LBL-23820 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 1 9 1987

LIBRARY AND
DOCUMENTS SECTION

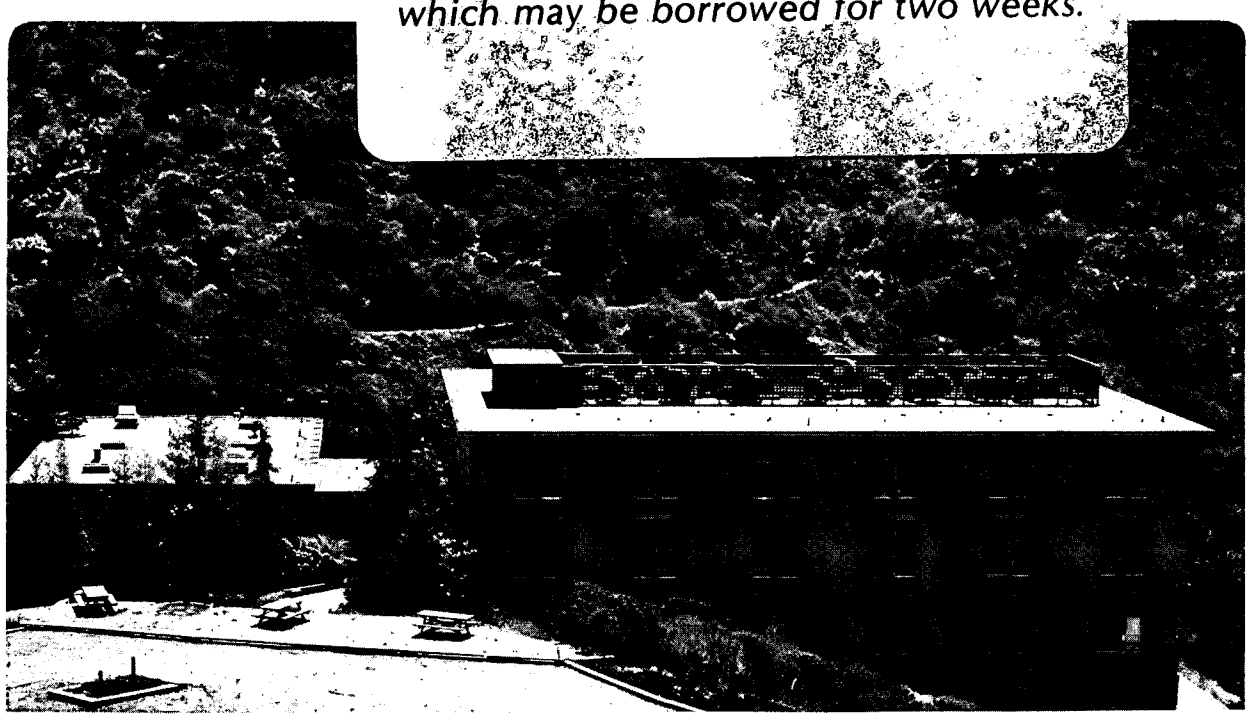
Submitted to Journal of the Electrochemical Society

Differential Diffusion Coefficients of Sodium Polysulfide Melts

S.D. Thompson and J. Newman

August 1987

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.



LBL-23820 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-23820

Differential Diffusion Coefficients of Sodium Polysulfide Melts

Susan D. Thompson[1] and John Newman

Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering,
University of California,
Berkeley, California 94720

August 27, 1987

Abstract

The method of restricted diffusion has been applied to sodium polysulfide melts in order to determine differential diffusion coefficients spanning the composition range of the single-phase liquid region (Na_2S_3 to Na_2S_5), at temperatures between 300 and 350°C. Molybdenum electrodes at the ends of the cell gave open-circuit potentials in response to the transient concentration difference. The shape of the potential-*versus*-time plots showed the expected dependence on the initial concentration profile.

The following expression summarizes the experimental data:

$$D = 0.0153 \exp(-5890/T) \exp(5.30x_e) \text{ cm}^2/\text{s}. \quad (1)$$

The diffusion coefficients showed a temperature dependence in harmony with viscosity data, but not conductivity data.

[1]Present address: Dow Chemical Company, Pittsburg, California.

Key words: high-temperature battery, molten salt.

Introduction

Importance of the Na/S Cell.—The sodium/sulfur secondary cell is probably the closest to commercial viability of all the molten-salt, high-temperature systems. It is a leading candidate 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 sytems.

For over twelve years, substantial effort has been devoted to the development of the sodium/sulfur system. The major technical problems concern safety, durability of the electrolyte and seals, and corrosion of the container materials. However, mass transport of reactants and products to and from the electrode surface is also important in the operation of the sulfur electrode. The rate of diffusion in sodium polysulfide melts is the focus of this research.

The sodium/sulfur cell consists of a negative sodium electrode and a positive sulfur electrode separated by a solid electrolyte. Both electrodes are molten, since the cell typically operates between 300 and 375°C. Sudworth and Tilley[1] have reviewed sodium/sulfur cells with β-alumina electrolytes.

Depending on the state of charge, the polysulfide composition in the sulfur electrode varies between pure S and Na_2S_3, or 100 to 60 atom% S. The size of the single-phase sulfur region does not extend below 99% S, and further discharge leads to a second liquid phase with a composition around $Na_2S_{5.2}$. If the sulfur content of the positive electrode drops below 72.2 atom%, or $Na_2S_{5.2}$, corresponding to a cell which is 60 percent discharged, the polysulfide becomes a single phase. Sodium/sulfur cells are considered fully discharged around 60 atom% S, since a solid Na_2S_2 phase starts to form at 58.5

atom% S. This second single-phase region, between the approximate overall melt compositions Na_2S_3 and $Na_2S_{5.2}$, is studied in this work.

Structure of the solution.—The sodium polysulfide melt has been described by both microscopic and macroscopic models. The melt is known to contain the ions $S_2^=$, $S_3^=$, $S_4^=$, $S_5^=$, and $S_6^=$,[2,3] and to be free of elemental sulfur.[4] The microscopic model thus deals with sodium cations and seven different polysulfide anions. However, if there is rapid equilibration among these polysulfide species, the melt can be treated as a binary solution for purposes of thermodynamics and transport phenomena. Stoichiometrically, the binary melt can be prepared from sodium sulfide electrolyte (Na_2S) and neutral sulfur solvent. Therefore, the macroscopic model considers sodium cations, monosulfide anions, and neutral sulfur solvent. In this work, the macroscopic model of the melt is used.

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_2S electrolyte (x_e). The compositions Na_2S_3 and Na_2S_5 correspond to values of x_e of 0.333 and 0.2, respectively. One can now apply the standard treatment and notation for a binary electrolyte.[5] Thus, the transport properties will consist of the viscosity, conductivity, diffusion coefficient, and one transference number. Note, however, that x_e is defined as the ratio of the moles of Na_2S to the sum of the moles of Na_2S and S, and c refers to the electrolyte concentration.

Literature data.—Tischer and Ludwig[2] combined experimental data of several investigators to determine a few diffusion coefficients which are internally self consistent. Rotating-disk data of Armstrong *et al.*[6] with the functional form $cD^{2/3}$, where c is the

concentration of the diffusing species involved in the electrode reaction, were combined with the stationary electrode chronopotentiometric data of South *et al.*[7] with the form $cD^{1/2}$ to obtain diffusion coefficients for Na_2S_5 of 2.4×10^{-7} cm^2/s at 300°C, and 6.3×10^{-7} cm^2/s at 350°C. The activation energy obtained from these results, 57.3 kJ/mol, is larger than the value of 46.9 kJ/mol obtained from viscosity data. Tischer and Ludwig also combined linear sweep and chronopotentiometric data at 350°C of South *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_2S_4 at 300°C.

Divisek *et al.*[8] 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 activation energy calculated from these results is 48.1 kJ/mol. 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_2S_4 and $Na_2S_{5.2}$, using labeled S-35 as a tracer. The results at 300°C were $D = 2.3 \times 10^{-5}$ cm^2/s for Na_2S_4 and 1.5×10^{-5} cm^2/s for $Na_2S_{5.2}$. 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 (simultaneous sulfide ion and sodium ion diffusion in the first case, and uncharged sulfur species movement in the second).

Armstrong *et al.*[9] determined diffusion coefficients at 350°C, from alternating-current impedance measurements made on a rotating-disk electrode. Their results, $D = 9.8 \times 10^{-6}$ cm^2/s for $Na_2S_{3.08}$ and $D = 1.4 \times 10^{-5}$ cm^2/s for $Na_2S_{4.86}$, 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 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's results, seem more reasonable since they also agree with results predicted from conductivity data. Tischer and Ludwig estimated a diffusion coefficient of 7 to 9×10^{-7} cm^2/s for Na_2S_4 at 300°C, from the equivalent conductance of the melt using the Nernst-Einstein relation. 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.

Restricted diffusion.—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 summarized in the next section 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.

In this method, an initial concentration profile is allowed to relax with time. At sufficiently long times, the concentration profile reduces to an exponential function of time. The time dependence of the concentration difference across the diffusion cell can then be described by the equation

$$\Delta c = c_{top} - c_{bottom} = 2A_1 \exp\left(\frac{-\pi^2 Dt}{a^2}\right) . \tag{2}$$

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_1; however, it has no effect on the diffusion coefficient being measured.

The concentration difference across the diffusion cell cannot be measured directly. However, any property of the sodium polysulfide melt which varies linearly with concentration will have a time dependence of the same form. The only difference will be the value of the coefficient. Refractive index[10,11,12] and conductance[13] 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.

Potential measurements.—It has been proposed[14] 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[4] have measured the *emf* of the following

concentration cell with transference:

$$C \mid Na_2S_x(l) \mid\mid Na_2S_5(l) + S(l) \mid C \tag{3}$$

for a large range of sodium polysulfide compositions. The *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.

Model of Restricted Diffusion

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 suggested the method of restricted diffusion, and Harned and French[13] developed the method in 1945. Newman and Chapman[10,11] performed a rigorous analysis for concentrated solutions.

Restricted Diffusion in Dilute Solutions.—Figure 1 is a schematic of a restricted-diffusion cell. 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_∞. In this problem the fluid velocity is zero, and the governing equation is simply Fick's second law in one dimension:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2}, \tag{4}$$

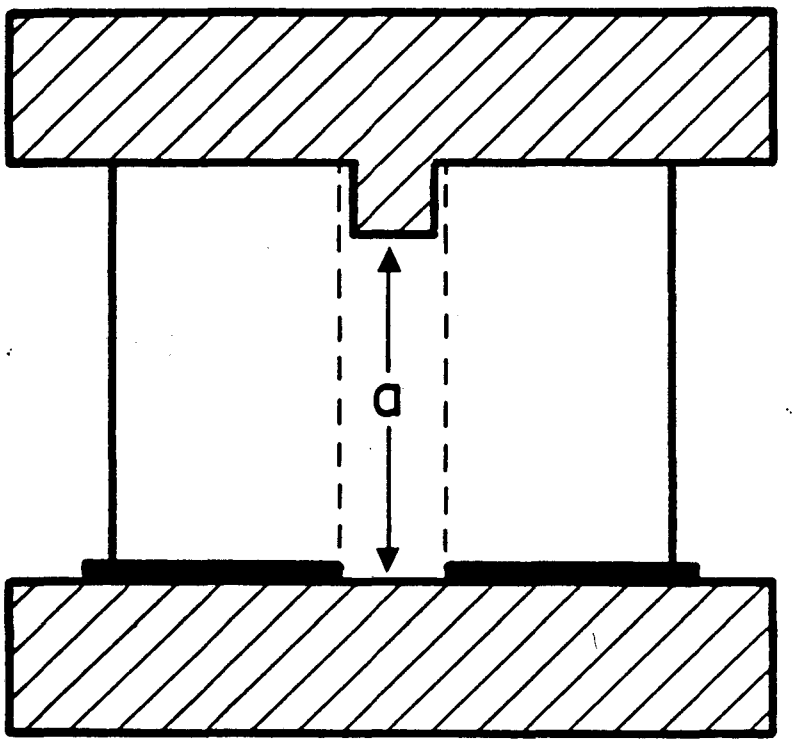


Figure 1. Schematic showing how the cell height, *a*, is measured. The cell top and bottom are molybdenum electrodes, and the cell body is a Pyrex cylinder. An aluminum gasket seals the cell at the bottom, and the top electrode is machined to extend into the hole in the Pyrex, to promote contact with the polysulfide melt.

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

$$\frac{\partial c}{\partial y} = 0 \quad \text{at } y = 0 \tag{5}$$

and

$$\frac{\partial c}{\partial y} = 0 \quad \text{at } y = a. \tag{6}$$

The solution to this problem[11,13] is the Fourier series

$$c = c_\infty + \sum_{n=1}^{\infty} A_n \exp\left(-\frac{n^2\pi^2 Dt}{a^2}\right) \cos\frac{n\pi y}{a}. \tag{7}$$

The values of the A_n coefficients depend on the initial concentration profile in the diffusion cell.

In the experimental system, we are interested in the concentration difference between any two convenient points in the diffusion cell. At long times the higher order terms become negligible compared to the first time-dependent term, and a plot of ln Δc *versus* time will be a straight line of slope $-\pi^2 D/a^2$. 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 conductance 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.

Restricted Diffusion in Concentrated Solutions.—Newman and Chapman[11] presented a rigorous analysis of restricted diffusion based on concentrated-solution-theory flux equations; it includes the effects of solvent flux and variable solution properties. They also developed an optical cell that can deal with concentrated solutions. Nişancioğlu and Newman[12] used this system for aqueous solutions of nitric acid.

As time approaches infinity, the concentration, density, and height of the liquid column approach the steady-state values c_∞, ρ_∞, and a_∞, respectively. The diffusion coefficient can be expanded in a Taylor series around c_∞:

$$D = D_\infty + \left.\frac{dD}{dc}\right|_{c_\infty} (c-c_\infty) + \frac{1}{2}\left.\frac{d^2D}{dc^2}\right|_{c_\infty} (c-c_\infty)^2 + \ldots \tag{8}$$

The manipulations are quite complicated, and therefore only the final results will be discussed here. The decay in time to a uniform composition is governed by the function ε:

$$\varepsilon = \exp\left(\frac{-D_\infty t\pi^2}{a_\infty^2}\right) . \tag{9}$$

This also appears as a factor in the dilute-solution result in equation 7. The resulting con-

centration difference between the top and the bottom of the cell is

$$\Delta c = c(0) - c(a) = 2A_1\varepsilon + 2(K+L)\varepsilon^3 + \dots , \tag{10}$$

where A_1 is a function of the initial concentration profile and K and L are complicated functions of the concentration derivatives of the solution properties. The results also show that the difference between a and a_∞ is very small.

It will take longer in principle for the higher order terms in equation 10 to become negligible, than it did for dilute solutions, since the second term in the series is of order ε^3 instead of ε^{25} or ε^9 as can be achieved with dilute-solution theory. However, at sufficiently long times, the differential diffusion coefficient D_∞, corresponding to the final cell concentration c_∞, can still be determined from a plot of $\ln\Delta c$ *versus* time.

Model of Concentration Profile Relaxation.—To predict the shape of the $\ln\Delta c$ *versus* time plot and the effect of the initial concentration profile, the concentration-profile relaxation was modeled using the concentration expression developed for dilute solutions (equation 7).

Three initial concentration profiles were considered: a cosine profile, 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 $(\Delta c)_o$. The A_n coefficients for the various concentration profiles were determined from the orthogonality property of the cosine function. The results are shown in figure 2 for sensors placed at the top and bottom of the cell. For the cosine profile the semi-log plot is linear over the entire time scale, and 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} cm^2/s,

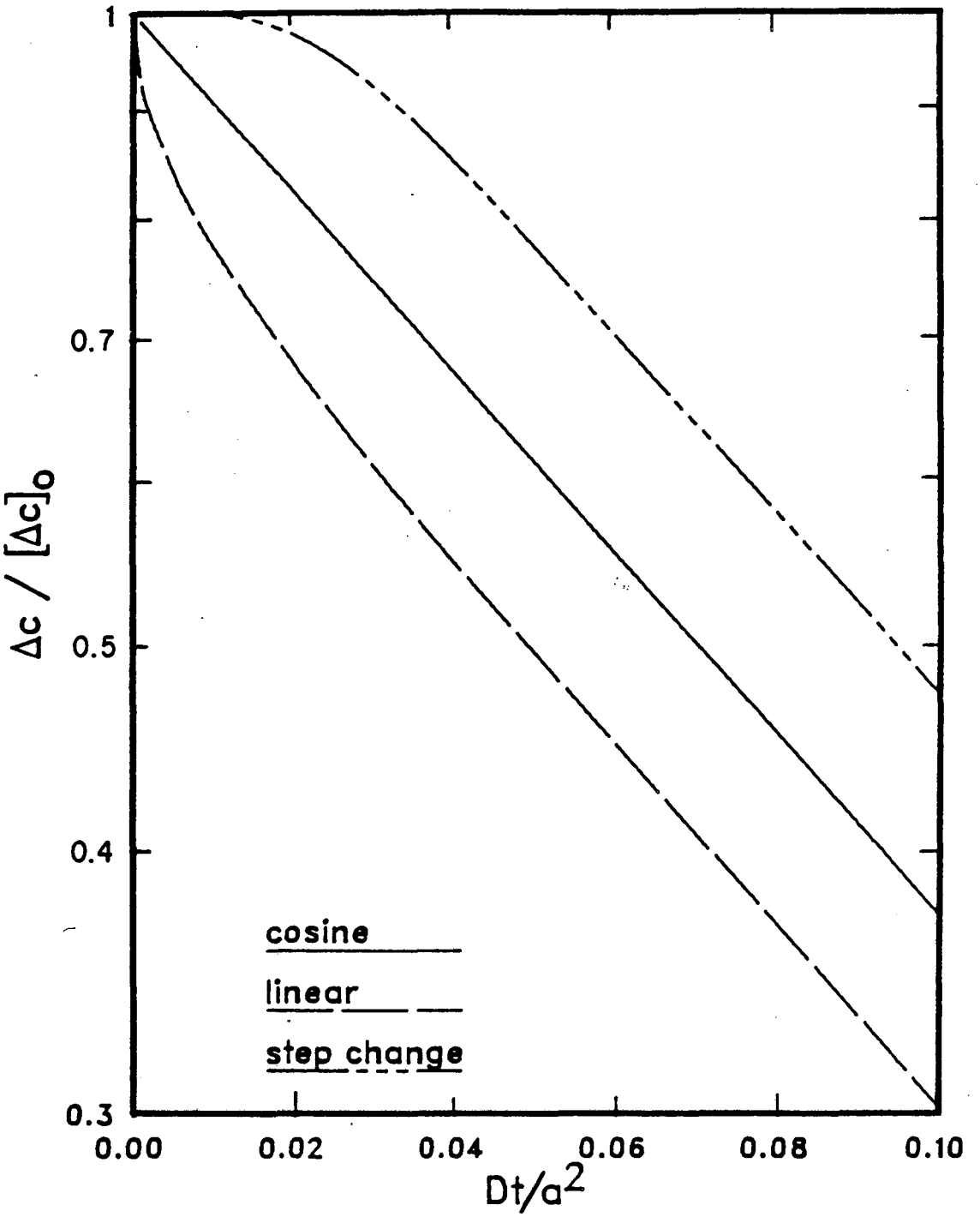


Figure 2. Concentration difference between the top and the bottom of the cell, plotted *versus* dimensionless time. $[\Delta c]_o$ is the initial concentration difference between the top and the bottom of the cell.

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 slopes of the curves are zero and infinite for the initially-sharp boundary and linear profile, respectively.

The location of the reference points in the diffusion cell also affects the shape of the $\ln\Delta c$ *versus* time plot. Figure 3 shows the results for reference points placed at $a/6$ and $5a/6$. The sensors are exposed to the entire applied concentration difference only for the case of the step-change profile, since $(\Delta c)_o$ 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. Straight-line behavior occurs considerably faster for this sensor arrangement due to the behavior of the cosine function. However, it is not always possible to design cells with sensors at these locations.

Experimental Equipment and Procedure

Cell Design.—A sketch of the diffusion cell is shown in figure 1. The cell is a 1 cm tall Pyrex disk with a 3.5 mm hole bored through the center and sandwiched between two 0.635 cm thick molybdenum electrodes. The cell size was chosen to limit the run time of each diffusion measurement to two days. The touching Pyrex and molybdenum surfaces were highly polished to ensure a tight seal. The sodium polysulfide melt is corrosive, and molybdenum is appropriate for the electrodes because its sulfide is stable and electronically conducting.

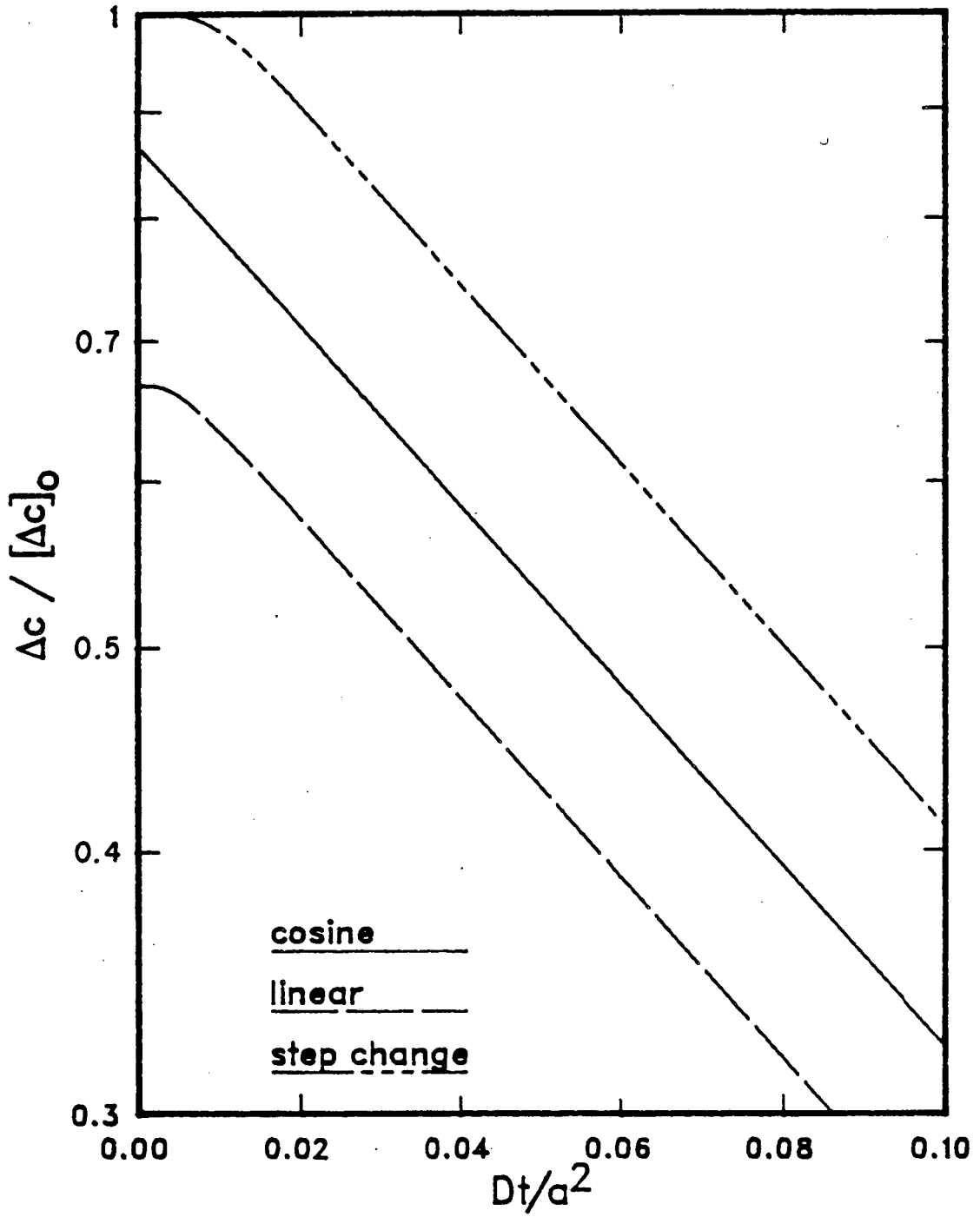


Figure 3. Concentration difference between the two points $y=a/6$ and $y=5a/6$, plotted *versus* dimensionless time. $[\Delta c]_o$ is the initial concentration difference between the top and the bottom of the cell.

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 4×10^{-4} ohm^{-1}–cm^{-1})[15] 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. An aluminum gasket was used for this seal since it introduced no impurities into the system.

The cell must have a uniform temperature profile because of the possibilities of natural convection and thermocouple effects. Natural convection is not accounted for in the theory of restricted diffusion, and the thermocouple effect would produce a potential offset across the cell. In the final apparatus, the diffusion cell was operated inside a brass block, a design improvement which reduced the equilibrium potential offset to less than 1 mV.

To obtain data faster, two Pyrex diffusion cells and their respective molybdenum reference electrodes were placed inside a common brass block. The upper electrodes were machined to extend approximately 2 mm into the top of the diffusion cells to account for the reduction in polysulfide density upon melting (see figure 1). Bolts were used to squeeze the diffusion cells closed; after the block was heated to the operating temperature, these bolts could be further tightened to compensate for thermal expansion and polysulfide density changes upon melting. A thermocouple and a voltmeter were used for temperature measurement. The temperature in the diffusion cell was controlled to about one kelvin, and no effect of natural convection was noticed in normal operation.

Sodium polysulfides are very hygroscopic. It was therefore necessary to do all materials handling and experiments within a helium-atmosphere glove box. Purification units controlled the concentrations of nitrogen, oxygen, and water. The water concentration was never greater than 1 ppm.

The brass block and diffusion cells were suspended in a furnace well that was 46 cm long and had a 15 cm inside diameter. Heat shields were placed above the diffusion cell to reduce convection and radiation in the furnace well.

Determination of the Cell Height.—Since the method of restricted diffusion yields directly the value of D/a^2, any error in the cell height will be doubled during the calculation of D. From figure 1 we see that the cell height (a) is the height of the Pyrex cell, plus the thickness of the aluminum gasket, minus the length of the extension on the upper electrode. The error due to the annular space between the extension on the upper electrode and the Pyrex diffusion cell was minimized by machining the electrode extension to approximately the same diameter as the Pyrex cell. A lower limit of uncertainty can be obtained by dividing the volume of the annular space by the closed cell volume, and multiplying by 100. With a value for a of 7 mm, a cell diameter of 3.6 mm, and a 2 mm electrode extension whose diameter is 0.13 mm less than that of the cell, we calculate an extra volume of 2 percent. This could lead to reported diffusion coefficients being 4 percent less than the real values.

From the coefficients of linear thermal expansion for aluminum, molybdenum, and Pyrex, one can estimate that the cell height is 0.11 percent larger at 325°C than at 25°C. The effect of thermal expansion on the cell height is negligible compared to the uncertainty due to the electrode extension. Consequently, the cell height was measured at room

temperature.

Polysulfide Preparation.—Cleaver[16] describes five methods used to prepare sodium polysulfides. For several of these methods, Brauer[17] provides more detail. For the more recent methods, electrochemical preparation and preparation from monosulfide and sulfur, the best references are Cleaver *et al.*[18] and Rosén and Tegman,[19] respectively.

The simplest technique is preparation from monosulfide and sulfur. For the restricted-diffusion experiments, the polysulfide composition is most accurately determined at the end of the diffusion-coefficient measurement. This method was used with anhydrous sodium sulfide purchased from the Noah Chemical Div. of Noah Industrial Corp. (grade 4N and analyzed to have a water concentration of 51 ppm when new) and grade 6N sulfur powder purchased from Electronic Space Products Inc.

The procedure suggested by Rosén and Tegman[19] was modified slightly for making the sodium polysulfide slugs. Stoichiometric amounts of sulfur and sodium sulfide were weighed, ground together with a mortar and pestle, and placed into the reaction tube, which was then evacuated and sealed. To avoid excessive sulfur vapor pressures, the mixture was first reacted as a solid at 200 to 230°C for 12 hours. To obtain a completely homogeneous polysulfide, the subsequent liquid reaction time recommended by Rosén and Tegman was increased to 24 hours at 375°C. A crystalline product was obtained by cooling the polysulfide slowly, eliminating any need for regrinding and tempering. A crystalline product is preferred because a glass slug would crack and shatter while being removed from the reaction tube.

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, heated and cooled back down several times before it was completely filled. However, the prepared slug of polysulfides was more efficient, since it requires only one cell filling.

Measurement of Diffusion Coefficients.—Once the molybdenum electrodes were polished and the polysulfide slug prepared, the diffusion cell was assembled inside the brass block, and the bolt which presses on the top electrode to close the diffusion cell was tightened. When the block reached the operating temperature, the cell was retightened. To ensure that the cell was completely filled, the cell resistance was measured with an ac bridge. This resistance measurement was repeated at least once a day to check for sulfur leaks.

A potential of 30 to 100 mV was 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 by the charging time. The top electrode was normally made positive with respect to the bottom electrode to produce the lower density polysulfide at the top of the cell and avoid natural convection.

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 the potential-*versus*-time data to measure the diffusion coefficient accurately. Potentials greater than 300 mV cannot be used because a second phase will form near one or both of the electrodes.

The power supply was then turned off, and the potential across the cell was monitored with time and recorded every 10 minutes using two buffer amplifiers and a

multimeter. The buffer amplifiers were unity-gain devices with input impedances greater than 10^{12} ohms. An electrometer with an input impedance of 10^{14} ohms was used periodically to check the potential measurements.

When the potential decayed to zero, typically after two days, the diffusion coefficient corresponding to the average, or final, cell concentration was obtained from the potential-*versus*-time data. Generally the potential leveled out around 0.5 or 1 mV, instead of zero, due to the temperature difference 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 was subtracted from the data before the diffusion coefficient was calculated. The temperature could 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 was determined at the end of the series of measurements. The sodium polysulfide analysis was primarily done by the UC Berkeley microanalytical laboratory. Sodium concentrations were measured using atomic absorption spectrophotometry. Sulfur was oxidized to sulphate and then precipitated as barium sulphate. Both Scott[20] and Fehér and Berthold[21] describe in detail this analytical method for sulfur.

Results and Discussion

With the method of restricted diffusion, differential diffusion coefficients were measured as a function of sodium polysulfide melt composition and temperature; these results are listed in table 1 and plotted in figure 4.

Effect of the Initial Concentration Profile.—Three types of initial concentration profiles were discussed earlier. 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. Experi-

Table 1. Experimental Diffusion Coefficients.

composition	temperature (K)	$D \times 10^6$ (cm^2/s)
$Na_2S_{2.89}$	573.15	3.26
		3.42
	622.65	6.35
$Na_2S_{3.43}$	573.15	1.10
		1.22
		1.34
	596.15	1.91
	597.15	1.80
	624.15	2.96
$Na_2S_{3.59}$	573.95	2.25
	598.25	3.65
~Na_2S_4	572.95	2.03
	576.55	2.24
	600.35	3.36
$Na_2S_{4.02}$	573.95	2.10
		2.12
$Na_2S_{4.76}$	573.15	1.57
		1.59
	598.15	2.31
		2.37
	623.15	3.63

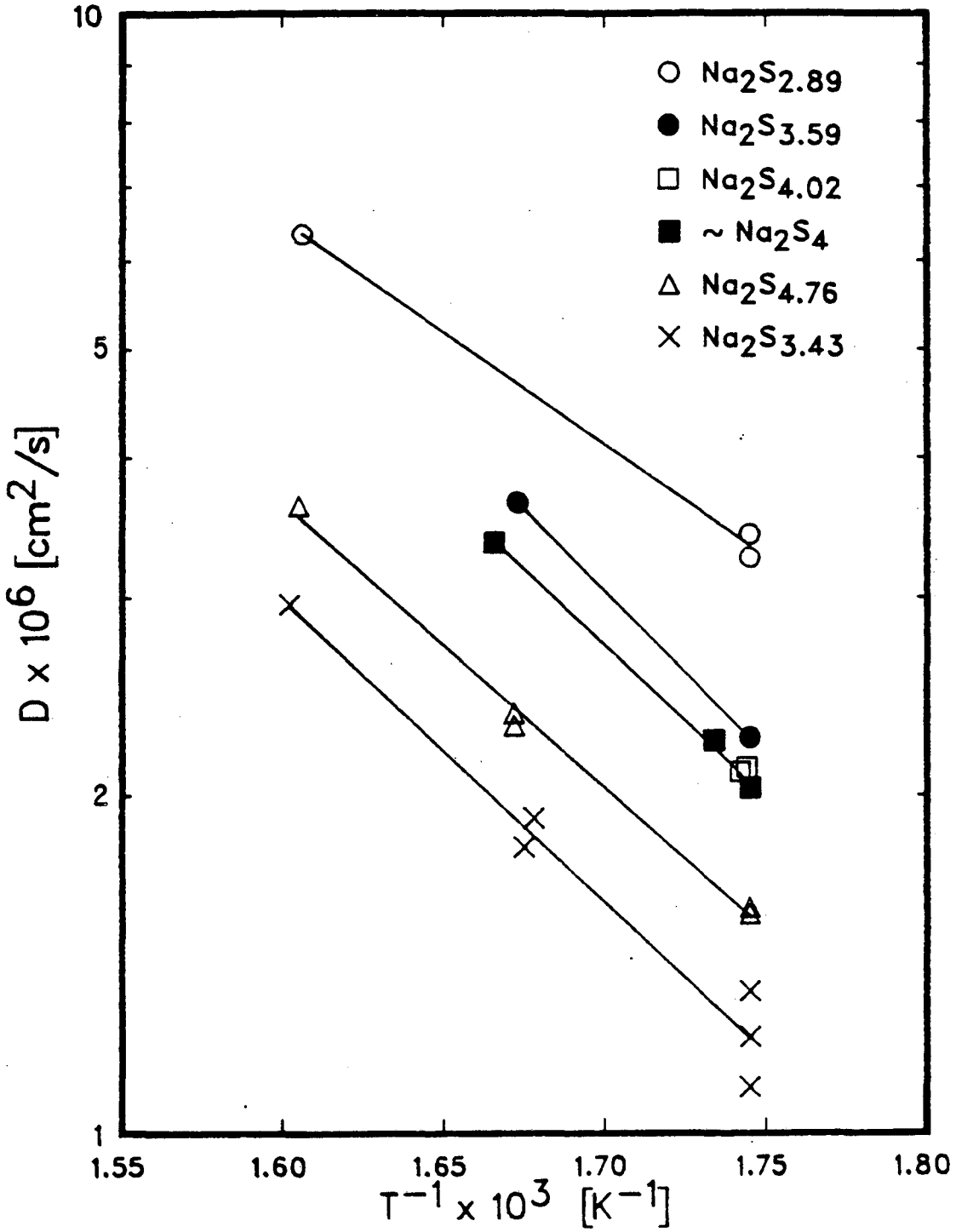


Figure 4. Diffusion coefficients determined experimentally, using the restricted diffusion method, plotted as a function of temperature.

mental potential data for linear and step-change initial concentration profiles are shown in figure 5; these are typical of the potential data generally measured. 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. Comparison with figure 2 shows that 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 resembles the modeling results for dimensionless times greater than about 0.04. The sharp potential drop at small times resulted from the brief application of a potential across the cell, during a direct-current resistance measurement. In later experiments, resistance measurements were made using an autobalance universal ac bridge, thereby minimizing the perturbation to the cell.

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. Values of D/a^2 measured in preliminary experiments for $Na_2S_{3.48}$ at 299°C showed that the results are not affected by either the potential used to charge the cell or the amount of time it was applied. The discrepancies among these results were of the same magnitude as the variation among identical runs. The data suggest that the standard error is about 3 percent.

Temperature and Composition Dependence.—The diffusion coefficients plotted in figure 4 appear to have a temperature dependence of the Arrhenius form, with nearly the same slope. The average activation energy E_A calculated from all of the experiments is 49.5 kJ/mol. In table 2, this value is compared to the results of Tischer and Ludwig and

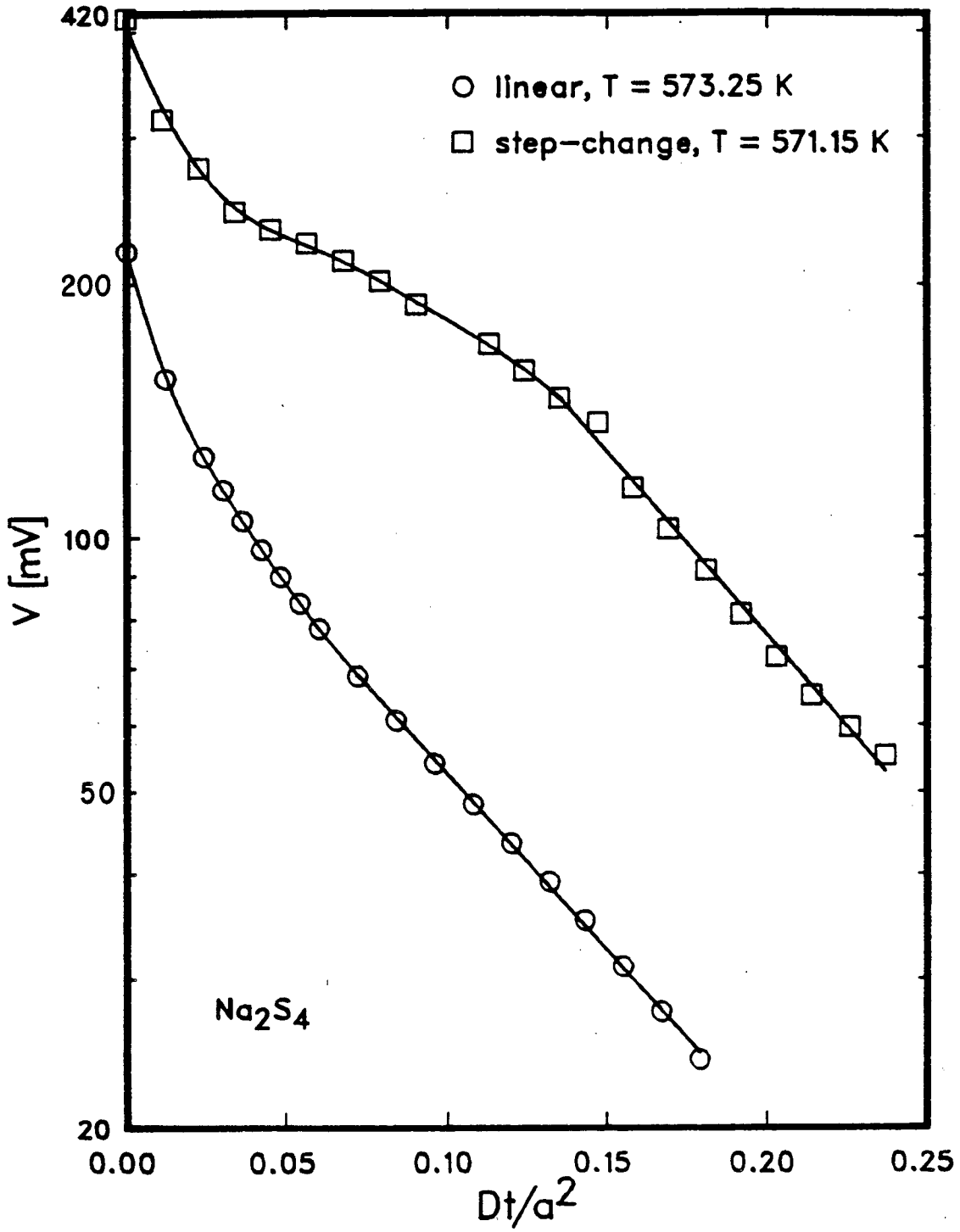


Figure 5. Decay of potential for two initial concentration profiles. The potential between the top and the bottom of the diffusion cell has been plotted *versus* dimensionless time.

of Divisek *et al.*, microscopic model predictions, and values calculated from viscosity and conductivity data.

The activation energy determined from the restricted diffusion experiments agrees with the results of Tischer and Ludwig and of Divisek *et al.* and the viscosity data. The microscopic model predictions[14,22] are based on the conductivity data, and all of these show activation energies disturbingly different from those of diffusion and viscous effects.

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. All of the restricted diffusion results at 300°C are between 1 and 4 × 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

Table 2. Values of the Activation Energy for Sodium Polysulfides.

Source	E_A kJ/mol	Composition
restricted diffusion	49.5	Na_2S_3 – Na_2S_5
Tischer and Ludwig[2]	57.3	Na_2S_5
Divisek *et al.*[8]	48.1	Na_2S_4
microscopic model[14]	27.8	Na_2S_3 – Na_2S_5
modified microscopic model[22]	30.6	Na_2S_3 – Na_2S_5
viscosity[23]	–46.9	Na_2S_3 – Na_2S_5
conductivity[18]	32.2	Na_2S_3 – Na_2S_5

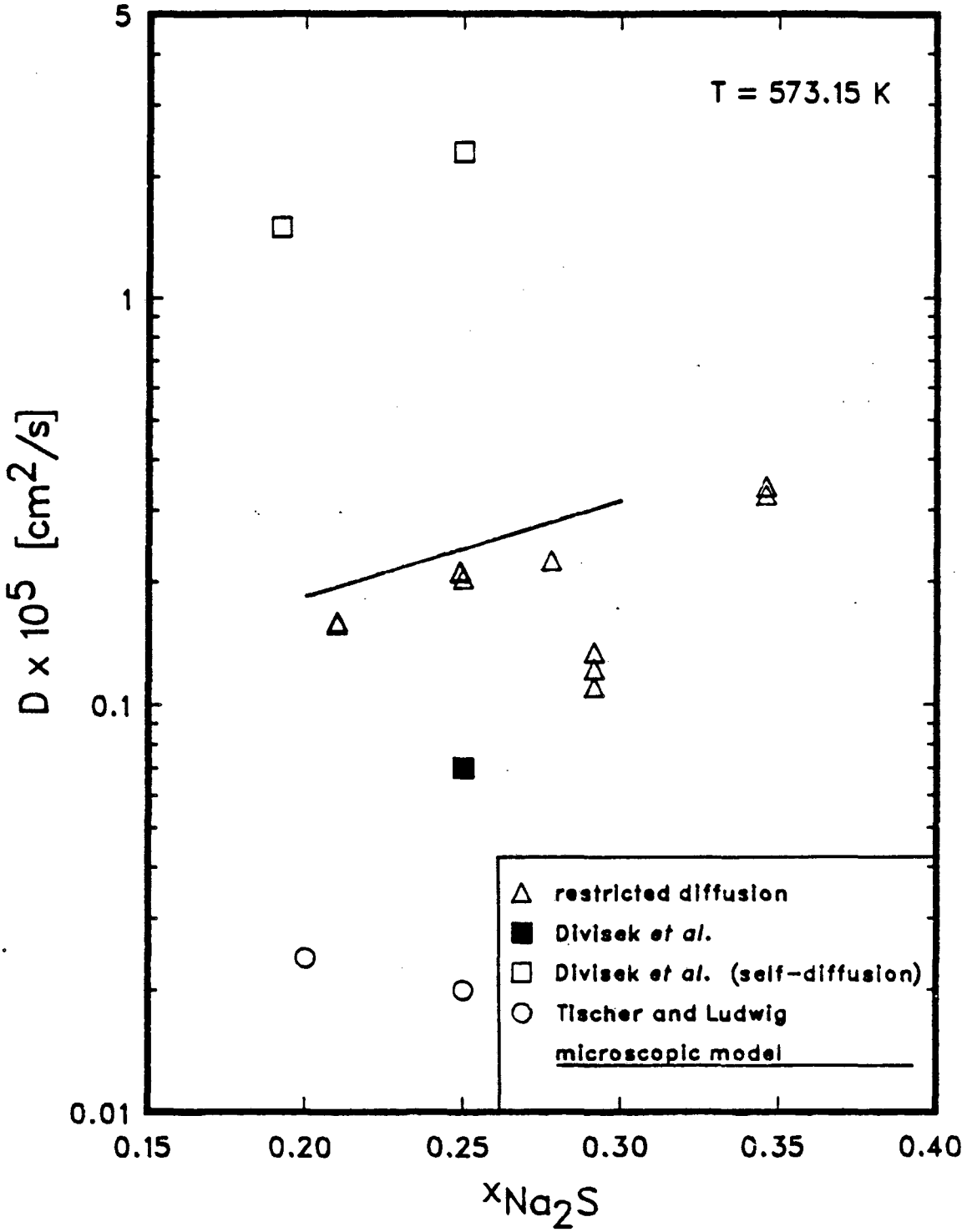


Figure 6. Comparison of the experimental diffusion coefficients to the results of other researchers and the predictions of the microscopic model, at a temperature of 573 K.

microscopic model predictions, both in value and composition dependence. However, the data from one cell (x_e = 0.292) lie well below the other data. The variation between runs is considerably larger in this cell than in the others, indicating that the cell was not behaving properly and that these results should be neglected.

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

$$D = 0.0153 \exp(-5890/T) \exp(5.30\, x_e)\ \mathrm{cm^2/s}. \tag{11}$$

The discrepant data obtained for $Na_2S_{3.43}$ were not considered since they vary by almost 3 standard deviations from this fit. The value of the activation energy, 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. The correlation is compared to the experimental data in figure 7.

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, and the density data of Cleaver and Davies[23] suggest that the density of the polysulfide will therefore be higher at the top of the diffusion cell. The relaxation of the concentration profile will then be enhanced by natural convection, and the diffusion coefficient measured in such an experiment will be higher than the true value.

Natural convection due to the positive density gradient increased the apparent diffusion coefficients by about 15 percent at a low value of x_e and more at higher values. The results are surprisingly reproducible, and the composition dependence at 573 K can be represented by changing the coefficient 5.30 in equation 11 to 7.54.

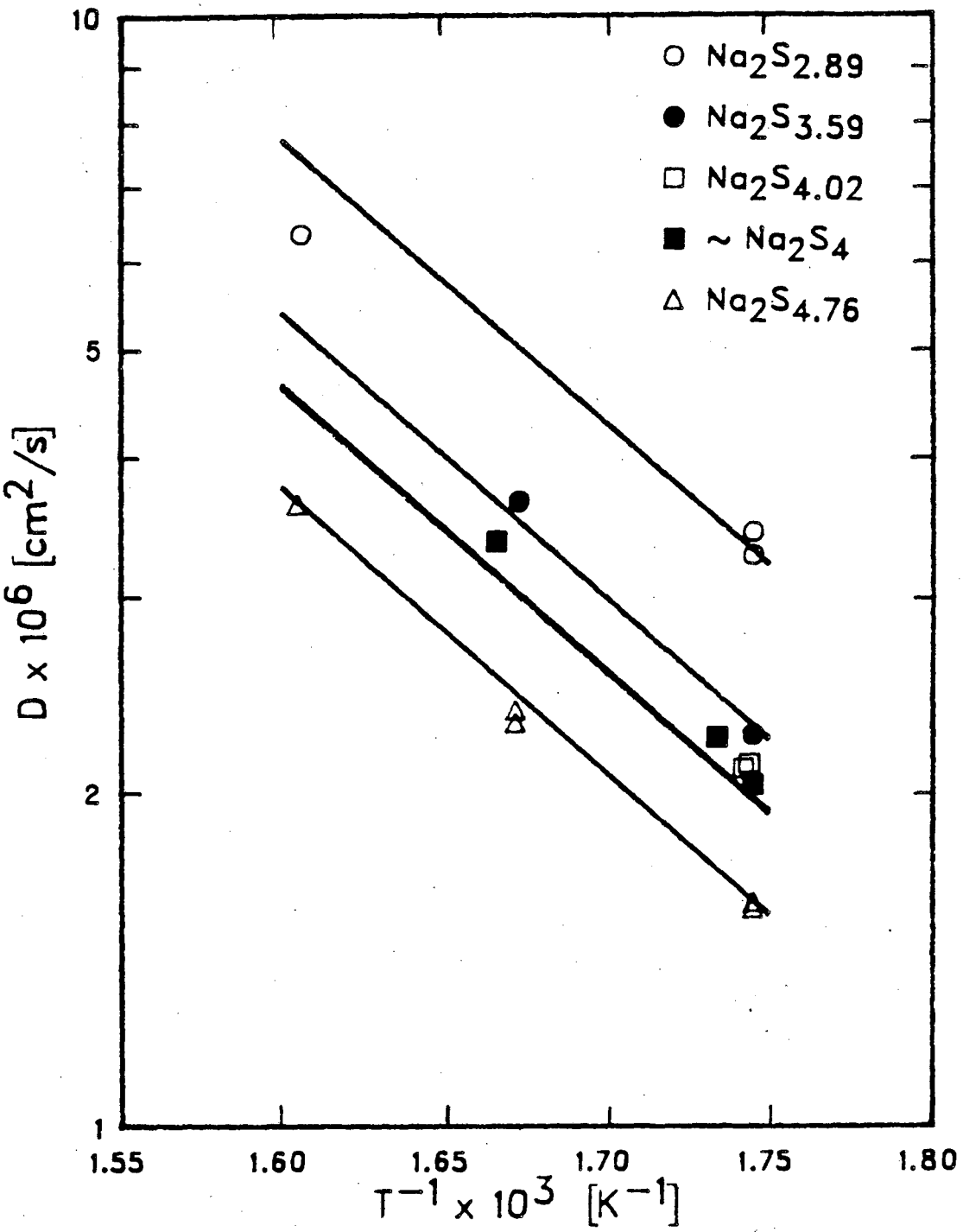


Figure 7. Comparison of the experimental data to the derived correlation. Solid lines represent the correlation $D = 0.0153 \exp(-5890/T) \exp(5.30x_e)$ cm^2/s. Discrepant-cell data are omitted.

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 percent were observed between cell runs. All of the results fall between the two groups of experimental data of the other researchers and generally agree with the microscopic model predictions. Although the activation energy of the experimental results is 80 percent greater than that predicted by the microscopic model, the diffusion coefficients from the two sources agree within 10 percent 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 in equation 11. Figure 8 shows the experimental deviations from the correlated dependence on temperature and composition. The discrepant-cell data have been included for comparison. The standard deviation in the quantity $De^{-5.30x_s}$ is 1.32×10^{-7} cm^2/s. Similarly, the standard deviation in the quantity $De^{5890/T}$ is 1.30×10^{-2} cm^2/s. The scatter in the data in both quantities is random, and equation 11 appears to be an acceptable fit of the data.

If the polysulfide melt is truly a binary mixture, that is, if equilibration among the polysulfide ions is rapid, the macroscopic diffusion coefficient reported is the only one which can be measured unambiguously. The microscopic model serves mainly for prediction of values of such macroscopic transport properties. In view of the discrepancy between viscosity and diffusion coefficient data on the one hand and conductivity data on the other, the power of the microscopic model should now, perhaps, be turned to the

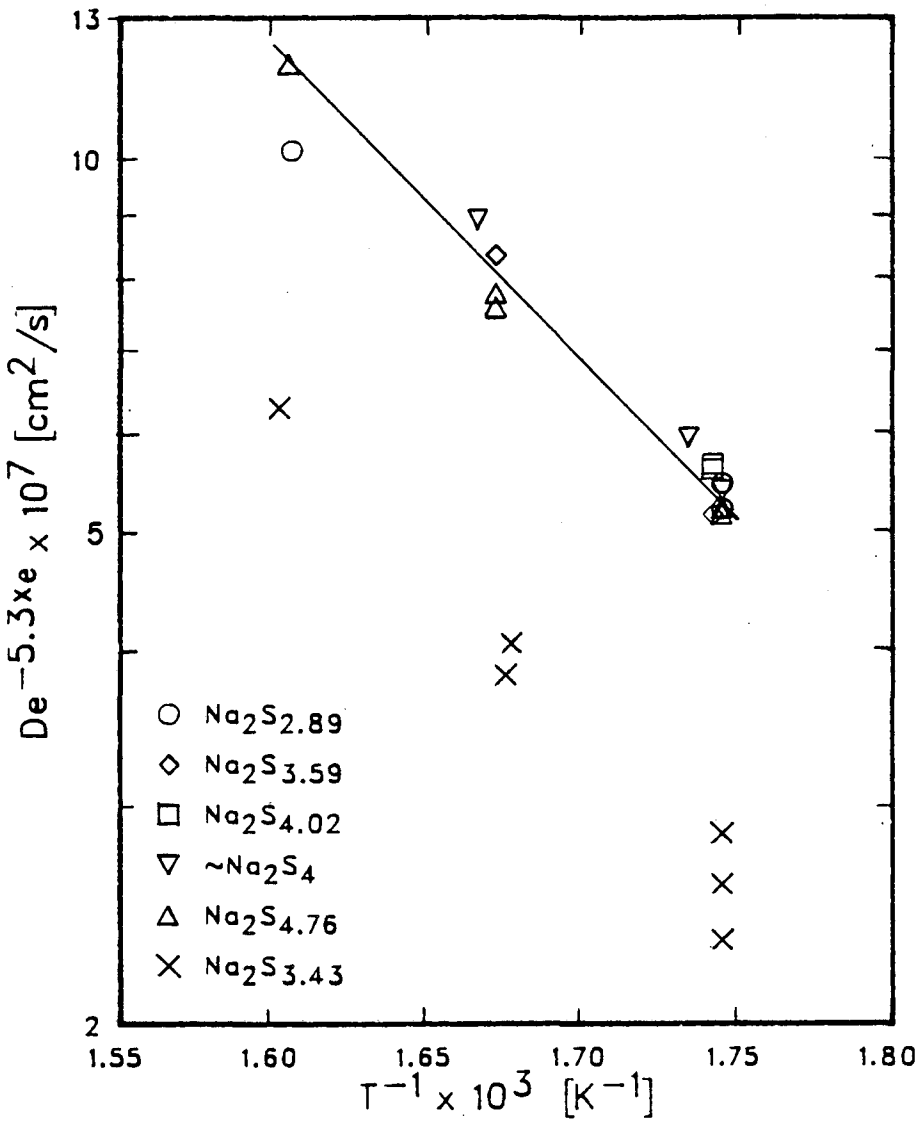


Figure 8. Reduced diffusion data; $De^{-5.30x}$, plotted as a function of temperature. Plot compares the correlated composition and temperature dependence to the data. Discrepant-cell data are also included.

Acknowledgment

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

List of Symbols

a	height of diffusion cell, cm
A_n	Fourier series coefficients defined by equation 7
c	concentration of electrolyte, mol/cm^3
D	diffusion coefficient of electrolyte based on concentration driving force, cm^2/s
E_A	activation energy, kJ/mol
F	Faraday's constant, 96,487 C/equiv
K,L	functions of concentration derivatives of the solution properties
R	universal gas constant, 8.3143 J/mol-K
t	time, s
T	absolute temperature, K
x	twice the ratio of sulfur to sodium in Na_2S_x
x_e	mole fraction of sodium sulfide

Greek letters

ε	function of time defined by equation 9
ρ	density, g/cm^3

Subscripts

o	initial value at zero time
∞	value at long times

References

1. J. L. Sudworth and A. R. Tilley, "The Sodium-Sulfur Battery with β-Alumina Electrolyte," R. P. Tischer, ed., *The Sulfur Electrode,* Academic Press, pp. 235-322 (1983).

2. R. P. Tischer and F. A. Ludwig, "The Sulfur Electrode in Nonaqueous Media," Heinz Gerischer and Charles Tobias, eds., *Advances in Electrochemistry and Electrochemical Engineering,* **10,** John Wiley and Sons, Inc., N.Y., 391-482 (1977).

3. Ragnar Tegman, "Thermodynamic Studies of High Temperature Equilibria," *Chemica Scripta,* **9,** 158-166 (1976).

4. B. Cleaver, and A. J. Davies, "Properties of Fused Polysulphides-III. *EMF* Measurements on the Sodium-Sulfur Cell, and Sulfur Activities and Constitution in Fused Sodium Polysulphides," *Electrochim. Acta,* **18,** 733-739 (1973).

5. John S. Newman, *Electrochemical Systems,* Prentice-Hall Inc., Englewood Cliffs, N. J. (1973).

6. R. D. Armstrong, T. Dickenson, and M. Reid, "Rotating Disk Studies of the Vitreous Carbon-Sodium Polysulfide Interface," *Electrochim. Acta,* **20,** 709-714 (1975).

7. K. D. South, J. L. Sudworth, and G. Gibson, "Electrode Processes in Sodium Polysulfide Melts," *J. Electrochem. Soc.,* **119,** 554-558 (1972).

8. J. Divisek, F. G. Bodewig, J. Mergel, and H. Lippert, "Mass Transport Phenomena in the Molten Sulfur-Sodium Polysulfide System," *J. Electrochem. Soc.,* **127,** 357-363 (1980).

9. R. D. Armstrong, T. Dickenson, and M. Reid, "Alternating Current Impedance Measurements of the Vitreous Carbon/Sodium Polysulfide Interphase at 350°C," *Electrochim. Acta,* **21,** 935-942 (1976).

10. Thomas W. Chapman, *The Transport Properties of Concentrated Electrolytic Solutions,* Ph.D. Thesis, University of California Berkeley, pp. 99-103 (November, 1967).

11. John Newman and Thomas W. Chapman, "Restricted Diffusion in Binary Solutions," *AIChE J.,* **19,** 343-348 (1973).

12. Kemal Nişancioğlu and John Newman, "Diffusion in Nitric Acid Solutions," *AIChE J.,* **19,** 797-801 (1973).

13. H. S. Harned and D. M. French, "A Conductance Method for the Determination of the Diffusion Coefficients of Electrolytes," *Annals New York Acad. Sci.,* **46,** 267 (1945).

14. Timothy Kent Risch, *The Transport Properties of Sodium Polysulfide Melts and a Theoretical Comparison of Flow-Through and Flow-By Porous Electrodes at the Limiting Current,* M.S. Thesis, University of California Berkeley (December, 1983).

15. H. M. Garfinkel, "Ion Exchange Properties of Borosilicate Glass Membranes in Molten Salts," *Physics and Chemistry of Glasses,* **11,** pp. 151-158 (1970).

16. B. Cleaver, "Properties of Polysulfide Melts," R. P. Tischer, ed., *The Sulfur Electrode,* Academic Press, pp. 35-43, (1983).

17. George Brauer, *Handbook of Preparative Inorganic Chemistry,* vol. 1, Academic Press, N.Y., pp. 358-367 (1963).

18. B. Cleaver, A. J. Davies, and M. D. Hames, "Properties of Fused Polysulfides-I. The Electrical Conductivity of Fused Sodium and Potassium Polysulfides," *Electrochim. Acta,* **18,** 719-726 (1973).

19. E. Rosén and R. Tegman, "A Preparative and X-Ray Powder Diffraction Study of the Polysulfides Na_2S_2, Na_2S_4, Na_2S_5," *Acta Chem. Scand.,* **25,** 3329-3336 (1971).

20. W. W. Scott, *Standard Method of Chemical Analysis,* Fifth Edition, vol. 1, Van Nostrand Company Inc., N.Y., pp. 908-911 (1939).

21. F. Fehér and H. J. Berthold, "Beiträge zur Chemie des Schwefels. XIII," *Fresenius' Zeitschrift für Analytische Chemie,* **138,** 245 (1953).

22. Susan Dale Thompson, *Mass Transport in Sodium Polysulfide Melts,* M.S. Thesis, University of California Berkeley (September, 1985).

23. B. Cleaver, and A. J. Davies, "Properties of Fused Polysulfides-II. The Density, Surface Tension and Viscosity of Fused Sodium Polysulfides," *Electrochim. Acta,* **18,** 727-732 (1973).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720