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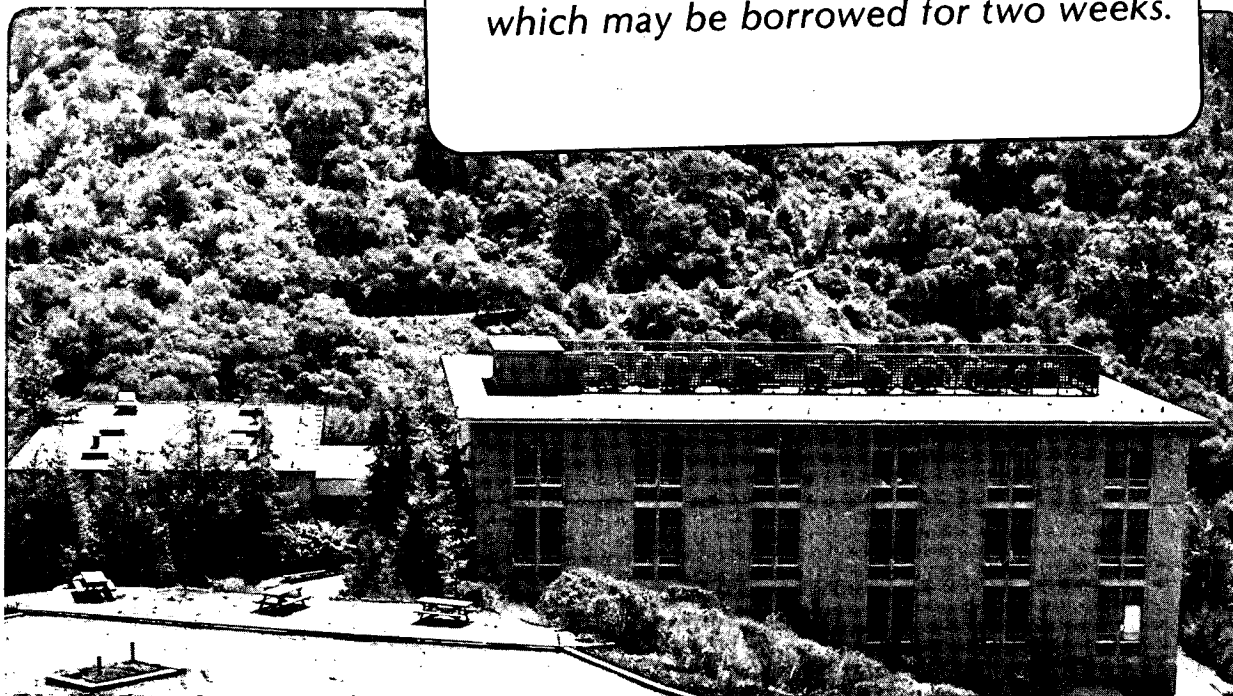
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Transference Number Calculations for Sodium Polysulfides

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January 4, 1988

Key words: Fused Salts, Battery, Current, Transport

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Abstract

Transference numbers for sodium cations and sulfur anions in sodium polysulfide melts are calculated from previously determined experimental data. Concentrated electrolyte theory assuming a binary electrolyte consisting of sodium anions, sulfide cations, in a neutral sulfur solvent is used to relate the transference numbers to fundamental solution transport properties. Slopes of open circuit potential measurements versus melt composition on sodium-sulfur cells with and without transference are used to determine the sulfur anion or sodium cation transference numbers. The transference number of sodium cations is calculated from previous experimental data for two temperatures, 573 and 633 K, and range from 0.88 to 0.93 for sodium sulfide mole fractions between 0.20 and 0.34. These values for transference numbers presented here are more accurate than previous interpretations of these data where unity sodium cation transference numbers were assumed. The results of this work are shown to be important in the design of sodium-sulfur cells.

Introduction

Recently, there has been a renewed interest in studying the transport processes within sodium polysulfide melts. The sulfur electrode in the sodium sulfur battery is seen by many as the foundation for an economical, long-lasting, and high energy battery system.

For proper design and scale-up of these cells, it is important to have accurate values for the transport properties of sodium polysulfides. Such values possess a great deal of practical value, as well as yielding useful information about the transport processes in complex molten salt electrolytes.

There have been relatively few studies in recent years both experimentally and theoretically quantifying needed design properties for melts of sodium polysulfides. The most comprehensive source for transport data on these compounds is the work of Cleaver and Davies.¹ Measurements of melt conductivity, viscosity and surface tension are presented in their work, but data for the transference number and the diffusion coefficient are not included. Some recent work by Yoshida and Nakajima² gives some values for transference number obtained from experimental measurements of the discharge potential of the sodium sulfur cell. However, the authors have incorrectly determined the transference number by not considering diffusion through the cell. Despite the need for accurate values of the transference numbers, there are no accurate values available in the open literature.

In this paper, our aim is to clarify the description of ionic movement in polysulfides induced by the passage of current. We present here a rigorous treatment of the transport processes founded on the idealistic assumption of a binary melt consisting of sodium cations and sulfide anions in a neutral sulfur solvent. While it is well documented that polysulfide melts contain sodium and several polysulfide ions, a binary melt is useful for defining and categorizing the transport processes. Our idealistic assumption will not prejudice the outcome of our results. These results may be used to describe the bulk movement of sodium and sulfur regardless of the actual nature of species present in the melt.

Definition of Transference Numbers

A generalized theory for transport in concentrated electrolytes has been developed by Newman, Bennion, and Tobias³ and has been expanded by Newman.⁴ The starting assumption asserts that the description of transport in concentrated electrolytic solutions can be expressed as a set of generalized flux equations of the form

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T D_{ij}} (\mathbf{v}_j - \mathbf{v}_i). \quad (1)$$

Equation 1 can be thought of as a force balance where $c_i \nabla \mu_i$ is the driving force per unit volume on species i . The driving force is opposed by the drag of species j exerted on i as a result of their relative motion and is given by the right side of Equation 1. Newton's third law of motion (action equals reaction) requires

$$D_{ij} = D_{ji}. \quad (2)$$

Thus for a mixture containing N species, Equation 1 above defines $N - 1$ independent equations with $1/2 N(N - 1)$ independent D_{ij} transport parameters.

This set of equations which expresses the driving forces as linear combinations of the velocities can be inverted into an equivalent set of flux equations explicit in the velocities. For a binary electrolyte in a solvent, the set of three flux equations and three independent transport parameters can be inverted to yield the following set of transport equations

$$N_+ = c_+ \mathbf{v}_+ = -\frac{\nu_+ D}{\nu RT} \frac{c_T}{c_o} c \nabla \mu_e + \frac{it_+^o}{z_+ F} + c_+ \mathbf{v}_o, \quad (3)$$

$$N_- = c_- \mathbf{v}_- = -\frac{\nu_- D}{\nu RT} \frac{c_T}{c_o} c \nabla \mu_e + \frac{it_-^o}{z_- F} + c_- \mathbf{v}_o, \quad (4)$$

$$N_o = c_o \mathbf{v}_o. \quad (5)$$

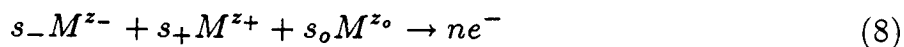
The subscripts $+$, $-$, and o denote the cation Na^+ , the anion S^- , and the solvent S respectively. In these equations $\nu = \nu_+ + \nu_-$ and $\mu_e = \nu_+ \mu_+ + \nu_- \mu_-$ where μ_e is the chemical potential of the electrolyte and taken to be Na_2S . The total solution concentration c_T is the sum of the cation concentration c_+ , the anion concentration c_- , and the the solvent concentration c_o . The diffusion coefficient of the salt, based on a thermodynamic driving force, is

$$D = \frac{D_{o+} D_{o-} (z_+ - z_-)}{z_+ D_{o+} - z_- D_{o-}}, \quad (6)$$

and the transference numbers with respect to the solvent velocity are

$$t_+^o = 1 - t_-^o = \frac{z_+ D_{o+}}{z_+ D_{o+} - z_- D_{o-}}. \quad (7)$$

For the potential in the solution, one can define the potential relative to a reference electrode. Application of thermodynamic principles to the following general half cell reaction



yields,

$$s_- \nabla \mu_- + s_+ \nabla \mu_+ + s_o \nabla \mu_o = -nF \nabla \Phi, \quad (9)$$

and can be used to obtain the following expression relating the current density to the gradient of potential and the gradient of chemical potential

$$\mathbf{i} = -\kappa \nabla \Phi - \frac{\kappa}{F} \left(\frac{s_+}{n\nu_+} + \frac{t_+^o}{z_+\nu_+} - \frac{s_o c}{nc_o} \right) \nabla \mu_e. \quad (10)$$

The solution conductivity κ can be expressed as

$$\frac{1}{\kappa} = -\frac{RT}{c_T z_+ z_- F^2} \left(\frac{1}{D_{+-}} + \frac{c_o t_-^o}{c_+ D_{o-}} \right). \quad (11)$$

In obtaining equation 3 through 11, we have used the definition for the current density

$$\mathbf{i} = F \sum_i c_i z_i \mathbf{v}_i, \quad (12)$$

and we have chosen the velocity of the solvent \mathbf{v}_o as the reference velocity. The superscript o on the transference number designates the solvent reference frame.

One may also choose other reference frames as bases for the flux equations. Two other possible reference velocities are the molar-average velocity \mathbf{v}^* and the mass-average velocity \mathbf{v} defined by

$$\mathbf{v}^* = \frac{1}{c_T} \sum_i c_i \mathbf{v}_i, \quad (13)$$

and

$$\mathbf{v} = \frac{1}{\rho} \sum_i \rho_i \mathbf{v}_i. \quad (14)$$

If the molar-average velocity is taken as the reference frame, the three independent flux equations may be written as

$$\mathbf{N}_+ = -\nu_+ c_T D \nabla x_e + \frac{\mathbf{i} t_+^*}{z_+ F} + c_+ \mathbf{v}^*, \quad (15)$$

$$\mathbf{N}_- = -\nu_- c_T D \nabla x_e + \frac{\mathbf{i} t_-^*}{z_- F} + c_- \mathbf{v}^*, \quad (16)$$

and

$$\mathbf{N}_o = \nu c_T D \nabla x_e + \left[\left(\frac{1}{z_-} + \frac{1}{z_+} \right) t_+^* - \frac{1}{z_-} \right] \frac{\mathbf{i}}{F} + c_o \mathbf{v}^*, \quad (17)$$

where the driving force has been rewritten in terms of the mole fraction of the electrolyte x_e . The variable D is a differential diffusion coefficient related to the thermodynamic diffusion coefficient \mathcal{D} by

$$D = \mathcal{D} \frac{c_T}{c_o} \left(1 + \frac{d \ln \gamma_{+-}}{d \ln m} \right) \quad (18)$$

where γ_{+-} is the mean molal activity coefficient and m is the molality. Alternatively, one may write the flux equations in terms of the mass-average velocity \mathbf{v} and the gradient of the mass fraction of the electrolyte ω_e as

$$\mathbf{N}_+ = -\nu_+ \rho D \nabla \omega_e + \frac{\mathbf{i} t_+}{z_+ F} + c_+ \mathbf{v}, \quad (19)$$

$$\mathbf{N}_- = -\nu_- \rho D \nabla \omega_e + \frac{\mathbf{i} t_-}{z_- F} + c_- \mathbf{v}, \quad (20)$$

and

$$\mathbf{N}_o = \nu \rho D \nabla \omega_e + \left[\left(\frac{1}{z_-} + \frac{1}{z_+} \right) t_+ - \frac{1}{z_-} \right] \frac{\mathbf{i}}{F} + c_o \mathbf{v}. \quad (21)$$

Finally, the velocity of any ionic species could be chosen as the reference velocity. Using the velocity of sodium cation \mathbf{v}_+ as the reference velocity gives the three independent flux equations as

$$\mathbf{N}_+ = c_+ \mathbf{v}_+, \quad (22)$$

$$\mathbf{N}_- = \frac{\mathbf{i}}{z_- F} + c_- \mathbf{v}_+, \quad (23)$$

and

$$\mathbf{N}_o = \frac{D}{\nu RT} \frac{c_o c_e}{c_T} \nabla \mu_o - \frac{c_o}{c_+} \frac{\mathbf{i} t_+^o}{z_+ F} + c_o \mathbf{v}_+. \quad (24)$$

In equations 15 through 24 above, the three definitions for the sodium cation transference number t_+^o , t_+^* , and t_+ depend upon the chosen reference velocity. Each of these, however, may be related to the transference number of sodium cations in the solvent reference frame by the following relationships

$$t_+^* = 1 - t_-^* = (c_- + c_o t_+^o) / c_T, \quad (25)$$

and

$$t_+ = 1 - t_- = (\rho_- + \rho_o t_+^o) / \rho. \quad (26)$$

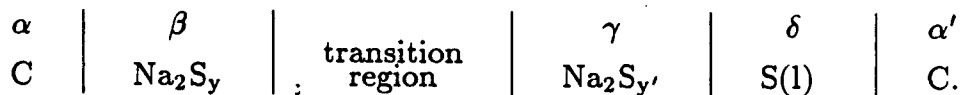
Thus, if the transference number for either the sodium cation or the sulfide anion in any reference frame is available, the transference numbers in any of the other reference frames defined above also may be calculated.

Calculation of Transference Numbers

The transference numbers for many common aqueous electrolytes can be measured from either the Hittorf method or the moving boundary method. For sodium polysulfide melts, each of these methods is impractical due to the high temperature and the opaque nature of the electrolyte. It is possible, however, to obtain transference number data in the single phase composition region from open circuit potential measurements on a cell with transference. Such a cell is made by combining two sulfur electrodes of different compositions with a "transition region" or diffusion junction separating the two. Cleaver and Davies¹ were the first to suggest such a method but did not perform any calculations. They assumed simply that $t_+^o = 1$. Here we present calculations which determine more accurately the values for cation and anion transference numbers in these melts.

Open circuit potential measurements have been performed on the following cell with transference

Cell 3*



The potential U_3 of this cell is shown in the Appendix to be given by

$$FU_3 = \frac{1}{2} \int_{\gamma}^{\beta} \left(t_+^o \frac{1-x_e}{x_e} + 1 \right) d\mu_o, \quad (27)$$

where x_e denotes the mole fraction of sodium sulfide. Differentiating this expression for the cell potential gives

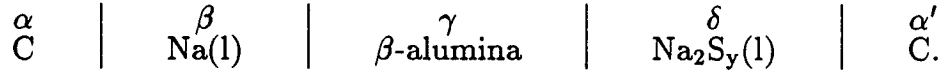
$$dU_3 = \frac{1}{2F} \left(t_+^o \frac{1-x_e}{x_e} + 1 \right) d\mu_o, \quad (28)$$

Provided the differential of the chemical potential of sulfur and the differential of the cell potential are known, the transference number can be determined.

The differential of the chemical potential of sulfur within the melt can be determined from the potential U_1 of the cell

* This cell numbering system is consistent with the original work of Cleaver and Davies.

Cell 1



This is

$$d\mu_o = 2Fx_e dU_1. \quad (29)$$

Combining Equation 28 and 29, the transference number of sodium ions relative to neutral sulfur is

$$t_+^o = \frac{-\frac{dU_3}{dx_e} \frac{dx_e}{dU_1} - x_e}{1 - x_e}. \quad (30)$$

A complete derivation of the cell potentials and the transference number is given in the Appendix. The important result of Equation 30 is that the transference number of sodium ions relative to neutral sulfur solvent can be related to the derivative of the two cell potentials with respect to the mole fraction of sodium sulfide.

Cleaver and Davies¹ present cell potential versus melt composition data for the cells described above (see Figures 2 and 3 in this reference). The potentials of the cells for two temperatures, 573 and 633 K are given. The essential feature of these curves is that the cell potential is very nearly linear with the mole fraction of sodium sulfide in the single phase region. The potential of the cells can therefore be described by the following relationships

$$U_1 = \alpha_1 + \beta_1 x_e \quad (31)$$

and

$$U_3 = \alpha_3 + \beta_3 x_e. \quad (32)$$

Thus

$$\frac{dU_3}{dx_e} \frac{dx_e}{dU_1} = \frac{\beta_3}{\beta_1} \quad (33)$$

and

$$t_+^o = \frac{-\frac{\beta_3}{\beta_1} - x_e}{1 - x_e}. \quad (34)$$

Values for the α 's and β 's for the two cells at the two temperatures are given in Table 1.

While Equation 34 gives the transference number for sodium ions relative to sulfur solvent, the value of this number is very close to one in agreement with Cleaver and Davies,

and it is more convenient to consider the transference number for sulfide ions. Figure 1 illustrates the transference number for sulfide ions as a function of melt composition for the two temperatures. This shows, subject to the stated assumptions, the transference number is nearly constant over the range of compositions encountered as per Cleaver and Davies assumption. Also, the transference number for sulfide ions is very small, indicating that in a melt of uniform composition, the majority of the current is carried by the sodium cations. The transference numbers for the molar-average or mass-average frame of reference may be determined from the relationships given in Equations 25 and 26.

Conclusions

We have derived the transport equations for concentrated binary electrolytes and applied these to the transport processes in sodium polysulfide melts. From these equations, we have defined transference numbers of sodium cations and sulfide anions for the solvent, mass-average, and molar-average velocity reference frames. We have shown that all binary transference numbers, regardless of the reference frame, can be related to the cation transference number with respect to the solvent velocity.

We have calculated transference numbers for sodium polysulfide melts at two temperatures using the experimental cell potential data of Cleaver and Davies. Although previous interpretation of data has assumed that the transference number of sodium cations with respect to the solvent velocity is near unity, we have more accurately determined new values from the calculations presented here.

Our results illustrate the predominant current carrying species in sodium-sulfur melts is the sodium cation. However, because the transference number of sulfur anions is not zero, sulfur anions will also migrate in the melt. We have also shown, that sodium ion transference numbers near one, do not necessarily suggest the absence of free sulfur in the melt. On the contrary, the idealistic binary electrolyte model presented here considers both free sulfur and sulfide ions in the melt and is not inconsistent with unity solvent based sodium ion transference numbers.

In practical sodium-sulfur cells, concentration gradients of sulfide anions as well as sodium cations will be created in the melt during cell operation by the migration of the sodium and sulfide ions. The extent of these concentration gradients will depend on the magnitude of transference numbers as well as the diffusivity of the individual ions that tend to counteract the movement of species by migration. Concentration gradients give rise to spatial variations of melt properties such as density and conductivity and will limit performance of cells by inhibiting the transport of critical reactants within the cell. Accurate sodium sulfur cell models must include the effects of concentration and property variations so that proper cell behavior can be simulated.

The framework presented here describing the transport of sodium cations and sulfur anions in polysulfide melts has improved the correlation of experimental data resulting in

more accurate values for fundamental transport properties. These results will improve the design of sodium sulfur cells by refining present cell performance models. Furthermore, this work is an important step forward in the knowledge of fundamental transport behavior in molten salt melts.

Acknowledgement

This work was supported by the Assistant Secretary of Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract DE-AC-03-76SF00098.

List of Symbols

English Characters

c	concentration of electrolyte, mol/cm ³
c_i	concentration of species i , mol/cm ³
c_T	total solution concentration = $c_+ + c_- + c_o$, mol/cm ³
D	measured diffusion coefficient of electrolyte, cm ² /s
D	diffusion coefficient of the electrolyte for a thermodynamic driving force, cm ² /s
D_{ij}	diffusion coefficient for interaction of species i and j , cm ² /s
F	Faraday constant, 96,485 coulombs/equiv
i	current density, A/cm ²
m	molality of electrolyte, kg/cm ³
M	arbitrary species
n	number of electrons
N_i	flux of species i , mol/cm ² -s
s_i	stoichiometric coefficient of species i in electrode reaction
t_i	transference number of species i with respect to the mass-average velocity
t_i^o	transference number of species i with respect to the solvent velocity
t_i^*	transference number of species i with respect to the molar-average velocity
U_1	thermodynamic cell potential of cell 1, V
U_3	thermodynamic cell potential of cell 3, V
v	mass-average velocity, cm/s
v_i	velocity of species i , cm/s
x_e	mole fraction of electrolyte, $Na_2S = c/c_T$
x_i	mole fraction of species $i = c_i/c_T$
z_i	charge number of species i , equiv/mol

Greek Characters

α_1	constant defined in Equation 5 describing the open circuit potential of cell 1, V
α_3	constant defined in Equation 6 describing the open circuit potential of cell 3, V
β_1	constant defined in Equation 5 describing the open circuit potential of cell 1, V

β_3	constant defined in Equation 6 describing the open circuit potential of cell 3, V
γ_{+-}	mean molal activity coefficient of an electrolyte
κ	conductivity of solution, $(\Omega\text{-cm})^{-1}$
μ_e	chemical potential of the electrolyte, J/mol
μ_i	chemical potential of species i , J/mol
μ_i^o	chemical potential of species i at the standard state, J/mol
ν	number of moles of ions into which a mole of electrolyte dissociates
ν_+, ν_-	numbers of cations and anions which a molecule of electrolyte dissociates
ρ	density of solution, g/cm^3
ρ	partial density of species i , g/cm^3
Φ	electric potential, V
ω_i	mass fraction of species $i = \rho_i/\rho$
ω_e	mass fraction of electrolyte, $\text{Na}_2\text{S} = (\rho_+ + \rho_-)/\rho$

Subscripts

e	the electrolyte, Na_2S
i	species i
j	species j
o	species o , neutral sulfur
n	reference species

Superscripts

o	denoting a reference frame based on the solvent velocity
$*$	denoting a reference frame based on the molar-average velocity

Table 1 Values for α and β describing the open circuit potential of cells 1 and 3 for the data of Cleaver and Davies.

Temp., K	α_1 , V	β_1 , V	Rel. Std. Dev., %	α_3 , V	β_3 , V	Rel. Std. Dev., %
573	2.4681	-1.9812	0.0007	-0.34955	1.8111	0.4
633	2.4632	-2.0253	0.05	-0.39371	1.9958	0.2

Figure Captions

Figure 1. Calculated sulfide ion transference numbers as a function of melt composition for 573 and 633 K.

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Appendix

Calculation of Transference Numbers for Sodium Polysulfide Melts

Consider the potential of Cell 3 which is given by

$$FU_3 = \mu_{e-}^{\alpha} - \mu_{e-}^{\alpha'} = \frac{1}{2}(\mu_{-}^{\beta} - \mu_{-}^{\gamma}) + \frac{1}{2}(\mu_{o}^{\delta} - \mu_{o}^{\beta}). \quad (\text{A} - 1)$$

Equation A-1 holds if equilibrium exists between phases α and β , and phases γ and δ and if the sulfur in phase δ is pure. Now Equation 16-3 from Newman⁵ is

$$\frac{1}{z_n} \nabla \mu_n = \frac{F}{\kappa} \mathbf{i} - \sum_i \frac{t_i^o}{z_i} \left(\nabla \mu_i - \frac{z_i}{z_n} \nabla \mu_n \right), \quad (\text{A} - 2)$$

which can be derived as a consequence of the independent flux equations. Here we will let species n be $S^=$ and transference numbers will be taken relative to neutral sulfur, S. Also we will take \mathbf{i} to be zero. This equation combined with the Gibbs-Duhem relation which requires

$$x_e d\mu_e + (1 - x_e) d\mu_o = 0, \quad (\text{A} - 3)$$

results in

$$\frac{1}{2} \nabla \mu_{-} = -t_{+}^o \cdot \frac{1 - x_e}{x_e} \nabla \mu_o. \quad (\text{A} - 4)$$

Integration of Equation A-4 from the composition in phase γ to the composition in phase β gives

$$\frac{1}{2} \int_{\gamma}^{\beta} \nabla \mu_{-} = \frac{1}{2} (\mu_{-}^{\beta} - \mu_{-}^{\gamma}) = -\frac{1}{2} \int_{\gamma}^{\beta} t_{+}^o \frac{1 - x_e}{x_e} \nabla \mu_o. \quad (\text{A} - 5)$$

This gives for the potential of the cell from Equation A-1

$$FU_3 = -\frac{1}{2} \int_{\gamma}^{\beta} \left(t_{+}^o \frac{1 - x_e}{x_e} + 1 \right) d\mu_o, \quad (\text{A} - 6)$$

which can be differentiated to yield

$$FdU_3 = -\frac{1}{2} \left(t_{+}^o \frac{1 - x_e}{x_e} + 1 \right) d\mu_o. \quad (\text{A} - 7)$$

The differential of the sulfur chemical potential can be obtained from the potential of cell 1. The expression for the cell potential is

$$FU_1 = \mu_{Na}^{\beta} + \frac{1}{2} \mu_S^{\delta} - \frac{1}{2} \mu_{e-}^{\delta}. \quad (\text{A} - 8)$$

When one takes the differential of Equation A-8 and applies the Gibbs-Duhem relation (A-3) this yields

$$FdU_1 = \frac{1}{2} \frac{1}{x_e} d\mu_o. \quad (\text{A} - 9)$$

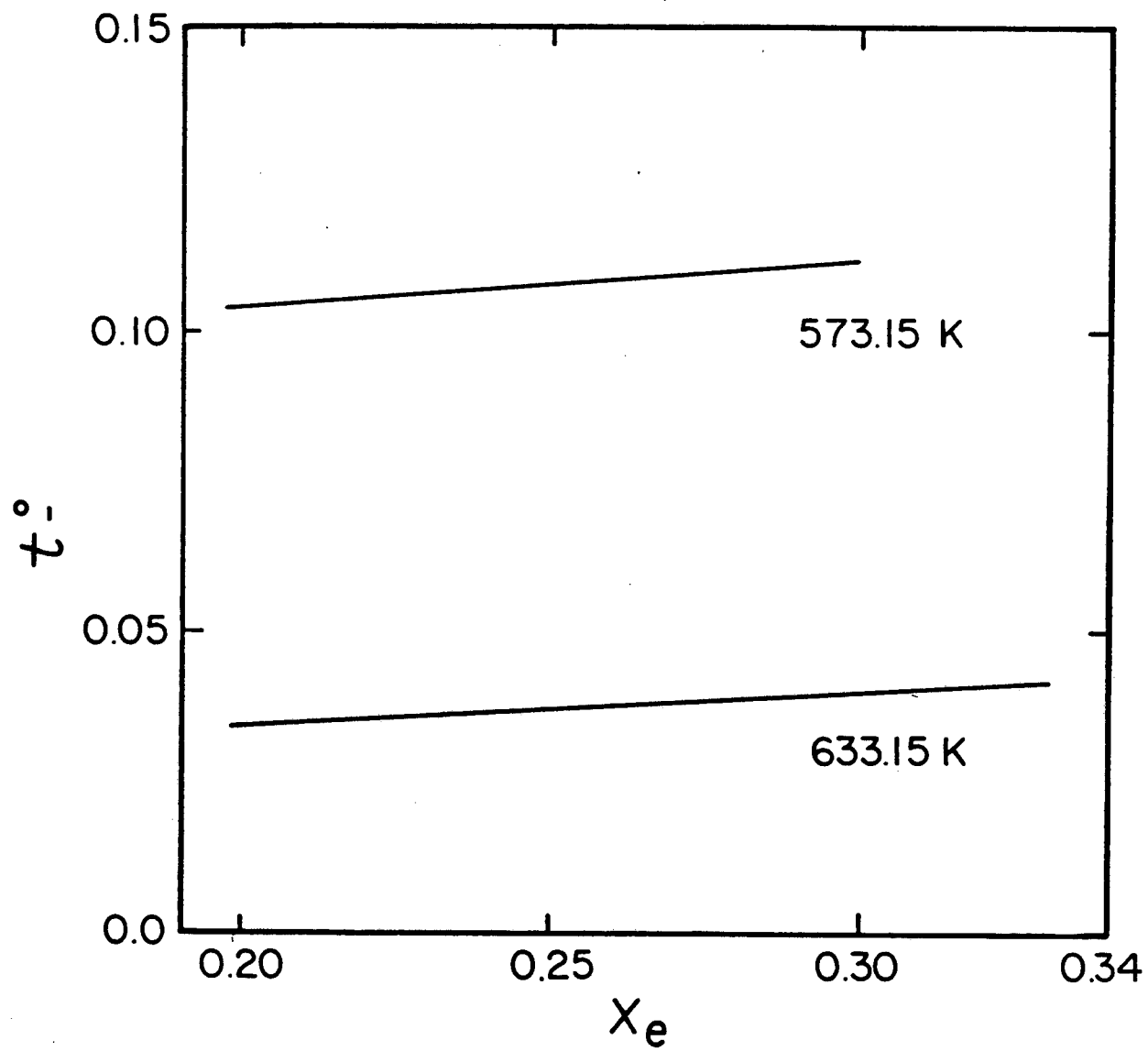
Using Equations A-7 and A-9 gives for the differential of potential of cell 3

$$dU_3 = - \left(t_+^o \frac{1 - x_e}{x_e} + 1 \right) x_e dU_1. \quad (\text{A} - 10)$$

The transference number of sodium ions relative to neutral sulfur is thus

$$t_+^o = \frac{-\frac{dU_3}{dx_e} \frac{dx_e}{dU_1} - x_e}{1 - x_e}. \quad (\text{A} - 11)$$

The two derivatives of cell potential with electrolyte mole fraction can be obtained from the slope of cell potential versus composition data.



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