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## Materials & Molecular Research Division

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November 30, 1983

TRANSPORT PROPERTIES OF CONCENTRATED SOLUTIONS

J. Newman

November 1983

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# Transport Properties of Concentrated Solutions

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November 30, 1983

## ABSTRACT

The analysis of mass-transport processes in battery systems requires accurate values of the transport properties of electrolytic solutions. A generally valid theory of mass transport is presented and described.

Mass-transport properties are defined by the theory one chooses to describe the flux of mobile species. A consistent set of transport equations have been developed for dilute solutions of electrolytes. This theory breaks down, however, in concentrated solutions. In concentrated-solution theory, the migration and diffusion fluxes are defined with respect to an average velocity of the fluid, and the driving force for these fluxes is the electrochemical potential. Unlike dilute solution theory, concentrated solution theory correctly defines the number of transport properites. The fundamental binary transfer coefficients defined by concentrated-solution theory may be calculated as functions of concentrations from independent measurements of diffusion coefficients, transference numbers, and conductivity.

The measurement of fringe displacements of diffusing solutions in an optical concentration cell is a method of determining diffusion coefficients. This method is described, and results for nitric acid solutions are given.

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## Transport Properties of Concentrated Solutions

(slide 1)

In the short time available, we want to introduce transport properties by means of their definitions--for both dilute and concentrated solutions. This will be followed by some rather old, but accurate measurements we made for diffusion coefficients of aqueous nitric acid solutions.

(slide 2)

For dilute solutions, three contributions to the flux density are singled out. These are migration, diffusion, and convection. By means of this equation, two transport properties are defined--the mobility and the diffusion coefficient of each solute species. Derived transport properties, such as the conductivity and the transference numbers, must be defined in terms of these more basic properties. The transport properties are similar to thermodynamic properties in that they can be functions of temperature and composition--and to a lesser extent of pressure. Part of the significance of the flux density equation is that the transport properties are independent of the gradients of concentration and electric potential.

For concentrated solutions, we must start again with a different equation--one relating the gradient of the electrochemical potential of a species (solute or solvent) to a linear combination of terms involving differences of velocities of this species with other species in the solution. Here the fundamental transport properties defined by this equation are the  $\bar{D}_{ij}$ , also called diffusion

coefficients. Again, these properties are dependent upon concentration, temperature, and pressure and are independent of the gradients. Again, conductivities and transference numbers can be expressed in terms of these more fundamental properties. There are also diffusion coefficients describing diffusion of neutral combinations of ions, like an electrolyte in a solvent, in the absence of the flow of electrical current. These can also be expressed in terms of the  $\bar{D}_{ij}$ . In the multicomponent diffusion equation for concentrated solutions, gradients of concentration and electric potential are combined into the gradients of electrochemical potentials.

(slide 3)

There are a number of improvements of the multicomponent diffusion equation over the dilute-solution equation. These include:

1. A reference velocity need not be specified in advance. In an application, one would be free to choose among the mass-average velocity, the molar-average velocity, the volume-average velocity, or the solvent velocity (or that of any one of the species).

2. The correct number of transport properties is defined by this equation.

3. The driving force is expressed in terms of electrochemical potentials, and the choice of an electric potential can be postponed until an application is encountered.

(slide 4)

However, there are still some compelling reasons for continuing to deal with dilute-solution theory and transport properties defined therein. These are:

1. Frequently there is an absence of data on the  $\mathfrak{D}_{ij}$ , particularly for multicomponent solutions. In this meeting we shall hear about the  $\text{ZnCl}_2\text{-KCl-H}_2\text{O}$  system for which there is an unusual amount of good, fundamental data on diffusion coefficients.

2. The dilute-solution theory continues to give a correct qualitative description of migration, convection, and diffusion in a manner which is comprehensible and frequently does justice to the available data without undue complication.

(slide 5)

The difference in the number of transport properties defined by the two transport equations illustrates the fundamental difference between them. For concentrated-solution theory, there are  $\frac{1}{2} n(n-1)$  different  $\mathfrak{D}_{ij}$  defined, versus  $2(n-1)$  for dilute solutions. The first value corresponds to one value for each pair of species in the solution. For dilute solutions, however, there are two for each solute species, and these describe basically the interactions of each species with the solvent. On the other hand, the concentrated-solution theory deals with the interaction of each species with every other species.

The numbers can be changed a little by bringing in other considerations. With the Nernst-Einstein relation, which should probably be regarded to be valid, the number of transport properties for

dilute-solution theory is reduced to one for each solute species. The multicomponent-diffusion equation as used involved the assumption of the Onsager reciprocal relation (that  $\bar{D}_{ij} = \bar{D}_{ji}$ ). Without this assumption there would be two  $\bar{D}_{ij}$  for each pair of species. There is still no way to make the numbers of transport properties agree. There is a fundamental difference between the two theories--although the multicomponent-diffusion equation can be made to reduce to the dilute-solution equation for dilute solutions.

In any event, the  $\bar{D}_{ij}$  defined by the multicomponent-diffusion equation must be regrouped in order to describe measured properties. They yield

1. a single conductivity  $\chi$ .
2. transference numbers in the number of  $n-1$  (since they add up to 1).
3.  $\frac{1}{2} (n - 1)(n - 2)$  diffusion coefficients corresponding to one for each pair of neutral combinations of ions, that one might encounter in diffusion problems in the absence of current. If we don't see right off how to apply the Onsager reciprocal relation to this problem, our counting of transport properties might get fouled up.

For a solution of a single solute, like zinc bromide, in water, the correct number of transport properties is three--the conductivity, the transference number of one of the ions, and the diffusion coefficient of zinc bromide in water. For a solution of two elec-



troytes, with a common ion, in water, there are a total of six transport properties.

(slide 6)

We might note that it is reasonably straightforward to calculate the applied transport properties (conductivity, transference numbers, and  $D_{ij}$ ) from a complete set of  $\bar{\mathcal{D}}_{ij}$ . This we could even do if we believe in a detailed solution model including complexing of ions--if we can assume that the homogeneous reactions among the species are equilibrated rapidly. It is certainly more difficult to go backwards and calculate the  $\bar{\mathcal{D}}_{ij}$  from the measured transport properties--particularly if we have an incomplete set or if we must deal with experimental uncertainty.

(slide 7)

Let us conclude with some accurate measurements of the diffusion coefficient of aqueous solutions of nitric acid. First we should relate the measured value  $D$  to the  $\bar{\mathcal{D}}_{ij}$  defined by the multicomponent-diffusion equation. We define a  $\bar{\mathcal{D}}$  in terms of the  $\bar{\mathcal{D}}_{ij}$  for the ion-solvent interactions. This we might think of as a fundamental diffusion coefficient of the electrolyte, based on a gradient of the chemical potential. Then we need to apply a correction factor involving the mean molal activity coefficient in order to yield a diffusion coefficient based on gradients of concentration.

(slide 8)

The optical cell used for observing concentration profiles is shown in this slide. The electrolyte diffuses relative to the

solvent in the vertical direction. The diffusion process is eventually constrained by the ends of the cell, and a cosine profile is obtained, which decays exponentially with time.

(slide 9)

This slide shows Rayleigh interference patterns which reveal, with great accuracy, the concentration profile. You may be able to see the cosine profile in the lower picture. This is an absolute method, by which we can obtain diffusion coefficients with no calibration necessary.

(slide 10)

Finally, here we see measured diffusion coefficients over a range of concentrations up to about 9 moles per liter. This method yields values with an estimated error of two or three tenths of a percent.

Other speakers will go over other relevant diffusion measurements --and these can be interpreted in terms of either dilute or concentrated solution theory. Thank you for your patience.

## **Transport Properties**

### **Definitions**

- **Dilute solutions**
- **Concentrated solutions**

### **Some measurements**

## Dilute-solution theory

$$\mathbf{N}_i = - z_i u_i F c_i \nabla \Phi - D_i \nabla c_i + c_i \mathbf{v}$$

migration      diffusion      convection

## Multicomponent diffusion equation

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (v_j - v_i)$$

## **Improvements over dilute-solution equations**

- No reference velocity needed
- Correct number of transport properties
- Driving force in electrochemical potentials

## Reasons for using dilute-solution equations

- Absence of data on  $\mathcal{D}_{ij}$
- Correct qualitative description of migration, convection, and diffusion

**Number of transport properties for mass transfer**

$$\frac{1}{2} n(n-1) \quad \text{vs.} \quad 2(n-1)$$

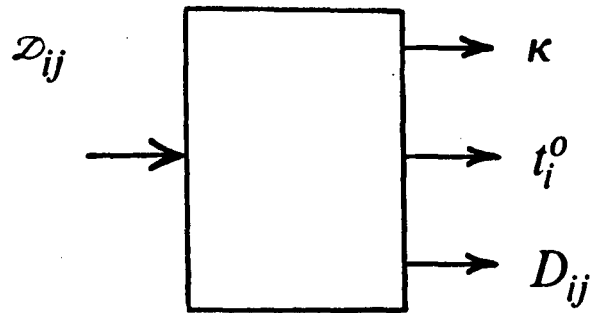
for dilute solutions.

Separate  $\varphi_{ij}$  into

$\kappa$  conductivity

$t_i^{(v)}$   $n-1$  transference numbers

$\frac{1}{2} (n-1)(n-2)$  diffusion coefficients



?



Can we go backwards?



## Measured D in a binary solution

$$D = \mathcal{D} \frac{c_T}{c_0} \left( 1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right)$$

where

$$\mathcal{D} = \frac{\mathcal{D}_{0+} \mathcal{D}_{0-} (z_+ - z_-)}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}}$$

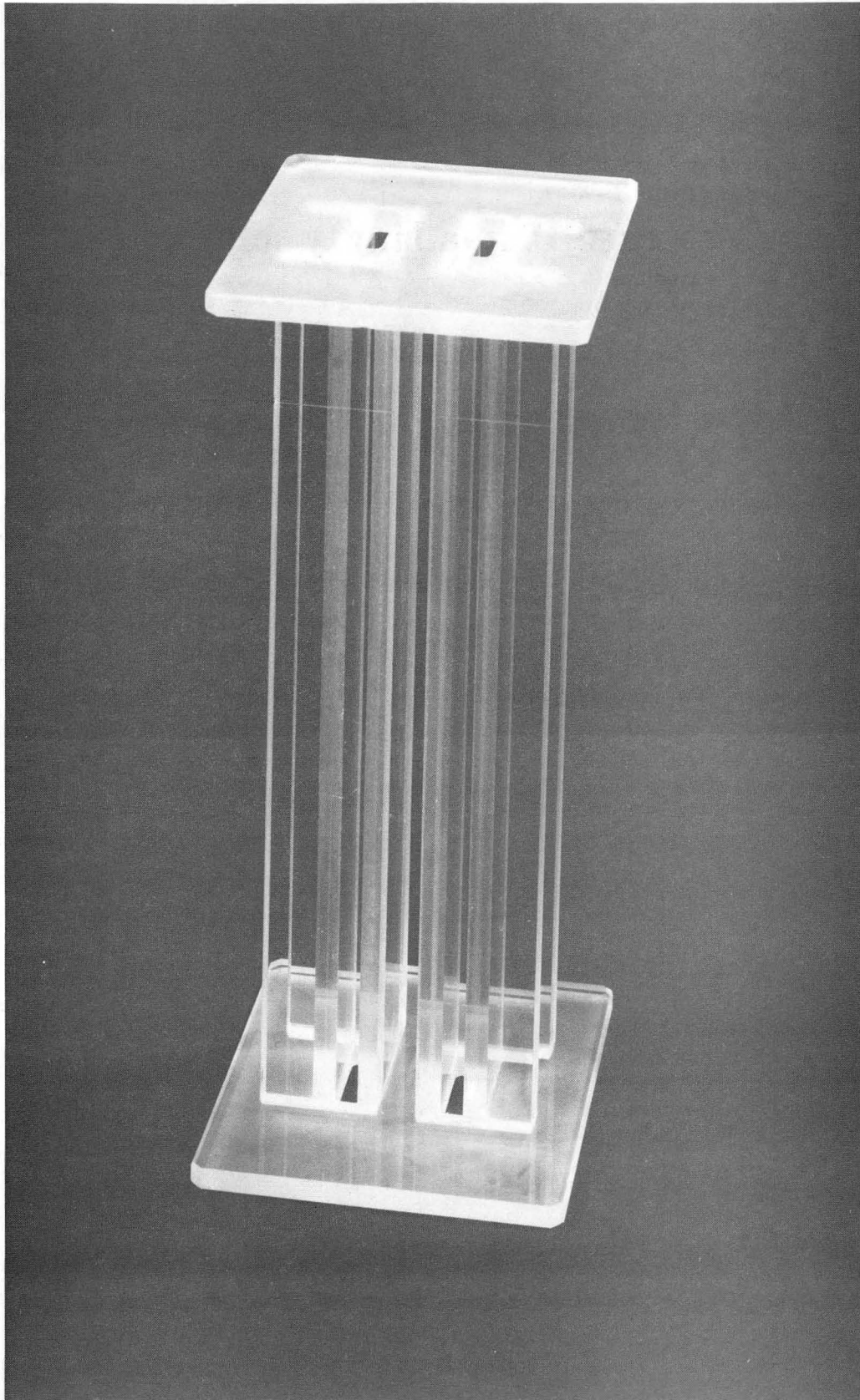
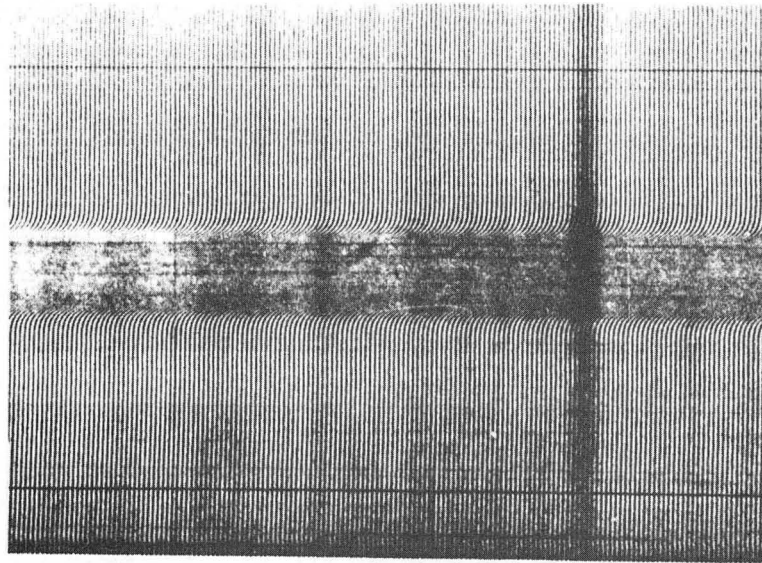
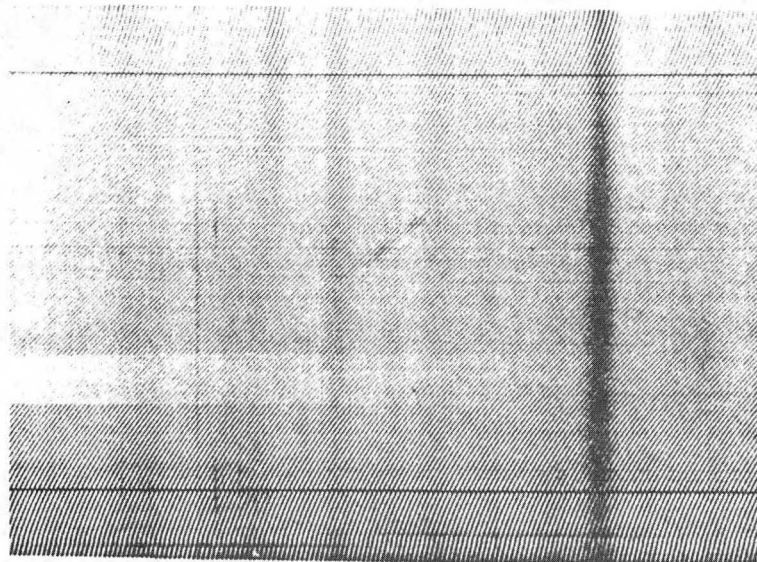


Figure 1. Optical cell.

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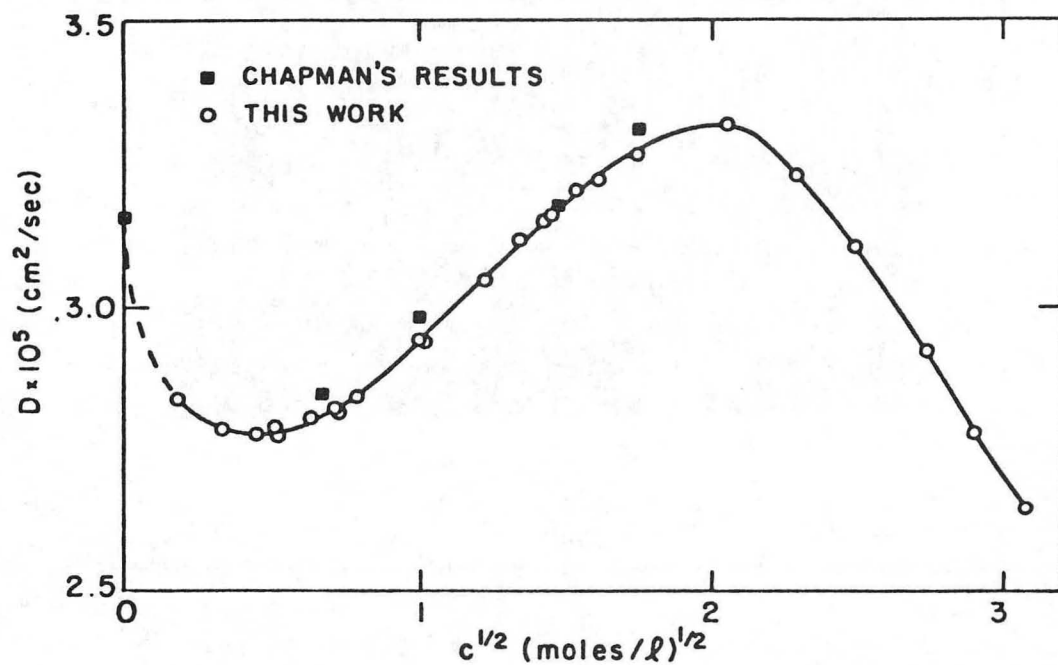


Fringe pattern about half an hour after the formation of the boundary. The fringes cannot yet be distinguished in the boundary. The scribed marks show up as horizontal lines.



Fringe pattern toward the end of the run.

XBB 6911-7618



XBL 6912-6668

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