

## Interferometric Studies of Boundary Formation and Deviations from Ideality in Diffusion Experiments

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Various types of diffusion cells have been studied by means of the birefringence interference method especially with regard to the methods used for producing a sharp interface. This method, which is very sensitive to small concentration differences, was found to give valuable information concerning the beginning of the diffusion process. Thus, the boundary formation has been compared for different types of cells. The small influence of convection, in spite of the small concentration differences used, was quite remarkable. The various factors influencing ideality in diffusion experiments using the birefringence interference method on very dilute solutions have been discussed in some detail.

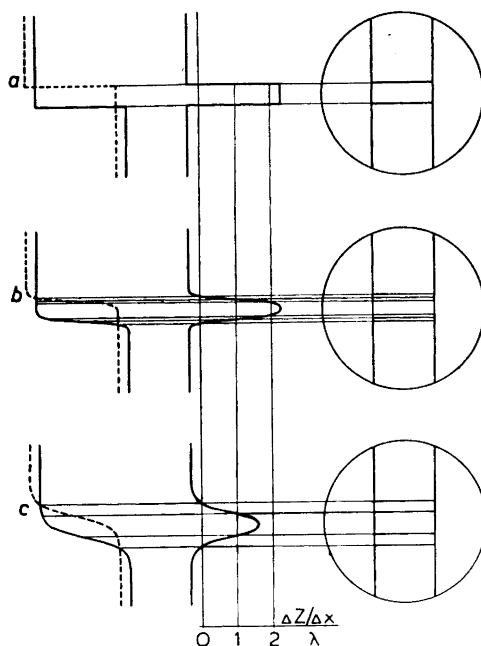
### STUDIES ON BOUNDARY FORMATION IN DIFFUSION CELLS

Optical methods are of great value in the study of liquid diffusion because of their precision and the great amount of information which they yield. One of the main problems in arranging diffusion experiments is the formation of an initially sharp interface.

This problem has been solved in many different ways. Diffusion cells belonging to the types mentioned below have been designed specially for registration by optical methods.

The diffusion equation is usually solved using the initial condition that the solution and solvent are separated by a sharp interface in an infinitely long tube at  $t = 0$ . Turbulence and other disturbing phenomena arising from the boundary formation process must therefore be suppressed. Thus, the way in which the boundary is formed has proved to be of great importance, since this is decisive for the magnitude of the zero-time correction and the lapse of time after which the first measurements can be taken.

The magnitude of the concentration difference influences the ideality of the initial gradient. With decreasing concentration difference, the density gradient decreases and the disturbances arising from the formation process disappear more slowly. On working with very dilute solutions it is consequently important that the disturbing phenomena be minimized. It will be shown below that sharp interfaces can be formed using the boundary-sharpening technique<sup>1</sup> even with very small concentration differences.



*Fig. 1.* (Left) The refractive index as a function of  $x$  for the concentration gradient. (Middle) The corresponding difference graph for the path differences between the two wave fronts produced by the Savart plate. (Right) The appearance of destructive interference in the object plane.

a) An ideal initial boundary gives rise to a concentration step which in this method is represented by a fringe pair.

b) At the beginning of the diffusion run, a record of the refractive index instead of its gradient is obtained because of the steepness of the concentration gradient.

c) As a rule, however, the photograph gives the derivative  $dn/dx$  directly due to the doubling of the wave front and no correction is necessary.

### I. OPTICAL METHOD

The shearing interferometer utilizing birefringence interferences<sup>2-4</sup> and giving an image of the whole diffusion column is very sensitive to small concentration differences and is also suitable for the registration of rapid processes. Studies of the beginning of the diffusion process have been performed with this recording interferometric method, the optical arrangement of which has been described in an earlier paper<sup>4</sup>.

By placing a birefringent double crystal plate (Savart plate) in parallel light behind the cell in the optical arrangement, a doubling of the wave front (representing the concentration curve) is effected (Fig. 1). If the crossed polarizers have their oscillation planes at  $45^\circ$  with respect to the principal planes of the Savart plate, the light is extinguished at those points where the optical path difference between the wave fronts is a whole number of wave lengths<sup>4</sup>. From Fig. 1a it is evident that an ideal boundary formation is represented

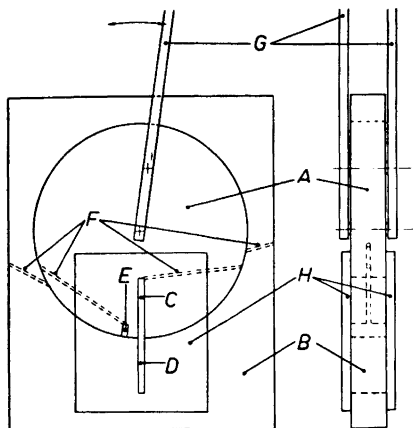


Fig. 2. Diffusion cell. By means of a lever *G* it is possible to turn the inner disk *A* until the two halves of the diffusion column *C* and *D* coincide. In this way the boundary will be formed and the diffusion started. The cell is tightened with silica lubricant at the glass plates *H* forming the walls of the diffusion cell.

by one horizontal fringe pair with a distance between the fringes equal to the displacement between the wavefronts. In Fig. 1 it is seen that at first the optical method gives a doubling of the integral curve and that later, when the refractive index gradient becomes broader, the method gives a record of the derivative  $dn/dx$ . Actually, the measurements give  $\Delta n/\Delta x$  but the correction for obtaining the derivative can be easily calculated<sup>2-4</sup>. The correction is as a rule very small and can be neglected<sup>2</sup>. Only at the start of the diffusion has one to pay attention to the correction term. Hence, if no measurements are made at the beginning, the method becomes quite convenient.

## II. DIFFUSION CELLS

In optical methods the following demands are made upon the diffusion cells:

- a) plane parallel, transparent, homogeneous walls in the light direction,
- b) a rectangular cross section to eliminate optical distortions,
- c) uniformly thick diffusion column forming no wedge.

Thanks to Prof. O. Lamm and Dr. H. Svensson who kindly put diffusion cells at our disposal, a fairly complete examination could be performed and the different ways of producing boundary layers compared.

The types of cells commonly used and examined here can be classified in three groups according to the technique of boundary formation:

*I "Draw-slide cell"* — usually referred to as the Lamm cell. A slide separating solution and solvent is drawn out — two cells of this type<sup>5</sup> with thicknesses of 1 cm (*Ia*) and 5 cm (*Ib*) were studied.

*II "Flowing-junction cell"*. The boundary is formed by allowing solution and solvent to flow out together through a narrow horizontal exit slit in the side wall of the cell<sup>6-9</sup>. The cell<sup>6</sup> examined here was 5 cm thick.

*III "Sliding-solvent cell"*. In this cell the interface is formed by sliding the solvent over the solution<sup>10-12</sup>.

After some unsuccessful experiments with cells of type *III* built according to descriptions found in the literature, the author decided to design a new cell of this type (Fig. 2). The material used was perspex, 1.2 cm thick. A circular disk *A* (diameter = 10 cm) was fitted into a corresponding hole in a plate *B*. Narrow slits *C* and *D* (3 mm) were cut and used as a diffusion column. A slit *E* was also cut for pouring in the bottom solution. Small channels *F* are bored to permit filling by means of a syringe. The boundary layer is formed by turning the disk until the slits *C* and *D* coincide.

### III. REGISTRATION

In order to get a complete mapping of the phenomena arising from the boundary formation process, two different photographic registration methods have been used.

1. A registration of the whole of the cell plane was performed at equal time intervals. The time of exposure was about 1 sec.

2. A continuous registration of the interference pattern gives much information about the symmetry and various disturbing phenomena and their influence. A narrow vertical strip of the image plane was reproduced on a film attached to a continuously moving drum. A film speed of 3 cm/min was employed.

Iford HPS film was used to attain a minimum of exposure.

### IV. EXPERIMENTS

Monochromatic light (5 461 Å) was used in all experiments. The solutions, always with distilled water as solvent, were carefully thermostated at a temperature of about 21°C.

The following experiments were carried out:

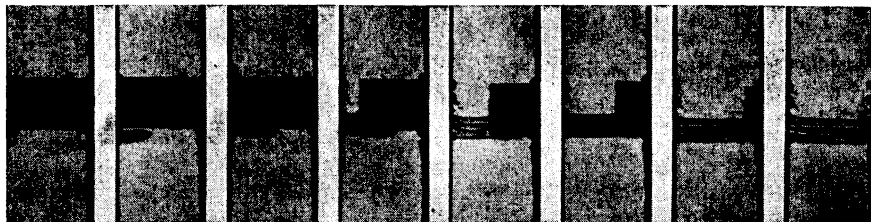
Run	Solution diffusing against water	g/100 ml	Cell thickness in cm	Zero-time correction in sec	
<i>Ia</i> , 1 *	glycine	0.0942	1.0	29	} Draw-slide cell
<i>Ib</i> , 1	sucrose	0.0503	5.0	22	
<i>Ib</i> , 2	sucrose	0.0503	5.0	18 (20)	
<i>II</i> , 1	sucrose	0.0500	5.0	4	} Flowing-junction cell
<i>II</i> , 2	sucrose	0.0500	5.0	3	
<i>III</i> , 1	sucrose	0.2508	1.2	20	} Sliding-solvent cell

### V. RESULTS

In all cases the concentration was chosen so as to give rise to 3–5 fringe pairs at the beginning of the run.

\* The first figure refers to the cell types described in Section II, and the last figure to the registration methods listed in Section III.

Run 1 a, 1



### I. "Draw-slide cell"

*Ia, 1.* The registrations were performed at 6 sec intervals. From the recordings it is seen how a region of mixing is developed below the slide. If the dividing wall is withdrawn at a uniform speed, a sucking effect acts upon the liquid so that a sharp boundary is formed. It should be added that the zero-time point (starting point of the diffusion run) will generally occur in the period between when the slide starts to leave the cell wall and when it is completely removed from the diffusion column. The slide was 2 mm thick.

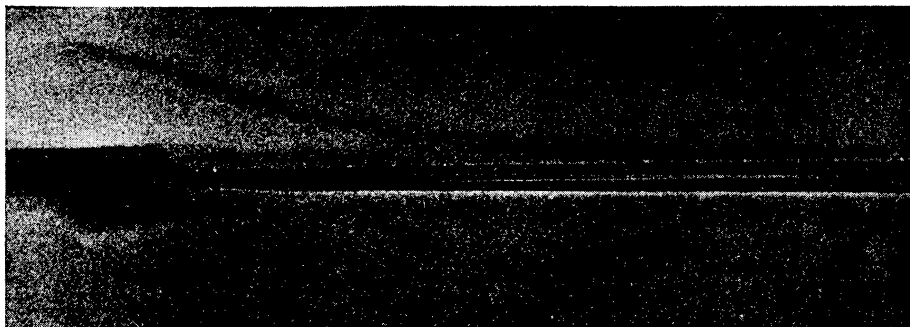
*Ib, 1.* The slide thickness here was 1 mm. A turbulent motion under the slide is also visible in this run. However, another phenomenon occurs - at the instant the slide leaves the cell wall a narrow beam of solution is forced up into the solvent layer. It spreads out at a definite height but sinks and disappears with time (*cf. Ib, 2*).

The influence of the slide velocity on the boundary formed has been examined. In the case of the 2 mm slide (*Ia*), only slow speeds (less than 0.2 mm/sec) are possible since turbulence sets in at higher speeds. A speed of 0.1 mm/sec gave a smooth symmetrical gradient and was found to be the

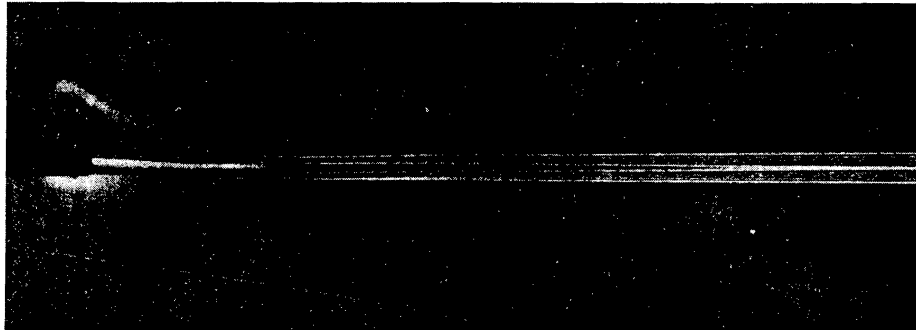
I b, 1



Run 1 b, 2



Run 1 b, 2



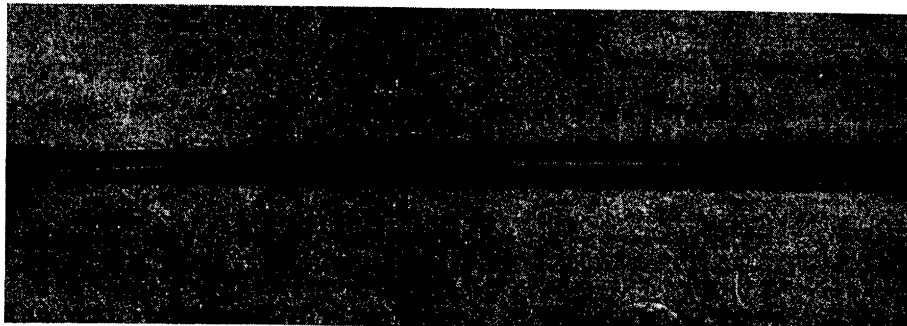
most suitable value. The cell with the 1 mm slide (*Ib*) gave a sharp boundary with a slide speed of 1 mm/sec. However, at this speed disturbing vibrations of the boundary occurred. The most satisfactory results were obtained with a value of about 0.2 mm/sec. The slide speed must not be too slow in order to avoid lateral skewness of the gradient.

*Ib, 2.* Two records showing the change in the interference pattern with time. Here the vanishing of the disturbing processes is clearly seen. The sharpness of the gradient is also apparent.

Run 11, 1



Run II, 2



### II. "Flowing-junction cell"

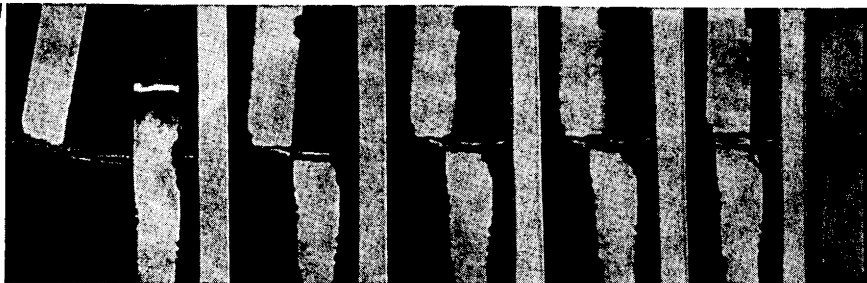
II, 1. The sharp gradient is obtained as a state of equilibrium. As is seen from the photographs, the boundary is sharper near the exit slit. The outflow rate considerably influences the symmetry of the gradient. The outflow was about one drop every two seconds. However, a continuous flow was obtained by placing the capillary outlet in a beaker of water. Different concentrations required different sized capillaries.

II, 2. No disturbances can be observed in this photograph. This cell gave the most ideal boundary obtained in this work. However, there is asymmetry due to incorrect focusing. This skewness of the gradient disappears if the camera is focused on a plane  $1/3$  of the cell thickness from the front wall<sup>13</sup>.

### III. "Sliding-solvent cell"

III, 1. This cell resembles cell type I but here the displacement of the upper column of liquid has been eliminated. The liquid column was moved with a speed of 0.3 mm/sec which was found to be the best one for this cell. Only small asymmetries along the gradient have been observed. Sharp boundaries were also obtained for very dilute solutions.

Run III, 1



These experiments confirm the possibility of forming sharp interfaces between solutions with very small density differences. The boundary-sharpening technique works well without leaving any disturbing convections and no superimposed thermal gradient is necessary to increase the density gradient. As is seen from the photographs of the formation of the interfaces, *all* the cells examined work very well and can be used for precise measurements at the smallest concentration differences.

It would perhaps be worth while investigating the possibility of improving the boundary-sharpening technique further by equipping the cell with two outflow slits opposite each other. By varying the outflows through the two slits, the optimum conditions could be obtained (*i.e.* the outflows need not necessarily be equal).

## DIGRESSION ON DEVIATIONS FROM IDEALITY IN DIFFUSION EXPERIMENTS

### VI. THE EFFECT OF THE MAGNITUDE OF THE DENSITY DIFFERENCE ON THE FORMATION OF IDEAL GRADIENTS

It is possible to sharpen the boundary using a transient, superimposed thermal gradient. This procedure cannot be used when working with very dilute solutions since the time for the disappearance of the thermal gradient is comparable to the length of the run.

The values of the parameters, *e.g.* slide speed, outflow rate and pressure difference, have proved to be very critical when working with small concentration differences. The adjustment of the different parameters is easiest with the flowing-junction cell. Initially sharp boundary layers have been observed with the flowing-junction cell down to a concentration difference (sucrose solution) corresponding to an optical path decrement of about 1 000 Å.

One may ask how great a concentration difference is necessary to form a sharp interface. Convection caused by transient temperature gradients, which cannot be totally eliminated by good thermostating, must be prevented by a sufficiently large concentration gradient.

An estimate of the amount of convection produced can be obtained from Grashof's number \* ( $Gr_1$ ) and another dimensionless number ( $Gr_2$ ) specifying the convection caused by a density gradient.

$$Gr_1 = \frac{l^3 g \gamma \Theta}{\nu^2}$$

$$Gr_2 = \frac{l^3 g \frac{1}{V} \left( \frac{\partial V}{\partial c} \right) \Delta c}{\nu^2}$$

The influence of the various parameters ( $l$  — characteristic length,  $\Theta$  — temperature difference,  $\Delta c$  — concentration difference,  $\nu$  — kinematic viscosity) on the convection can be obtained using these numbers.

\* See, *e. g.*, *Lexikon der Physik*, H. Franke, Stuttgart 1950, p. 593.



The following notations are used:  $g$  — gravity,  $\gamma$  — thermal expansion coefficient,  $V$  — volume,  $c$  — concentration,  $\rho$  — density of the solution.

$Gr_1 = Gr_2$  gives the concentration gradient necessary to counteract a transient thermal gradient ( $\Theta$ ).

$$\frac{\Theta}{\Delta c} = \frac{\partial V / \partial c}{V\gamma} = \frac{1}{\gamma} \frac{\partial \ln V}{\partial c} = - \frac{1}{\gamma} \frac{\partial \ln \rho}{\partial c} \quad (1)$$

A rather trivial fact also apparent from Grashof's number is that the cell should be as narrow as possible if the convection is to be a minimum.

#### VII. ADVANTAGES OF PERFORMING DIFFUSION EXPERIMENTS WITH SMALL CONCENTRATION DIFFERENCES

Working with small concentration differences diminishes most of the problems pertaining to the non-linear relation between refractive index and concentration as well as to the concentration dependance of the diffusion coefficient.

The time necessary for performing a diffusion run by the birefringence interference method is greatly dependant upon the concentration difference. Small concentration differences make possible a saving of time and the use of smaller amounts of materials which may be difficult to obtain or purify.

With systems having a density maximum or minimum at a certain concentration, it is necessary to work in a range where the density-concentration curve is monotonic and this can always be achieved by working with very small concentration differences.

#### VIII. FACTORS DECISIVE FOR THE LENGTH OF TIME BEFORE MEASUREMENTS CAN BE PERFORMED

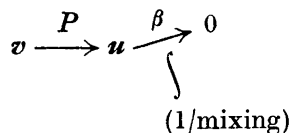
No measurements can be performed before the lapse of a sufficient period of time to allow:

1) disturbing processes arising from the shearing procedure to die out (see Section X, a),

2) the aberrations to decrease to 1/50 of a light wavelength (the critical time of diffusion of Svensson)<sup>14</sup>.

However, even working with such low concentration differences as those here, the critical time is surprisingly small, about a few seconds, and can be left out of consideration. What sets a limit to measurements at the beginning of the diffusion process are consequently the disturbances arising from the formation of the boundary. It is difficult to give a strict mathematical treatment of this.

An intuitive conception may be conveyed by the following picture:



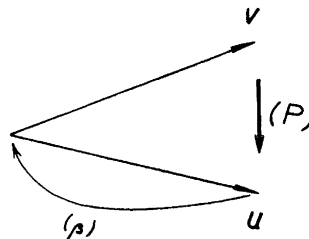


Fig. 3. Velocity field representation in Hilbert space  $l^2$  (projected in two dimensions).

where  $v$  represents the velocity field of the liquid during the formation process,  $u$  the velocity field after closing the outflow or removing the slide and  $\beta$  = damping factor of the liquid. The extent of mixing is inversely proportional to  $\beta$ .  $P$  indicates a transformation (operator) of the velocity field in function space and  $\beta$  is related to the decay of the vector field  $u$  \*. A "projection" of function space (Hilbert space) on the twodimensional subspace represented by the plane of the paper (Fig. 3) shows that the question — "How long will the decay of the turbulent field take?" — is answered as soon as the operator  $P$  and  $\beta$  can be formulated. A more detailed study of this question would be of great value in suggesting new ways for the further improvement of the cell construction.

\* Let us denote the velocity of flow at a single point by  $v$ .  $v$ , which is a vector function of the position vector, can be expanded in an infinite series of mutually orthogonal vector functions  $\bar{\varphi}_i$ , satisfying the same boundary conditions as  $v$ :

$$v = \sum_{i=1}^{\infty} a_i \bar{\varphi}_i$$

Now, the functions  $v$  and  $\bar{\varphi}_i$  can be regarded as elements of a so called Hilbert space. The infinite sequence

$$v = \{a_i\}_1^{\infty} (= \{a_1, a_2, a_3, \dots, a_i, \dots\}),$$

where the  $a_i$  are the same as above, is an element of another Hilbert space ( $l^2$  called). It can be shown that there is a one to one correspondence between the two Hilbert spaces mentioned. In this way the whole of the velocity field  $v$  can be represented by a single point in Hilbert space. With the use of these concepts the kinetical energy of the streaming liquid may be regarded as a so called functional of points in Hilbert space:

$$\Phi = \Phi(v)$$

If on closing the outflow the velocity field  $v$  goes over into another velocity field,  $u$ , with the same energy, then

$$\Phi(u) = \Phi(v),$$

and the transformation from  $v$  to  $u$  may be thought of as effected by an operator,  $P$ :

$$u = P v.$$

Thus, by an operator, a point of one Hilbert space is assigned to each point of another Hilbert space in a one to one fashion in exactly the same manner as an ordinary function  $y = f(x)$  assigns a point on the  $y$ -axis to each point of the  $x$ -axis.

## IX. ZERO-TIME CORRECTION

From the registrations it is evident that the smallest zero-time correction is obtained with the flowing-junction cell. Two principles for determining the zero-time correction are possible, namely

- 1) insertion of the real initial condition into Fick's law, and
- 2) extrapolation to zero time from the points obtained.

Our findings prove that the second method is the most reliable since all cell types show deviations from the ideal process during the first part of the run. Methods for obtaining the zero-time correction in these experiments are found in Ref.<sup>4</sup>

## X. THE INFLUENCE OF DEVIATIONS FROM IDEALITY ON THE MEASUREMENTS

When studying free diffusion by measuring the refractive index gradient in the diffusion cell as a function of time, one has to take the following factors into consideration in order to obtain accurate measurements:

- 1) occasional skewness arising from the boundary formation process,
- 2) the Wiener skewness (an optical effect),
- 3) deviations from the linear relation between refractive index and solute concentration,
- 4) the concentration dependance of the diffusion coefficient,
- 5) deviations from ideality due to polydispersity or impure preparations.

*a. Solution of Fick's equation with an asymmetrical initial condition.* A skew gradient caused by the mechanical boundary formation process (occasional skewness) leads to the problem of solving Fick's second equation with an asymmetrical initial condition, e.g. of the form  $c(\xi, 0) = c_0(1 - e^{-\xi/a})$  for  $\xi > 0$  and  $c(\xi, 0) = 0$  for  $\xi < 0$ , where  $\xi$  is the coordinate in the diffusion direction and  $a$  is a parameter proportional to the amount of asymmetry.

The influence of the skewness on the measurements can be estimated by the solution of the diffusion equation with an unsymmetrical initial condition. The solution has the following form<sup>15</sup>

$$c(x, t) = \int_{-\infty}^{+\infty} \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{(x-\xi)^2}{4Dt}} c(\xi, 0) d\xi \quad (2)$$

With  $c(\xi, 0) = c_0(1 - e^{-\xi/a}) U(\xi)$ , where  $U$  is the "unit step function"

$$U(\xi) = \begin{cases} 1 & \text{for } \xi > 0 \\ 1/2 & \text{for } \xi = 0 \\ 0 & \text{for } \xi < 0 \end{cases}$$

we get

$$c(x, t) = \int_0^{\infty} \frac{c_0}{2\sqrt{\pi Dt}} e^{-\frac{(x-\xi)^2}{4Dt}} (1 - e^{-\xi/a}) d\xi \quad (3)$$

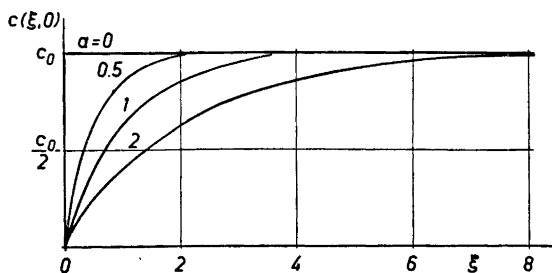


Fig. 4. Initially skew concentration distribution with the asymmetry parameter  $a = 0$  (ideal distribution), 0.5, 1, and 2, respectively.

The solution can be written in the form

$$c(x,t) = \frac{c_0}{2} \left\{ 1 + \operatorname{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \right\} - \frac{c_0}{2} \exp \left( \frac{Dt}{a^2} - \frac{x}{a} \right) \left\{ 1 - \operatorname{erf} \left( \frac{\sqrt{Dt}}{a} - \frac{x}{\sqrt{4Dt}} \right) \right\} \quad (4)$$

where the first term is the ordinary solution (for  $c(x,0) = U(x)$ ) and the second term is the correction due to the skewness.

An asymptotic expansion of the expression for the correction term in (4) shows that the correction will approach zero for large values of  $t$ .

A quantitative estimation of the influence of an occasional skewness on the diffusion coefficient determined by the present method can be obtained as follows.

Derivation of (4) gives

$$\frac{\partial c(x,t)}{\partial x} = \frac{c_0}{2a} \exp \left( \frac{Dt}{a^2} - \frac{x}{a} \right) \left\{ 1 - \operatorname{erf} \left( \frac{\sqrt{Dt}}{a} - \frac{x}{\sqrt{4Dt}} \right) \right\} \quad (5)$$

In Fig. 4 the initial concentration distributions are shown for some values of the asymmetry parameter  $a$ . Fig. 5 shows the derivative curve for the same values of  $a$ .

In the method of evaluation described in Ref. 4 an unsymmetrical gradient will cause a small error in the measured value of  $2x$  and accordingly in the diffusion coefficient\*. Now a theoretical explanation of the appearance of the experimental curves in Figs. 8 and 11 of Ref. 4 is possible. In the neighbourhood of the inflexion point (see Fig. 5) an asymmetrical gradient will give too small a value of  $2x$  while, on the other hand, measurements on the outermost fringe pairs correspond to the lower part of the Gaussian curve. Fig. 8 refers to measurements near the inflexion points and it is seen that the curves break down for small values of  $(2x)^2$ . In Fig. 11 too high a value for the

\* The distances  $2x$  between corresponding fringes in the interference pattern are measured. Following a definite fringe pair with time, we may plot  $(2x)^2$  vs.  $t$  and the diffusion coefficient is then obtained from a value of  $(2x)^2$  and its corresponding times  $t_1$  and  $t_2$  by the equation

$$D = \frac{(2x)^2(1/t_1 - 1/t_2)}{8 \ln t_2/t_1}$$

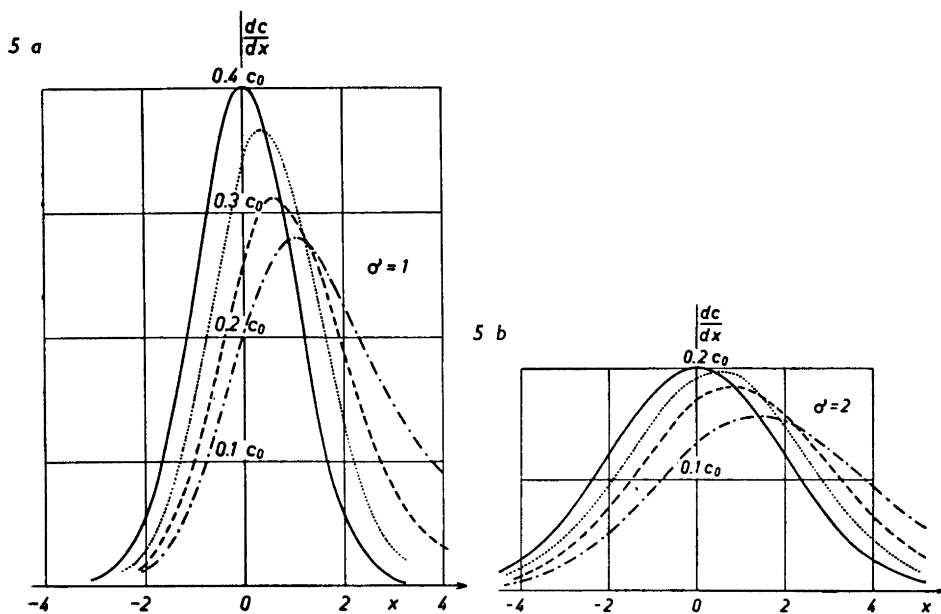


Fig. 5.  $dn/dx$  curves corresponding to the curves of Fig. 4 plotted for  $\sigma = 1$  and 2, respectively ( $\sigma = \sqrt{2Dt}$ ). -.-.-  $a = 2$ ; ---  $a = 1$ ; .....  $a = 0.5$ ; —  $a = 0$ .

diffusion coefficient is obtained; here however, the corrections are not so large owing to a more ideal boundary formation, (*i.e.* a smaller zero-time correction).

Generally, measurements are performed in the neighbourhood of the inflexion points of the Gaussian curve, where  $x = \sigma = \sqrt{2Dt}$ . Knowing the slope at the inflexion points it is possible to estimate the error in the determination of  $2x$ , and from this an estimation of the error in  $D$  can be made, *viz.*  $\Delta D/D = 2\Delta(2x)/2x$ .

From Fig. 6 it is possible to obtain a convenient expression for the displacement ( $\delta_+$ ) of the fringes from the ideal curve.

With the notation of Fig. 6 we conclude

$$f(x_a) = f_0(x_i) \approx f(x_i) + (x_a - x_i) f'_0(x_i)$$

$$\text{and hence } \delta_+ = x_a - x_i \approx \frac{f_0(x_i) - f(x_i)}{f'_0(x_i)} \quad (6)$$

for positive  $x$ -values and correspondingly for negative values of  $x$ .

$$\Delta(2x) = \delta_+ - \delta_- \text{ and hence } \frac{\Delta D}{D} = \frac{\delta_+ - \delta_-}{x}$$

From Fig. 7  $\Delta D/D$  can be read as a function of  $a$  and  $\sigma$ .

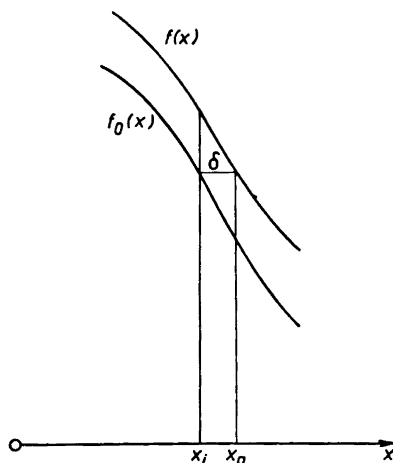


Fig. 6. Illustration of the method used for calculating  $\delta$  in the neighbourhood of an inflexion point of the ideal curve ( $f_0(x)$ ) and the actual curve ( $f(x)$ ).

From the character of the curves in Fig. 7 it is seen, following a horizontal line, how fast the corrections due to an asymmetrical initial condition die out. The great amount of asymmetry which can be tolerated is surprising.

It is obvious, however, when working with very dilute solutions and thus rapid diffusion experiments, that the initial skewness must be minimized if satisfactory results are to be obtained. In fact the demands on the symmetry are nearly inversely proportional to the time of experiment.

From Fig. 7 the impossibility of using the beginning of a diffusion run for extrapolation to zero-time is apparent. For a run with an occasional skewness (fixed  $a$  in Fig. 7), an estimation of the correction as a function of time can be obtained. Since this function is non-linear for small time values, the extrapolation to zero-time fails, as can be seen from the appearance of the curve (increasing correction on going to smaller time values). In practice this must be taken into account, especially when working with very dilute solutions.

*b. Elimination of the Wiener skewness.* Svensson<sup>13,16</sup> has shown that the aberration causing the Wiener skewness disappears if the camera is focused on a plane  $1/3$  of the cell thickness from the front wall.

*c. The influence of the concentration dependance of the diffusion coefficient.* In order to obtain a better interpretation of the data from optical interferometers, attempts have been made to solve the second equation of Fick in the case of a concentration dependant diffusion coefficient using a series expansion method<sup>17</sup>. For sucrose, *e.g.*, there is a variation of 2% in  $D$  between 1.5% solution and infinite dilution<sup>18</sup>.

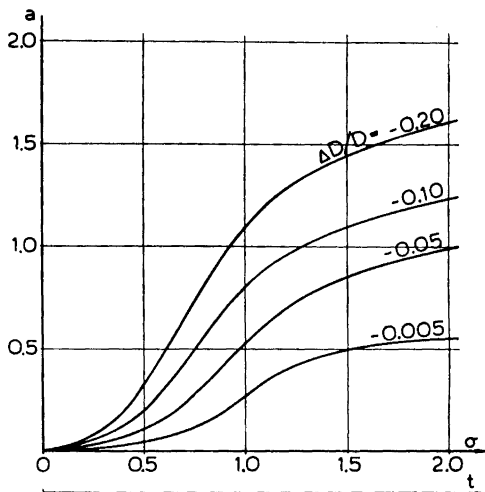


Fig. 7. Illustration of the influence of an asymmetrical initial condition on the diffusion coefficient measured.

In order to examine the influence of a concentration-dependant diffusion coefficient on the appearance of the interference pattern in *this method*, the solution of Fick's equation for the case of an exponential variation of the diffusion coefficient with concentration was studied.

If we put

$$D(c) = D_0 e^{ac} \quad (7)$$

for the diffusion coefficient, then the Fick equation takes on the following form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (D_0 e^{ac} \frac{\partial c}{\partial x}) \quad (8)$$

An approximate solution of this equation has been derived by Clarke<sup>19</sup>. Of interest here is the solution for small concentration differences

$$\left(\frac{\partial c}{\partial x}\right)_{\Delta c \text{ small}} \approx \frac{\Delta c}{2\sqrt{\pi D_0 t}} e^{-\frac{x^2}{4D_0 t}} \left\{ 1 - a\bar{c} \left( \frac{1}{2} - \frac{x^2}{4D_0 t} \right) + \frac{a^2 \bar{c}^2}{8} \left[ 7 - 8 \frac{x^2}{4D_0 t} + 4 \left( \frac{x^2}{4D_0 t} \right)^2 \right] \right\} \quad (9)$$

where  $\bar{c} = \frac{c_I + c_{II}}{2}$  (the arithmetic mean of the concentrations of the upper and the lower solution).

It should be noted that according to this expression, the position of the maximum point is the same as for the ideal case with a constant diffusion coefficient.

In the neighbourhood of the inflexion points ( $x = \sigma = \sqrt{2Dt}$ ) we have

$$\frac{\partial c}{\partial x} = \frac{\Delta c}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}} \left\{ 1 + \frac{\alpha^2 c^2}{2} \right\} \quad (10)$$

Using (6) we obtain the following expression for the error in (2x)

$$\Delta(2x) = 2\delta = \frac{\sigma\alpha^2 c^2}{2} \quad (11)$$

and consequently

$$\frac{\Delta D}{D} = 2 \frac{\Delta(2x)}{2x} = \frac{\alpha^2 c^2}{2} \quad (12)$$

In Ref.<sup>4</sup> diffusion runs with sucrose are described with concentration differences from 0.01 to 0.1 % sucrose. From eqn. (12) we conclude the corresponding values of ( $\Delta D/D$ ) to be from 0.0001 to 0.01 %, which can be left out of consideration.

A number of mathematical methods has been devised to compensate for effects 3 and 4 which cause rather large deviations if the experiments are performed with large concentration differences. Effects 3 and 4 give rise to a skew deviation of the refractive index gradient curve from the ideal Gaussian curve. These two sources of skewness may occasionally cancel<sup>17</sup> but there are also systems in which these effects act in the same direction and in such cases the resulting effect cannot be neglected.

The possibility of using quite small concentration differences in experiments with the birefringence interference method<sup>4</sup> reduces the magnitude of these errors substantially. The corrections necessary are much smaller and the mathematical difficulties correspondingly less.

## XI. REMARKS ON SOME TECHNICAL DETAILS

A very great advantage of the flowing-junction cell over the other cell types is that no moving mechanical parts are situated in the optical field. Thus, the optical field is clear and the tightening problems are simplified. The flowing-junction cell is very convenient for volatile organic solutions since it can easily be tightened with teflon packings<sup>9</sup> (there are indeed sparingly soluble lubricants but no ideal ones).

Another advantage of the flowing-junction cell is that one is in control of the formation of the boundary and can study the interface before starting the diffusion run. On the other hand, the flowing-junction cell is more sensitive to impurities in the liquids, but by inserting sintered glass filters in the input tubes to remove grease and other impurities, this disadvantage can probably be eliminated.

A disadvantage of the draw-slide cell is the trace of lubricant which is always left on the glass walls at the position where the slide is drawn out. The same criticism applies to the sliding-solvent cell.

The adsorption danger must be taken into account in diffusion experiments. In Ref.<sup>4</sup> the difficulty of performing diffusion runs with glycine in



cell *Ia* (a stainless steel cell) was pointed out. Lamm<sup>5</sup> describes an apparent downward drift of the diffusion coefficient of pentaerythrite during a run which he ascribes to the adsorption of pentaerythrite on the elastolite side walls of the cell used.

## XII. RECOMMENDATION FOR FUTURE INVESTIGATIONS

In addition to the present method there are numerous others, the most important of which are the scale- and schlieren methods of Lamm, the Gouy-interferometer, the Rayleigh-Calvet-Philpot interferometer, the Jamin interferometer and a modified schlieren method utilizing a Wolter phase plate<sup>20</sup> instead of a slit or an edge. All these methods are used side by side and so far no really satisfactory attempt has been made to compare the accuracy attainable by various methods. There is, however, indication that the present method should be superior to at least some of the earlier ones. There are two reasons for this. Firstly the method employs interferences with only a few wave-length differences. The advantage of this has been pointed out elsewhere<sup>2</sup>. Secondly it is characterised by what Wolter calls "Minimistrahlkennzeichnung"<sup>21</sup> which is advantageous from a measuring point of view. (Wolter ascribes the advantage of the "Minimistrahlkennzeichnung" to the so called wave uncertainty principle, the application of which is questionable).

It seems to the author that a satisfactory theory, which permits a quantitative calculation of the accuracy attainable by various methods would be highly desirable.

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