

(see above). As Kauzmann<sup>32,33</sup> has already pointed out in connection with the urea denaturation of BSA, the numerous disulfide bonds are probably at least in part responsible for this limit, and perhaps also for the reversibility of the expansion.

**Expansion in Alkaline Solution.**—Reference has been made a number of times in this paper to the fact that expansion of BSA occurs above  $pH$  10.5 as well as below  $pH$  4.3. This conclusion is based on the decrease in  $w$  occurring above  $pH$  10.5, and on the behavior of optical rotation<sup>9</sup> and fluorescence polarization<sup>6</sup> above that  $pH$ , which parallels that below  $pH$  4.3. We have made only a few exploratory viscosity measurements in this region, and have observed both an increase in viscosity and time dependence. It is probable that the expansion in alkaline solution will not show the plateau

observed in Fig. 1, for the higher charge at which the first stage occurs should result in a high enough electrostatic free energy even at the higher ionic strengths so that there is immediate expansion of the expandable form. It is possible that the entire process in alkaline solution will be more difficult to study, because of the readiness with which aggregation initiated by the ionized sulfhydryl group is likely to take place.

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## Studies of Free Diffusion in Liquids with the Rayleigh Method. I. The Determination of Differential Diffusion Coefficients in Concentration-dependent Systems of Two Components

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The work described gives expressions relating the deviations between ideal and observed fringe positions in Rayleigh diffusion interferograms to the various coefficients describing the concentration-dependence of both the diffusion coefficient and the refraction increment; rigorous methods are given for the calculation of differential diffusion coefficients in such systems. The expressions have been tested by using them to predict the deviations to be expected in the cases of sucrose, glycine and butanol, where adequate concentration-dependence data are already available. Reasonable success has been achieved in this prediction. Some of the likely sources of error in Rayleigh diffusion work are examined, and two examples are given of a comparison between Gouy and Rayleigh results obtained in the same experiment.

In diffusion experiments conducted between solutions of two different concentrations  $C_1$  and  $C_2$ , of the same solute, it has frequently been found<sup>3,4</sup> that for systems where the concentration-dependence of the diffusion coefficient is relatively small, the *mean concentration*  $\bar{C} = (C_1 + C_2)/2$  of the experiment is the concentration corresponding to the measured diffusion coefficient, the latter being independent of the actual magnitude of the concentration increment  $\Delta C = C_2 - C_1$ . Such experiments are therefore taken to yield the differential diffusion coefficient,  $D_{\bar{C}}$ , corresponding to the mean concentration. Recently, however, results obtained on the markedly non-ideal butanol-water system by Lyons and Sandquist<sup>5</sup> indicated a dependence, albeit small, of the diffusion coefficient upon  $\Delta C$  at constant  $\bar{C}$ , so that unambiguous values of  $D_{\bar{C}}$  may not be obtained directly in this way.

Furthermore much interest has arisen recently<sup>6,7</sup> in the question whether the Gouy and Rayleigh optical interference methods now in widespread use do in fact yield identical results when applied to

similar systems; in attempting to answer this question, it is clearly important that experimental data be analyzed to give results in terms of well-defined quantities and that any approximation introduced be closely scrutinized and estimated. The work of Fujita and Gosting<sup>8</sup> has shown how diffusion coefficients measured by the "height-area" method may be corrected for concentration-dependence of diffusion coefficient and of specific refraction increment to yield the true differential diffusion coefficient; the purpose of this paper is to show how parts of Fujita and Gosting's<sup>8</sup> theoretical development may be used to provide a basis whereby the results of Rayleigh diffusion experiments upon non-ideal systems may be similarly corrected. The work has shown, in addition, how the results may be treated to give an estimate of the concentration-dependence of the diffusion coefficient.

### Theory

(a) **Ideal Systems.**—For the purposes of this analysis, ideal systems are defined as those in which both the diffusion coefficient and the refraction increment are independent of the concentration. For experimental systems where concentration is measured as a function of height in the diffusion cell, the relevant solution of Fick's<sup>9</sup> law is, in the ideal case, an expression of the form

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- (3) E.g., L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1998 (1949).
- (4) M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).
- (5) P. A. Lyons and C. L. Sandquist, *ibid.*, **75**, 3896 (1953).
- (6) L. G. Longworth, private communications to L. J. Gosting.
- (7) F. J. Gutter and G. Kegeles, *THIS JOURNAL*, **75**, 3893 (1953).

- (8) H. Fujita and L. J. Gosting, *ibid.*, in press.
- (9) A. Fick, *Pogg. Ann.*, **94**, 59 (1855).

$$\frac{2(C - \bar{C})}{\Delta C} = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\beta^2} d\beta \quad (1)$$

where  $C$  is the concentration at the point distance  $x$  (positive downwards) from the initial infinitely sharp boundary separating the two solutions,  $t$  the time and  $D$  the diffusion constant. As the concentration function on the left of equation 1 will be extensively employed in what follows, for the sake of brevity it will be written  $g(C)$ ; thus the equation

$$\frac{2(C - \bar{C})}{\Delta C} = g(C) \quad (2)$$

serves to define this function. Secondly, the reduced variable  $z = x/2\sqrt{Dt}$  is introduced, so that the right-hand side of equation 1 is simply written  $H(z)$ , the symbol  $H$  denoting the probability integral.

The Rayleigh optical system<sup>10-12</sup> used for diffusion experiments yields a record of refractive index (in terms of interference fringes) as a function of cell displacement; denoting the number of a fringe as  $j$  (counting from the less concentrated solution) and the total number of fringes as  $J$ , a "reduced fringe number" function  $f(j)$  may be defined by the equation

$$\frac{2j - J}{J} = f(j) \quad (3)$$

The assumption of ideality implies that the refractive index of the solution is a linear function of the solute concentration, when the two functions  $g(C)$  and  $f(j)$  are equal, and accordingly

$$f(j) \rightarrow H(z)$$

Tables of probability functions<sup>13</sup> are then used to obtain  $z$  from the  $H(z)$  values, and knowing  $x$  and  $t$  from the experiment,  $D$  may be calculated from the equation defining  $z$ . This procedure has been used by Svensson,<sup>14</sup> and particularly by Longworth<sup>15,16</sup> for the determination of diffusion coefficients. In order to avoid locating the original starting position ( $z = 0$ ), separations between pairs of fringes are usually determined: Longworth's<sup>15</sup> procedure involved keeping  $\Delta j$  approximately constant, so that fringe 2 out of a system with  $J = 100$  would be compared with fringe 52, 4 with 54, etc.

The direct use of the fringe number function to obtain  $z$  values is clearly invalid if the refractive index is a non-linear function of the concentration; the function retains its usefulness, however, for in spite of any such effect, it may always be employed to define an ideal, normalized displacement  $z^*$  for the fringe numbered  $j$  by the relation

$$f(j) = H(z^*) \quad (4)$$

and the following treatment of concentration-dependence will employ  $z^*$  as one of the two fundamental parameters.

(b) **Concentration-dependent Systems.**—We shall consider the effect on the experimental record

(10) J. St. L. Philpot and G. H. Cook, *Research*, **1**, 234 (1948).

(11) H. Svensson, *Acta Chem. Scand.*, **3**, 1170 (1949).

(12) L. G. Longworth, *Rev. Sci. Instr.*, **21**, 524 (1950).

(13) "Tables of Probability Functions," Federal Works Agency, Works Project Administration, Supt. of Documents, Washington, D. C., 1941.

(14) H. Svensson, *Acta Chem. Scand.*, **5**, 72 (1951).

(15) L. G. Longworth, *This Journal*, **74**, 4155 (1952).

(16) L. G. Longworth, *ibid.*, **75**, 5705 (1953).

of boundary shape of concentration-dependence of diffusion coefficient and of specific refraction increment; following Fujita and Gosting<sup>8</sup> we write for the former

$$D = D\bar{C} [1 + k_1(C - \bar{C}) + k_2(C - \bar{C})^2 + \dots] \quad (5)$$

where  $D$  is the diffusion coefficient at concentration  $C$ ,  $D\bar{C}$  that at  $\bar{C}$  and  $k_1$  and  $k_2$  are coefficients related to, and determinable from, the experimental data for  $D$  vs.  $C$ . For the refractive index  $n$  of a solution of concentration  $C$  we write

$$n = n\bar{C} + R\bar{C}(C - \bar{C})[1 + a_1(C - \bar{C}) + a_2(C - \bar{C})^2 + \dots] \quad (6)$$

where  $R\bar{C}$ ,  $a_1$  and  $a_2$  are similar coefficients, defined by Fujita and Gosting.<sup>8</sup>

Using series methods mentioned in the general treatment by Fujita<sup>17</sup> of free diffusion when  $D$  varies with  $C$ , Fujita and Gosting<sup>8</sup> derived general equations<sup>18</sup> relating both the concentration and concentration gradient to the cell displacement for cases where  $D$  was a function of  $C$ , as given by 5; for the integral, concentration case, the result was

$$g(C) = \phi_0 + k_1 \left( \frac{\Delta C}{2} \right) \phi_1 + \left( k_1 \frac{\Delta C}{2} \right)^2 \phi_2 + k_2 \left( \frac{\Delta C}{2} \right)^2 \phi_3 + \dots \quad (7)$$

where  $\phi_0$  represents the (normalized) ideal concentration distribution (thus  $\phi_0 = H(z)$ ), and  $\phi_1$ ,  $\phi_2$  and  $\phi_3$ , which have been given by Fujita and Gosting,<sup>8</sup> are rather complex functions of  $z$ , which is itself defined in this connection by the relation<sup>19</sup>

$$z = x/2\sqrt{D\bar{C}t} \quad (8)$$

The use of equation 7 in the form stated to interpret Rayleigh diffusion records demands prior knowledge of  $D\bar{C}$ , and, of course, a relation between  $g(C)$  and  $f(j)$ ; moreover, individual fringe displacements from the original  $x = 0$  position would be required. Because of experimental limitations, the solution desired is one explicit in  $z$ , so that displacements may be paired directly (in this way it is possible to utilize the high accuracy with which fringe separations may be measured). For these reasons, therefore, the direct solution of 7 in terms of  $z$  was not attempted; instead an expression was derived in the quite general form of the Taylor expansion in  $z$ , at constant  $f(j)$

$$z = z^* + \left[ k_1 \left( \frac{\partial z}{\partial k_1} \right) + a_1 \left( \frac{\partial z}{\partial a_1} \right) \right] + \left[ \frac{k_1^2}{2} \left( \frac{\partial^2 z}{\partial k_1^2} \right) + \frac{a_1^2}{2} \left( \frac{\partial^2 z}{\partial a_1^2} \right) + k_1 a_1 \left( \frac{\partial^2 z}{\partial k_1 \partial a_1} \right) + k_2 \left( \frac{\partial z}{\partial k_2} \right) + a_2 \left( \frac{\partial z}{\partial a_2} \right) \right] + \dots \quad (9)$$

The reason for the particular grouping of terms in

(17) H. Fujita, *J. Colloid Sci.*, **9**, 269 (1954).

(18) Recently, J. Gillis and O. Kedem (*J. Polymer Sci.*, **11**, 545 (1953)) have examined the case of linear dependence of  $D$  upon concentration, and have given an equation in which the first-order term is essentially equivalent to the corresponding term in (7). As their treatment was based on an expansion about the diffusion coefficient at zero concentration,  $D_0$ , and it is clearly desirable in this case to have solutions about  $D\bar{C}$ , the relations derived by Fujita and Gosting<sup>8</sup> have been preferred in the subsequent derivations in this paper.

(19) Although this restricted definition of  $z$  should strictly be acknowledged by the addition of some distinguishing mark to the symbol, this will be omitted for the sake of clarity, it being understood, in all that follows, that  $z$  is always defined by equation 8.

this equation<sup>20</sup> will be apparent shortly; the restriction of constant  $(f)j$  in this expansion implies that fringe displacements are being expressed in terms of  $z^*$ , the displacement that the same fringe would have in an ideal diffusion system ( $k_1, k_2, a_1, a_2 \dots$  all zero) characterized by possession of the same total number of fringes  $J$  and governed by a diffusion constant  $D = D_c$ .

The required derivatives are obtained by making use of the generality

$$\left(\frac{\partial z}{\partial y}\right)_{f(j)} = - \left(\frac{\partial z}{\partial f(j)}\right)_y \left(\frac{\partial f(j)}{\partial y}\right)_z, \quad (10)$$

where  $y$  is one of the four variables  $k_1, k_2, a_1, a_2$ . This requires an explicit relation between  $f(j)$ ,  $z$  and the variables "y"; such an expression may be derived from equations 6 and 7 and the definition of  $f(j)$ , equation 4, in the following way.

Since the fringe number is a direct measure of refractive index difference, we may write

$$f(j) = \frac{2j - J}{J} = \frac{2(n - \bar{n})}{\Delta n} \quad (11)$$

where  $\bar{n} = (n_1 + n_2)/2$  and  $\Delta n = n_2 - n_1$ ,  $n_1$  and  $n_2$  being the refractive indices of solutions of concentration  $C_1$  and  $C_2$ .

Equation 6 may be rewritten in terms of  $g(C)$ , utilizing equation 2

$$n = n_c + R_c \left(\frac{\Delta C}{2}\right) \left[ g(C) + a_1 \left(\frac{\Delta C}{2}\right) [g(C)]^2 + a_2 \left(\frac{\Delta C}{2}\right)^2 [g(C)]^3 + \dots \right] \quad (12)$$

also we have

$$n_1 = n_c - R_c \left(\frac{\Delta C}{2}\right) \left[ 1 - a_1 \left(\frac{\Delta C}{2}\right) + a_2 \left(\frac{\Delta C}{2}\right)^2 + \dots \right] \quad (13a)$$

and

$$n_2 = n_c + R_c \left(\frac{\Delta C}{2}\right) \left[ 1 + a_1 \left(\frac{\Delta C}{2}\right) + a_2 \left(\frac{\Delta C}{2}\right)^2 + \dots \right] \quad (13b)$$

so that

$$\bar{n} = n_c + a_1 R_c \left(\frac{\Delta C}{2}\right)^2 + \dots \quad (14a)$$

and

$$\Delta n = 2R_c \left(\frac{\Delta C}{2}\right) \left[ 1 + a_2 \left(\frac{\Delta C}{2}\right)^2 + \dots \right] \quad (14b)$$

Combining equations 11, 12 and 14, and simplifying

$$f(j) = g(C) + a_1 \left(\frac{\Delta C}{2}\right) \{ [g(C)]^2 - 1 \} + a_2 \left(\frac{\Delta C}{2}\right)^2 \{ [g(C)]^3 - [g(C)] \} + \dots \quad (15)$$

The expression required is then obtained on substitution for  $g(C)$  from equation 7

(20) Although not indicated in equation 9 it is, of course, implied that each partial derivative is to be taken (i) at constant  $f(j)$  and (ii) holding all variables constant other than the particular one under consideration; furthermore, the limiting value, as all the variables  $k_1, a_1$ , etc., tends to zero, is required. Thus the complete specification of the first term in  $k_1$  would be

$$\left[ \left(\frac{\partial z}{\partial k_1}\right)_{f(j), k_2, a_1, a_2 \dots} \right]_{k_1, k_2, a_1, a_2 \dots \rightarrow 0}$$

$$f(j) = \phi_0 + \left(\frac{\Delta C}{2}\right) [k_1 \phi_1 + a_1(\phi_0^2 - 1)] + \left(\frac{\Delta C}{2}\right)^2 [k_1^2 \phi_2 + 2a_1 k_1 \phi_0 \phi_1 + k_2 \phi_3 + a_2(\phi_0^3 - \phi_0)] + \dots \quad (16)$$

The reason for the particular grouping of terms in equation 9 is now apparent; it should be observed that as equation 16 is complete up to and including terms of order  $(\Delta C/2)^2$ , only the derivatives indicated in equation 9 need be considered if the expression for  $z$  is to be accurate to the same limit (terms of order  $(\Delta C/2)^3$  and higher are negligible under the experimental conditions generally adopted, where  $J$  is not much greater than 100).

Equation 16 may be differentiated simply to yield each of the derivatives indicated in equation 10. In the following treatment use will be made of the equalities

$$\phi_0 = H(z) \quad (17a)$$

$$\frac{dH(z)}{dz} = H'(z) \left( = \frac{2}{\sqrt{\pi}} e^{-z^2} \right) \quad (17b)$$

$$\frac{dH'(z)}{dz} = H''(z) = -2zH'(z) \quad (17c)$$

$$\frac{d \left[ \frac{1}{H'(z)} \right]}{dz} = \frac{2z}{H'(z)} \quad (17d)$$

It will be convenient to defer precise definition of the functions  $\phi_1, \phi_2$  and  $\phi_3$  until the derivatives have been obtained.

Owing to the restrictions discussed above,<sup>20</sup> a single expression for the derivative of (16) with respect to  $z$  is applicable in all four cases; the expression is

$$\left(\frac{\partial f(j)}{\partial z}\right)_{k_1, k_2, a_1, a_2} = H'(z) + \left(\frac{\Delta C}{2}\right) \left[ k_1 \left(\frac{\partial \phi_1}{\partial z}\right) + 2a_1 H(z) H'(z) \right] + 0 \left[ \left(\frac{\Delta C}{2}\right)^2 + \dots \right] \quad (18)$$

which for subsequent purposes is more conveniently written

$$\left(\frac{\partial f(j)}{\partial z}\right)_{k_1, k_2, a_1, a_2} = H'(z) \left\{ 1 + \left(\frac{\Delta C}{2}\right) \left[ \frac{k_1}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) + 2a_1 H(z) \right] \right\} + \dots \quad (19)$$

For the variable  $k_1$ , equation 16 gives the expression

$$\left(\frac{\partial f(j)}{\partial k_1}\right)_{z, k_2, a_1, a_2} = \left(\frac{\Delta C}{2}\right) \phi_1 + \left(\frac{\Delta C}{2}\right)^2 [2k_1 \phi_2 + 2a_1 H(z) \phi_1] + \dots \quad (20)$$

Combining equations 17 and 19

$$\left(\frac{\partial z}{\partial k_1}\right)_{f(j), k_2, a_1, a_2} = - \left\{ \left(\frac{\Delta C}{2}\right) \frac{\phi_1}{H'(z)} + \left(\frac{\Delta C}{2}\right)^2 \left[ \frac{2k_1 \phi_2}{H'(z)} + \frac{2a_1 H(z) \phi_1}{H'(z)} \right] \right\} \times \left\{ 1 - \left(\frac{\Delta C}{2}\right) \left[ \frac{k_1}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) + 2a_1 H(z) \right] \right\} + \dots \quad (21)$$

$$= - \left(\frac{\Delta C}{2}\right) \frac{\phi_1}{H'(z)} + \left(\frac{\Delta C}{2}\right)^2 \left[ \frac{k_1 \phi_1}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) - \frac{2k_1 \phi_2}{H'(z)} \right] + \dots \quad (22)$$

The expression for the second derivative may be obtained from equation 22, acknowledging that all functions of  $z$  are implicit functions of  $k_1$

$$\left(\frac{\partial^2 z}{\partial k_1^2}\right)_{f(j), k_2, a_1, a_2} = -\left(\frac{\Delta C}{2}\right) \left[ \frac{1}{H'(z)} \frac{\partial \phi_1}{\partial k_1} + \phi_1 \frac{\partial}{\partial k_1} \left[ \frac{1}{H'(z)} \right] \right] + \left(\frac{\Delta C}{2}\right)^2 \left[ \frac{\phi_1}{[H'(z)]^2} \left(\frac{\partial \phi_1}{\partial z}\right) - \frac{2\phi_2}{H'(z)} \right] + \dots \quad (23)$$

The expression in the first bracket may be simplified by making use of (17d) and the relation

$$\left(\frac{\partial}{\partial k_1}\right)_{f(j)} = \left(\frac{\partial}{\partial z}\right)_{f(j)} \left(\frac{\partial z}{\partial k_1}\right)_{f(j)} \quad (24)$$

when we obtain, on simplification

$$\left(\frac{\partial^2 z}{\partial k_1^2}\right)_{f(j), k_2, a_1, a_2} = \left(\frac{\Delta C}{2}\right)^2 \left[ \frac{2z\phi_1^2}{[H'(z)]^2} + \frac{2\phi_1^2}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) - \frac{2\phi_2}{H'(z)} \right] + \dots \quad (25)$$

Denoting the function  $\phi_1/H'(z)$  as  $R(z)$ , we obtain the limiting values of the derivatives from equations 22 and 25.

$$\left(\frac{\partial z}{\partial k_1}\right)_{f(j), k_2, a_1, a_2} = -\left(\frac{\Delta C}{2}\right) R(z) + \dots \quad (26)$$

and

$$\left(\frac{\partial^2 z}{\partial k_1^2}\right)_{f(j), k_2, a_1, a_2} = \left(\frac{\Delta C}{2}\right)^2 \left[ 2z[R(z)]^2 + \frac{2R(z)}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) - \frac{2\phi_2}{H'(z)} \right] + \dots \quad (27)$$

For simplicity, the function of  $z$  in the outermost square brackets on the right of equation 27 will be denoted  $S(z)$ .

For  $a_1$ , similar reasoning gives

$$\left(\frac{\partial f(j)}{\partial a_1}\right)_{z, k_1, k_2, a_2} = \left(\frac{\Delta C}{2}\right) [ [H(z)]^2 - 1 ] + \left(\frac{\Delta C}{2}\right)^2 [ 2k_1 H(z) \phi_1 ] + \dots \quad (28)$$

which on combining with equation 19 and simplifying gives

$$\left(\frac{\partial z}{\partial a_1}\right)_{f(j), k_1, k_2, a_2} = \left(\frac{\Delta C}{2}\right) \left[ \frac{1 - [H(z)]^2}{H'(z)} \right] - \left(\frac{\Delta C}{2}\right)^2 \left\{ 2a_1 H(z) \left[ \frac{1 - [H(z)]^2}{H'(z)} \right] + 2k_1 H(z) R(z) + \frac{k_1}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) \left[ \frac{1 - [H(z)]^2}{H'(z)} \right] \right\} + \dots \quad (29)$$

The second-order derivative is obtained in the same manner used for the case of  $\partial^2 z / \partial k_1^2$ , making use of an expression in  $a_1$  of the form of equation 24. Defining

$$U(z) = \frac{1 - [H(z)]^2}{H'(z)} \quad (30)$$

the results for the limiting values are

$$\left(\frac{\partial z}{\partial a_1}\right)_{f(j), k_1, k_2, a_2} = \left(\frac{\Delta C}{2}\right) U(z) - \left(\frac{\Delta C}{2}\right)^2 k_1 \left[ \frac{U(z)}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) + 2H(z) R(z) \right] + \dots \quad (31)$$

and

$$\left(\frac{\partial^2 z}{\partial a_1^2}\right)_{f(j), k_1, k_2, a_2} = \left(\frac{\Delta C}{2}\right)^2 U(z) [ 2zU(z) - 4H(z) ] + \dots = \left(\frac{\Delta C}{2}\right)^2 W(z) + \dots \quad (32)$$

An expression for the cross derivative  $\partial^2 z / \partial a_1 \partial k_1$

may be obtained from either of equations 22 or 31 (giving the same result)

$$\left(\frac{\partial^2 z}{\partial a_1 \partial k_1}\right)_{f(j), k_1, a_2} = -\left(\frac{\Delta C}{2}\right)^2 U(z) \left[ \frac{1}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) + 2zR(z) \right] + \dots \quad (33)$$

The two remaining first-order derivatives are obtained very simply in a similar fashion

$$\left(\frac{\partial z}{\partial k_2}\right)_{f(j), k_1, a_1, a_2} = -\left(\frac{\Delta C}{2}\right)^2 \frac{\phi_3}{H'(z)} + \dots = -\left(\frac{\Delta C}{2}\right)^2 T(z) + \dots \quad (34)$$

and

$$\left(\frac{\partial z}{\partial a_2}\right)_{f(j), k_1, k_2, a_1} = \left(\frac{\Delta C}{2}\right)^2 H(z) U(z) + \dots \quad (35)$$

The limiting values of the derivatives given in equations 26, 27, 32, 34, and 35 in no case contain any terms involving any of the parameters  $a_1, k_1$ , etc., and are therefore identical with those required<sup>20</sup> in equation (9); for the derivative  $(\partial z / \partial a_1)$  only the first term in equation (31) is required, the sole cross-term coefficient being that given in (33). For simplicity, therefore, the function  $V(z)$  is defined:

$$V(z) = \frac{U(z)}{H'(z)} \left(\frac{\partial \phi_1}{\partial z}\right) + 2zR(z) \quad (36)$$

so that the results of this treatment may conveniently be expressed in terms of the summation:

$$z = z^* + \left(\frac{\Delta C}{2}\right) [ a_1 U(z^*) - k_1 R(z^*) ] + \left(\frac{\Delta C}{2}\right)^2 \left[ \frac{a_1^2}{2} W(z^*) - a_1 k_1 V(z^*) + a_2 U(z^*) H(z^*) + \frac{k_1^2}{2} S(z^*) - k_2 T(z^*) \right] + \dots \quad (37)$$

(This expression may be checked by writing the error function  $z^*$  as Taylor expansion in  $z$ , when equation 16 is obtained.)

It should be noted first that as all derivatives were obtained as the relevant coefficient vanished, all terms are in  $z^*$  and not the reduced displacement  $z$ . Secondly, both the functions  $U(z)$  and  $R(z)$  (see below) are symmetrical about  $z = 0$ —*i.e.*, for example  $U(z) = U(-z)$ . This is a most important conclusion, for it enables the first-order effects of concentration-dependence to be eliminated by comparing fringe displacements symmetrically about  $f(j) = 0$ —*i.e.*, in a 100 fringe system, fringe 2 would be compared with 98, 4 with 96, etc. As the second-order effect is negligible when either  $(\Delta C/2)$  or the constants are small (as is very frequently the case for simple substances) this procedure will give  $\Delta z$  values which are identical with the corresponding  $\Delta z^*$  values; the differential diffusion coefficient at the mean concentration may then be calculated directly, using equations 4 and 8; such a determination does not involve the use of any data concerning concentration-dependence of either the refraction increment or the diffusion coefficient. In certain special cases, or where the concentration increment is large, errors in  $D\bar{c}$  will still result from the application of the symmetrical "comparison" procedure, and the relevant concentration-depend-

ence coefficients must be employed if a rigorous analysis is desired.<sup>21</sup>

**The Determination of Concentration-dependence of  $D$ .**—For systems where  $a_1$  is negligible, and the concentration increment fairly small, the constant  $k_1$  may readily be determined from the relation between the observed and ideal fringe displacements. For example, equation 37 applied to such a case gives for the displacement of two fringes  $j_1$  and  $j_2$

$$(z_2 - z_1) - (z_2^* - z_1^*) = -k_1 \left( \frac{\Delta C}{2} \right) [R(z_2^*) - R(z_1^*)] + \dots \quad (38)$$

where  $z_1^*$  is obtained from  $H(z_1^*) = (2j_1 - J)/J$ , etc. The requisite data for this determination therefore are: knowledge of the fringe number  $j$  and the total number of fringes  $J$ , the concentration increment  $\Delta C$  (if  $k_1$  is to be expressed in concentration units), the function  $R(z)$ , and finally the experimentally observed reduced fringe separation  $\Delta z$ . The latter may be determined from the known time (subject to suitable zero time correction) and the differential diffusion coefficient calculated from the symmetrical separations. However, knowledge of the diffusion coefficient and time is not a pre-requisite, for it may be observed that

$$\frac{1}{n} \sum_1^n \left( \frac{x_{j-1} - x_j}{z_{j-1}^* - z_j^*} \right) = 2\sqrt{D\bar{c}t} \quad (39a)$$

is a constant for a particular time; here the summation covers  $n$  such quantities as  $(x_{98} - x_2)/(z_{98}^* - z_2^*)$ ,  $(x_{98} - x_4)/(z_{98}^* - z_4^*)$ , etc., in a 100-fringe system.

Equation 39a, involving the cell displacements  $x_1$  and  $x_2$ , is more useful if expressed in terms of the (arbitrary) comparator readings  $X_1$  and  $X_2$  for the fringes  $j_1$  and  $j_2$ , thus

$$\frac{1}{n} \sum_1^n \left( \frac{X_{j-1} - X_j}{z_{j-1}^* - z_j^*} \right) = 2M\sqrt{D\bar{c}t} = \bar{Y}_t \quad (39b)$$

Here  $M$ , the camera plate-to-cell magnification, is defined as  $\Delta X/\Delta x$ .  $\bar{Y}_t$  is, of course, the fundamental characteristic of the fringe pattern for the particular time.

Thus, employing equations 8 and 39b, a substitution may be made for  $z$  in equation 38, giving the relation

$$\frac{X_2 - X_1}{\bar{Y}_t} - (z_2^* - z_1^*) = -k_1 \left( \frac{\Delta C}{2} \right) [R(z_2^*) - R(z_1^*)] + \dots \quad (40)$$

and  $k_1$  may accordingly be determined from the slope of a plot of the difference function on the left-hand side *vs.* the difference in  $R(z^*)$  values (henceforward denoted  $\Delta R(z^*)$ ) on the right. Within limitations discussed below, departure from linearity of this plot indicates either that one of the other

(21) The parallel with the case of diffusion coefficient determination from refractive index *gradient* measurement is instructive. Thus Fujita and Gosting<sup>8</sup> find that the "height-area" value  $D_A$  differs from  $D\bar{c}$  only by a second-order quantity, so that  $D_A$  values will in general approximate to  $D\bar{c}$ 's, but further data are required before the correction factor can be applied. The Rayleigh fringe method may have an advantage over the Gouy in this connection, as concentration-dependence of  $D$  produces a more easily observed effect, so that an indication is obtained at once as to whether second-order effects should be considered.

coefficients  $a_1$ ,  $k_2$ , etc., is significant, and hence that other data must be considered, or that the term in  $k_1^2$  is significant. The curve in the central region, about  $\Delta R(z^*) = 0$ , will generally be sufficiently close to linear to give a preliminary value of  $k_1$ , when computations of  $(k_1^2/2)S(z)$  will immediately reveal the significance or otherwise of this term.

Where it is known that  $a_1$  is significant and  $a_2$  negligible, an alternative to the direct computation of  $a_1U(z)$  is to compute  $g(C)$  values from the  $f(j)$ 's and  $a_1$  when the three terms in  $a_1$  in equation 37 drop out, leaving a more easily manipulated relationship involving only  $k_1$  and  $k_1^2$ . This approach is further discussed in the results section.

Values of the requisite functions are given in the subsequent tables. As it is anticipated that the function  $R(z)$  (to be used in determinations of  $k_1$  when other factors are negligible) will be of most interest, values are given to five significant figures for intervals of 0.02 in  $z$  over the range 0–1.5; linear interpolation then leads to errors not exceeding one in the fourth place. Over the range 1.5 to 3.0 where the function is given only at intervals of 0.1 in  $z$ , linear interpolation will not produce errors of more than one in the third place (where given). It may be noted that  $R(z) \rightarrow -\infty$  as  $z \rightarrow \pm\infty$ .

The other functions are given only to four significant figures, at intervals of 0.1 in  $z$ . Smooth curves drawn through the points given will in general allow a function to be estimated to three-place accuracy, which will be sufficient for many cases.

### Experimental

In all this series of experiments, the Gouy diffusiometer equipment described by Gosting, *et al.*,<sup>22,23</sup> was employed as the basic apparatus. The conversion to the integral, Rayleigh, form of apparatus was effected by (a) rotation of the light source about the optic axis to give a vertical slit, (b) substitution of a vertical pair of masking slits (each of which was 1" long  $\times$  1/16" wide, separation between centers 1/4") for the Gouy masking devices, and (c) the insertion of a cylindrical lens with axis horizontal between the cell and the camera.

The vertical masking slits were fixed permanently to the cell frame, on the side nearer the source slit, while additional masking slits could be moved over them, by a rack and pinion device, to enable Gouy fringes and relevant reference fringes to be photographed for the same experiment. In order to produce a reference pattern, two pairs of short vertical slits were employed, displaced to one side of, and extending above and below, the main pair. This arrangement (illustrated in Fig. 1a) thus placed one of the main vertical slits opposite the cell, the other opposite its extension window,<sup>16</sup> while light traversing the upper and lower pair of reference slits came only through the water of the thermostat bath; by this means the extension fringes at the edges of the cell fringe pattern (a typical example is shown in Fig. 1b) were produced.

The cylindrical lens unit consisted of two similar plano-convex lenses,<sup>24</sup> each of focal length 130 cm., mounted on a single stand; each lens could be adjusted independently both for vertical motion and for rotation about the optic axis. The lenses had a minimum separation between the inner (curved) surfaces of approx. 1 mm. The stand was clamped to the lathe bed which also held the camera.

The focusing of the cylindrical lens unit is rather critical; the procedure finally adopted was as follows. The plane surface of the lens adjacent to the camera was adjusted to be parallel to the bath window, using a telescope with reflecting

(22) L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

(23) L. J. Gosting and P. J. Dunlop, *THIS JOURNAL*, **75**, 5073 (1953).

(24) Obtained from Frank Pearson Associates, New York.

TABLE I  
FUNCTIONS OF  $z$  FOR CONCENTRATION-DEPENDENCE EQUATIONS

$z$	$R(z)^a$	$z$	$R(z)$	$z$	$R(z)$	$z$	$R(z)$	$z$	$R(z)$	$z$	$R(z)$
0.00	+0.16102										
± .02	.16086	±0.32	+0.12056	±0.62	+0.01703	±0.92	-0.13148	±1.22	-0.30453	±1.60	-0.5350
.04	.16037	.34	.11546	.64	.00828	.94	.14250	1.24	.31654	1.70	.5955
.06	.15957	.36	.11009	.66	-.00063	.96	.15353	1.26	.32856	1.80	.6557
.08	.15845	.38	.10443	.68	.00974	.98	.16472	1.28	.34056	1.90	.7151
.10	.15699	.40	.09851	.70	.01903	1.00	.17600	1.30	.35267	2.00	.7746
.12	.15522	.42	.09231	.72	.02851	1.02	.18736	1.32	.36478	2.10	.8334
.14	.15315	.44	.08587	.74	.03815	1.04	.19879	1.34	.37686	2.20	.8922
.16	.15075	.46	.07916	.76	.04797	1.06	.21028	1.36	.38899	2.30	.9491
.18	.14806	.48	.07219	.78	.05792	1.08	.22188	1.38	.40113	2.40	1.004
.20	.14503	.50	.06500	.80	.06803	1.10	.23354	1.40	.41330	2.50	1.06
.22	.14168	.52	.05757	.82	.07828	1.12	.24525	1.42	.42547	2.60	1.11
.24	.13806	.54	.04990	.84	.08867	1.14	.25700	1.44	.43763	2.70	1.18
.26	.13413	.56	.04201	.86	.09919	1.16	.26884	1.46	.44975	2.80	1.23
.28	.12990	.58	.03390	.88	.10984	1.18	.28071	1.48	.46192	2.90	1.30
.30	.12537	.60	.02557	.90	.12059	1.20	.29258	1.50	.47420	3.00	1.36

TABLE II

$z$	$U(z)^b$	$S(z)^c$	$T(z)^d$	$V(z)^b$	$W(z)^e$	$z$	$U(z)$
0.00	+0.8862	0.0000	0.0000	0.0000	0.0000	1.60	+0.5358
+ .10	.8838	+0.0042	+0.0097	-0.0673	-0.2413	1.70	.5128
.20	.8767	.0075	.0173	.1320	.4735	1.80	.4910
.30	.8650	.0092	.0208	.1918	.6881	1.90	.4708
.40	.8491	.0086	.0187	.2453	.8782	2.00	.4519
.50	.8297	.0051	.0099	.2925	1.039	2.10	.4338
.60	.8071	-.0019	-.0064	.3343	1.168	2.20	.4169
.70	.7820	.0115	.0303	.3728	1.264	2.30	.4008
.80	.7551	.0248	.0617	.4111	1.329	2.40	.3881
.90	.7270	.0413	.0998	.4526	1.366	2.50	.3765
1.00	.6983	.0606	.1440	.5013	1.379	2.60	.3609
1.10	.6694	.0825	.1931	.5608	1.371	2.70	.3490
1.20	.6409	.1062	.2463	.6344	1.348	2.80	.3377
1.30	.6130	.1320	.3025	.7252	1.313	2.90	.3272
1.40	.5860	.1592	.3611	.8353	1.271	3.00	.3174
1.50	.5603	.1875	.4211	.9667	1.223		

<sup>a</sup>  $R(z) = \phi_1/H'(z)$ , where  $\phi_1 = -1/2\{[H(z)]^2 + zH(z)H'(z) + 1/2[H'(z)]^2 - 1\}$ . <sup>b</sup>  $U(z)$  and  $V(z)$  are defined by equations 30 and 36, respectively. <sup>c</sup>  $S(z)$  is defined by equation 27 where  $d\phi_1/dz = 1/2H'(z)[(2z^2 - 3)H(z) + zH'(z)]$ .  $\phi_2 = 1/4\{2[H(z)]^3 - (z^3 - 9/2z)[H(z)]^2H'(z) - (z^2 - 3)H(z)[H'(z)]^2 - 1/4z[H'(z)]^3 - zH'(z) - \frac{3\sqrt{3}}{\pi}H(\sqrt{3}z) + \left(\frac{3\sqrt{3}}{\pi} - 2\right)H(z)\}$ . <sup>d</sup>  $T(z) = \phi_3/H'(z)$  where  $\phi_3 = -1/6\{2[H(z)]^3 + 3z[H(z)]^2H'(z) + 3H(z)[H'(z)]^2 - \frac{6\sqrt{3}}{\pi}H(\sqrt{3}z) + (6\sqrt{3}/2\pi - 2)H(z)\}$ . <sup>e</sup>  $W(z)$  is defined by equation 32.

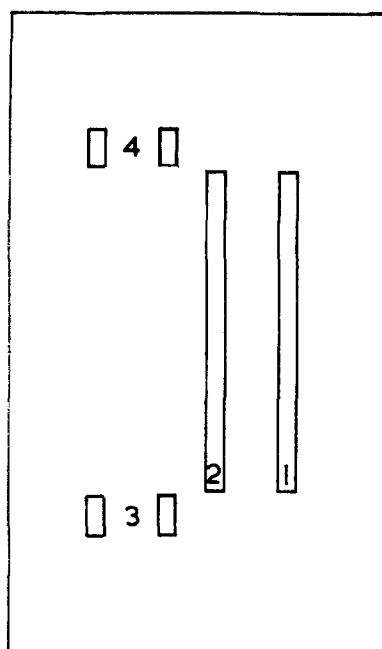
Gauss eyepiece. Then using four vertical slits in the cell position (source slit also vertical), this lens was twisted about the optic axis until the interference pattern viewed from the camera was best defined (the use of four slits in this manner gives a complex interference pattern which is considerably more sensitive to maladjustment than the first-order Rayleigh pattern obtained from two slits). This single lens was then placed at the correct height above the lathe bed by focusing a cross hair placed at the center of the main spherical lens upon the optic axis. The second cylindrical lens was then put in place and adjusted similarly for rotation and height. Finally, the combined unit was focused by placing a very narrow horizontal slit in the cell frame suspension at exactly the cell-center position, and using a Toepler "schlieren" knife edge at the camera end. Kodak "CTC" panchromatic half-tone plates were used throughout; the mercury green 5461 Å. line was isolated as described.<sup>23</sup>

Diffusion experiments were conducted according to the usual procedure.<sup>15,22</sup> Photographic records were obtained of the fringe pattern (a) after the sharpening capillary was inserted and before sharpening was commenced, (b) after the boundary was fully sharp, 50-100 ml. of liquid being withdrawn (these records (a) and (b) suffice to determine the fringe fraction), (c) immediately after the capillary was withdrawn and the cell closed off (both bottom and top sections of the cell could be moved, but not the central section)—the "diffusion reference" pictures, and finally, (d) as diffusion proceeded; 8 exposures, at approximately regular intervals, were generally taken allowing about 25% of

the total time of the diffusion to elapse before the first exposure was made. The diffusion process was generally allowed to proceed until  $\sqrt{Dt}$  was approximately 0.3 cm. In addition, a separate record was obtained of the cell and reference fringes when the cell was filled with water alone; this is termed the "cell blank."

All records were measured with a Gaertner Toolmaker's Microscope fitted with projection screen, described by Akeley and Gosting.<sup>25</sup> After lining up the plate with the aid of the reference fringe patterns, the fringe fraction is determined from records (a) and (b), approximately four recordings being made of the position of each of the four minima in the central part of the diffraction envelope at (plate) distances about 3-5 mm. either side of the center. Record (a) gives the small permanent displacement of the upper part of the envelope with respect to the lower, and record (b) the displacement corresponding to the fringe fraction. The fringe separation with this system is 260  $\mu$  and measurements may be made to approximately 2  $\mu$ , leading to a possible accuracy of about 1% in the fringe fraction. Secondly, the cell blank is measured to give a record of the displacement  $\delta_R$  of one cell fringe, as a function of distance from the top of the cell, with respect to the mean position of the two central reference minima (see Fig. 1b). The "cell deviation plot" so obtained which should be constant for a perfect optical system, actually varied by about 20-25  $\mu$

(25) D. F. Akeley and L. J. Gosting, *THIS JOURNAL*, **75**, 5685 (1953).



A

Fig. 1.—A, masking diaphragm for production of Rayleigh interferograms: (1) slit opposite diffusion channel; (2) slit opposite extension window; (3,4) pairs of slits producing reference patterns.



B, Rayleigh interferogram with reference patterns: (1,2) interference minima in region conjugate to homogeneous solvent, either of which may be taken as the "zeroth" fringe; (3) arrow indicates direction of cross-axis motion.

along the length of the cell fringes. It is somewhat analogous to the " $\delta'$ " correction employed in the Gouy procedures. Finally the diffusion records are measured: a few measurements on the diffusion reference picture in a region remote from the boundary serve to relate the displacement of the solvent fringes in the particular experiment (denoted  $\delta'_R$ ) to the cell deviation plot, the latter being considered non-varying for all experiments conducted with the same cell assembly. That is,  $\delta'_R$ , the displacement for a particular experiment, may differ from  $\delta_R$ , but it is found that this difference is independent of the distance along the cell fringes, so a graph of  $\delta_R$  vs. the cell coordinate may be employed for all experiments, when corrected by the small discrepancy between  $\delta_R$  and  $\delta'_R$ . This rather complicated procedure was designed to enable the reference point for the fringe measurements (*e.g.*, the zeroth minimum, Fig. 1b) to be selected in a reproducible manner from experiment to experiment, while avoiding the laborious task of obtaining a correction curve of  $\delta'_R$  vs. cell coordinate in each case. Reproducibility in this respect is important, as an error of 3 or 4  $\mu$  (which may easily be made in any single setting of the comparator cross axis motion) will produce serious errors in concentration-dependence determinations.

The diffusion exposures, after lining up and recording the reference minima positions as above, were measured up in the conventional manner,<sup>15</sup> but with constant reference to the  $\delta'_R$  correction values: *e.g.*, if measurements were required on  $j = 1.00, 2.00, 3.00 \dots$ , the first minimum would be approximately located, the  $\delta'_R$  value appropriate to the distance from the end of the cell fringes obtained from the correction graph, and the cross axis motion of the comparator set accordingly. This minimum would then be located

accurately. The positions of successive minima as they coincide with the cross hairs may then be recorded, the cross axis setting being altered as necessary: a variation of  $\delta'_R$  of up to 2  $\mu$  is tolerated without alteration of the cross axis. In practice this means that the cross axis setting must be adjusted for every whole fringe from 0.5 to 3.0, and then for every 10th fringe; the outer fringes, having a much lower slope (see Fig. 1b) than those nearer the center, are very much more sensitive to small variations in  $\delta_R$ . The importance of this continuous adjustment, if use is to be made of the outer fringes, must be emphasized strongly; the variation in  $\delta_R$  though corresponding only to about  $1/10$  of the fringe separation and thus implying that the optical qualities are reasonably good, will nevertheless introduce serious errors into the measurement of fringe separations, if not allowed for.

For most purposes the cross axis reading is altered as the  $J/2$  position is passed so that alignment is now on the  $J$ th minimum; this results in readings being obtained for (exactly) equal and opposite  $f(j)$  values, so that only one set of  $z^*$  values has to be looked up.

Diffusion coefficients were determined by calculating the regression of  $(\bar{Y}_t')^2$  upon  $t'$  by the method of least squares, thus

$$D\bar{c} = \frac{1}{4M} \frac{d[(\bar{Y}_t')^2]}{dt'}$$

In this equation,  $\bar{Y}_t'$ , is the quantity corresponding to  $\bar{Y}_t$ , defined by equation 30 but referred to  $t'$ , the time elapsed after boundary-sharpening ceased; as this method eliminates the need to consider "zero time" corrections,<sup>26</sup> the prime notation will henceforth be omitted, it being understood that all  $t$  and  $Y_t$  values quoted are strictly  $t'$  and  $Y_t'$ , respectively.

This procedure was adopted as being most consistent with experimental practice, as it was considered that (a) all values of  $t$  are equally reliable, (b) errors are located almost

exclusively in  $\bar{Y}_t$ , (c) errors in  $\bar{Y}_t$  are approximately proportional to its magnitude.

The magnification factor,  $M$ , is equivalent, in the Rayleigh method, to the "b" distance<sup>25,27</sup> in the Gouy and the accuracy of its determination, in any attempt at comparison of the methods, is obviously of first importance. In these experiments, the magnification was determined by placing a horizontally graduated reticle in the position optically equivalent to the cell-center, narrowing the vertical slit opposite the graduations to  $\sim 0.5$  mm., and photographing the resultant image; the reticle having very narrow graduations was measured to the full accuracy of the comparator, and the recorded image to about 5  $\mu$ . A series of 28 corresponding pairs of arbitrary comparator readings were thus obtained, the magnification being determined from the regression of the image values upon the object values. A subsequent check of the  $M$  values so obtained showed that errors in the position of the image lines did not generally exceed the known error of measurement. As the outermost reticle graduations were separated by  $\sim 2.5$  cm. giving a separation to the corresponding image marks of  $\sim 5.5$  cm., the average error of a single determination should not exceed about 1 in 5000, and the "best value" corresponding approximately to 27 such pairs should certainly be more reliable than this. The reproducibility of duplicate determinations confirmed this estimate.

**Materials and Solutions.**—The sucrose and urea were part of the same samples previously described.<sup>25</sup> The glycine (Pfanstiehl) was used as received; the butanol was the cen-

(26) L. G. Longworth, *THIS JOURNAL*, **69**, 2510 (1947).

(27) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

TABLE III

## ANALYSIS OF FRINGE DATA FOR 1.5% SUCROSE

 $\Delta C = 1.4880$  g./100 ml.,  $\bar{C} = 0.7440$  g./100 ml.,  $J = 97.80$ ,  $t = 15,570$  sec.,  $T = 25.00_3^\circ$ .

1	2	3	4	5	6	7	8	9	10	11	12
Fringe No. $j_1$	Fringe No. $j_2$	Separation $X_2 - X_1$ cm.	Ideal displacement $z_1^* (= -z_2^*)$	$Y_t^a = \frac{X_2 - X_1}{2z_2^*}$ cm.	$j_2'$	Separation $X_2' - X_1$ cm.	$\frac{X_2' - X_1}{(z_2^*)' - z_1}$ cm.	$\frac{\Delta z^* = X_2 - X_1}{\bar{Y}_t}$	$\frac{\Delta z^*}{(z_2^*)' - z_1^*}$	$\frac{\Delta z^*}{(\times 10^4)}$	$\Delta R(z^*)$
0.5	97.3	4.7410	-1.8158	1.3055	57.8	2.5886	1.3084	1.9834	1.9785	(+49)	+0.8155
1.0	96.8	4.2768	1.6391	1.3046	61.8	2.4556	1.3080	1.8815	1.8773	(42)	.6970
1.5	96.3	3.9886	1.5283	1.3049	65.8	2.4134	1.3082	1.8491	1.8448	(43)	.6127
2.0	95.8	3.7744	1.4457	1.3054	69.8	2.4132	1.3082	1.8490	1.8447	(43)	.5399
3.0	94.8	3.4513	1.3230	1.3043	73.8	2.3677	1.3080	1.8141	1.8102	(39)	.4362
4.0	93.8	3.2118	1.2306	1.3050	77.8	2.3719	1.3073	1.8173	1.8144	29	.3432
5.0	92.8	3.0153	1.1555	1.3048	79.8	2.3426	1.3073	1.7949	1.7919	30	.2760
6.0	91.8	2.8483	1.0914	1.3049	81.8	2.3315	1.3067	1.7864	1.7842	22	.2129
7.0	90.8	2.7029	1.0353	1.3054	83.8	2.3371	1.3061	1.7907	1.7893	14	.1510
8.0	89.8	2.5716	0.9850	1.3054	85.8	2.3590	1.3059	1.8075	1.8064	11	.0886
9.0	88.8	2.4520	.9393	1.3052	87.8	2.3972	1.3053	1.8367	1.8365	2	.0230
10.0	87.8	2.3420	.8972	1.3052	88.8	2.3978	1.3056	1.8372	1.8365	-7	-.0230
12.0	85.8	2.1434	.8214	1.3047	89.8	2.3560	1.3043	1.8052	1.8064	12	.0886
14.0	83.8	1.9676	.7540	1.3048	90.8	2.3334	1.3041	1.7879	1.7893	14	.1510
16.0	81.8	1.8090	.6928	1.3056	91.8	2.3258	1.3036	1.7820	1.7842	22	.2129
18.0	79.8	1.6621	.6364	1.3059	92.8	2.3348	1.3030	1.7889	1.7919	30	.2760
20.0	77.8	1.5245	.5838	1.3057	93.8	2.3644	1.3031	1.8116	1.8144	28	.3432
24.0	73.8	1.2724	.4872	1.3058	94.8	2.3560	1.3015	1.8052	1.8102	(50)	.4362
28.0	69.8	1.0419	.3990	1.3056	95.8	2.4031	1.3027	1.8413	1.8447	(36)	.5399
32.0	65.8	0.8261	.3165	1.3051	96.3	2.4013	1.3017	1.8399	1.8448	(49)	.6127
36.0	61.8	0.6220	.2382	1.306	96.8	2.4432	1.3014	1.8720	1.8773	(53)	.6970
40.0	57.8	0.4250	.1627	1.306	97.3	2.5774	1.3027	1.9748	1.9785	(37)	.8155

<sup>a</sup>  $\bar{Y}_t = 1.3051$  (average of  $Y_t$  values in column 5, omitting first two and last five values). Average value of quantity in column 8, omitting first two and last two values = 1.3051.

ter cut from a fractional distillation of dried (CaSO<sub>4</sub>) Baker C.P. material. All solutions were made up by weight, using calibrated weights; the density of solid glycine was taken as 1.601 and of butanol at 25° as 0.8055 g./ml. The solution density data of Gosting and Morris<sup>3</sup> for sucrose, Gosting and Akeley<sup>28</sup> for urea, Lyons and Thomas<sup>4</sup> for glycine and Lyons and Sandquist<sup>5</sup> for butanol were employed in determining corrected concentrations.

In several experiments, parallel records of the Gouy fringes were obtained so that a direct comparison of the two methods was possible; diffusion coefficients were calculated in the conventional manner.<sup>3</sup>

### Results

Most interest in this work must lie in the accuracy with which  $\bar{Y}_t$  and, hence, differential diffusion coefficients, may be determined, and in the ability of the theory to predict deviations in the diffusion of non-ideal solutes. The following experimental results have been chosen for detailed description, as they demonstrate both the potentialities and limitations of the Rayleigh method in these respects.

(a) **Sucrose.**—Table III summarizes the way in which experimental observations are arranged for the calculation of both  $D\bar{C}$  and  $k_1$ . Similar tabulations are made for each exposure. Columns 1 and 2 give the fringe numbers for which recordings were made, column 6 is identical with  $j_2$  in the reverse order. Column 3 gives the corresponding measured separations, and column 4 the ideal displacements calculated from the fringe numbers by use of equation 4. These are combined to give the  $Y_t$  values in column 5, and it is immediately evident that a very high degree of constancy of  $Y_t$  is obtained. If the experiment were to be used solely for the calculation of  $D\bar{C}$ , measurements would

have been concentrated in the region  $j_1$  10–24 (with  $j_2$  87.8–73.8) where fewer precautions are necessary to obtain accurate measurements, but the values given have been chosen to show that the symmetrical arrangement allows reliable determinations of the fringe separation to be made for the outermost fringes, even down to the region  $j = 0.5$ . These regions, while the least easy to measure up, are very important in the analysis of deviations from ideal behavior due to the presence of impurities in the solute.<sup>29</sup>

Column 7 gives the separations obtained when the same comparator figures are arranged non-symmetrically, keeping  $\Delta j$  more nearly constant, after Longworth<sup>15</sup> ( $X_2'$  is the comparator reading for fringe  $j_2'$ ), while column 8 gives the corresponding normalized values equivalent to  $Y_t$ . Here the skewness of the boundary is clearly demonstrated, although the average of all values is the same as  $\bar{Y}_t$ . The remaining figures refer to the determination of  $k_1$ , the first-order coefficient of concentration-dependence of the diffusion coefficient. Column 9 gives the result of normalizing the non-symmetrical separations (column 7) through division by  $\bar{Y}_t$  to give an estimate of  $\Delta z$  (equations 39b and 40), while the corresponding  $\Delta z^*$  values (obtained from combining the values given in column 4 with  $(z_2^*)'$ , the value given on reading the column upwards) are given in column 10; the difference between these two quantities is given in column 11 (the figures here are equivalent to experimental deviations in microns when  $Y_t = 1.00$  cm.) while,

(29) J. M. Creeth, report presented to the 126th National Meeting, American Chemical Society, New York, N. Y., Sept. 17, 1954, and to be published.



finally, column 12 gives the appropriate  $\Delta R(z^*)$  values obtained from the  $z^*$  values and Table I. A plot of  $(\Delta z - \Delta z^*)$  vs.  $\Delta R(z^*)$  now reveals that while the values corresponding to the inner fringes lie on a fair straight line, those for the outermost fringes are considerably displaced from the line, and are bracketed to indicate their unreliability.

As the experiments described below will show, this is not evidence of a failure in the theory, but rather of the limitations inherent in the procedure of comparing fringes of greatly differing slopes. Denoting the error in  $\delta_R$  (experimental section) as  $\epsilon$ , the resulting error  $\epsilon'$  in  $z$  will be given by the relation

$$\epsilon' = \epsilon/H'(z)$$

As  $H'(z)$  tends to zero for high  $z$  values, the error  $\epsilon'$  becomes excessively high: for the outermost points in this case,  $\epsilon' = 25 \epsilon$ . As  $\epsilon$  can hardly be less than 1 or 2  $\mu$ , it is clear that comparisons involving these fringes will be highly unreliable, particularly in the relatively unfavorable case of sucrose, where the expected deviations are small. (It should be noted that this error is independent of  $k_1$  so that determinations will become progressively more accurate as  $k_1$  increases). For this reason, no attempt has been made to utilize the deviations corresponding to  $z$  values greater than 1.3 (for which  $\epsilon' = 5\epsilon$ ) in determinations of concentration-dependence coefficients.

It is clear also from these results that while some error is undoubtedly present in  $\delta_R$ , this is quite constant throughout the measurement, and so cancels completely when symmetrical fringes are compared. This emphasizes the importance of the symmetrical procedure for the determination of differential diffusion coefficients, in that not only are the real effects due to non-ideality eliminated, but also that all consistent errors in  $\delta_R$  and personal errors in locating an interference minimum are likewise obviated. (The error will only cancel in the alternative procedure<sup>15</sup> when the average of all pairs has been taken.)

The scatter evident in the unbracketed values in column 11 of the table is minimized when the results of four exposures (all obtained during the last half of the diffusion time) are averaged, and the resulting values are shown in Fig. 2. The line, which represents the expected deviations, was calculated from equation 38 and the value for  $k_1$  of  $-1.494 \times 10^{-3}$  obtained from the data of Gosting and Morris<sup>3</sup> and the value of  $D\bar{c}$  of  $5.172 \times 10^{-8}$  cm.<sup>2</sup> sec.<sup>-1</sup> (corrected to 25.000°) given by the experiment itself. The value of  $k_1$  corresponding to the least-squared straight line through the points is  $1.384 \times 10^{-2}$ , which may be considered a reasonable agreement. The value of  $D$  (similarly corrected) calculated from the Gouy fringes in this experiment was  $5.178 \times 10^{-6}$  cm.<sup>2</sup> sec.<sup>-1</sup>, which agrees better with the earlier results of Gosting and Morris<sup>3</sup> (5.175) than the more recent results of Akeley and Gosting<sup>25</sup> (5.170).

(b) **Glycine.**—In this case, both  $a_1$  and  $k_1$  are significant, while other coefficients may be ignored.<sup>4</sup> As  $k_1$  for glycine is considerably greater than for sucrose, the experiment provides a potentially better test of the theory respecting  $k_1$  deter-

minations, and accordingly it was desired to obviate the complicating effect of refractive increment variation; this was done in the following manner. From an expression relating refractive index to concentration (e.g., equation 6) it is possible to calculate the concentration corresponding to any particular fringe if the relevant constants are known. Values of  $\bar{C}$  so obtained may then be used in a direct computation of the  $g(\bar{C})$  function (equation 2) from which modified "ideal displacements,"  $z^\ddagger$ , may be obtained and employed exactly as was done for the  $f(j)$  and  $z^*$  values in the sucrose example. These "ideal displacements" are not true  $z^*$  values as the latter are strictly defined only by equation 4, whereas the definition of  $z^\ddagger$  is given by the closely analogous relation

$$g(\bar{C}) = H(z^\ddagger) \quad (41)$$

It will be apparent that  $z^*$  and  $z^\ddagger$  are identical for systems in which  $\Delta n/\Delta C$  is independent of  $C$ , when  $g(\bar{C}) = f(j)$ . By this means, the computation of the expected deviations in fringe position may be accomplished without using the  $U(z)$  function, when the resulting comparison between observed and expected deviations should constitute a more rigorous check of the  $R(z)$  function.

In the cases examined here, the experimental conditions have been such that  $C_1 = 0$  (i.e., diffusion occurs between a solution of original concentration  $C_2$  and pure solvent) and  $\Delta n/\Delta C$  is linear in  $C$  (i.e., that  $a_2$  and all higher coefficients in equation 6 are negligible). In these circumstances, it is more convenient to use an expansion of the refractive index-concentration relation about  $n_0$  (the value corresponding to the solvent) than  $n\bar{c}$ , as was done in 6. Thus, starting from the equation

$$n = n_0 + R_0 C [1 + a_1' C + \dots] \quad (42)$$

the expression for the refraction increment becomes

$$\frac{\Delta n}{\Delta C} = R_0 [1 + 2a_1' \bar{C} + \dots] \quad (43)$$

The constants  $R_0$  and  $a_1'$  are readily obtained when experimental refraction increment data are expressed as a function of  $\bar{C}$ .<sup>30</sup>

The solution of (42) for the concentration  $C_1$  at a point corresponding to a certain fringe  $j$ , where the refractive index is  $n_j$  (thus  $C_j \equiv C_2$  in the earlier nomenclature) is given by the expression

$$C_1 = \frac{n_j - n_0}{R_0} - \frac{a_1'(n_j - n_0)^2}{R_0^2} + \dots$$

(30) A relation between  $a_1$  and  $a_1'$  may be obtained as follows: the expression for the refraction increment derived from equation 6 is, when  $a_2$  is negligible

$$\frac{\Delta n}{\Delta C} = R\bar{c} + \dots$$

so that, from equation 43

$$R_C = R_0 [1 + 2a_1' \bar{C} + \dots]$$

From equation 42

$$a_1' = \frac{1}{2R_0} \left( \frac{\partial^2 n}{\partial C^2} \right)_{C=0}$$

whereas from 6

$$a_1 = \frac{1}{2R\bar{c}} \left( \frac{\partial^2 n}{\partial \bar{C}^2} \right)_{C=\bar{c}}$$

The two second derivatives may be equated under these conditions, when it follows that

$$a_1 = a_1' (1 - 2a_1' \bar{C} + \dots)$$

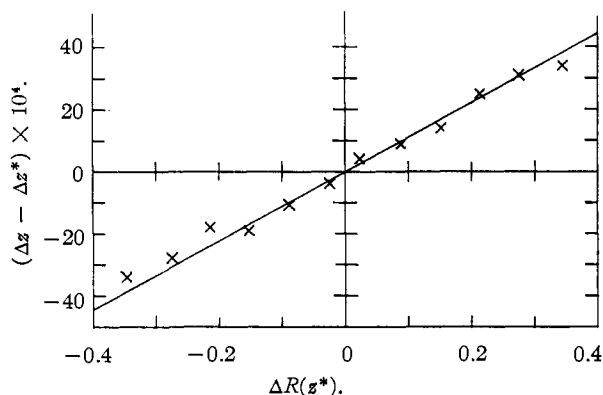


Fig. 2.—Fringe deviation diagram for sucrose. Crosses are average experimental values, determined at four different times. Solid line represents expected deviations on basis of known value of  $k_1$ .

However, using the substitution

$$\frac{j\lambda}{d} = n_1 - n_0$$

(where  $\lambda$  is the wave length and  $d$  the thickness of the diffusion cell along the optic axis), the calculation of separate refractive index values may be avoided.

Using the values for  $R_0$  and  $a_1'$  given by Lyons and Thomas,<sup>4</sup> and equation 41 to obtain the  $z^\pm$  values, the deviation between ideal and observed fringe positions were thus obtained as a function of the parameter  $\Delta R(z^\pm)$ , and are shown in Fig. 3. The agreement between expected deviations, as represented by the straight, solid line, and those experimentally observed is very satisfactory; the slope obtained by drawing the best straight line through the points gives  $k_1 = -2.55 \times 10^{-2}$ , which compares with the value of  $2.45 \times 10^{-2}$  (obtained from Lyons and Thomas' results<sup>4</sup>) used to plot the solid line. The differential diffusion coefficient (corrected to 25.000°) obtained in this experiment ( $\bar{C} = 0.6101$  g./100 ml.) was  $1.0451 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>, while simultaneous Gouy records gave  $D = 1.0458 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>. The values for this concentration obtained from the data of Lyons and Thomas<sup>4</sup> and of Dunlop<sup>31</sup> are, respectively,  $1.0479 \times 10^{-5}$  and  $1.0446 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>.

(c) **Butanol.**—Lyons and Sandquist's data<sup>5</sup> on butanol-water systems show that in the concentration region around 0.10  $M$ , at 25°, the coefficients  $a_1$ ,  $k_1$  and  $k_2$  are likely to be significant, while  $a_2$  is essentially zero. In the experiment, a solution of butanol of concentration 0.2828  $M$  was allowed to diffuse against water, giving  $J = 99.66$ , equivalent to  $\Delta n/\Delta C$  value of  $766.5 \times 10^{-5}$ , which is in rather poor agreement with Lyons and Sandquist's value for this concentration of  $761.2 \times 10^{-5}$ . In order to use these workers' data, therefore, the mean concentration of the experiment was taken as  $\bar{C} = 0.1423 M$ ; expressing their results about this value, the equations

$$\left(\frac{\Delta n}{\Delta C}\right) \times 10^5 = 761.2 + 101.3(C - 0.1423), C \leq 0.3006$$

(31) P. J. Dunlop, THIS JOURNAL, 77, in press.

and

$$D \times 10^6 = 9.255 - 3.20_3(C - 0.1423) + 0.278_5(C - 0.1423)^2, C \leq 0.7001$$

are obtained, from which  $a_1' = 6.782 \times 10^{-2}$ ,  $a_1 = 6.651 \times 10^{-2}$ ,  $k_1 = -3.461 \times 10^{-1}$  and  $k_2 = 3.009 \times 10^{-2}$ .

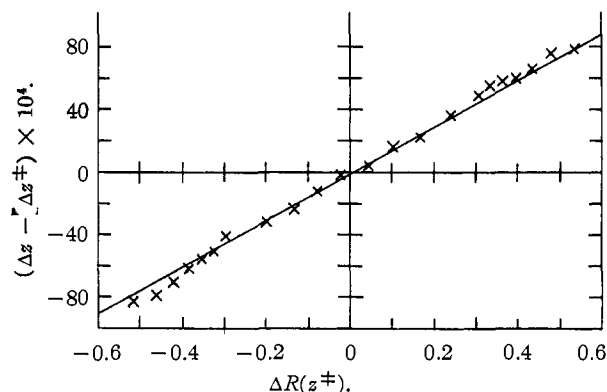


Fig. 3.—Fringe deviation diagram for glycine. Crosses are average experimental values, determined at four different times. Solid line represents expected deviations on basis of known value of  $k_1$ , effects due to refraction increment variation having been eliminated.

From these values and the values of the functions in Table II, it is evident that the theory predicts that all the second-order effects are very small, amounting always to less than  $5 \times 10^{-4}$  in  $(\Delta z - \Delta z^*)$  and hence largely beyond experimental detection. This was borne out in the experiment, the quantity  $Y_1$  being at least as constant as in the sucrose experiment (Table III, Column 5) for  $j$  values between 3.00 and 96.66, and it is therefore justifiable to treat the results in the manner of the glycine experiment, using the refractive index data above to enable  $g(C)$  values to be calculated from the  $f(j)$ 's, so that a value of  $k_1$  could be determined from the experiment for comparison with the known value. The plot thus prepared showed a closely linear relation between the deviations and the appropriate  $\Delta R(z^\pm)$  function, giving a value of  $k_1$  of  $3.213 \times 10^{-1}$ , *i.e.*, about 7% lower than expected, a discrepancy which is probably about the magnitude of the experimental error for this system.

In order to demonstrate the magnitude of the skewness caused by variation of the refraction increment (which is a question of some interest<sup>16</sup>), and moreover to provide an illustration of the rigorous analysis which would be required were the second-order effects much larger, a detailed calculation has been made of the deviations predicted by the theory for the two first-order effects and the four second-order effects considered in the butanol experiment. Some of the values so obtained are given in Table IV. The  $z^*$  values given are those corresponding to some of the fringes recorded in the experiment (thus  $z^* = 1.3288$  corresponds to fringe 96.66). The remainder of the table is self-explanatory: column 8 gives the total predicted deviation, from all six effects considered, for positive  $z^*$  values and column 9 the corresponding deviations for  $z^*$  taken as negative.

TABLE IV  
EXPECTED DEVIATIONS<sup>a</sup> FOR BUTANOL EXPERIMENT

$z^*$	2 $\left(\frac{\Delta C}{2}\right)^{a_1} U(z^*) \times 10^4$	3 $\left(\frac{\Delta C}{2}\right)^{k_1} R(z^*) \times 10^4$	4 $\frac{a_1^2}{2} \left(\frac{\Delta C}{2}\right)^2 W(z^*) \times 10^4$	5 $\left(\frac{\Delta C}{2}\right)^{a_1 k_1} V(z^*) \times 10^4$	6 $\frac{k_1^2}{2} \left(\frac{\Delta C}{2}\right)^2 S(z^*) \times 10^4$	7 $\left(\frac{\Delta C}{2}\right)^{k_2} T(z^*) \times 10^4$	8 Total <sup>b</sup> for $+z^*$ $\times 10^4$	9 Total <sup>b</sup> for $-z^*$ $\times 10^4$
1.3288	57.4	182.3	-0.6	3.6	-1.7	-2.0	-128.8	-121.0
1.1619	61.6	133.0	- .6	2.9	-1.2	-1.3	- 74.8	- 68.0
0.9922	66.2	84.5	- .6	2.4	-0.7	-0.9	- 21.1	- 15.5
.9048	68.7	60.7	- .6	2.2	- .5	- .7	+ 5.4	+ 10.6
.7624	72.5	24.2	- .6	1.9	- .2	- .3	45.9	50.7
.6456	75.3	- 2.9	- .6	1.7	.0	- .1	76.0	80.4
.5442	77.6	-23.7	- .5	1.5	.0	.0	99.3	103.3
.4530	79.4	-40.1	- .5	1.3	.0	+ .1	125.5	128.9
.3286	81.5	-58.3	- .4	1.0	+ .1	.1	138.2	141.4
.2136	82.8	-70.3	- .3	0.6	.1	.1	152.0	154.2
.1041	83.7	-77.1	- .1	0.3	.0	.0	160.4	161.2
.0682	83.8	-78.4	- .1	0.2	.0	.0	161.9	162.5

<sup>a</sup> Calculated using values of  $a_1$ ,  $k_1$ ,  $k_2$  and  $\Delta C$  given in text. <sup>b</sup> As calculated by use of equation 37.

It may be noted that deviations produced by refraction increment variation of the first order (column 2) are of considerable magnitude in the  $z^*$  range considered; when the values are paired non-symmetrically (*e.g.*, as for the sucrose experiment) however, the effect is little more than one-tenth of the magnitude of the corresponding deviations produced by the first-order variation of the diffusion coefficient. Secondly, the term in  $k_1^2$ , like the other second-order effects, is very small, even though  $k_1$  is itself rather large. This is due to the fact, evident from Table II, that  $S(z)$  is a much smaller function than the others.

For a rigorous calculation of  $D_{\bar{c}}$ , it would be necessary to compute all the second-order effects for, say, 6 or 8  $z^*$  values equivalent to fringes in the region 10-24 for  $J = 100$ . Then as all second-order functions change sign as  $z$  changes (thus  $S(z) = -S(-z)$ ), symmetrical pairing of fringe measurements enables the relation

$$(X_{j-i} - X_i)/2M\sqrt{D_{\bar{c}}t} = 2z_j^* + 2\left(\frac{\Delta C}{2}\right)^2 \sum \left[ \frac{k_1^2}{2} S(z_j^*) + \dots \right] \quad (44)$$

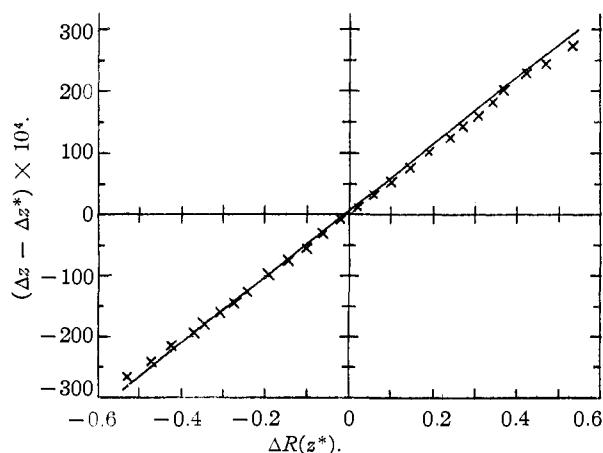


Fig. 4.—Fringe deviation diagram for butanol. Crosses are average experimental values, determined at four different times. Solid line (almost linear) represents expected deviations on basis of known values of  $a_1$ ,  $k_1$  and  $k_2$ .

(where the summation covers all second-order effects) to be employed and hence  $D_{\bar{c}}$  determined. For the results given in Table IV, where the difference between corresponding values in columns 8 and 9 represents twice the sum of the second-order effects, it is clear that these are negligible in this case, and accordingly the direct procedure for determining  $D_{\bar{c}}$  was employed, leading to the result (at 25.000°)  $D_{\bar{c}} = 9.255 \times 10^{-6}$  cm.<sup>2</sup> sec.<sup>-1</sup>, in exact agreement with the data of Lyons and Sandquist.

Finally, a direct comparison between the total calculated deviations (columns 8 and 9, Table IV) and those experimentally observed, after suitable non-symmetrical pairing, is shown in Fig. 4. The deviations<sup>32</sup> have been plotted as before against  $\Delta R(z^*)$  and it is apparent firstly that the theoretical relationship (solid line in the figure) is still very closely linear, even though about 10% of the deviation is produced by refraction increment variation; this shows that it would be quite impossible in practice to separate the two first-order effects. This behavior is to be expected from the similarity of form of the functions  $U(z)$  and  $R(z)$  over the range  $z = 0-1.3$ .

Secondly, it will be noticed that the theoretical displacement curve is shifted slightly from the origin; this is due to the second-order terms considered, which do not cancel at this point (equation 44). Finally, it is clear from the diagram that the average experimental points fall very closely on the theoretical line, although a straight line drawn through them would have a slope slightly lower than the slope of the (linear) central part of the theoretical curve.

This near coincidence of theoretical and observed deviations constitutes an indirect check on the accuracy of the expression for  $U(z)$ , when considered

(32) In experiments with butanol-water systems, it is necessary to have the butanol solution *above* the water, owing to the negative density increment of this solute. As this causes a natural reversal of the sign of  $z^*$ , the usual convention that  $x$  is measured positive downwards has been abandoned in this case. As  $k_1$  for the system, as defined by equation 5, is negative, it has been necessary also to reverse the convention concerning the sign of  $\Delta C$ , which has been taken to be positive. Accordingly, the deviation graph has the same form as those for sucrose and glycine.

together with the result, discussed previously, of *eliminating* deviations due to refraction increment variation, for in the one case the function has been used to compute part of the deviations, while in the other it has not. The other results, particularly those for glycine, go far to demonstrate the correctness of the  $R(z)$  function. Experiments on more highly concentration-dependent solutes would be required for an adequate test of the second-order functions, as the blurring of the fringes for high concentration increments, discussed by Longworth,<sup>15</sup> precludes the use of high  $\Delta C$  values.

In the determination of concentration-dependence effects, any comparison between different apparatus would be of great interest, and the results of Longworth<sup>16</sup> on butanol allow an attempt to be made in this direction. This experiment was used by Longworth in an ingenious application of the numerical solutions derived by Stokes<sup>33,34</sup> for linear concentration-dependence of  $D$ , a calculation which represents the first use of Rayleigh diffusion records in this type of estimation. The result was obtained in terms of the ratio of the diffusion coefficient at concentration  $C_2$  to that at zero concentration. (When put in the form used in this paper, the figure ( $D_2/D_0 = 0.942$ ) give  $k_1 = -4.44 \times 10^{-1}$ , a figure, which being calculated from the total skewness of the observed boundary, must include some effect due to variation of refraction increment). Through the kindness of Dr. Longworth in making available the comparator recordings of this experiment, the writer was able to apply the theoretical treatment developed in this paper; the results obtained showed firstly that the  $Y_1$  values were as constant as those reported in this work, the  $D_{\bar{c}}$  was almost identical with that obtained by Longworth, while the differences ( $\Delta z - \Delta z^*$ ) when plotted against the  $\Delta R(z^*)$  function gave a good linear relation, with about the same amount of scatter. The slope obtained was  $3.36 \times 10^{-2}$ , compared with the slope of  $2.46 \times 10^{-2}$  which was calculated for this experiment, using Lyons and Sandquist's data and values of  $U(z)$  and  $R(z)$  from the tables, and assuming a linear relation, as before. Thus, as Longworth's treatment suggested, the observed skewness here is rather greater than expected; it should also be pointed out that this experiment was performed with less than half the concentration increment used in the work reported here, so that the fringe separation measurements were much smaller and hence unavoidably more susceptible to error.

**Possible Anomalies in These Procedures.**—It has always been observed, with both settings of the cylindrical lens (see below), that the early Rayleigh pictures (*i.e.*, those taken up to about  $\sqrt{Dt} =$

(33) R. H. Stokes, *Trans. Faraday Soc.*, **49**, 887 (1952).

(34) An interesting point emerges from a comparison of Stokes' results with the treatment developed here: thus Stokes found that in all cases of linear dependence of  $D$  upon  $C$ , the concentration-distance curves had a common point at which they coincided with the ideal, non-concentration-dependent curve. This occurred at  $z = \pm 0.66$ , and it is noteworthy that the zeros of the  $R(z)$  function (corresponding to the points at which the concentration is unaffected by linear variation of  $D$ ) occur at  $z = \pm 0.657$ . It may be shown also that if Fujita and Gosting's result (equation 7 of this paper) is expressed in the forms used by Stokes, values of the "relative concentration" may be obtained which are very close to those in Stokes' Table 2.

0.1 cm.) showed appreciably less skewness than the later ones. For this reason, the estimates of concentration-dependence reported here have all been determined from exposures obtained during the last half of the experiments, when no drift of the  $\Delta z$  values with time could be observed. An entirely similar effect was observed with the records of the butanol experiment performed by Dr. Longworth. Although anomalies of this type might well be due to small imperfections in the cylindrical lenses, being most easily observed when the lens is used at high aperture (corresponding to early diffusion photographs) and negligible at low aperture (later diffusion photographs) it seems probable that the effect is real in the sense that it is due to those aberrations of the optical system which have recently been considered by Svensson.<sup>35,36</sup> For the type of optical system used here, where the cylindrical lens unit is focused on the geometrical center of the cell, Svensson found a finite correction to the equation for the path difference between the solution in the cell and the reference solution (bath-water in this case). This correction (equation 41 and Table II of reference 35) varies linearly with the square of the refractive index gradient, and so would be inversely time-dependent; moreover its effect would be greatest for the central fringes in a Rayleigh interferogram, which would undergo a shift quite independent of any concentration-dependence effect. From the equation cited, it appears that the central fringes in the sucrose experiment should suffer a displacement, relative to the outer fringes with which they are compared in Fig. 2, of approximately  $14 \times 10^{-4}$ , at the time of the earliest exposure used in the computations (8535 sec.). This aberration drops to about  $8 \times 10^{-4}$  for the last exposure used: the sign of the corrections is such as to increase the magnitude of the observed skewness, so it is possible that part of the small discrepancy between the observed and calculated values of  $k_1$  in this case may be ascribed to the operation of the effect. The time-variation of this aberration,  $6 \times 10^{-4}$ , is so small that it would be obscured by the natural scatter of the results; only in the case of the sucrose experiment is the effect<sup>37</sup> of significant magnitude.

**Comparison of Gouy and Rayleigh Results.**—On the basis of the theory outlined in this paper, differential diffusion coefficients obtained with the Rayleigh method should be identical with the Gouy values from the same experiment whenever the second-order effects are negligible. However, it is evident that the Gouy results for the sucrose and glycine experiments described are approximately 0.1% higher than the Rayleigh values, and a discrepancy of this magnitude has been observed consistently throughout the series (the mean discrepancy for six experiments, in most of which sucrose

(35) H. Svensson, *Optica Acta*, **1**, 25 (1954).

(36) H. Svensson, *ibid.*, **1**, 90 (1954).

(37) The procedure used by Svensson<sup>35</sup> in an experimental test of the theory of these aberrations apparently involved the assumption that the position of the maximum refractive index gradient, in the diffusion of 2% sucrose against water, does not vary with time; it may be shown from Fujita and Gosting's theory that, in fact, this ordinate undergoes a displacement which, though small in comparison with the optical length  $d$  of the cell, is first order in  $(k_1, \Delta C)$ , and so should perhaps be considered.

was the solute, was 0.12%). As the constants in the equation used for calculating Gouy values are independent of any lens characteristics and, moreover, the theoretical basis of the determination has been so rigorously examined,<sup>3,8,27,38</sup> the Gouy values are to be taken as the more reliable. The cause of the small error in the Rayleigh values is as yet undetermined: it cannot be due to aberrations of the type considered by Svensson,<sup>35</sup> for such displacement errors will cancel when the fringes are compared symmetrically. It seems unlikely also that it can be ascribed to direct errors in the magnification (*vide* the discussion in the experimental section) although this is the most obvious source of error. There seems to be no doubt that it is correct to focus the geometrical center of the cell in the camera plane.<sup>27,35,36</sup>

In the absence of such direct errors, and accepting the above conclusion as to the identity of Gouy and Rayleigh values, it is necessary to postulate an anomaly arising from the fact that, in the determination of the magnification, somewhat different demands are made upon the cylindrical lens from those concerned in the recording of the interferograms. Thus in the latter case, it appears that light traversing the center of the diffusion boundary will be largely restricted to the lower half of the lens, whereas in the former case, all parts of the lens are used more or less equally. Although no independent evidence for the existence of lens imperfections or errors of mutual alignment has been found (apart from the variable skewness at early times discussed above) further weight is given to this possibility by observations made in an earlier series of measurements, when one of the two cylindrical lenses was inverted (relative to the orientation employed throughout this work), but the focusing procedure was otherwise identical. In this case, the diffusion results obtained showed a consistent discrepancy from the Gouy values recorded in the same experiment of +0.3%, although

(38) L. J. Gosting and L. Onsager, *THIS JOURNAL*, **74**, 6066 (1952).

the apparent skewness was of the correct order, and no other anomalies were evident. Whatever the true origin of this minor discrepancy may be, it does serve to emphasise the difficulty of accurate alignment and focusing of a pair of cylindrical lenses of such long focal length.

In assessing the reliability of the apparatus in its present form, three criteria may be considered important. These are (a) the constancy of  $Y_1$  values, (b) the correct prediction of observed skewness, and (c) the accuracy of the differential diffusion coefficients. As the apparatus clearly meets the first two requirements (both of which, it may be noted, are *independent* of the particular value of the magnification), the slight anomaly in the third has been ignored, and it is therefore concluded that the apparatus, when used with the precautions outlined in this paper, does at least meet the minimum requirements for Rayleigh diffusion experiments; it is to be regretted that no conclusion can be drawn from this work as to the identity or otherwise of diffusion coefficients obtained with the two optical systems considered.

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