

ring deuterated toluenes in the 2260 to 2288 cm.^{-1} region. There should be only one fundamental frequency in this region, but two lines are observed in toluene-4-*d*. It is postulated that this doubling is due to Fermi resonance of the deuterium valence-stretching vibration with the combination $1493 + 784 = 2277 \text{ cm.}^{-1}$. Since the 2266 cm.^{-1} line appears with greater intensity than the 2288 cm.^{-1} line, the 2266 cm.^{-1} line must retain a greater resemblance to the deuterium valence-stretching frequency. The deuterium frequency must be Class A_1 ; thus, the 1493 cm.^{-1} line must belong to Class A_1 also, if this postulate is correct. Presumably, resonance would not take place in the case of toluene-2-*d* or that of toluene-3-*d* since the deuterium vibration would belong to a symmetry class different from that of the combination. The 1493 cm.^{-1} line and corresponding lines in the other deuterated toluenes have been observed by Nance⁶ in the infrared.

The measured frequencies show that the deuterium atom is held more tightly in the meta

position than it is in the ortho position; the possibility of Fermi resonance leaves the condition of the para position in doubt.

A Raman spectrograph is currently under construction for use in the extension of this investigation to benzyl chloride, benzal chloride and benzotrichloride. The infrared spectra of these compounds are being measured.

Summary

The Raman spectra of the deuterated toluenes have been measured and compared with the infrared spectra. Examination of the frequencies in the region of the C-D stretching frequencies indicates that doubling in the spectrum of toluene-4-*d* is due to Fermi resonance with the combination $1493 + 784$. This implies that the 1493 cm.^{-1} band belongs to symmetry class A_1 .

The C-D stretching frequencies also indicate that the C-H force constant in the meta position is larger than the corresponding constant for the ortho position.

BATON ROUGE, LA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Diffusion of Sucrose in Supersaturated Solutions

BY A. C. ENGLISH¹ AND MALCOLM DOLE

Introduction

As far as we are aware there have never been any successful measurements of diffusion coefficients in supersaturated solutions although Van Hook and Russell,² realizing the importance of diffusion data in the supersaturated range for the interpretation of the kinetics of crystallization, attempted to measure diffusion coefficients of sucrose in supersaturated solutions using the Northrop³-McBain⁴ porous disk technique, but "only irregular and unreliable results were realized"—probably due to crystallization induced by sharp edges or irregularities in the porous disk. It occurred to us that the Foucault-Toepler schlieren⁵ method of observing refractive index and hence concentration gradients could be profitably applied to diffusion measurements in the supersaturated region just as it had been in the region of dilute solutions by a number of investigators.⁶

During the preliminary stages of the investiga-

tion⁷ a new optical method for the determination of diffusion coefficients was developed in this country by Longworth,⁸ and Kegeles and Gosting⁹ and in Great Britain by Coulson, Cox, Ogston and Philpot.¹⁰ In the present research we have tried both methods as described below. We have also developed a diffusion cell particularly suitable for the highly viscous solutions with which we have had to deal.

Experimental

Part A: The Schlieren Method.—The optical components of the Longworth-Tiselius electrophoresis apparatus were purchased from the Klett Manufacturing Company and were used as received after installation of a lens of the correct focal length in the camera.

Our first diffusion cell was a modified Neurath⁸ type, but one with which we experienced the following difficulties: leakage troubles, due to areas of short distance between the diffusion channel and the water-bath, crystallization difficulties arising from impurities, grease, etc., which squeezed out the glass-metal contact zone into the diffusion channel, and the production of swirls and eddies in

(7) This research was started by J. J. Josephs during the academic year 1945-1946, but for reasons beyond our control, it was not resumed until the fall of 1947 by A. C. English. We wish to acknowledge the aid of Dr. Josephs in the early stage of development.

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

(9) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947); L. J. Gosting, E. M. Hanson, G. Kegeles and Margaret S. Morris, *Rev. Sci. Instrument*, **20**, 209 (1949); L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1998 (1949).

(10) C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc.*, **A192**, 382 (1948).

(1) Department of Chemistry, University of Kentucky, Lexington, Kentucky.

(2) A. Van Hook and H. D. Russell, *THIS JOURNAL*, **67**, 370 (1945).

(3) J. H. Northrop and M. L. J. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(4) J. W. McBain and T. H. Liu, *THIS JOURNAL*, **53**, 59 (1931).

(5) The technique of this method is extensively discussed by L. G. Longworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

(6) See the review by H. Neurath, *Chem. Rev.*, **30**, 357 (1942).

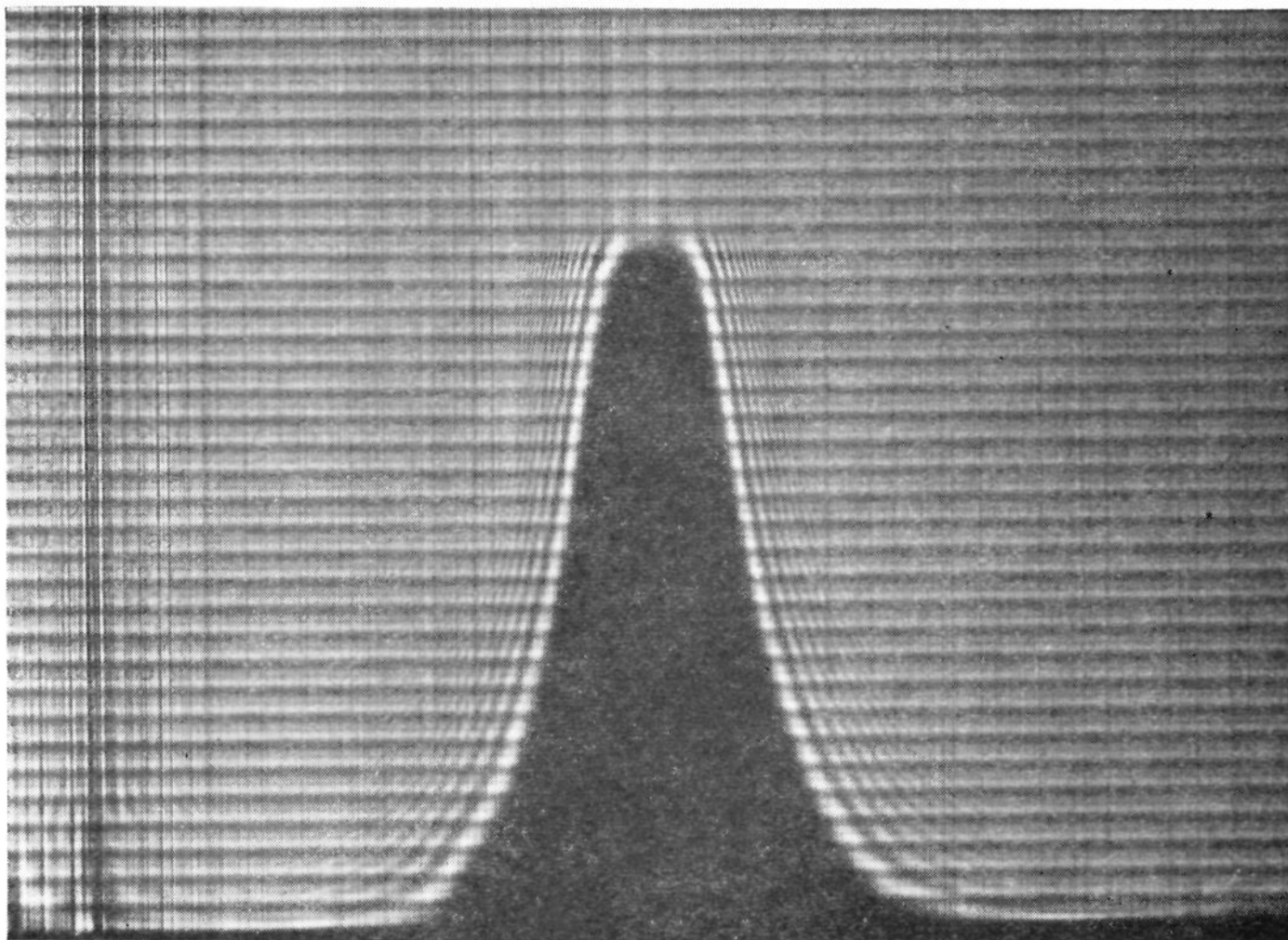


Plate I.

forming the boundary in the case of the more viscous solutions. Nevertheless a number of experiments was carried out with this cell.

Part B: Interpretation of the Schlieren Data.—Neurath⁶ has described methods of calculating the diffusion coefficient from the schlieren photographs such as illustrated in Plate I. For the integrated form of Fick's diffusion equation to be true, it is necessary that D , the diffusion coefficient, be independent of the concentration c . This is not true, but for the concentration difference across the boundary used by us, 0.5 to 1.0 weight per cent. sucrose, the diffusion coefficient changes only 2.5 to 5%, which is too small a change to invalidate Fick's law as can be seen from Fig. 1 where $1/h_{\max}^2$ is plotted against the time. Despite this seemingly excellent test of Fick's law, there is considerable uncertainty in the absolute magnitude of D as calculated from the slope of the line in Fig. 1 because of the fact that the area, A , of the shadow such as depicted in Plate I, which must be known, is uncertain. If the edges of the shadow are carefully examined, it can be seen that the edges are not sharp, nor is the peak sharp,

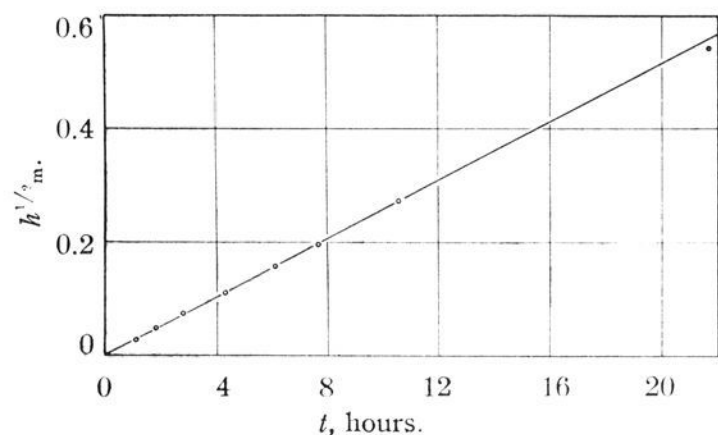


Fig. 1.—Test of Fick's law: 60.3% sucrose average concentration.

so that there is considerable personal latitude in the selection of both the height and the area.¹¹ In Plate I, the horizontal lines which look like a Venetian blind resulted from a slightly warped screw rod which moved the photographic plate non-uniformly across the opening in the camera. The vertical lines represent either scratches in the glass plates of the cell or perhaps tiny air bubbles.

A second method of computing D from the schlieren photographs is to plot $\log h$, h measured at various x values, against x^2 , at constant time; a straight line should result from whose slope D can be calculated. In this measurement x must be known correctly in terms of centimeters, but the scale used in measuring h is arbitrary. Figure 2 illustrates the application of this second method of obtaining D from the schlieren photographs. Again it is seen that the integrated form of Fick's law is valid. Another test of the law is to plot the slopes of the straight lines of Fig. 2 as a function of $1/t$; from the slope of the resulting rectilinear curve, D can also be calculated. Figure 3 illustrates this relation.

If the straight lines of Fig. 2 are extrapolated back to zero x , $\log h_{\max}$ is obtained; hence we have here a method of checking our selection of h_{\max} from the schlieren photographs. When this test of our first choice of h_{\max} was made, it was found that the h_{\max} values computed from the curves of Fig. 2 were definitely higher than those previously measured. The difference between the two amounted to a whole unit in D , the diffusion coefficient. On examining the schlieren photographs carefully, see Plate I, it was noticed that the diffraction fringes along the edge of the shadow seemed to end abruptly¹² at about

(11) The measurements of height and area were made on a dividing engine in the Dearborn Observatory of Northwestern University. We are greatly indebted to Dr. K. A. Strand, Director, for making this instrument available to us.

(12) This phenomenon has also been observed recently by A. Distèche, *Biochimica et Biophysica Acta*, **3**, 146 (1949), who similarly makes use of the disappearance of the fringes to fix the position of the maximum height.

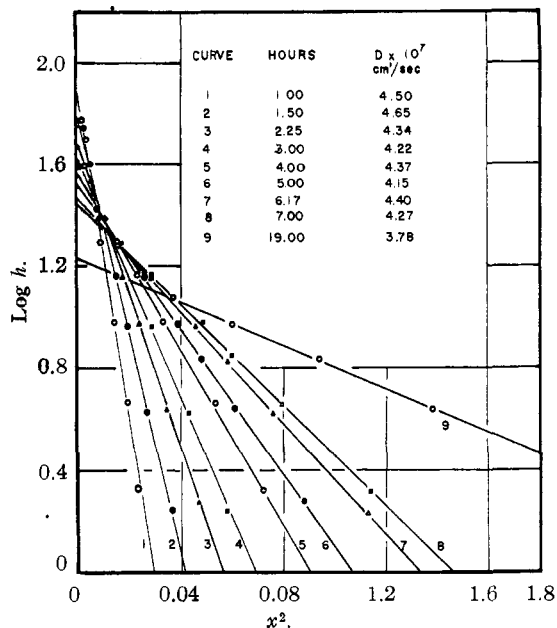


Fig. 2.—Test of Fick's law, 74.4% sucrose.

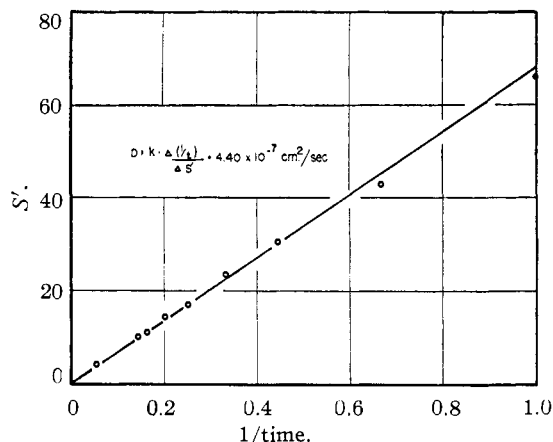


Fig. 3.—Test of Fick's law, 74.4% sucrose.

the h_{max} value predicted from the lines of Fig. 2. It was decided, therefore, to choose h_{max} at the point of disappearance of these diffraction fringes. Agreement between the two methods of computing D was improved by this procedure. Table I gives the data at 25° obtained from the schlieren photographs.

TABLE I
DIFFUSION COEFFICIENTS OF SUCROSE AT 25°, SCHLIEREN PHOTOGRAPH DATA

Wt. % sucrose		Av. concn., moles H ₂ O per mole sucrose	D in sq. cm./sec. $\times 10^7$		
Concn.	Dilute		h_{max} method	Slope method	Average
60.61	60.01	12.50	11.6	12.5	12.0
66.60	66.26	9.60	8.8		8.8
70.70	70.26	7.96	6.9	6.6	6.8
71.90	71.56	7.49	5.9	5.9	5.9
72.90	72.60	7.12	5.5	5.6	5.55
74.55	74.20	6.54	4.4	4.4	4.4

Although these data gave a smooth curve when plotted as a function of the weight per cent., see Fig. 4 solid circles, we had considerable doubt as to the reliability of their absolute values because of the uncertainty in the choice of the edge of the shadow in the schlieren photograph. For this reason we decided to repeat our measurements using the new interference fringe method. Also we wished to redesign our diffusion cell to make it more useful for viscous liquids.

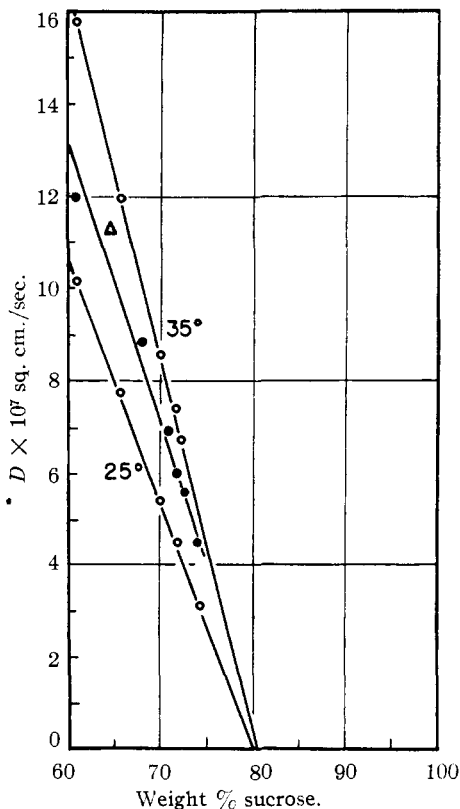


Fig. 4.—Open circles show interference fringe method; closed circles Schlieren method at 25°; triangle result of Van Hook and Russell.

Part C: The New Diffusion Cell.—Our new diffusion cell¹³ had the following features over the modified cell initially used. The optically flat glass windows of the cell were rigidly attached to the cell and sealed with rubber gaskets to prevent water leakage. The boundary was not formed by sliding the lower block under the upper, but by removing a thin sliding partition between the upper and lower liquids in the manner of Lamm.¹⁴ The boundary was then sharpened by a flowing technique¹⁵ making use of exit channels on both sides of the diffusion cell and controlling the flow by adjusting the slit openings by means of a movable inner block. When visual observation of the

(13) A complete description of this cell including engineering drawings with dimensions can be obtained from the doctoral dissertation of A. C. English, Northwestern University, 1949, or by request from the authors.

(14) Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Ser. IV, 10, No. 6 (1937).

(15) Kahn and A. Polson, *J. Phys. Colloid Chem.*, **51**, 816 (1947). sharpened their boundary by slowly sucking up solution through a capillary tip placed close to the boundary, as did Gosting and Morris.⁹ In the work of Coulson, *et al.*,¹⁰ the boundary was formed and sharpened by a flowing technique in which the two solutions flowed out of the diffusion cell through an exit on one side of the channel.

boundary by means of the schlieren camera showed that a sharp boundary existed, the diffusion was started by closing the exit channels.

Part D: The Interference-Fringe Method.—By making some rather obvious changes, the Klett optical system may be modified for use in the interference-fringe method, as Longworth has done.⁸ Instead of using a step-filter in front of the camera plate as recommended by Longworth, we varied the exposure of the photographic plate by moving an opaque shield over the light source at a speed controllable by an electric motor. In this way a gradual change in the blackening of the photographic plate was obtained, or as many step-wise exposures as desired.

A piece of optical glass was mounted rigidly on the support plate of the schlieren lens in order to deflect¹⁰ upward slightly the light which passed through the two optical stops on the side of the cell. In this way a set of reference fringes was produced on the photographic plate about two millimeters above the normal undeviated image of the source slit. Duplicate measurements of the distance between the reference fringes and fringes produced by light passing through stops in front of the diffusion cell filled with distilled water agree on the average to ± 1.4 microns. On removing and then replacing the stops in front of the cell, the error rose to ± 1.8 microns. However, on comparing distances measured with the stops over the upper, middle and lower part of the diffusion cell, the deviation was ± 8 microns. This represents the resultant of optical imperfections in the water-bath windows, the cell windows and the schlieren lens. Tests showed that about half of this discrepancy was due to the cell windows so that optically flat cell windows were ordered. They did not arrive in time for this research. In actual practice, however, photographs of the slit image were taken with a fine slit width at an early stage of diffusion in each experiment using light passing near the center of the cell. In this case the error in estimating the distance between the reference fringes and the cell fringes is believed to be about ± 5 microns. As the distance between the undeviated image and the diffusion fringes varied in the useful range between one and five centimeters, an uncertainty of 5 microns amounts only to 0.05%.

One of the most difficult problems involved in the interference fringe method of diffusion constant determinations is the estimation of j_m values.¹⁶ Two methods were employed; in the first, we placed a brass plate with a double slit in it over the diffusion boundary so that the slit system straddled the boundary, and took photographs while the boundary was still very sharp, usually while the solutions were still flowing. The shift in the fringes from the position they would have had if both solutions had been identical divided by the distance between two fringes gave the fractional part of j_m . From a rough estimate of the number of fringe minima, using the j plus $3/4$ approximation (strictly valid only for the middle fringes), the integral part of j_m could be deduced. The second method gave j_m by an extrapolation procedure. By plotting the num-

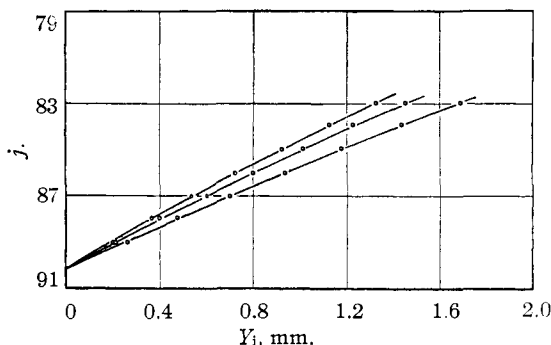


Fig. 5.—Run 11.

(16) We are using the symbols of Longworth⁸ and Kegeles and Gosting.⁹

ber of fringe minima, counting the lowest fringe minimum as zero, as a function of the distance from the undeviated slit image, by extrapolating the curve so obtained to the position of the undeviated slit image, and by adding unity, j_m was obtained. The theory as applied to the middle fringes would require the addition of 0.75 if valid for fringes near the undeviated image, but empirically more consistent values of C_t and better agreement between the two methods of estimating j_m resulted from the addition of unity. An example of the graphical method of estimating j_m is shown in Fig. 5 where Y_j is the distance from the undeviated slit image. From this graphical method j_m was estimated to be 91.1 ± 0.05 while from the Rayleigh interference method 91.1 ± 0.03 was obtained. Taking 91.1 for j_m , the values of C_t given in Table II were calculated. Except for some of the C_t data at the 60th fringe, the numbers are reasonably constant. It was not always possible to obtain such good agreement between the two methods of determining j_m . In such experiments, the j_m as obtained by the extrapolation procedure was the value adopted.

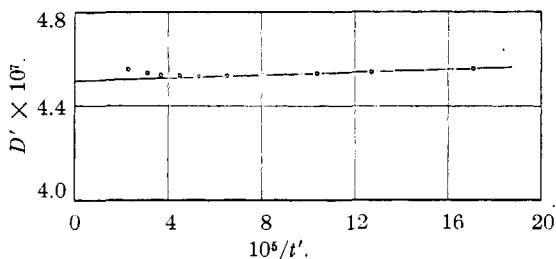


Fig. 6.—Run 11: 72.2% sucrose average concentration.

Following Longworth's procedure the diffusion constants, calculated from C_t , j_m and the optical constants of the equipment, were plotted as a function of $1/t'$ in order to determine whether any correction to t' for a slight mixing at the boundary at the start of the experiment should be applied. Figure 6 illustrates such a plot for the data of Table II.

TABLE II

C_t VALUES FOR EXPERIMENT NO. 11 AT 25°

c_1 , 71.79% sucrose; t' in seconds; c_2 72.62%

$t' \rightarrow$	5845	7885	9625	12,445	15,205	27,565
0	4.9285	4.2522	3.8502	3.3902	3.0671	2.2765
2	4.9298	4.2511	3.8500	3.3899	3.0664	2.2770
4	4.9307	4.2523	3.8501	3.3903	3.0680	2.2771
6	4.9276	4.2516	3.8492	3.3899	3.0671	2.2769
8	4.9309	4.2521	3.8497	3.3907	3.0679	2.2769
10	4.9311	4.2535	3.8510	3.3903	3.0672	2.2769
20	4.9321	4.2535	3.8519	3.3902	3.0683	2.2775
40	4.9296	4.2485	3.8498	3.3900	3.0680	2.2782
60	4.9275	4.2437	3.8425	3.3897	3.0659	2.2777
"Av." C_t	4.9300	4.2521	3.8500	3.3902	3.0673	2.2770
$D' \times 10^7$	4.557	4.541	4.538	4.526	4.526	4.530

The method of calculating D' from the C_t values making use of Airy integral tables was the same as that of Gosting and Morris.¹⁷

In addition to the constancy of the C_t values as a criterion of reliability of the data, another test of our results is to compare them with previously published determinations of Gosting and Morris. For this purpose we performed a special experiment in the low concentration range, using a 1.46% sucrose solution diffusing into pure water at 25°. Apparently there was a larger initial disturbance at the boundary than in most of our experiments (this test was made before a pressure equalizing groove was cut in the sliding cut-off of our new cell), but the C_t values became constant at the longer times and on

(17) L. J. Gosting and Margaret S. Morris, THIS JOURNAL, **71**, 1998 (1949).

extrapolation of the D' data to infinite time we obtained $5.174 \pm 0.005 \times 10^{-6}$ for D as compared to $5.178 \pm 0.0015 \times 10^{-6}$ calculated from Gosting and Morris's data at our average concentration. This extrapolation was carried out by means of an equation with constants determined by the least squares method.

Part E: Results of the Interference Fringe Method.—Experiments were carried out at 25 and 35° up to about 74% sucrose. At this concentration, which is about 6% more concentrated at 25° and 4.5% more concentrated at 35° than a saturated solution, crystallization difficulties began to interfere. We hope, however, to extend the concentration range in the future. Table III contains our final results. The values of Δt are the estimated corrections to the zero time to allow for the initial disturbance at the boundary.

TABLE III

DIFFUSION COEFFICIENTS OBTAINED BY THE INTERFERENCE-FRINGE METHOD

Concentration, wt. per cent. c_1	c_2	wt. per cent. $c_{av.}$	Moles H ₂ O/ mole sucrose	Δt , sec.	$D \times 10^7$ sq. cm./sec.
25°					
0	1.457	0.729	2587	231	51.74
60.61	61.48	61.05	12.1	251	10.71
65.77	66.66	66.22	9.69	0	7.80
70.05	70.82	70.44	7.97	90	5.42
71.79	72.62	72.21	7.31	68	4.51
74.15	74.84	74.50	6.50	398	3.14
35°					
60.61	61.48	61.05	12.1	144	15.88
65.49	66.41	65.95	9.81	12	12.00
70.00	70.79	70.40	7.99	213	8.61
71.77	72.63	72.20	7.32	39	7.33
72.38	73.16	72.77	7.11	114	6.70

Discussion of the Data

All of the significant data obtained in this research by both methods are plotted as a function of the weight per cent. of sucrose in Fig. 4. It is interesting to note how well the interference-fringe results fall on straight lines in contrast to the schlieren data which scatter somewhat more. In other words, the interference-fringe method gives diffusion coefficient values which are more accurate from the point of view of internal consistency than the schlieren method results. It should also be noted that the interference-fringe data are all lower by about one unit in the 1×10^{-7} diffusion coefficient units than the schlieren data. Because of the uncertainty in knowing where to select the maximum height in the schlieren photographs and because of the uncertainty in the measurements of the areas, we believe that the interference-fringe diffusion coefficient values are more correct on an absolute basis.

Also plotted in Fig. 4 is one result estimated from the graphs of Van Hook and Russell.² It is nearly three units higher than the interference-fringe values; any disturbances in the diffusion process through the porous disk, such as convection currents or mixing due to vibration would tend to increase D , so that we believe that our lower values of D are more reliable than the results of Van Hook and Russell.

Gosting and Morris¹⁷ demonstrated that the diffusion of sucrose molecules in dilute solution is a true diffusion process because of agreement of the observed data with diffusion coefficients calculated from the Gordon equation¹⁸

$$D = D_0 \left[1 + \frac{d \ln f}{d \ln c} \right] \eta_0 / \eta \quad (1)$$

whereas Van Hook and Russell² in their test of this equation in the concentrated range found that it gave values which were only a third to a fifth of the observed. Equation (1) contains two factors, a thermodynamic factor represented by the term in the brackets and a kinetic factor represented by the viscosity ratio η_0/η . To test equation (1) we have calculated η_0/η using viscosity data for sucrose solutions published by the National Bureau of Standards.¹⁹ The thermodynamic factor in terms of activity coefficients based on the molal concentration unit may be written in the equivalent forms

$$\left[1 + \frac{\log \gamma}{\log m} \right] \left[\frac{V}{n_1 \bar{V}_1} \right] \quad (2)$$

or

$$\partial \log m \gamma / \partial \log c \quad (3)$$

Scatchard, Hamer and Wood²⁰ have calculated the activity coefficients of sucrose in aqueous solutions up to saturation from isopiestic vapor pressure measurements. Using these activity coefficients and available density data,¹⁹ we have been able to compute the kinetic and thermodynamic factors necessary to test equation (1). Table IV contains the results of these calculations.

TABLE IV

m	Wt. % sucrose	η_0/η	$1 + \frac{\partial \log \gamma}{\partial \log m}$	$\frac{V}{n_1 \bar{V}_1}$	$D_{\text{calc.}} \times 10^7$ sq. cm./sec.
1.0	25.50	0.4085	1.208	1.236	32.0
2.0	40.64	.1634	1.386	1.454	17.2
3.0	50.66	.06652	1.560	1.673	9.08
4.0	57.79	.02782	1.691	1.894	5.22
5.0	63.12	.01193	1.791	2.115	2.36
6.0	67.25	.005245	1.840	2.337	1.18

Note that the decrease in the kinetic factor, η_0/η , with increase of concentration is considerably greater than the increase in the thermodynamic factor (2). The last column gives the calculated diffusion coefficients taking D_0 to be 52.3×10^{-7} at 25°.¹⁷

In Fig. 7 we have plotted our diffusion coefficients at 25° along with those of Gosting and Morris¹⁷ as a function of weight per cent. Although there is a long gap between our range of concentration and that of Gosting and Morris, the data of both investigations seem to fit very well on a smooth curve, leaving little uncertainty as to the change of the diffusion coefficient with

(18) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

(19) "Polarimetry, Saccharimetry and the Sugars," Circular C 440, National Bureau of Standards, Washington.

(20) G. Scatchard, W. J. Hamer and S. E. Wood, *THIS JOURNAL*, **60**, 3061 (1938).

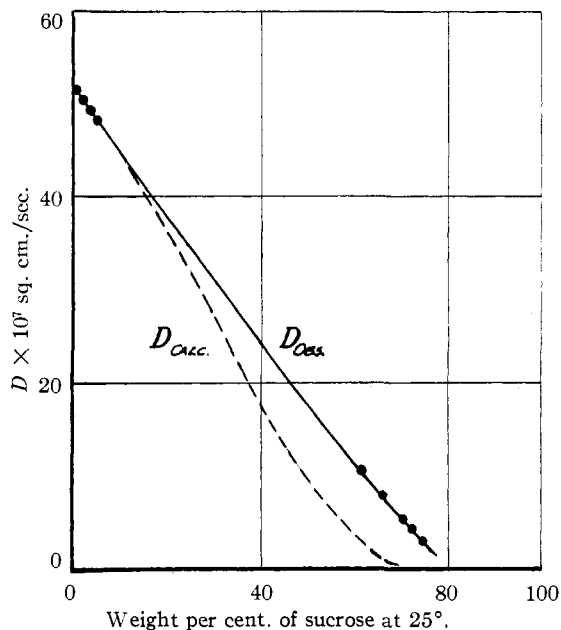


Fig. 7.

concentration up to 75% sucrose. Inasmuch as the curve extrapolates to zero for the diffusion coefficient at about 81% sucrose at both 25 and 35° (Fig. 4), it would be interesting to measure D in this range. (D may be vanishingly small if not exactly zero at 81% sucrose.) We hope to do this at a later date. The dotted line of Fig. 7 represents the diffusion coefficients calculated from Gordon's equation (1); the marked disagreement between the observed and calculated values at sugar concentrations 40% and higher is readily seen.

Gosting and Morris¹⁷ also make use of the Stokes-Einstein relation

$$D_0 = kT/6\pi\eta r \quad (4)$$

in discussing their data. If D_{33}/D_{25} is computed from equation (4) assuming r to remain constant, and if this result is inserted into equation (5), an activation energy of about 4600 cal./mole results. Our values of 7000 to 8000 cal./mole given below are considerably higher.

From activation energies we obtain another point of view in considering the diffusion data. Thus, from the equation

$$\Delta E_{\text{act}} = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{D_2}{D_1} \quad (5)$$

we can calculate the activation energy for the diffusion process and from the equation

$$\Delta E_{\text{act}} = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{\eta_2}{\eta_1} \quad (6)$$

a similar activation energy may be obtained for viscous flow at the same weight per cent. of sugar. The activation energies for these two processes are plotted as a function of the concentration in Fig. 8 where it can be seen that the higher the

concentration the more the activation energy for viscous flow deviates from that for diffusion.

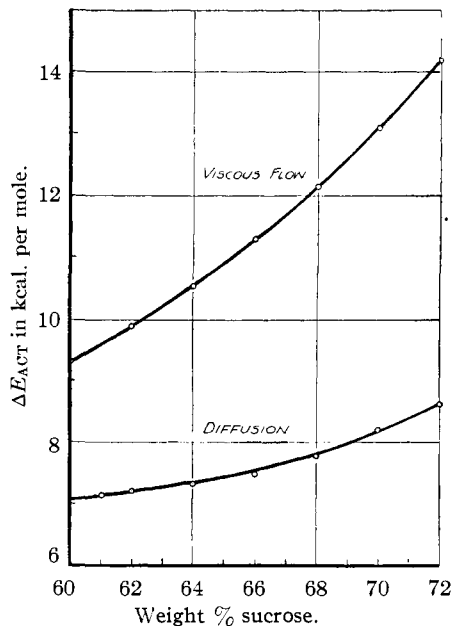


Fig. 8.

It is quite possible that the hydration of the sugar molecule is responsible for these discrepancies between observation and the theory valid for dilute solutions. The number of moles of water per mole of sucrose at 81 wt. per cent. where the curves of Fig. 4 extrapolate to zero diffusion coefficient is about 4.5. If these water molecules are bound so firmly to sugar molecules that they cannot diffuse, diffusion would no longer exist although viscous flow could still occur. Such a mechanism could explain a vanishingly small diffusion coefficient. However, in the range of concentrations studied, the diffusion coefficient is greater than that predicted by the Gordon equation. This must be the result of a diffusion mechanism which differs from that of viscous flow. Perhaps the water molecules are transferred through the solution by rotation of sugar molecules and the transfer of water from one sugar molecule to another in a sort of "Grotthus chain" transfer. In this way water could diffuse through the solution, without, however, having to displace the sugar molecules bodily, as presumably occurs in viscous flow.

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and Miss Jean Thomas of the University of Wisconsin for further details concerning construction and manipulation of their optical system and diffusion cell. Our thanks are also due to Mr. Stanley Cassid, instrument maker, for many helpful suggestions and for his careful construction of our diffusion cell.

Summary

1. The diffusion coefficient of sucrose in highly concentrated and supersaturated solutions has been measured at 25 and 35° by two optical methods, the usual schlieren method and the new Gouy interference-fringe method. The latter

method gave more accurate results from the standpoint of internal consistency and on an absolute basis also, we believe.

2. A new diffusion cell is described.

3. The diffusion coefficients decrease linearly with increase in weight per cent. of sucrose extrapolating to zero at 81% sugar at both temperatures, but they are all higher by 5–10 fold than diffusion coefficients calculated from Gordon's equation. We believe this to be due to a possible difference in mechanism between the viscous flow and diffusion processes as the solution becomes highly concentrated.

EVANSTON, ILLINOIS

RECEIVED OCTOBER 10, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Kinetics of Hydrolysis of β -Propiolactone in Acid, Neutral and Basic Solutions¹

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The hydrolysis of lactones to give hydroxy acids is usually considered to be a typical case of ester hydrolysis. This appears to be valid for γ -lactones which give the expected hydroxide ion and acid catalyzed reactions. However with β -lactones an added reaction with water enters.² With β -butyrolactone Olson and co-workers^{3,4} have shown that the hydrolysis in basic and in strongly acid solutions results in the expected acyl-oxygen fission and retention of configuration of the β -carbon. However, in the pH range of from 1 to 7 the only observable reaction is a pH independent hydrolysis which splits the alkyl-oxygen bond and inverts the configuration of the β -carbon.

Since Olson and co-workers were primarily interested in the mechanisms of the hydrolysis of β -butyrolactone they did not investigate the kinetics very fully. This is particularly true of the acid catalyzed reaction. Consequently we have investigated the hydrolysis of the related β -propiolactone in acid, basic and neutral solutions with emphasis on the temperature coefficients of the reactions and on the kinetics of the acid catalyzed reaction. The reactions of β -propiolactone with hydroxide ion and water have been studied at 25° by Johansson²; the acid catalyzed hydrolysis has not been previously investigated.

Materials and Procedures.—The β -propiolactone used in these studies was obtained from the B. F. Goodrich Chemical Company. It was stored at 5° and from 30 to 50 ml. were redistilled at reduced pressure from time to time. Its freezing point was found to be -33.4°. Its equivalent weight was determined by addition of excess base

and back titration with acid and was found to be 71.93, indicating a purity of 99.8% or better.

Since the β -propiolactone has a marked tendency to polymerize,⁵ preliminary tests were made to see if this would complicate the hydrolysis experiments. It was concluded that in the dilute (not over 0.1 molar) aqueous solutions used in these studies, the polymerization was too slow to be of any consequence.

The study of the bimolecular reaction of the β -lactone with hydroxide ion was followed by a conductivity method similar to that used by Hegen and Wolfenden.⁶ The cells were typical conductivity cells with platinized platinum electrodes. They were kept at constant temperature by using a regulated oil-bath. The conductivity bridge was a somewhat simplified version of the Jones bridge. All conductivity studies were made with carbon dioxide-free solutions.

The equation used to calculate the rate constant is⁶

$$k_b = \frac{(R_2 - R_1)(R_\infty - R_0)R_\infty}{a(t_2 - t_1)(R_\infty - R_2)(R_\infty - R_1)R_0}$$

where a is initial concentration of base and lactone in moles per liter and R_0 , R_1 , R_2 and R_∞ are measured resistances at times 0, t_1 , t_2 and ∞ , respectively. R_0 was taken as the resistance of a solution of sodium hydroxide of concentration a . R_∞ was determined in two ways. In some cases the conductivity cell for the rate experiment was removed from the bath, kept at room temperature overnight and then brought back to bath temperature and the resistance measured. In other cases solutions identical with those for the rate experiments were made up at room temperature, permitted to react for several hours, put into the conductivity cell, brought to temperature and

(1) Presented in part at the 116th meeting of the American Chemical Society, Atlantic City, N. J., Sept. 19–23, 1949.

(2) Johansson, *Chem. Zentr.*, **87**, 11, 558 (1916).

(3) Olson and Miller, *THIS JOURNAL*, **60**, 2687 (1938).

(4) Olson and Hyde, *ibid.*, **63**, 2359 (1941).

(5) Gresham, Jansen and Shaver, *ibid.*, **70**, 998 (1948).

(6) Hegen and Wolfenden, *J. Chem. Soc.*, 508 (1939).