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Introduction

Mass transport by diffusion is important in electrodeposition and in many other forms of crystal growth occurring in solution.¹ Since the coefficients of diffusion of important species are not always known, especially at temperatures other than 25 C, it is essential to have available apparatus for measuring them.

A convenient device for measuring diffusion coefficients is the diaphragm cell, which has become standard in the field since its introduction in 1929.² The heart of any diaphragm cell consists of two well stirred solution compartments on opposite sides of a porous glass frit. When solutions of differing concentration are placed in the compartments, diffusion occurs across the frit. Since the porosity of the frit is not known a priori, the diaphragm cell must be calibrated before it can be used with solutions with unknown diffusion coefficient. In standard practice, the cell is calibrated with an aqueous solution of 0.5 M KCl at 25 C, a system for which the diffusion coefficient has been determined with great accuracy.³

For the purpose of determining diffusion coefficients as required for electrodeposition studies and other applications, we have constructed a diaphragm cell and an isothermal water bath. This system is currently being calibrated as described above.

In studying previous work, we found that a rigorous theory for the operation of the diaphragm cell was not available except in the special case the diffusion coefficient was independent of concentration.^{3,4} This situation is usually encountered in practice, however, only in the limit of infinite dilution. At high concentration, most solutions are thermodynamically non-ideal, which causes the diffusion coefficient to be concentration dependent. Since crystals are grown from supersaturated solutions, it is often the high concentration value of the diffusion coefficient which is the most important for interpreting the rate of mass transport observed in the growth process.

In order to extend the applicability of the diaphragm cell to the important high concentration regime, we have developed a rigorous series integration of the equation of motion governing the cell.⁵ Let $c_1(t)$ and $c_2(t)$ be the solute concentrations at time t , observed below and above the diaphragm, respectively. If the solution volumes below and above the diaphragm are identical, the mean concentration, $\bar{c} = (1/2)[c_1(t) + c_2(t)]$, is independent of time. Let $D(c)$ be the diffusion coefficient, taken as a function of concentration, and let $\Delta c(t) = c_1(t) - c_2(t)$ represent the concentration difference measured across the diaphragm. We have found that t and Δc are related by the equation,

$$t = A_0 + A_1 \ln(\Delta c) + A_2 (\Delta c)^2 + A_4 (\Delta c)^4 + \dots \quad (1)$$

where the coefficients, A_n , $n = 0, 1, 2, \dots$, depend upon $D(c)$ and various derivatives of $D(c)$ evaluated at $c = \bar{c}$. The coefficient, A_1 , is the most important, since it satisfies the equation,

$$D(\bar{c}) = \frac{1}{\beta A_1} \quad (2)$$

where β is the cell constant, which is determined by the calibration.

In the high concentration applications, which we envisage, the cell will be started at $t = 0$ with a certain value of Δc . Subsequently, Δc will be measured as a function of t , and the t vs Δc data fitted to Eq.(1) by least squares. The least squares value obtained for A_1 will be used to determine $D(\bar{c})$ at the mean concentration of the cell using Eq. (2). To change the value of \bar{c} , the experiment is repeated, starting from a different initial condition. If this procedure is repeated through a sufficient number of cycles, it should serve to map out the entire functional form of $D(c)$.

We note that, when $D(c)$ is independent of c , all coefficients in Eq. (1) except for A_0 and A_1 are identically zero, and our result is the same as that which is well known for this case.³ As written including the higher order terms, however, Eq. (1) is entirely new and serves to resolve all the ambiguities, which were pointed out more than 30 years ago⁴ as being associated with the operation of a diaphragm cell at high concentration. Aside from their intrinsic value in crystal growth, the functional forms of $D(c)$ obtained for various solutes by our method should be useful also in addressing problems in the theory of molecular transport⁶ and in the theory of solutions.⁷

Three calibration runs on the diaphragm cell were completed. On the basis of these runs, we may conclude conservatively that the cell constant $\beta = 0.12$ cm⁻². Other calibration runs are in progress, which when complete should permit the cell constant to be determined with an accuracy of one percent.

References

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