

## PHYSICAL CHEMISTRY

DIFFUSION IN TERNARY SYSTEMS CONSISTING OF  
TWO ISOTOPIC FORMS OF A SUBSTANCE IN SOLUTION

## PART I. — THEORY

BY

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*Summary*

For ternary systems containing two isotopic forms of the same chemical species, solutions of the diffusion equations, for free diffusion boundary conditions, are discussed. These solutions are derived on the basis of two different assumptions concerning the concentration dependence of diffusion coefficients. The diffusion of labeled molecules in a gradient of the total solute concentration is described with the aid of the mutual and self-diffusion coefficient. The measurement of this diffusion can be used to determine these coefficients. The results apply to solutions of non-electrolytes as well as to electrolyte solutions.

## 1. INTRODUCTION

The application of isotopically labeled molecules has become of considerable importance in the study of diffusion. In this connection the terms "self-diffusion" and "tracer-diffusion" are often used in the literature, whereas recently ALBRIGHT and MILLS [1] introduced another term: "intradiffusion". In order to avoid ambiguity and to relate the present work to previous publications in the field, a few remarks on nomenclature will first be made.

In a diffusion experiment in which no use is made of labeled molecules, there are always finite concentration gradients and gradients of the activity coefficients of the components in the system. Such an experiment, when performed in a binary system, gives one coefficient which is called the "mutual diffusion coefficient" or the "interdiffusion coefficient".

The term "tracer-diffusion" is often used in connection with the application of a trace amount of a labeled component, whereas in "intradiffusion" this amount is not necessarily small. For detailed definitions, the reader is referred to the work of ALBRIGHT and MILLS [1] who confine the use of the term "self-diffusion" to the special case in which two isotopic forms are the only components present in the system (e.g. benzene and  $^{14}\text{C}$ -labeled benzene). Other authors [2, 3], however, also use "self-diffusion" when there are more than two components.

Tracer-diffusion and intradiffusion experiments have one important common feature, in contradistinction to experiments in which no labeled

components are applied; this is that the molecules, the diffusion of which is measured, move in an essentially homogeneous environment, the activity coefficient of all components being practically constant. Therefore, a tracer- and an intradiffusion experiment, if performed at the same composition of the mixture, are expected to give the same diffusion coefficient. Since the difference between these two experiments is of experimental rather than of fundamental nature, it is doubtful whether the distinction between tracer- and intradiffusion coefficients adds much to clarity in nomenclature. In the present work, the term "self-diffusion coefficient" is used also for multicomponent systems. It should be kept in mind that this coefficient is a function of the composition of the mixture.

The purpose of the present work is to consider the diffusion of labeled molecules or ions in systems not subject to the condition of a homogeneous environment for these molecules or ions. In order to do this, we have chosen the simplest possible ternary system, consisting of two isotopic forms of one chemical species and a third component, the solvent. An example would be the diffusion of  $^{14}\text{C}$ -labeled sucrose in a gradient of total sucrose in water. It will be shown that this diffusion can be described by a combination of mutual- and self-diffusion. As a consequence of this, it is possible to measure both the mutual- and the self-diffusion coefficient of a solute in situations in which there is a gradient of the total solute concentration. This may be of some practical value because in the usual type of measurement, the mixtures on both sides of the diffusion boundary have equal or only very slightly different densities, which may cause errors in the measurements due to convection.

In this paper, solutions of the diffusion equations are discussed. The results apply to solutions of non-electrolytes as well as to electrolyte solutions. In a subsequent paper some experimental results will be presented.

## 2. THEORY

### 2.1. *Diffusion equations for a ternary system*

When there is diffusion in one direction only (the  $x$ -axis) in a ternary system of uniform temperature and pressure, the diffusion process can be described quite generally by an extension of Fick's law

$$(1) \quad J_i = - \sum_{j=1}^2 D_{ij} \frac{\partial c_j}{\partial x} \quad (i = 1, 2).$$

Here 1 and 2 denote two of the three components which could be called the solutes. In general, the four diffusion coefficients  $D_{ij}$ , are functions of both  $c_1$  and  $c_2$ , the concentration in *moles/volume*. The flows  $J_i$  are taken with respect to the volume-fixed reference system [4]. Equation (1) applies to solutions of non-electrolytes and to electrolyte solutions. In the latter case, the components are neutral salts.

It will be assumed that the partial molar volumes of all components vary so little with concentration, or that the concentration differences across the diffusion boundary are so small, that volume changes caused by mixing can be neglected. Then, the volume-fixed frame of reference does not move with respect to the diffusion cell, the flows become equal to the experimental flows, and the coefficients  $D_{ij}$  are those determined directly by experiment. (The same will be true for the other diffusion coefficients to be discussed). Furthermore, under this condition, eqn. (1) can be combined with the continuity equation, to give the partial differential equations [5, 6]

$$(2) \quad \frac{\partial c_i}{\partial t} = \sum_{j=1}^2 \frac{\partial}{\partial x} \left( D_{ij} \frac{\partial c_j}{\partial x} \right) \quad (i=1, 2).$$

Solutions of these equations subject to the "free diffusion" boundary conditions will be discussed. In free diffusion, a sharp boundary is formed (at  $x=0$  and time  $t=0$ ) between two solutions of different concentration say, in a cylinder long enough to prevent the development of concentration gradients at the ends of the cylinder. Then, the initial and boundary conditions are

$$(3) \quad \left. \begin{array}{l} c_i = c_i'' \text{ for } x > 0 \\ c_i = c_i' \text{ for } x < 0 \end{array} \right\} t=0 \quad (i=1, 2)$$

and

$$(4) \quad \left. \begin{array}{l} c_i = c_i'' \text{ for } x = +\infty \\ c_i = c_i' \text{ for } x = -\infty \end{array} \right\} t > 0 \quad (i=1, 2),$$

where  $c_i'$  and  $c_i''$  are the initial concentrations on each side of the boundary.

## 2.2. Ternary diffusion of solvent + two isotopic forms of the same substance

The general equations given thus far, will now be applied to the special ternary system to be discussed here. Then, the subscripts 1 and 2 denote the labeled and the unlabeled form of the same chemical species, respectively. In the case that the solutes are electrolytes, the subscript 1 denotes the neutral salt containing a labeled ion.

It will be assumed that isotope effects can be neglected as far as diffusion is concerned. Using only this assumption, ALBRIGHT and MILLS [1] derived certain relations between the coefficients  $D_{ij}$  which are valid for the special ternary system under consideration, and by which eqns. (2) can be simplified.

In order to do this, first a mutual- and a self-diffusion coefficient have to be defined for our system. The mutual diffusion coefficient,  $D$ , is defined by

$$(5) \quad J_s = -D \frac{\partial c_s}{\partial x},$$

where

$$(6) \quad J_s = J_1 + J_2$$

and

$$(7) \quad c_s = c_1 + c_2.$$

The following equation defines the self-diffusion coefficient,  $D^*$ .

$$(8) \quad J_1 = -D^* \frac{\partial c_1}{\partial x} \quad c_s = \text{constant}.$$

The relations, referred to, derived by ALBRIGHT and MILLS for non-electrolyte solutions, are

$$(9) \quad D^* = D_{11} - D_{12} = D_{22} - D_{21}$$

and

$$(10) \quad D = D_{11} + \frac{c_2}{c_1} D_{12} = D_{22} + \frac{c_1}{c_2} D_{21},$$

which imply

$$(11) \quad c_2 D_{12} = c_1 D_{21},$$

$$(12) \quad D = D_{11} + D_{21} = D_{22} + D_{12}$$

and

$$(13) \quad D_{ij} = \frac{c_i}{c_s} (D - D^*) + \delta_{ij} D^* \quad (i=1, 2),$$

where  $\delta_{ij}$  is the Kronecker  $\delta$ .

It has been recently remarked by MILLER [7] that these relations apply equally to electrolyte solutions (see also ref. 8, appendix I). Then,  $D$  and  $D^*$  are the mutual diffusion coefficient of the neutral salt and the self-diffusion coefficient of the labeled ion, respectively.

### 2.3. *Solutions of the diffusion equations for constant diffusion coefficients*

#### *a. $D_{ij}$ independent of concentration*

The differential equations (2) can be solved analytically only by means of simplifying assumptions concerning the concentration dependence of the coefficients  $D_{ij}$ . A solution for general ternary systems of these equations, subject to the boundary conditions (3) and (4), was presented by FUJITA and GOSTING [9], who used the assumption that the coefficients  $D_{ij}$  are independent of the concentrations. Their solution can be simplified for our special ternary system by the substitution of eqns. (13). However in this special case, the assumption concerning the coefficients  $D_{ij}$  is inconsistent with the general boundary conditions (3) and (4). Obviously, by eqn. (11), the assumption implies that  $c_1/c_2$  should be constant. This

demands a very special choice of the initial concentrations which is not taken in general. Nevertheless, the solution has been applied successfully by GOSTING, DUNLOP and others [10-16] in the calculation of the four coefficients  $D_{ij}$  from the results of diffusion measurements. These coefficients were found to be consistent [8, 13-18] with the ONSAGER reciprocal relation in the thermodynamics of irreversible processes [19]. For this reason, the solution given by Fujita and Gosting, although it can not be exact for the general initial condition (eqn. (3)), might be a useful approximation for the special system that is considered here, and its utility might be tested by experiment.

We only give the final result of the substitution of eqns. (13) into the original solution given by Fujita and Gosting. It reads

$$(14) \quad c_i = \left\{ \bar{c}_i + \frac{\Delta c_i}{2} \operatorname{erf} \left( \frac{x}{2\sqrt{D^*t}} \right) \right\} \frac{\bar{c}_s + \frac{\Delta c_s}{2} \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)}{\bar{c}_s + \frac{\Delta c_s}{2} \operatorname{erf} \left( \frac{x}{2\sqrt{D^*t}} \right)}, \quad (i=1, 2),$$

in which

$$(15) \quad \bar{c}_i = \frac{c_i'' + c_i'}{2} \quad (i=1, 2, s)$$

and

$$(16) \quad \Delta c_i = c_i'' - c_i' \quad (i=1, 2, s).$$

The meaning of erf (z) (or error function of z) is given by

$$(17) \quad \operatorname{erf} (z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\alpha^2} d\alpha$$

in which  $\alpha$  is an integration variable.

In the derivation of eqn. (14), we used the following expression for  $c_s$ .

$$(18) \quad c_s = \bar{c}_s + \frac{\Delta c_s}{2} \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right).$$

This is the well known solution of the diffusion equation for binary systems with constant  $D$  [20]. The use of eqn. (18) is permitted, since it follows from eqns. (9) and (12) that  $D^*$  and  $D$  are constant if the coefficients  $D_{ij}$  are constant.

The expression for  $c_i$  (eqn. (14)) is seen to be the product of the solution of the diffusion equation for constant  $D^*$ , and a factor which approaches unity for large values of  $\bar{c}_s$ , small values of  $\Delta c_s$  or when the difference between  $D$  and  $D^*$  is small.

#### b. $D$ and $D^*$ independent of concentration

Another possible solution of eqns. (2) can be derived for our special system when it is assumed that the coefficients  $D$  and  $D^*$  are constant.

This assumption allows the choice of much more general initial conditions rather than restricting them to the trivial case, where the isotopic ratio  $c_1/c_2$  has the same value all over the cell. When isotope effects in diffusion may be neglected,  $D$  and  $D^*$  only depend on  $c_s$ . From experimental values of  $D$  and  $D^*$  one can see that the assumption is reasonable as long as  $c_s$  does not vary too much in the experiment and thus for small values of the concentration difference,  $\Delta c_s$ , across the boundary.

In order to find a solution of the diffusion equations for constant  $D$  and  $D^*$ , first eqns. (13) are substituted into eqns. (1). The result is

$$(19) \quad J_i = -D^* \frac{\partial c_i}{\partial x} - \frac{c_i}{c_s} (D - D^*) \frac{\partial c_s}{\partial x} \quad (i=1, 2).$$

These equations were already derived in a different way by VAN GEET and ADAMSON [21]. Equations (19) are combined with the continuity equation to give partial differential equations which for constant  $D$  and  $D^*$  can be written as

$$(20) \quad \frac{\partial c_i}{\partial t} = D^* \frac{\partial^2 c_i}{\partial x^2} + (D - D^*) \frac{\partial}{\partial x} \left( \frac{c_i}{c_s} \frac{\partial c_s}{\partial x} \right) \quad (i=1, 2).$$

The solution of this set of coupled differential equations seems difficult at first sight. However, it should be remembered that  $c_s$  in eqns. (20) is a known function of  $x$  and  $t$ , given by eqn. (18), which is the solution of the equation.

$$(21) \quad \frac{\partial c_s}{\partial t} = D \frac{\partial^2 c_s}{\partial x^2}.$$

The partial differential eqns. (20) can be reduced to ordinary differential equations by introducing a new variable

$$(22) \quad \eta = \frac{x}{2\sqrt{Dt}}.$$

The substitution of the variable is permitted [22] when  $c_1$  and  $c_2$  are functions of  $x/t^{\frac{1}{2}}$  only. This was recently shown to be true, by MIJNLIEFF and VREDENBERG [6], for the boundary conditions (3) and (4), in systems with a similar concentration dependence of the coefficients  $D_{ij}$  as in our case. We therefore substitute eqn. (22) into (20) and (21) and find

$$(23) \quad -2\eta \frac{dc_i}{d\eta} = \frac{D}{D^*} \frac{d^2 c_i}{d\eta^2} + \frac{(D - D^*)}{D} \frac{d}{d\eta} \left( \frac{c_i}{c_s} \frac{dc_s}{d\eta} \right) \quad (i=1, 2)$$

and

$$(24) \quad -2\eta \frac{dc_s}{d\eta} = \frac{d^2 c_s}{d\eta^2},$$

respectively. Now, another variable

$$(25) \quad r_i = \frac{c_i}{c_s} \quad (i=1, 2)$$

is substituted into eqns. (23), to give

$$(26) \quad -2\eta c_s \frac{dr_i}{d\eta} - 2\eta r_i \frac{dc_s}{d\eta} = \frac{D^*}{D} c_s \frac{d^2 r_i}{d\eta^2} + r_i \frac{d^2 c_s}{d\eta^2} + \frac{(D+D^*)}{D} \frac{dc_s}{d\eta} \cdot \frac{dr_i}{d\eta}.$$

Next, eqn. (24) is multiplied by  $r_i$  and subtracted from eqns. (26). After division by  $c_s D^*/D$ , the result is

$$(27) \quad \frac{d^2 r_i}{d\eta^2} + \left\{ 2\eta \frac{D}{D^*} + \left( \frac{D}{D^*} + 1 \right) \frac{d \ln c_s}{d\eta} \right\} \frac{dr_i}{d\eta} = 0 \quad (i=1, 2).$$

By integrating these equations, we obtain

$$(28) \quad \frac{dr_i}{d\eta} = E_i e^{-\eta^2(D/D^*)} \left( \frac{c_s}{\bar{c}_s} \right)^{-[(D/D^*)+1]} \quad (i=1, 2),$$

where  $E_i$  is an integration constant. The final solutions of eqns. (20) is found by integrating eqns. (28) between the boundaries 0 and  $\eta$ . The result is

$$(29) \quad r_i(\eta) - r_i(0) = E_i \int_0^\eta e^{-\beta^2(D/D^*)} \left( \frac{c_s}{\bar{c}_s} \right)^{-[(D/D^*)+1]} d\beta \quad (i=1, 2),$$

where  $\beta$  is an integration variable and  $c_s(\beta)$  is given by eqn. (18) with  $\frac{1}{2}x/(Dt)^{\frac{1}{2}}$  replaced by  $\beta$ . The constants  $E_i$  and  $r_i(0)$  are determined by the boundary conditions which are expressed in terms of  $r_i$  and  $\eta$  by

$$(30) \quad r_i = r_i' = \frac{c_i'}{c_s'} \quad \text{for } \eta = -\infty \quad (i=1, 2)$$

and

$$(31) \quad r_i = r_i'' = \frac{c_i''}{c_s''} \quad \text{for } \eta = +\infty \quad (i=1, 2).$$

With the aid of these conditions and writing  $I(\eta)$  for the integral in eqns. (29), we obtain the following expressions for  $E_i$  and  $r_i(0)$ .

$$(32) \quad E_i = \frac{r_i'' - r_i'}{I(+\infty) - I(-\infty)} \quad (i=1, 2)$$

and

$$(33) \quad r_i(0) = \frac{r_i' I(+\infty) - r_i'' I(-\infty)}{I(+\infty) - I(-\infty)}.$$

It should be noted that  $r_i(0)$  is not necessarily equal to  $\bar{c}_i/\bar{c}_s$  in this case.

The integral  $I(\eta)$  can only be evaluated numerically. Values of  $D$ ,  $D^*$  and  $\Delta c_s/\bar{c}_s$  have to be chosen first. It is convenient to use tables of the error function and its derivative [23] for the evaluation, since these are just the functions occurring in the integrand of eqns. (29).

#### 2.4. Equations for a measurable quantity

A complete test and comparison of the two solutions presented (cf. eqns. (14) and (29)) would demand the measurement of the total concentration distribution of  $c_1$  in a number of diffusion experiments. It is, however, easier to measure the amount of the labeled component that has been transported across the plane  $x=0$  in time  $t$ . For comparison we first calculate the total amount of solute transported across this plane in an ordinary mutual diffusion experiment. This is done by integrating the flow of solute, described by Fick's law (cf. eqn. (5)), at the plane  $x=0$ , between time 0 and  $t$ . Using eqn. (18) we obtain (cf. ref. 20, p. 22)

$$(34) \quad (J_s)_{x=0} = -\frac{\Delta c_s}{2} \left( \frac{D}{\pi t} \right)^{\frac{1}{2}}.$$

We now define an experimental quantity  $Q_s$  by

$$(35) \quad Q_s = \frac{1}{\bar{c}_s} \int_0^t (J_s)_{x=0} dt = -\frac{\Delta c_s}{\bar{c}_s} \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}}.$$

The mutual diffusion coefficient,  $D$ , can be calculated from this expression when  $Q_s$  is determined by experiment.

Next, we consider a free diffusion experiment with the special ternary system under study, in which the amount of the labeled component transported across the plane  $x=0$  is measured. As in the previous case, expressions for this quantity are easily derived from the solutions of the differential equations for the system (eqns. (14) and (29)). First eqns. (14) (for  $i=1$ ) and (18) are differentiated with respect to  $x$  and the resulting expressions for  $(\partial c_1/\partial x)_{x=0}$  and  $(\partial c_s/\partial x)_{x=0}$  are substituted into the flow eqn. (19) (for  $i=1$ ) to give

$$(36) \quad (J_1)_{x=0} = -\frac{\Delta c_1}{2(\pi t)^{\frac{1}{2}}} \left\{ D^{*\frac{1}{2}} + (D^{\frac{1}{2}} - D^{*\frac{1}{2}}) \frac{\bar{c}_1}{\Delta c_1} \frac{\Delta c_s}{\bar{c}_s} \right\}.$$

In the derivation of this equation we used the equalities  $(c_1)_{x=0} = \bar{c}_1$  and  $(c_s)_{x=0} = \bar{c}_s$  which follow from eqns. (14) and (18). Next, we define two quantities,  $Q_1$  and  $D_m$  by an equation similar to eqn. (35), but with the subscript  $s$  replaced by 1, and  $D$  replaced by  $D_m$ . From a comparison of eqns. (34) and (36), it is concluded that  $D_m$  which might be considered as an apparent diffusion coefficient, is given by

$$(37) \quad D_m = \left\{ D^{*\frac{1}{2}} + (D^{\frac{1}{2}} - D^{*\frac{1}{2}}) \frac{\bar{c}_1}{\Delta c_1} \frac{\Delta c_s}{\bar{c}_s} \right\}^2.$$

A similar derivation is now given, starting from the other solution, eqn. (29) or its derivative with respect to  $\eta$ , eqn. (28). First eqn. (19) (for  $i=1$ ) is transformed, using  $r_1 = c_1/c_s$ , into

$$(38) \quad J_1 = -D^* c_s \frac{\partial r_1}{\partial x} - D r_1 \frac{\partial c_s}{\partial x}.$$

Expressions for the partial differential quotients in this equation are easily derived from eqns. (18) and (28). After substitution of these expressions, the final result can be written as

$$(39) \quad (J_1)_{x=0} = -\frac{\Delta c_1}{2(\pi t)^{\frac{1}{2}}} \left\{ \frac{(\pi)^{\frac{1}{2}} E_1 \bar{c}_s D^* + r_1(0) \Delta c_s D}{\Delta c_1 D^{\frac{1}{2}}} \right\}.$$

From a comparison of eqns. (34) and (39), we conclude that

$$(40) \quad D_m = \left\{ \frac{(\pi)^{\frac{1}{2}} E_1 \bar{c}_s D^* + r_1(0) \Delta c_s D}{\Delta c_1 D^{\frac{1}{2}}} \right\}^2.$$

The expressions (37) and (40) which are the result of two different assumptions concerning the concentration dependence of diffusion coefficients, can be compared and tested by experiment.

### 3. DISCUSSION

A first test and comparison of the equations obtained, can be performed by the substitution of two special initial conditions. The first of these is expressed by

$$(41) \quad \Delta c_s = 0$$

which is the condition for a self-diffusion experiment. It is easily shown that the substitution of this condition into eqns. (14) and (29) gives the same result, namely

$$c_i = \bar{c}_i + \frac{\Delta c_i}{2} \operatorname{erf} \left( \frac{x}{2\sqrt{D^*t}} \right), \quad (i=1, 2)$$

which is the solution of the binary diffusion equation for constant  $D^*$ . Furthermore, when condition (41) is applied to eqns. (37) and (40), both give  $D_m = D^*$  as was to be expected. It is not surprising that eqn. (14) gives the correct result in this case: the derivation of differential equations as given by Fujita and Gosting finally resulting in eqns. (14), can be shown to be exact if  $D$  and  $D^*$  are constant and condition (41) is satisfied.

The second initial condition we substitute into eqns. (14) and (29) is

$$(43) \quad c_1'/c_s' = c_1''/c_s''.$$

Again, the result is the same for both equations: we obtain eqn. (18) with the subscript  $s$  replaced by  $i$ , whereas both eqns. (37) and (40) give  $D_m = D$ . This result was to be expected, since eqn. (29) combined with condition (43) immediately gives  $c_1'/c_s' = c_1''/c_s'' = c_1/c_s = \text{constant}$ . This is the only case for which the four coefficients,  $D_{ij}$ , are constant, and therefore eqn. (14) gives the correct result.

In a subsequent paper, it will be explained how the quantities  $Q_1$  and  $D_m$  are determined by experiment. Experiments, when performed in systems with known values of  $D$ ,  $D^*$ ,  $c_s'$ ,  $c_s''$ ,  $c_1'$  and  $c_1''$ , provide a test

of eqns. (37) and (40) (and therefore of eqns. (14) and (29)). On the other hand, it is possible to calculate both  $D$  and  $D^*$  by using values of  $D_m$  which are obtained from experiments in which there is a gradient in the total solute concentration. It is interesting to investigate what will be the difference in the results if eqn. (37) or eqn. (40) is used for such calculations.

For example, two experiments (to be denoted by the indices I and II) could be carried out, with the same values of  $c_s'$  and  $c_s''$ , but different values of  $c_1'$  and  $c_1''$ . Let the results of these experiments be  $D_{mI}$  and  $D_{mII}$ , respectively, then,  $D$  and  $D^*$  can be solved from the two eqns. (37) for the two experiments. Writing  $q_s$  for  $\Delta c_s/\bar{c}_s$  and  $q_1$  for  $\Delta c_1/\bar{c}_1$ , we obtain

$$(44) \quad \sqrt{D^*} = \frac{q_1^I \sqrt{D_{mI}} - q_1^{II} \sqrt{D_{mII}}}{q_1^I - q_1^{II}}$$

and

$$(45) \quad \sqrt{D} = \frac{q_1^{II}(q_1^I - q_s) \sqrt{D_{mII}} - q_1^I(q_1^{II} - q_s) \sqrt{D_{mI}}}{q_s(q_1^I - q_1^{II})}.$$

Similarly,  $D$  and  $D^*$  can be solved from the eqns. (40) for the two experiments and use can be made of eqns. (32) and (33) for the constants  $E_1$  and  $r_1(0)$  in eqn. (40). Then for  $\sqrt{D^*}$  a complicated expression is obtained, which still contains the integrals  $I(+\infty)$  and  $I(-\infty)$ . However, in the expression for  $\sqrt{D}$ , these integrals drop out and the final result is just eqn. (45). In other words, eqns (37) and (40), when used to calculate  $D^*$  and  $D$  from experimental values of  $D_m$ , only give different results for  $D^*$  but not for  $D$ .

For the purpose of illustration, we have calculated the dimensionless quantity  $D_m/D^*$  for a number of chosen values of  $q_s$ ,  $D/D^*$  and  $q_1$ . The integrals, necessary for these calculations with eqn. (40), were evaluated numerically, using Simpson's rule. The results for  $q_1 = \pm 2$  are presented in tables 1-3. We chose these values of  $q_1$  because it is convenient in practice to perform experiments in which either  $c_1'$  or  $c_1''$  is zero.

Using the values of  $D_m/D^*$  obtained from eqn. (40) for  $q_1 = +2$  and  $q_1 = -2$ , we calculated the quantity  $D^*$  (eqn. 44)/ $D^*$ . The results are given in the last column of the tables. If eqn. (40) is considered as the correct equation, these results give an impression of the inaccuracy in the values

TABLE 1

$q_s = \Delta c_s/\bar{c}_s = -0.2$

$D/D^*$	$D_m/D^*$	$(q_1 = -2)$	$D_m/D^*$	$(q_1 = +2)$	$D^*$ (eqn.44)/ $D^*$
	eqn. 37	eqn. 40	eqn. 37	eqn. 40	
0.50	0.9423	0.9435	1.0594	1.0610	1.0014
0.75	0.9737	0.9739	1.0270	1.0276	1.0006
1.125	1.0122	1.0120	0.9879	0.9877	0.9998
1.25	1.0238	1.0234	0.9765	0.9761	0.9996
1.50	1.0455	1.0434	0.9556	0.9532	0.9978

TABLE 2

$$q_s = \Delta c_s / \bar{c}_s = -0.6667$$

$D/D^*$	$D_m/D^*$	$(q_1 = -2)$	$D_m/D^*$	$(q_1 = +2)$	$D^*$ (eqn. 44)/ $D^*$
	eqn. 37	eqn. 40	eqn. 37	eqn. 40	
0.50	0.8143	0.8238	1.2048	1.2280	1.0158
0.75	0.9127	0.9171	1.0913	1.1009	1.0069
0.875	0.9574	0.9592	1.0435	1.0476	1.0029
1.125	1.0409	1.0385	0.9600	0.9564	0.9970
1.25	1.0802	1.0768	0.9229	0.9164	0.9950
1.50	1.1554	1.1495	0.8558	0.8455	0.9917

TABLE 3

$$q_s = \Delta c_s / \bar{c}_s = -1.2$$

$D/D^*$	$D_m/D^*$	$(q_1 = -2)$	$D_m/D^*$	$(q_1 = +2)$	$D^*$ (eqn. 44)/ $D^*$
	eqn. 37	eqn. 40	eqn. 37	eqn. 40	
0.50	0.6794	0.6992	1.3824	1.4967	1.0605
0.75	0.8457	0.8552	1.1672	1.2124	1.0260
1.125	1.0741	1.0751	0.9285	0.9136	0.9903
1.25	1.1467	1.1386	0.8634	0.8357	0.9813
1.50	1.2879	1.2736	0.7485	0.7055	0.9687

of  $D^*$  calculated with the inexact eqn. (37). The quantity  $D^*$  (eqn. 44)/ $D^*$  was also calculated using values of  $q_1$  different from  $\pm 2$ . The results were practically the same as those presented in the last column of the tables.

For many systems it is observed experimentally that  $0.75 < D/D^* < 1.25$ , whereas, except at very low values of  $\bar{c}_s$  it will be easy to perform experiments in which  $|q_s| < 2/3$ . It was already observed that the eqns. (37) and (40) give the same result when used in the calculation of  $D$ . So, in many practical cases eqn. (37) will give sufficient accuracy in the calculation of both  $D$  and  $D^*$ . Although the derivation of eqn. (40) is better justified from a theoretical point of view, its application in the calculation of  $D^*$  from experimental values of  $D_m$  involves much more numerical work than the use of eqn. (37).

In conclusion, from the assumption that the four coefficients  $D_{ij}$ , used in the description of ternary diffusion, are constant, a solution of the diffusion equations for our system is obtained which is not exact for the free diffusion boundary conditions. This solution, however, can be applied in many cases to calculate both  $D$  and  $D^*$ , with acceptable accuracy, from the result of diffusion experiments. We hope to have illustrated the limitations of its applicability, by a comparison with the results of another solution which was derived on the assumption that  $D$  and  $D^*$  are constant.

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## PHYSICAL CHEMISTRY

### DIFFUSION IN TERNARY SYSTEMS CONSISTING OF TWO ISOTOPIC FORMS OF A SUBSTANCE IN SOLUTION

PART II. – EXPERIMENTS WITH THE SYSTEM  $\text{Na}^{36}\text{Cl} - \text{NaCl} - \text{H}_2\text{O}$  at 25° C.

BY

Y. WIERSEMA AND J. TH. G. OVERBEEK

(Communicated at the meeting of November 30, 1968)

#### *Summary*

A glass diffusion cell of the shearing type is described. Some experiments with the system labeled urea–urea–water and labeled sucrose–sucrose–water show that the accuracy of results obtained with this cell is better than  $\pm 1\%$ . Measurements of the diffusion of the  $^{36}\text{Cl}$ -ion in a gradient of the total NaCl concentration with the system  $\text{Na}^{36}\text{Cl}$ –NaCl– $\text{H}_2\text{O}$ , confirm the theory given in part I of this publication.

#### 1. INTRODUCTION

In part I of this series [1], diffusion in a special type of ternary systems was studied. The two solutes in these systems are two isotopic forms of the same substance which were assumed to behave identically in diffusion. It is well known that labeled compounds are used in experiments to determine self-diffusion coefficients. (For reasons given in part I the use of “self-diffusion” instead of “tracer-diffusion” or “intradiffusion” is preferred). In such experiments the total solute concentration is kept constant or nearly constant. In part I, however, situations were also studied in which the labeled component diffuses in a gradient of the total solute concentration. Solutions for the diffusion equations were discussed and it was concluded that the diffusion of the labeled component can be described with the aid of two diffusion coefficients: the mutual diffusion coefficient and the self-diffusion coefficient. It was shown to be possible, in principle, to determine these coefficients from measurements of the diffusion of a labeled component in a gradient of the total solute concentration. These conclusions apply to solutions of non-electrolytes and to electrolyte solutions.

It is the purpose of this part, to show that experiments with the system  $\text{Na}^{36}\text{Cl}$ –NaCl– $\text{H}_2\text{O}$  are in agreement with the theory. A diffusion cell, used in these experiments, will be described.

#### 2. THEORY

##### 2.1. *Equations for a measurable quantity*

In this section, equations will be given, which are used in order to calculate diffusion coefficients from measured quantities. Suppose, a

diffusion experiment is performed in a cylinder of cross section  $A$ , and length  $2l$ .

The axis of the cylinder is called the  $x$ -axis; the middle is at  $x=0$  and the ends are at  $x=\pm l$ . A sharp boundary is formed, at  $x=0$  and time  $t=0$ , between two solutions of different concentrations. When the cylinder is sufficiently long to prevent the development of concentration changes at the ends, the boundary conditions are those of so-called free diffusion. Then, in the case of a binary system, the total amount of solute which has been transported across the plane  $x=0$  in the time  $t$  can be easily calculated [2].

Here, we are interested in the amount of the labeled component which is transported across the plane  $x=0$  during time  $t$  in an experiment with the special ternary system under consideration. For this system we adopt the following notation. The subscripts 1, 2 and  $s$  will be used for the labeled component, its unlabeled chemical equivalent and their sum, respectively.

Furthermore,  $c_i'$  and  $c_i''$  ( $i=1, 2, s$ ) denote the initial concentrations in the cylinder for  $x<0$  and  $x>0$ , respectively, whereas we write  $\Delta c_1$  for  $c_1'' - c_1'$  and  $\bar{c}_1$  for  $(c_1'' + c_1')/2$ .

In part I, we defined the quantities  $Q_1$  and  $D_m$  by the equation

$$(1) \quad Q_1 = \frac{1}{\bar{c}_1} \int_0^t (J_1)_{x=0} dt = -\frac{\Delta c_1}{\bar{c}_1} \left( \frac{D_m t}{\pi} \right)^{\frac{1}{2}},$$

in which  $J_1$  is the flow per unit cross section of the labeled component and  $D_m$  can be considered as an apparent diffusion coefficient. It will be clear that  $A$  times the integral in this equation equals the amount of the labeled component which is transported across the plane  $x=0$  during time  $t$ . If the amount of this component present at time  $t$  in the parts of the cylinder extending from  $x=0$  to  $x=-l$  and from  $x=0$  to  $x=+l$  are denoted by  $M(t)$  and  $N(t)$ , respectively, the following equation can be written

$$(2) \quad \frac{Q_1}{2l} = \frac{N(t) - N(0)}{2Al\bar{c}_1} = \frac{M(0) - M(t)}{2Al\bar{c}_1} = \frac{N(t) - N(0)}{M(0) + N(0)} = \frac{N(t) - N(0)}{M(t) + N(t)}.$$

Combining eqns. (1) and (2), we obtain

$$(3) \quad \frac{M(0) - M(t)}{M(t) + N(t)} = \frac{N(t) - N(0)}{M(t) + N(t)} = -\frac{\Delta c_1}{2\bar{c}_1 l} \left( \frac{D_m t}{\pi} \right)^{\frac{1}{2}}.$$

The left-hand side of this equation is measurable, since the amounts of the labeled component are proportional to the amounts of radioactivity. The factor  $\Delta c_1/2\bar{c}_1$  can, if necessary, be obtained from

$$(4) \quad \frac{\Delta c_1}{2\bar{c}_1} = \frac{N(0) - M(0)}{M(0) + N(0)}.$$

In actual practice, however, it is convenient to put either  $c_1'$  or  $c_1''$  equal

to zero. Then,  $\Delta c_1/2\bar{c}_1$  becomes equal to  $+1$  or  $-1$ , respectively, and eqn. (3) is written as

$$(5) \quad \frac{M(t)}{M(t) + N(t)} = \frac{1}{l} \left( \frac{D_m t}{\pi} \right)^{\frac{1}{2}} \quad \text{for } c_1' = 0$$

or

$$(6) \quad \frac{N(t)}{M(t) + N(t)} = \frac{1}{l} \left( \frac{D_m t}{\pi} \right)^{\frac{1}{2}} \quad \text{for } c_1'' = 0.$$

In part I, two equations for the quantity  $D_m$  are given. The first is:

$$(7) \quad D_m = \left\{ D^{*\frac{1}{2}} + (D^{\frac{1}{2}} - D^{*\frac{1}{2}}) \frac{\bar{c}_1}{\Delta c_1} \frac{\Delta c_s}{\bar{c}_s} \right\}^2,$$

in which  $D$  and  $D^*$  are the mutual- and the self-diffusion coefficient of the solute. If  $D$  and  $D^*$  are assumed to be constant, eqn. (7) is only exact for two special choices of the initial conditions, i.e. when  $c_1'/c_2' = c_1''/c_2''$  or when  $\Delta c_s = 0$ .

It is easily verified that then, eqn. (7) reduces to  $D_m = D$  or to  $D_m = D^*$ , respectively. For all other choices of the initial conditions eqn. (7) should be considered as an approximation. Therefore, another equation for  $D_m$  was derived, using the assumption that  $D$  and  $D^*$  are constant, and which is exact for all initial conditions. It reads

$$(8) \quad D_m = \left\{ \frac{(\pi)^{\frac{1}{2}} E_1 \bar{c}_s D^* + r_1(0) \Delta c_s D}{\Delta c_1 D^{\frac{1}{2}}} \right\}^2.$$

Expressions for the constants  $E_1$  and  $r_1(0)$  ( $r_1(0)$  equals  $(c_1/c_s)_{x=0}$ ) are given in ref. 1.

The equations (7) and (8) can be used to calculate  $D$  and  $D^*$  from experimental values of  $D_m$ . It was concluded in part I that they give the same result for  $D$  but not for  $D^*$ , although eqn. (7) may give acceptable results for  $D^*$  in many cases.

## 2.2. The duration of the experiments.

The duration of a diffusion experiment with a cylinder as described above, is an important factor. If  $t$  in eqn. (5) and (6) is taken too small, the amount of material transported from one compartment to the other is too small to be measured with sufficient accuracy. On the other hand, when  $t$  is chosen too large, the free diffusion boundary conditions are no longer satisfied and eqns. (5) and (6) are not valid any more. A suitable compromise is found by the following reasoning.

When  $t$  is too large, the situation becomes one of "restricted diffusion". Then the right-hand side of eqn. (3) should be replaced by a more complicated function. Using the method of "reflection and superposition" [3] (see also ref. 2, p. 23) this function can be developed into a convergent

series of which we have calculated the first three terms. With these, and using eqn. (4), eqn. (3) changes into

$$(13) \quad \left\{ \frac{N(t) - N(0)}{M(0) - N(0)} = \frac{1}{l} \sqrt{\frac{D_m t}{\pi}} - \left\{ \frac{\sqrt{D_m t}}{l} \operatorname{erf}' \left( \frac{l}{\sqrt{D_m t}} \right) + 2 \operatorname{erf} \left( \frac{l}{\sqrt{D_m t}} \right) - 2 \right\} + \right. \\ \left. + \left\{ \frac{\sqrt{D_m t}}{l} \operatorname{erf}' \left( \frac{2l}{\sqrt{D_m t}} \right) + 4 \operatorname{erf} \left( \frac{2l}{\sqrt{D_m t}} \right) - 4 \right\} + \dots \right.$$

where erf and erf' are the error function and its derivative. When the value of  $\sqrt{D_m t}/l$  is chosen such that the first term equals 0.25, a calculation of the second and third terms with the aid of tables of the error function and its derivative [4] gives

$$(14) \quad \frac{N(t) - N(0)}{M(0) - N(0)} = 0.25 - \{0.246 \times 10^{-3}\} + \{0.29 \times 10^{-10}\} + \dots$$

From this it is seen that by choosing  $t \leq (0.25 l)^2 \pi / D_m$ , the second term contributes less than 0.1 percent of the first, whereas the third and higher terms are completely negligible.

The over-all experimental error in the left-hand side of eqn. (13) is about 0.4 percent, so that the error caused by neglecting the second and higher terms, with this choice of  $t$ , is sufficiently small. This choice implies that one quarter of the total amount of radioactivity, which was originally present only in one compartment of the cylinder, has diffused into the other compartment, at the end of an experiment.

### 3. EXPERIMENTAL

The diffusion cells used in this work are of the so-called shearing type, which means that a sharp boundary is formed by sliding two cell halves, containing solutions of different concentrations, on top of each other. In some respects our cells resemble the one used earlier in our laboratory by COHEN and BRUINS [5] and other cells described by WANG and KENNEDY [6] and by MEYERHOF and MEIER [7].

The cell is constructed as follows, starting from two circular plate glass disks having a thickness of 6 mm and a diameter of 67 mm. Besides a hole in the centre, two sets of four holes, all at the same distance from the centre are drilled into each disk with the aid of a diamond drill. The angles between the holes of one set are 90°, but there is an angle of 55° or 35° between the holes of the two sets. (fig. 1). The two disks are placed on top of each other and two sets of four precision bore glass capillaries, one set with 1.5 mm and one with 2.5 mm bore diameter, all 65 mm in length, are inserted into the holes. The capillaries are cemented to the disks with epoxy resin. During the setting of the resin, glass spacers (thickness 3 mm) are placed between the disks. Care is taken that the parts of the capillaries, sticking out of the disks are equal in length, and that the capillaries are perpendicular to the disks. Then, two flanged brass bearings A and B

(fig. 1) are cemented into the central holes of the glass disks. A stainless steel shaft C (thickness 8 mm) keeps the bearings (which exactly match the shaft) aligned during the setting of the resin. The bearing B is fixed to the shaft by means of a conic pin, sticking through holes in the flange and the

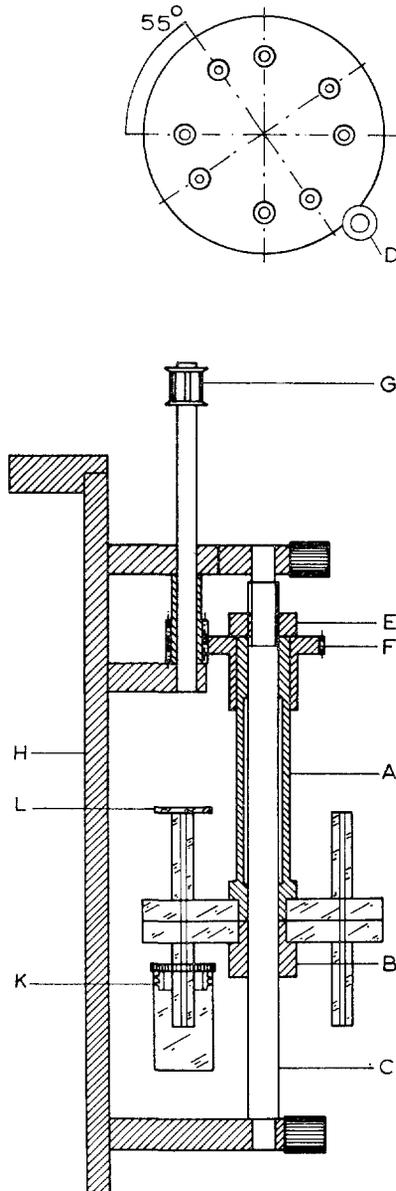


Fig. 1. Diffusion cell.

Upper part: horizontal cross section. Lower part: vertical cross section.

A, B, brass bearings; C, stainless steel shaft; D, hollow brass cylinder, to fix glass disks in diffusion position; E, nut; F, gear-wheel; G, pulley; H, brass cell holder; K, polyethylene stopper fixing container to capillary; L, glass platelet.

shaft. The capillaries, which hold the disks together, are then cut with a diamond saw, sliding into the 3 *mm* space between the disks. The faces of the glass disks are ground and polished until they are flat within 0.01 *mm*. The same is done with the ends of the capillaries that stick out of the disks. Care is taken to make the lengths of the capillaries (30 *mm*) in each cell half, equal to each other within 0.01 *mm*.

When the cell is constructed as described above, one can slide the upper half of the cell over the lower half, until in one position, the capillaries are exactly on top of each other. This position is fixed with a stainless steel rod fitting exactly in the bore of two hollow brass cylinders, which are cemented to the glass disks at D.

One set of capillaries, either those with the 2.5 *mm* bore or those with the 1.5 *mm* bore, is used for the measurement, while the other set is used to fill or empty the measuring capillaries. Since the two sets are at angles of 55°, there is always a position of the disks at which the capillaries of one set in one cell half can be filled or emptied through the capillaries of the other set in the other cell half, while the remaining capillaries stay closed. Before an experiment is started, a very small amount of grease and a few drops of the solution used in the experiment are placed between the disks. By means of a nut E and a rubber ring between the nut and the gear-wheel F, the two disks are pressed together, leaving a thin transparent film of solution between the disks. This liquid film prevents air bubbles from being trapped in the capillaries when the disks are rotated with respect to each other. The open ends of the measuring capillaries are closed with small polished glass platelets using a very small amount of grease. The capillaries are filled with the aid of a glass tube which is, at one end, drawn out to a thin capillary, and, at the other end, connected to a hypodermic syringe.

First the two disks are rotated with respect to each other over an angle of 55°, and the capillaries in one cell half are filled. The capillaries in the other cell half can be filled after a rotation over 20° in the opposite direction and by turning the cell upside down. The solution with the highest density is always put into the capillaries of the lower cell half. When the cell has been filled, the disks are rotated with respect to each other in such a way that all capillaries are closed. An advantage of our cell over similar other types, is that any air bubbles left in the capillaries can be easily observed and removed.

The cell is put into a water thermostat, the shaft being fixed in the cell holder H, which is tightly clamped to the wall of the thermostat bath. The cell is allowed to stand for about one hour to establish temperature equilibrium. During this period a small amount of solution escapes from the capillaries into the liquid film between the disks, due to the expansion of the liquid.

To start an experiment, the upper half of the cell is rotated by means of the gear assembly at F and a pulley G, (which is driven by a flexible

belt connected to an electromotor) until the capillaries are exactly on top of each other. At this moment, which is taken as zero time for the experiment, the stainless steel rod just slides into the bore of the cylinders at D. The speed of rotation is such that there are five minutes between the moment of first contact of the 2.5 *mm* bore capillaries and the moment of complete coverage.

At the end of an experiment, the upper half of the cell is rotated by means of the electromotor until all capillaries are closed. The time of the experiment is taken from zero time to the moment when the capillaries just loose contact during the rotation at the end of the experiment. In this way a partial correction is applied for the times, at the beginning and at the end of the experiment, during which the capillaries cover each other incompletely. The cell is taken from the thermostat and the set of capillaries which is not used for the measurement is provided with small glass containers connected to the capillaries by means of polyethene stoppers as shown at K. The contents of the measuring capillaries are then transferred to the glass containers, simply by sliding the small glass platelets L away, after which the platelets and the capillaries are rinsed with one *ml* of water. Finally, the containers are placed into sample bottles for a liquid scintillation counter.

The thermostat, a Perspex box with double walls and a Perspex cover, is placed on a heavy stone table in the basement of the laboratory. From a second thermostat, water is pumped, through a flexible rubber tubing, into the lower part of the first one; the water flows back into the second thermostat by means of an overflow device.

The second thermostat, which holds the devices for temperature control and the circulation pump, is placed on a console-table fixed to the wall of the basement. In this way, vibrations are reduced to an acceptable minimum. The temperature is kept at  $25.00 \pm 0.01^\circ\text{C}$ .; usually the fluctuations are less than  $0.003^\circ\text{C}$ . Six cell holders are placed in the thermostat, so that six experiments can be performed simultaneously. The electromotor driving the gear assemblies of these cell holders, is supported by a heavy steel tube, fixed to the wall.

Analytical reagent ("AnalaR") B.D.H. chemicals and distilled water were used to prepare the solutions. The radioactive chemicals were supplied by the Radiochemical Centre, Amersham, England. The solutions were made up by volume or by weight; in the latter case, the concentrations were converted into mole/volume units with the aid of tabulated densities.

The samples were counted in a Nuclear Chicago Mark I liquid scintillation counter. The counting liquid mixture consisted of: 1 *l* 1,4-dioxane; 110 *g* naphthalene; 6 *g* P.P.O. (2,5-diphenyloxazole) and 50 *mg* P.O.P.O.P. (p-bis-[2-(5-Phenyloxazolyl)]-benzene). Corrections for background and quenching were applied in the usual way.

## 4. RESULTS AND DISCUSSION

In order to test the cells used in this work, some measurements were performed with the systems  $^{14}\text{C}$ -labeled urea-urea-water and  $^{14}\text{C}$ -labeled sucrose-sucrose-water at  $25^\circ\text{C}$ . Both  $D$  and  $D^*$  for these systems are reported in the literature. The results which are listed in tables 1 and 2, were obtained with four different cells. The same cells were used in the measurement with the system  $\text{Na}^{36}\text{Cl}-\text{NaCl}-\text{H}_2\text{O}$ . In the tables we give mean values, obtained from the four capillaries in one experiment, together with the standard deviation. The value obtained from each capillary usually differed less than 2 % from the mean. For all measurements, the 2.5 mm bore capillaries were used.

In the tables we have marked with an asterisk the side of the boundary at which the radioactive material was originally present. Tables 1 and 2 only give results of experiments in which either  $c_s''=0$  or  $c_s'=c_s''$ ; this corresponds to  $D_m=D$  or to  $D_m=D^*$ , respectively. The literature values are given at the mean concentration  $\bar{c}_s$ .

TABLE 1  
Diffusion of urea in water at  $25^\circ\text{C}$ .

cell no.	$c_s'$ g/100 ml	$c_s''$ g/100 ml	$D \times 10^5$ $\text{cm}^2/\text{sec}$	$D^* \times 10^5$ $\text{cm}^2/\text{sec}$	lit. value
3	1.00*	0.00	$1.36 \pm 0.01$		1.37 [8, 9]
4	1.00*	0.00	$1.37 \pm 0.02$		
3	1.00*	1.00		$1.38 \pm 0.01$	1.37 [9]
4	1.00*	1.00		$1.39 \pm 0.01$	

TABLE 2  
Diffusion of sucrose in water at  $25^\circ\text{C}$ .

cell no.	$c_s'$ g/100 ml	$c_s''$ g/100 ml	$D \times 10^6$ $\text{cm}^2/\text{sec}$	$D^* \times 10^6$ $\text{cm}^2/\text{sec}$	lit. value
2	0.50*	0.00	$5.21 \pm 0.02$		5.21 [10, 11]
1	1.00*	0.00	$5.18 \pm 0.03$		5.19 [10, 11]
3	1.00*	1.00		$5.08 \pm 0.05$	
1	2.00*	2.00		$5.01 \pm 0.05$	compare
1	3.00*	3.00		$4.94 \pm 0.03$	ref. 12,
4	4.00*	4.00		$4.80 \pm 0.02$	13 and
1	5.00*	5.00		$4.72 \pm 0.03$	text.
1	7.00*	7.00		$4.52 \pm 0.02$	

In general the agreement with literature data is good. The self-diffusion coefficients of sucrose confirm (within 1 %) the data recently published by TILLEY and MILLS [12], but are substantially higher than the results of IRANI and ADAMSON [13]. Our values of  $D^*$  may be somewhat high due to the error caused by convection during the formation of the boundary. In order to estimate the magnitude of this error, we have done three

short-time self-diffusion experiments with the urea-water system at  $c_s = 0.01$  g/ml. The durations of these experiments were 315, 1960 and 7640 sec., respectively. A straight line could be drawn through values of  $D^*t$  when plotted versus  $t$ . By extrapolation, a zero time correction of 200 sec was obtained, which is only about 0.2 % of the times used in the experiments in table 1. The error caused by convection will probably be lower in cases where  $c_s' \neq c_s''$ . It may be concluded that the diffusion cells used in this work, give a precision better than  $\pm 1$  % for measurements in which  $c_s' \neq c_s''$ .

In order to test the equations (7) and (8), two groups of four experiments ( $2 \times 16$  capillaries) were performed with the system  $\text{Na}^{36}\text{Cl}-\text{NaCl}-\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . In one group, the flow of radioactive material has the same sign as the total solute flow, whereas in the other group these flows have opposite signs. In the calculation of  $D_m$  with the aid of eqns. (7) and (8), we used the following literature data for  $D$  and  $D^*$  at the mean concentration ( $\bar{c}_s = 0.625$  g/100 ml):  $D_{\text{NaCl}} = 1.484 \times 10^{-5}$   $\text{cm}^2/\text{sec}$  [14] and  $D^*_{\text{Cl}^-} = 1.94 \times 10^{-5}$   $\text{cm}^2/\text{sec}$  [15].

The last value was checked by doing two self-diffusion experiments with our cells. The results were:  $D^*_{\text{Cl}^-} = 1.93_0$  and  $1.93_8 \times 10^{-5}$   $\text{cm}^2/\text{sec}$ . In table 3, calculated and experimental values of  $D_m$  are listed. The experimental values are mean values from 16 capillaries; the standard deviation of the mean is given between brackets.

TABLE 3  
Diffusion of the  $^{36}\text{Cl}$ -ion in  $\text{NaCl} + \text{H}_2\text{O}$  at  $25^\circ\text{C}$ .

$c_s' = 1.000; c_s'' = 0.250^* \text{ (g/100 ml)}$			$c_s' = 1.000^*; c_s'' = 0.250 \text{ (g/100 ml)}$		
$D_m \times 10^5 \text{ (cm}^2/\text{sec)}$			$D_m \times 10^5 \text{ (cm}^2/\text{sec)}$		
exp.	calc.		exp.	calc.	
	eqn. (7)	eqn. (8)		eqn. (7)	eqn. (8)
2.30 <sub>3</sub>	2.249	2.325	1.67 <sub>4</sub>	1.659	1.677
( $\pm 0.003$ )			( $\pm 0.006$ )		

The difference between experimental values and values calculated from eqn. (7) is clearly beyond experimental error. The calculated values may be somewhat high due to the fact that the value for  $D^*_{\text{Cl}^-}$  used in the calculations is probably too high.

Some results calculated in part I can now be used for a comparison with the results of our experiments. Table 3 of part I (ref. 1) was computed for the same value of  $\Delta c_s/\bar{c}_s$  as in our experiments for which  $\Delta c_s/\bar{c}_s = -0.75/0.625 = -1.2$ , whereas the value  $D/D^* = 0.75$  is close to the experimental value:  $D/D^* = 1.484/1.94 = 0.765$ . When  $D$  and  $D^*$  are calculated, using eqn. (7), from experimental values of  $D_m$  (compare eqns. (44) and (45), ref. 1), we expect the correct value for  $D$ , but too high a value for  $D^*$ . The result indeed is  $D = 1.48_7 \times 10^{-5}$   $\text{cm}^2/\text{sec}$  and  $D^* = 1.97_6 \times 10^{-5}$   $\text{cm}^2/\text{sec}$ .

There are several ways to find a better result for  $D^*$ , using eqn. (8). Here we discuss two possibilities. In the first, the error in  $D^*$  ( $D^*$  calculated with eqn. (7)) is computed as a function of  $D/D^*$ , using eqn. (8). Table 3, ref. 1, is suitable for that purpose. From this table it is seen that the error is +2.6 % for  $D/D^*=0.75$ , which is close to the value 0.765 for our system. When  $D^*$  is corrected for this error, we obtain  $D^*=1.92_6 \times 10^{-5}$   $cm^2/sec$ .

Using the same table, the quotient of the two values for  $D_m$  (for  $\Delta c_1/\bar{c}_1 = \pm 2$ ) can be calculated as a function of  $D/D^*$ . The logarithm of this quotient, when plotted versus  $D/D^*$  gives approximately a straight line. This suggests another method to obtain the value of  $D^*$ . We computed the quotient, with the aid of eqn. (8), for two values of  $D/D^*$  close to the experimental value 0.765, namely  $D/D^*=0.75$  (already computed for table 3, ref. 1) and  $D/D^*=0.78125$  (chosen for convenience in desk calculations). Using the experimental value of the quotient,  $2.303/1.674 = 1.376$ , we obtained  $D/D^*=0.770$  for the system under study, by linear interpolation in a logarithmic plot. Substituting the experimental result for  $D$ , we find  $D^*=1.48_7 \times 10^{-5}/0.770 = 1.93_1 \times 10^{-5}$   $cm^2/sec$ , which agrees quite well with the results of our self-diffusion experiments.

We conclude that the experiments with the system  $Na^{36}Cl-NaCl-H_2O$  confirm the theory given in part I, and that it is possible in practice to obtain both  $D$  and  $D^*$  from experiments in which there exists a gradient in the total solute concentration. It should be stressed that the theory is a purely phenomenological one. We have not, for example, attempted to give a more physical explanation for the fact that the two values of  $D_m$ , obtained from the experiments with the system studied, differ substantially from the self-diffusion coefficient of the chloride ion. For this, the gradient of the electric potential (sometimes called the diffusion potential) in the diffusion boundary is mainly responsible.

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