melt as a combination of sodium sulfide electrolyte and neutral sulfur solvent, the two diffusion coefficients can be related by the expression

\[
D = \mathfrak{D} \frac{c_T}{c_0} (1 + \frac{d \ln \gamma_x}{d \ln \mathfrak{m}}),
\]

where \( \mathfrak{m} \) is the molality of the electrolyte, \( \gamma_x \) is the mean molal activity coefficient, \( c_0 \) is the concentration of the solvent, and \( c_T \) is the total solution concentration. As discussed in chapter 2, values of the thermodynamic activity coefficient factor, \( (1 + \frac{d \ln \gamma_x}{d \ln \mathfrak{m}}) \), can be calculated from Cleaver and Davies's open-circuit potential data for a sodium/sulfur cell. These data are available at 300 and 360°C. Since the restricted diffusion experiments were
performed in the 300 to 350°C temperature range, only thermodynamic based diffusion coefficients corresponding to 300°C can be calculated directly. Results for other temperatures will be calculated by assuming a form for the temperature dependence of the thermodynamic activity coefficient factor.

The multicomponent transport properties $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ can then be calculated from the thermodynamic based diffusion coefficient and transference number data, using equations 2-10 and 2-11. For temperatures other than 300°C it will be necessary to assume a linear temperature dependence for the transference numbers.

The binary interaction coefficient between the cation and the anion, $\mathcal{I}_{+-}$, can then be determined using equation 2-12. These calculations require sodium polysulfide density and conductivity data in addition to the transference number data. Since the experimental errors in all of these physical properties will be compounded in this calculation, the $\mathcal{I}_{+-}$ values will be less accurate than the other results.

### 6.4.3.2. Concentrations

To calculate $\mathcal{D}$ values from the experimental diffusion data, we first need to calculate the concentration ratio $c_r/c_0$. The total solution concentration and the solvent concentration can be calculated as a function of the overall melt composition from density data. The melt composition will again be defined in terms of the mole fraction of sodium sulfide, $x_s$.

First we need to define an average molecular weight of the melt in terms of the molecular weights of the electrolyte and the solvent:

$$M_{av} = x_e M_e + (1-x_e) M_0 \quad \text{(6-5)}$$

Then the concentration of the electrolyte and the solvent can be represented as
The expressions for the concentrations of the cations and anions are then simply

$$c_+ = \nu_+ c = \frac{\rho}{M_{av}} \nu_+ x_e,$$  \hspace{1cm} (6-8)

and

$$c_- = \nu_- c = \frac{\rho}{M_{av}} \nu_- x_e.$$  \hspace{1cm} (6-9)

The total solution concentration is the sum of all the species concentrations:

$$c_T = \nu c + c_0 = \left[1+(\nu-1)x_e\right] \frac{\rho}{M_{av}}.$$  \hspace{1cm} (6-10)

Therefore, the ratio of the total solution concentration to the solvent concentration:

$$\frac{c_T}{c_0} = \frac{\left[1+(\nu-1)x_e\right] \frac{\rho}{M_{av}}}{\left(1-x_e\right) \frac{\rho}{M_{av}}} = \frac{\left[1+(\nu-1)x_e\right]}{(1-x_e)},$$  \hspace{1cm} (6-11)

do not depend on density and can be calculated directly from the melt composition.

6.4.3.3. Diffusion Coefficients Based on a Thermodynamic Driving Force

We can now directly calculate values for the thermodynamic based diffusion coefficient at 300°C. The results are similar to the values predicted using the microscopic model, as shown in figure 6-8. However, the experimental results vary linearly with composition, unlike the microscopic model predictions which include a shallow minimum.

To calculate thermodynamic diffusion coefficients at 325 and 350°C, we must assume a form for the temperature dependence of the thermodynamic
Figure 6-8. Values of the diffusion coefficient based on a thermodynamic driving force versus melt composition, at a temperature of 573 K. Dashed line represents the experimental diffusion coefficients. Solid curve calculated using the microscopic model.
activity coefficient factor. The factor is calculated from Cleaver and Davies's open-circuit potential data using equation 2-39. We will assume that the derivative of the open-circuit cell potential with respect to the melt composition, \( \frac{dU}{dz} \), varies linearly with temperature. Then values for the thermodynamic based diffusion coefficient at 325 and 350°C can be calculated using the values for \( \frac{dU}{dz} \) given in equations 2-40 and 2-41. The results are plotted in figure 6-9 and compared to the values calculated in a similar manner using the diffusion coefficient correlation.

6.4.3.4. Multicomponent Transport Properties

The interaction coefficients between the solvent and the cations (\( \Theta_0^+ \)), and the solvent and the anions (\( \Theta_0^- \)), can be calculated from the thermodynamic diffusion coefficient and either transference number using the two expressions

\[
\Theta = \frac{\Theta_0^+ \Theta_0^- (z_+ - z_-)}{z_+ \Theta_0^+ - z \Theta_0^-}
\]

and

\[
t_0^+ = 1 - t_0 = \frac{z \Theta_0^+}{z_+ \Theta_0^+ - z \Theta_0^-}
\]

Then the interaction coefficient between the cation and the anion, \( \Theta_+^- \), can be calculated from the expression

\[
\frac{1}{\kappa} = \frac{-RT}{c_+ z_+ z_- F^2} \left( \frac{1}{\Theta_+^-} + \frac{c_0 t_0^+}{c_+ \Theta_0^-} \right)
\]

using conductivity, transference number, and density data.

Transference number data can be obtained from open-circuit potential measurements on a cell with transference. Cleaver and Davies\(^8\) measured the \( \text{emf} \) of the following cell with transference:

\[
C || Na_2S_4(l) || Na_2S_8(l) + S(l) || C,
\]

but did not calculate the transference numbers. Newman and Risch\(^38\) have
Figure 6-9. Values of the diffusion coefficient based on a thermodynamic driving force versus melt composition. Solid lines calculated using the diffusion coefficient correlation given in equation 6-3.
calculated transference numbers from the open-circuit potential data. The calculated transference numbers for 300 and 360°C are plotted in figure 8-10.

These transference data have been used in conjunction with the thermodynamic diffusion coefficients to obtain values for the multicomponent transport properties, at 300°C, as a function of melt composition. Transference numbers for 325 and 350°C were obtained by linearly interpolating the data given in figure 6-10. The values of $\mathcal{D}_{0-}$ and $\mathcal{D}_{0+}$ calculated using these transference numbers are shown in figure 6-11. The solid lines were calculated using equation 6-3, values of the thermodynamic activity coefficient factor, and transference data. Once again the correlation is a satisfactory representation of the data.

The interaction coefficient between the cation and the anion can now be calculated from equation 6-14. The ratio of the solvent concentration to the cation concentration is simply a function of the melt composition:

$$\frac{c_0}{c_+} = \frac{1-x_a}{\nu_x x_a}$$

(6-15)

However, calculation of the total solution concentration requires knowledge of the melt density (see equation 6-10). Therefore, these calculations will require conductivity and density data besides the transference data which have been discussed previously.

Cleaver and Davies have measured the conductivity of several different polysulfide melts as a function of temperature. They have correlated the data for discrete melt compositions using an empirical function of temperature:

$$\kappa = A e^{-\frac{E_\kappa}{R(T-T_o)}}$$

(6-16)

The values of $A, T_o,$ and $E_\kappa$ are functions of melt composition and are given in table 6-7.
Figure 6-10. Calculated sulfide ion transference numbers relative to neutral sulfur solvent plotted as a function of sodium polysulfide melt composition.
Figure 6-11. Calculated binary interaction coefficients versus melt composition for the temperatures 573, 598, and 623 K. Solid lines calculated using the diffusion coefficient correlation given in equation 6-3.
Table 6-7. Values of the Parameters in Equation 6-16

<table>
<thead>
<tr>
<th>Melt</th>
<th>$x_e$</th>
<th>Temp. range (K)</th>
<th>$A$ (ohm-cm)$^{-1}$</th>
<th>$E^*$ (kJ/mol)</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>2$S$</em>{2.1}$</td>
<td>0.476</td>
<td>728-940</td>
<td>5.478</td>
<td>3.079</td>
<td>499</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{2.9}$</td>
<td>0.345</td>
<td>642-898</td>
<td>3.863</td>
<td>2.478</td>
<td>456</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{3.0}$</td>
<td>0.333</td>
<td>582-893</td>
<td>7.033</td>
<td>5.893</td>
<td>329</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{3.2}$</td>
<td>0.313</td>
<td>458-694</td>
<td>7.048</td>
<td>5.854</td>
<td>330</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{3.6}$</td>
<td>0.263</td>
<td>428-694</td>
<td>7.056</td>
<td>6.438</td>
<td>325</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{4.2}$</td>
<td>0.238</td>
<td>456-671</td>
<td>6.279</td>
<td>6.183</td>
<td>341</td>
</tr>
<tr>
<td>Na$<em>2$S$</em>{5.1}$</td>
<td>0.196</td>
<td>477-681</td>
<td>5.815</td>
<td>6.329</td>
<td>344</td>
</tr>
</tbody>
</table>

A plot of the melt conductivity at 300, 325, and 350°C is shown in figure 6-12. The linear regression fits of the data which were used are

at 300°C, $\kappa = -0.1051 + 1.572x_e$. \hspace{1cm} (6-17)

at 325°C, $\kappa = -0.0993 + 1.946x_e$. \hspace{1cm} (6-18)

and at 350°C, $\kappa = -0.0739 + 2.272x_e$. \hspace{1cm} (6-19)

Cleaver and Davies's\textsuperscript{37} density data are plotted for several temperatures in figure 6-13. The data exhibit a strange dependence on composition. It has been suggested\textsuperscript{35} that the data are best represented using a function of temperature only. Furthermore, the data for Na$_2$S$_{3.7}$ ($x_e = 0.270$) are particularly suspect and should be neglected. The correlation which was used to represent this density data is

$$\rho = 2.295 - 6.866 \times 10^{-4} T \text{ g/cm}^3,$$ \hspace{1cm} (6-20)

which has a maximum error of 0.018 g/cm$^3$ if the Na$_2$S$_{3.7}$ data are neglected.

The $\mathcal{J}_{p-}$ interaction coefficients calculated using equation 6-14 are listed in table 6-8. Negative values were obtained for the temperatures 300 and 325°C. The negative interaction coefficients imply that the sodium and sulfur ions are moving in the same direction. This is not very likely. A more reasonable explanation for the negative values is that the experimental transference numbers, and possibly the density data, are not very accurate. It can be shown using equation 6-14, that positive values of $\mathcal{J}_{p-}$ would be obtained at
Figure 6-12. Sodium polysulfide conductivity as a function of melt composition. Experimental data from Cleaver and Davies.31
Figure 6-13. Sodium polysulfide density as a function of melt composition, plotted for several temperatures. Data from Cleaver and Davies. 37
300 and 325°C if the anion transference numbers were about 50 and 25% smaller, respectively.

Table 6-8. Values of \( \mathcal{J}_+ \)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Melt</th>
<th>( x_+ )</th>
<th>( \mathcal{J}_+ \times 10^8 \text{ cm}^2/\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>Na(<em>2)S(</em>{2.89})</td>
<td>0.346</td>
<td>-2.57</td>
</tr>
<tr>
<td></td>
<td>Na(<em>2)S(</em>{3.59})</td>
<td>0.278</td>
<td>-1.37</td>
</tr>
<tr>
<td></td>
<td>Na(_2)S(_4)</td>
<td>0.25</td>
<td>-1.26</td>
</tr>
<tr>
<td></td>
<td>Na(<em>2)S(</em>{4.02})</td>
<td>0.249</td>
<td>-1.38</td>
</tr>
<tr>
<td></td>
<td>Na(<em>2)S(</em>{4.76})</td>
<td>0.21</td>
<td>-0.956</td>
</tr>
<tr>
<td>598</td>
<td>Na(<em>2)S(</em>{3.59})</td>
<td>0.278</td>
<td>-16.7</td>
</tr>
<tr>
<td></td>
<td>Na(_2)S(_4)</td>
<td>0.25</td>
<td>-2.26</td>
</tr>
<tr>
<td></td>
<td>Na(<em>2)S(</em>{4.76})</td>
<td>0.21</td>
<td>-5.26</td>
</tr>
<tr>
<td>623</td>
<td>Na(<em>2)S(</em>{2.89})</td>
<td>0.346</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>Na(<em>2)S(</em>{4.76})</td>
<td>0.21</td>
<td>3.89</td>
</tr>
</tbody>
</table>

6.5. Conclusions

The method of restricted diffusion was successfully used to determine differential diffusion coefficients in sodium polysulfide melts. Although the method is inherently accurate, variations of up to 5% were observed between cell runs. The results fall between the two groups of experimental data of the other researchers and generally agree with the microscopic model predictions. Although the temperature dependence of the experimental results is 80% greater than that predicted by the microscopic model, the diffusion coefficients from the two sources agree within 10% at 300°C. Considering that prior experimental results differed by greater than one order of magnitude, this agreement is quite good.

The experimental diffusion coefficients have been summarized by the correlation

\[ D = 0.0153 \exp(-5.89 \times 10^3 / T) \exp(5.30 x_+) \text{ cm}^2/\text{s}. \]  

(6-21)

Figures 6-14 and 6-15 show the experimental deviations from the correlated
Figure 6-14. Reduced diffusion data $D_e^{5890}/T$ plotted versus melt composition. Plot compares the correlated temperature dependence to the data.
Figure 6-15. Reduced diffusion data $D_e^{-5.30s}$ plotted as a function of temperature. Plot compares the correlated composition dependence to the data.
dependence on temperature and composition. The discrepant cell data have been included for comparison. In figure 6-14 the factor $D e^{5890/\theta}$ has been plotted versus melt composition. The standard deviation of this factor is $1.30 \times 10^{-2}$ cm$^2$/s. Similarly, the factor $D e^{-5.302\phi}$ is plotted as a function of temperature in figure 6-15; the standard deviation is $1.32 \times 10^{-7}$ cm$^2$/s. The scatter in the data in both figures is random, and equation 6-21 appears to be an acceptable fit of the data.

Values for the diffusion coefficient based on a thermodynamic driving force were calculated from the experimental data, using only open-circuit potential data for the sodium/sulfur cell. The binary interaction coefficients $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ were then evaluated using the calculated $\mathcal{D}$ values and transference number data. All of these results appear reasonable, and they generally agree with the microscopic model predictions.

Values of $\mathcal{D}_{0-}$ were then calculated with the use of density and conductivity data. Negative results were obtained for the temperatures 300 and 325°C. The physical significance of these results should not be emphasized. Rather, the negative results should probably be attributed to the limited transference number data. These results suggest a need for more accurate transference data, and possibly density data, for sodium polysulfide melts.
## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>height of diffusion cell, cm</td>
</tr>
<tr>
<td>( A )</td>
<td>constant in the expression for conductivity, equation 6-16</td>
</tr>
<tr>
<td>( A_m )</td>
<td>Fourier series coefficients defined by equation 4-8</td>
</tr>
<tr>
<td>( c )</td>
<td>concentration of electrolyte, mol/cm(^3)</td>
</tr>
<tr>
<td>( c_{av} )</td>
<td>average concentration defined by equation 3-6</td>
</tr>
<tr>
<td>( c_i )</td>
<td>concentration of species ( i ), mole/cm(^3)</td>
</tr>
<tr>
<td>( c_T )</td>
<td>total solution concentration, mole/cm(^3)</td>
</tr>
<tr>
<td>( C )</td>
<td>constant in equation 6-1, cm(^2)/sec</td>
</tr>
<tr>
<td>( C_1, , C_2 )</td>
<td>coefficients in equation 6-2</td>
</tr>
<tr>
<td>( D )</td>
<td>diffusion coefficient of electrolyte based on concentration driving force, cm(^2)/s</td>
</tr>
<tr>
<td>( D_i )</td>
<td>diffusion coefficient of species ( i ) based on concentration driving force, cm(^2)/s</td>
</tr>
<tr>
<td>( D_m )</td>
<td>diffusion coefficient defined by equation 4-29</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>diffusion coefficient of electrolyte based on thermodynamic driving force, cm(^2)/s</td>
</tr>
<tr>
<td>( \Phi_{ij} )</td>
<td>interaction coefficient between species ( i ) and ( j ), cm(^2)/s</td>
</tr>
<tr>
<td>( E_A )</td>
<td>activation energy, kJ/mol</td>
</tr>
<tr>
<td>( E_\varepsilon )</td>
<td>constant in conductivity expression, equation 6-16</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday's constant, 96,485 C/equiv</td>
</tr>
<tr>
<td>( G )</td>
<td>free energy per mole, J/mol</td>
</tr>
<tr>
<td>( H )</td>
<td>enthalpy per mole, J/mol</td>
</tr>
<tr>
<td>( i )</td>
<td>current density, A/cm(^2)</td>
</tr>
<tr>
<td>( K, L, M )</td>
<td>functions of concentration derivatives of the solution properties</td>
</tr>
<tr>
<td>( K_i )</td>
<td>equilibrium constant for reaction ( i ), atm(^{-\frac{(i-1)}{2}})</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$K_{ij}$</td>
<td>friction coefficient for interaction between species $i$ and $j$, J-s/cm$^5$</td>
</tr>
<tr>
<td>$m$</td>
<td>molality of electrolyte, mol/kg</td>
</tr>
<tr>
<td>$M_{av}$</td>
<td>average molecular weight defined in equation 6-4, g/mol</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molecular weight of species $i$, g/mol</td>
</tr>
<tr>
<td>$n_i$</td>
<td>particle fraction of species $i$</td>
</tr>
<tr>
<td>$N$</td>
<td>number of species present in solution</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avagadro's number, $8.023 \times 10^{23}$/mol</td>
</tr>
<tr>
<td>$N_i$</td>
<td>flux of species $i$, mol/cm$^2$-s</td>
</tr>
<tr>
<td>$P_{S_2}$</td>
<td>vapor pressure of ideal diatomic sulfur, atm</td>
</tr>
<tr>
<td>$r_i$</td>
<td>ionic radius of species $i$, cm</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, 8.314 J/mol-K</td>
</tr>
<tr>
<td>$R_i$</td>
<td>rate of homogeneous reaction of species $i$, mol/cm$^3$-s</td>
</tr>
<tr>
<td>$S$</td>
<td>entropy per mole, J/mol-K</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
<tr>
<td>$t_i$</td>
<td>transference number of species $i$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature, K</td>
</tr>
<tr>
<td>$T_0$</td>
<td>reference temperature in conductivity expression, equation 6-16</td>
</tr>
<tr>
<td>$v$</td>
<td>fluid velocity, cm$^2$/s</td>
</tr>
<tr>
<td>$v_i$</td>
<td>velocity of species $i$, cm$^2$/s</td>
</tr>
<tr>
<td>$V_i$</td>
<td>partial molar volume of species $i$, cm$^3$/mol</td>
</tr>
<tr>
<td>$x$</td>
<td>twice the ratio of sulfur to sodium in Na$_2$S$_x$</td>
</tr>
<tr>
<td>$x_s$</td>
<td>mole fraction of sodium sulfide</td>
</tr>
<tr>
<td>$x_S$</td>
<td>mole fraction of sulfur</td>
</tr>
<tr>
<td>$y$</td>
<td>mean activity coefficient of electrolyte on a concentration basis</td>
</tr>
<tr>
<td>$z_i$</td>
<td>charge number of species $i$, equiv/mol</td>
</tr>
</tbody>
</table>
Greek Symbols:

\[ \gamma_e \]  mean molal activity coefficient of electrolyte

\[ \Delta G_i \]  change in free energy for reaction \( i \), J/mol

\[ \Delta H_i \]  change in enthalpy for reaction \( i \), J/mol

\[ \Delta S_i \]  change in entropy for reaction \( i \), J/mol-K

\( \epsilon \)  function of time defined by equation 4-31

\( \epsilon_1, \epsilon_2 \)  parameters defined in equation 2-30 and 2-31, respectively

\( \kappa \)  conductivity, (ohm-cm)\(^{-1}\)

\( \mu_i \)  electrochemical potential of species \( i \), J/mol

\( \nu \)  number of moles of ions into which a mole of electrolyte dissociates

\( \nu_+, \nu_- \)  number of cations and anions respectively, into which a molecule of electrolyte dissociates

\( \rho \)  density, g/cm\(^3\)

Subscripts:

0  neutral sulfur solvent

1  \( S^= \) species

\( e \)  electrolyte

\( i \)  species number \( i \)

\( j \)  species number \( j \)

\( N \)  species number \( N \), \( Na^+ \) ions

\( o \)  initial value at zero time

+  cation

-  anion

Superscripts:

0  with respect to solvent velocity
References


Appendix A. Derivation of an Expression Relating the Sodium/Sulfur Cell Potential to the Activity of Sulfur

We are looking for a relationship between the activity of sulfur and the equilibrium potential \( U \) of a sodium-sulfur cell:

\[
C \mid Na(l) \mid \text{beta-alumina} \mid Na_2S_x(l) \mid C.
\]

If we represent the cell as

\[
\begin{array}{cccccc}
\alpha & \beta & \gamma & \delta & \alpha' \\
C & Na(l) & \beta \text{-alumina} & Na_2S + (x-1)S(l) & C,
\end{array}
\]

the equilibrium cell potential is

\[
FU = F(U_S - U_{Na}) = \mu^\alpha_{e^-} - \mu^\alpha'_{e^+}. \tag{A-1}
\]

Using the equilibrium relations among the various phases:

\[
\begin{align*}
\mu^\beta_{Na} &= \mu^\gamma_{Na^+} + \mu^\alpha_{e^-} \tag{A-2} \\
\mu^\delta_{S} &= 2 \mu^\alpha_{e^-} + \mu^\delta_{S}, \tag{A-3}
\end{align*}
\]

the cell potential can be rewritten as

\[
FU = \mu^\alpha_{e^-} - \mu^\alpha'_{e^+} = \mu^\beta_{Na} - \mu^\gamma_{Na^+} - \frac{1}{2} \mu^\delta_{S} + \frac{1}{2} \mu^\delta_{S}. \tag{A-4}
\]

Assuming sodium metal in phase \( \beta \) to be pure, and the sodium ions in the \( \gamma \) and \( \delta \) phases to be equilibrated, we find

\[
FU = \mu^\beta_{Na} + \frac{1}{2} \mu^\delta_{S} - \frac{1}{2} \mu^\delta_{S}. \tag{A-5}
\]

Differentiating, and using the Gibbs-Duhem equation (equation 2-35) and the definition of the chemical potential of sulfur:

\[
\mu_S = \mu^\delta_{S} + RT \ln a_S, \tag{A-6}
\]

we obtain the final expression

\[
FdU = \frac{1}{2} (1 + \frac{x_S}{x_e}) d \mu_S = \frac{RT}{2x_e} d \ln a_S. \tag{A-7}
\]
Appendix B. Raw Material Analysis

The lot analysis for the raw materials, sodium sulfide and sodium metal, are given in tables B-1 through B-3. The 100 mesh, grade 4N, anhydrous sodium sulfide was purchased from the Noah Chemical Division of Noah Industrial Corp. Two different lots of sodium sulfide were used. Lot 38022 was opened just prior to its use, whereas lot 22719 was stored in the He-atmosphere glove box for two years prior to the experiments. A water analysis was obtained from the manufacturer for lot 38022. The lump sodium metal was purchased from J. T. Baker Company.

Table B-1. Lot Analysis for Sodium Sulfide, lot number 38022

<table>
<thead>
<tr>
<th>Material</th>
<th>Spectrographic Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>40 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>7 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>3 ppm</td>
</tr>
<tr>
<td>Mg</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Mo</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Water</td>
<td>51 ppm</td>
</tr>
</tbody>
</table>

Table B-2. Lot Analysis for Sodium Sulfide, lot number 22719

<table>
<thead>
<tr>
<th>Material</th>
<th>Spectrographic Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Cd</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>2 ppm</td>
</tr>
<tr>
<td>K</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Mg</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>
Table B-3. Lot Analysis for Sodium Metal, lot number 14332

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum Level Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>20 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>20 ppm</td>
</tr>
<tr>
<td>Phosphates</td>
<td>3 ppm</td>
</tr>
<tr>
<td>Heavy Metals</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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