Acknowledgment.—The work reported in this paper was supported by a grant from the government.

Summary

The solubility products of cupric trihydroxychloride, sulfate and nitrate are determined in the corresponding potassium salt solutions at 25°.

It has been shown that cupric oxide is stable in dilute cupric perchlorate solutions with moderate sodium perchlorate concentrations. On the basis of this it has been possible to determine the solubility product of cupric oxide directly with the aid of pH measurements. The solubility product of cupric hexahydroxyperchlorate, stable in more concentrated cupric and sodium perchlorate solutions, is also measured.

The precipitation curve of cupric ion with alkali hydroxide is further studied. As a new result it may be mentioned that the cupric trihydroxynitrate first precipitated from the dilute cupric nitrate solution turns into cupric oxide before the corresponding end-point of the titration.

The equilibrium in the presence of two solid phases, hydroxysalt and oxide, is further interpreted by means of the solubility products.

HELSINKI, FINLAND RECEIVED MAY 19, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Diffusion Studies on Dilute Aqueous Sucrose Solutions at 1 and 25° with the Gouy Interference Method[1]

BY LOUIS J. GOSTING AND MARGARET S. MORRIS

The recent revival[2,3] of interest in the Gouy interference phenomenon[4] as a means of studying diffusion in liquid systems may be ascribed to its inherent sensitivity to the refractive index gradient of a diffusion boundary. In this country the development of theory[5] and apparatus[6,7] for the Gouy interference method for diffusiometry has emphasized increased precision, while other workers[3] have stressed a significant increase in speed of measurement.

The purposes of this research were to test further the theory of this method and with its aid to measure the diffusion coefficients of sucrose as functions of the concentration at 1 and 25°. In this method the cell, in which an initially sharp boundary between solution and solvent spreads by diffusion, is placed in the path of light from a lens that is illuminated with monochromatic light from a horizontal slit, and the interference fringes formed in the focal plane of the lens are photographed at intervals. In the evaluation of the diffusion coefficient, D, from the spacing of the fringes at a given time after the formation of the boundary, two essential parameters to be evaluated are the position, Y^0, of the undeviated slit image, *i. e.*, the image formed when the cell is filled with homogeneous solution, and the total number, j_m, of fringes in the pattern. Since j_m is a compound number, of which only the integral part, I, is obtained directly from the number of fringes in the pattern, it is necessary to evaluate the fractional part, F, independently. In the present research both Y^0 and F have been obtained with the aid of Rayleigh double slits as will be described below, and an independent check on F was made using a separate refractometer cell.

In addition to the foregoing refinements in experimental procedure, improved interference conditions are derived for the lower fringes.

Experimental

Preparation of Solutions.—Merck reagent grade sucrose, weighed by difference, was dissolved and diluted volumetrically with water at the temperature of measurement. Since refractometric data at 1° presented below indicated that variation in the amount of dissolved air could introduce appreciable errors, standard treatment of each sample of doubly-distilled water included saturation with air near the temperature at which it would be used. The computed weight *in vacuo* of the sucrose was taken as its dry weight when computing concentrations since a sample lost less than 0.01% in weight during evacuation for a week over phosphorus pentoxide. The volumetric flasks used to make up solutions for diffusion and viscosity determinations had been calibrated within about 0.01%, with correction made for thermal expansion between the two temperatures. All solutions were used promptly after their preparation.

Diffusion Procedure.—Only a brief discussion of the equipment and experimental procedure will be given here as a detailed description is presented elsewhere.[7] Green light from a mercury AH4 lamp illuminated the horizontal source slit which was focused, through a constant temperature water-bath regulating to about ±0.005°, on a photographic plate by means of a 170 cm. focal length compound lens. In the converging light through the bath was placed a tall center section Tiselius cell[8,9,10] which served as the diffusion cell. The boundary between solution and solvent (or less concentrated solution) was shifted to the center of the section and sharpened at the optic axis by withdrawing liquid from the cell through a capillary inserted to this level as suggested by Polson.[11] To ensure attainment of maximum boundary sharpness with the flow rates of from 1.0 to 1.6 ml. per minute used, at least 75 ml. of liquid were withdrawn in each experiment.

---

(1) Including material presented at the Meeting of the American Chemical Society, April 22, 1948, Chicago, Illinois.

(2) Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).

(3) Coulson, Cox, Ogston and Philpot, *Proc. Roy. Soc. (London)*, **A192**, 382 (1948).

(4) Gouy, *Compt. rend.*, **90**, 307 (1880).

(5) Kegeles and Gosting, THIS JOURNAL, **69**, 2516 (1947).

(6) Longsworth, *ibid.*, **69**, 2510 (1947).

(7) Gosting, Hanson, Kegeles and Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(8) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(9) Longsworth, *Ann. N. Y. Acad. Sci.*, **41**, 267 (1941).

(10) Longsworth, *Chem. Revs.*, **30**, 323 (1942).

(11) Kahn and Polson, *J. Phys. Colloid Chem.*, **51**, 816 (1947).

The fractional part, F, of the total number of fringes, j_m, was measured during the boundary sharpening process by modifying the optical system so that it served as a form of Rayleigh interferometer. This conversion consisted simply of sliding a mask, with two horizontal slits of about 1 cm. separation, in line with the cell so that the slits were symmetrically spaced above and below the optic axis. Thus with the sharpened boundary on the optic axis, light from the lower slit traversed pure solution while light from the upper slit passed through pure solvent. At the photographic plate the downward displacement of the Rayleigh interference fringes within the fixed central diffraction envelope, compared with their position when pure solution was in front of both slits, should have given the fractional part, F, of j_m. However, photographs taken during the boundary sharpening procedure could not be compared directly with each other since random relative movement of optical elements in the system exceeded the tolerance of about 0.001 mm. This difficulty was overcome by taking a reference picture immediately before or after each refractometric and diffusion photograph and making each measurement relative to that reference. The reference picture consisted of the Rayleigh fringes from a double slit adjacent to the cell so that light forming these fringes passed only through bath-water. In this Rayleigh pattern the center of the central bright fringe corresponded to the position of the center of the image of the source slit. A light weight vane on the frame supporting the cell could be turned to cover either the cell or the reference Rayleigh slits, while superposition of fringe systems at the photographic plate was prevented by simultaneous movement of a mask designed to expose adjacent vertical strips of the plate as desired.

It was found that the Rayleigh fringes of the reference were not quite in alignment with the Rayleigh fringes from the cell when filled with homogeneous solution. Therefore measurements of the fringe fraction, F, were further improved by determination of a zero correction for the reference immediately after the boundary sharpening capillary was inserted. This zero correction, consisting of the vertical displacement of reference Rayleigh fringes from those obtained through the cell containing homogeneous solution, may be attributed to the capillary and to slight prismatic effects in the cell and/or bath windows. On adding the small reference zero correction algebraically to fringe displacements from the references for the 6 to 8 photographs taken during the boundary sharpening procedure, and dividing the corrected average downward displacement by the fringe width, the fringe fraction, F, was obtained with an average deviation of about 0.01 fringe.

The corresponding correction, δ, for the diffusion Rayleigh reference pattern was determined before inserting the capillary when the cell center section was in its diffusion position. A double slit of about 3.3 mm. vertical separation was placed on the optic axis behind the cell, and the upward displacement of the center of the central bright fringe in this pattern from the center of the central bright fringe in the reference pattern was determined. Figure 1 presents these values of δ as a function of concentration of homogeneous sucrose solution in the cell for the 1° experiments. A similar plot of δ was made for the 25° experiments, though the data for the two temperatures agreed within 2 microns. All values of Y_j in the experiments reported below consist of the sum of δ, for that concentration and temperature, and the measured displacement of each diffusion fringe below the slit image position, $Y^0 - \delta$, given by the reference.

The first diffusion photograph of each experiment was taken soon after the fringe system was completely in view. This was followed by additional pictures, usually taken after successively longer intervals of time, until the product of the time and the diffusion coefficient of the material was about 0.10 cm.^{2}. Tri-X Panchromatic plates, Type B, were used for early photographs, while later pictures were taken on these or on the slower Kodaline CTC Pan plates.

The Refractometer Cell.—In order to test for possible small errors in F, owing to edges of the boundary overlapping the Rayleigh slits, solutions from several diffusion determinations were studied in an auxiliary cell designed to eliminate contact between solutions being compared.[12] For these experiments the diffusion cell and mask were merely replaced in the optical system by the auxiliary refractometer cell with its accompanying double slit mask, and the optical principles of the modified Rayleigh interferometer[3,5] were applied.

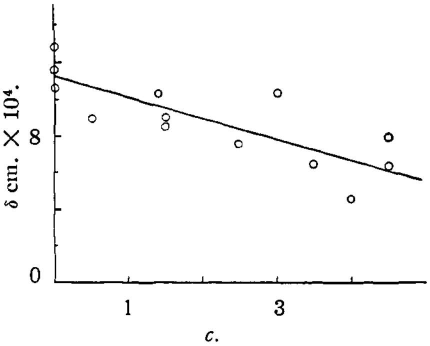

Fig. 1.—Measured values of δ at 1° as a function of the sucrose concentration, c, expressed as g. per 100 ml. of solution.

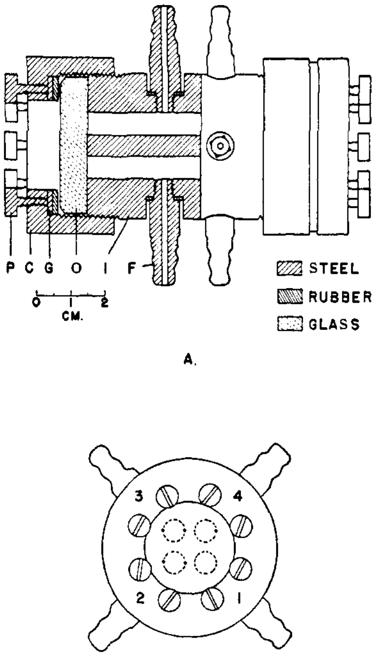

Fig. 2.—Auxiliary refractometer cell: P, pressure screw; C, screw cap; G, guard ring; O, optical flat; I, insert; F, filler screw.

In the diagram, Fig. 2a shows the cell viewed lengthwise from a 45° angle with the horizontal and partly bisected, and Fig. 2b affords a front view, as seen from the photographic plate. All metal parts were machined from 18–8 stainless steel and then made passive by heating at 80°

---

[12] This general type of cell was proposed by Dr. Gerson Kegeles. Similar cells have been used by McBain, Ford and Mills, *Rev. Sci. Instruments*, **7**, 341 (1936), and Claesson, *Arkiv. Kemi, Mineral., Geol.*, **23A**, No. 1 (1946).

for two hours in concentrated nitric acid.[13] Gum rubber tubing connected the cell chambers 1, 2 and 3, and permitted closure of chambers 1, 3 and 4. In the experiments reported, chambers 1, 2 and 3 were filled with the denser of the solutions that had been prepared for the diffusion experiment, and chamber 4 was filled with the corresponding lighter solution or water. Thus the interference fringes formed by light from the double slits immediately behind chambers 2 and 3 constituted a reference,[7] while fringes from light passing through 1 and 4 were displaced downward through a distance related to j_m in a manner given under "Refractometer Cell Results."

Density and Viscosity Determinations.—Specific gravities were obtained by determining the loss in weight of a 3 ml. Pyrex bob suspended in the solutions and in water and were used to compute absolute densities from the accepted density of water at the same temperature. Flow times from an Ostwald viscometer were converted to relative viscosities after correcting in each case for the small kinetic energy term.

Equations and Improved Interference Conditions

The general theory[5] for the Gouy interference method for diffusiometry showed that the fringe displacement equation

$$Y_j = \{ab(n_s - n_0)/(2\sqrt{\pi Dt})\}e^{-z_j^2} \qquad (1)$$

could be used to determine the diffusion coefficient, D, for an ideal diffusion. Here Y_j represents the displacement below the undeviated slit image of the jth intensity zero or maximum, when the lowest maximum and minimum are each assigned the number zero. Thickness of the diffusion cell along the direction of the light path is denoted by a, while b represents the optical distance from the center of the diffusion cell to the photographic plate, and n_s and n_0 are the refractive indices, referred to vacuum, of the original liquids below and above the initial boundary, respectively. The time since the formation of the infinitely sharp initial boundary is denoted by t, and the "reduced height," z, in the cell is related to the actual height, x, by $z = x/2\sqrt{Dt}$.

Letting λ denote the wave length *in vacuo* of the light used, the total number, j_m, of fringes in the system is defined as

$$a(n_s - n_0)/\lambda = j_m = I + F \qquad (2)$$

where I represents the integral part and F the fractional part of j_m. Then denoting the maximum downward displacement of light at the photographic plate *if the light followed geometrical optics* by C_t, where[5,6]

$$C_t = j_m\lambda b/(2\sqrt{\pi Dt}) \qquad (3)$$

equation (1) becomes

$$Y_j = C_t\,e^{-z_j^2} \qquad (4)$$

For an ideal diffusion, C_t computed from this equation should be constant at a given time for all fringes of the system.

The remaining quantity, $e^{-z_j^2}$, needed to solve for C_t (or D) from each fringe has been obtained from a table of $e^{-z_j^2}$ *versus* a function, $f(z_j)$,[14] after values of $f(z_j)$ were obtained from the simple approximate interference conditions[5]

$$(j + 3/4) \cong j_m f(z_j) = v_m/\pi \qquad j = 0,1,2\ldots \qquad (5)$$

for intensity zeros and

$$(j + 1/4) \cong j_m f(z_j) = v_m/\pi \qquad j = 0,1,2,\ldots \qquad (6)$$

for intensity maxima. Here v_m is the maximum in the phase difference function, v, when plotted against z.

Interference Conditions from the Airy Integral.—Calculation of more nearly exact interference conditions for the lower fringes[15] is possible now that extensive tables of the Airy integral,

$$Ai(u) = (1/\pi)\int_0^\infty \cos\left(\tfrac{1}{3}p^3 + up\right)\mathrm{d}p \qquad (7)$$

its zeros, and its turning values have become available.[16]

It follows from the previous theory[5] that the relative intensity, I_Y, at any level in the fringe system a distance Y below the undeviated slit image is given by the proportionality

$$I_Y \propto \left[\int_0^\infty \cos v\,\mathrm{d}z\right]^2 \qquad (8)$$

when diffraction from the masks at the ends of the cell is neglected. Now let V denote a cubic in z

$$V = g(\tfrac{1}{3}z^3 + hz) \qquad (9)$$

which may be made to fit any true phase difference function, v, at (0,0) and at its maximum by suitable adjustment of the negative constants g and h.[17] By defining u and p such that $z = p/\sqrt[3]{g}$ and $hg^{2/3} = u$, equation (9) reduces to

$$V = \tfrac{1}{3}p^3 + up$$

corresponding to the form of the Airy integral. The maximum, V_m, in this function is seen to be

$$V_m = (2/3)(-u)^{3/2} = v_m \qquad (10)$$

Table III of the Airy integral tables[16] lists values of u which give the first 50 zeros and turning values of $Ai(u)$. Since the fringe system intensity integral (equation (8)) is also of this form, within the limits of error of curve-fitting v with V, and since the curve-fitting procedure has made V_m exactly equal to v_m, these values of u provide accurate interference conditions for the

---

(13) Edsall, *et al.*, *Rev. Sci. Instruments*, **15**, 243 (1944).

(14) $f(z_j) = (2/\sqrt{\pi})\int_0^{z_j} e^{-\beta^2}\,\mathrm{d}\beta - (2/\sqrt{\pi})z_j\,e^{-z_j^2}$

(15) Equations (5) and (6) were derived by approximating the phase difference function, $v = v(z)$, by parabolas fitting at their maxima and then assuming that the Fresnel integrals, $C(\sqrt{2v_m/\pi})$ and $S(\sqrt{2v_m/\pi})$, were both equal to one-half. As one goes to lower minima and maxima the value of v_m decreases and the latter assumption becomes increasingly inaccurate. Furthermore, as indicated by equation (26) and associated discussion in the original report (ref. 5), v is more nearly a cubic than a quadratic for these fringes. Consequently, interference conditions calculated from the Airy integral may be expected to be more accurate for the lower fringes than those given by equations (5) and (6).

(16) "The Airy Integral," British Association for the Advancement of Science Mathematical Tables, Part-Volume B. University Press, Cambridge, 1946.

(17) This treatment differs from that of Coulson and Philpot (ref. 3) who expanded the phase difference function so their cubic expression has the same slope at the origin as the true v function. In the present treatment V is made to fit v at its maximum because the greatest contribution to the intensity comes from that region.

lower fringes. Values of $v_m/\pi = (2/3\pi)(-u)^{3/2}$ are tabulated as Z_j and M_j for a number of fringe system intensity zeros and maxima, respectively, in Table I. Combining the exact parts of equations (5) and (6) with these results gives the final form of the interference conditions derived from the Airy integral.

TABLE I

AIRY INTEGRAL REFINEMENT OF THE "QUARTER WAVE" APPROXIMATION FOR THE INTERFERENCE CONDITIONS

M_j and Z_j correspond to maxima and minima, respectively.

j	M_j	Z_j
0	0.21822	0.75867
1	1.24229	1.75395
2	2.24565	2.75254
3	3.24698	3.75187
4	4.24769	4.75148
5	5.24813	5.75122
6	6.24843	6.75104
7	7.24864	7.75091
8	8.25881	8.75080
9	9.24894	9.75072
10	10.24904	10.75065
12	12.24920	12.75055
14	14.24931	14.75048
16	16.24939	16.75042
18	18.24946	18.75038
20	20.24951	20.75034
22	22.24956	22.75031
24	24.24959	24.75028
26	26.24962	26.75026
28	28.24965	28.75024
30	30.24967	30.75023
40	40.24976	40.75017

$$f(z_j) = Z_j/j_m \qquad j = 0,1,2,\ldots \tag{11}$$

for intensity zeros, and

$$f(z_j) = M_j/j_m \qquad j = 0,1,2,\ldots \tag{12}$$

for intensity maxima. The fact that these relations become nearly identical with equations (5) and (6) for large values of j indicates that for this region the true v functions need not be fitted exactly to give accurate results. Furthermore, the values in Table I may be used to indicate the smallest value of j for which the "quarter wave" approximations illustrated by equations (5) and (6) are sufficiently accurate for a particular experiment.

Zero-Time Correction.—Since the infinitely sharp initial boundary required for rigorous application of the equations cannot be obtained experimentally, the observed time after formation of a boundary is denoted by t'. Then a small constant increment, Δt, is added[6] to t' to approximate the time, t, at which the boundary was apparently formed.

$$t = t' + \Delta t \tag{13}$$

A diffusion coefficient, D', is computed by using t' in equation (3).

$$D' = (j_m^2\lambda^2 b^2)/(4\pi C_t^2 t') \tag{14}$$

The true diffusion coefficient, D, is related to D' by the expression

$$D' = D(1 + \Delta t/t') \tag{15}$$

and D and Δt are readily obtained from a plot of D' *vs.* $1/t'$.

Results

For each experiment values of $f(z_j)$ were determined for intensity zeros from equation (11) by using Table I and the value of j_m obtained by adding the Rayleigh value of F to the integer, I, determined by the number of fringes observed in the diffusion pattern.[7] Corresponding values[18] of $e^{-z_j^2}$, together with the values of Y_j[19] for those fringes, were inserted in equation (4) to compute C_t. To obtain D' from any photograph an average value of C_t was calculated from the lower minima and inserted in equation (14), together with the values $\lambda = 5462.2 \times 10^{-8}$ cm. and $b = 306.45$ cm. for 1° or $b = 305.55$ cm. for 25°. Since no fringes higher than $j/j_m = 0.25$ were used to determine diffusion coefficients, the calculation procedure corresponds to the conventional height and area method. Fringe numbered zero was also omitted from each average since its broad, unsymmetric, nature may result in loss of accuracy.

The calculations for a typical diffusion fringe photograph are illustrated in Table II by data from a picture from a 1° experiment. When the

TABLE II

ILLUSTRATIVE DIFFUSION DATA AT 1.00°

$c_0 = 3.0034$[a] $j_m = 100.21$
$c_s = 4.5052$[b] $t' = 20280$ sec.

j	Y_j, cm.	C_t, cm.
0	2.1016	2.2037
1	2.0251	2.2031
2	1.9645	2.2044
4	1.8604	2.2037
6	1.7720	2.2039
8	1.6918	2.2029
10	1.6193	2.2035
12	1.5510	2.2030
14	1.4868	2.2025
16	1.4263	2.2027
18	1.3684	2.2025
20	1.3130	2.2023
30	1.0652	2.2027
40	0.8517	2.2026
50	.6632	2.2023
60	.4948	2.2023
70	.3437	2.2018
80	.2085	2.199
90	.0904	2.199

$$D' = 2.274_8 \times 10^{-6}$$

[a] c_0 = g. sucrose per 100 ml. solution above the initial boundary. [b] c_s = g. sucrose per 100 ml. solution below the initial boundary.

---

(18) An enlarged form of Table I of ref. (5) has been computed by Dr. Gerson Kegeles and was very useful in evaluating $e^{-z_j^2}$ from $f(z_j)$.

(19) Corrected with the factor (δ) as described under "Diffusion Procedure."

values of D' for all photographs of this experiment were plotted against $1/t'$, the graph shown in Fig. 3 was obtained. On determining the best straight line through these points by the method of least squares, the intercept gave a value of 2.2704×10^{-6} for D while the slope, $D\Delta t$, indicated that Δt was thirty-five seconds.

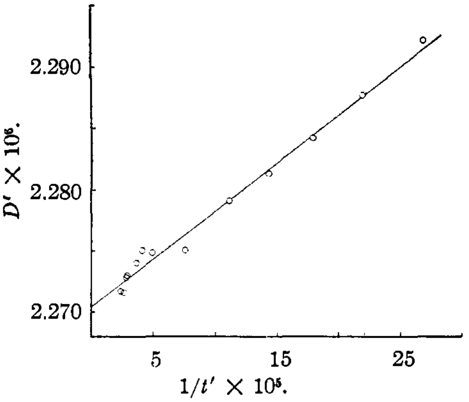

Fig. 3.—The calculated diffusion coefficient, D', at 1.00° as a function of the reciprocal of the experimental time, t': $c_0 = 3.0034$, $c_s = 4.5052$, $j_m = 100.21$.

A value of D for each experiment was obtained in this manner and these values at 1° are tabulated in column 7 of Table III and at 25° in the same column of Table IV. The average deviation of experimental points about each straight line of D' *vs.* $1/t'$ is given in column 8 of each table. The sharpness of the starting boundaries is illustrated by the low values of the zero time correction, column 5. Subsequent data showed that sharpening with a two-prong capillary resulted in a zero time correction of about one-third the value obtained with a single capillary, while the value of D was not appreciably affected.

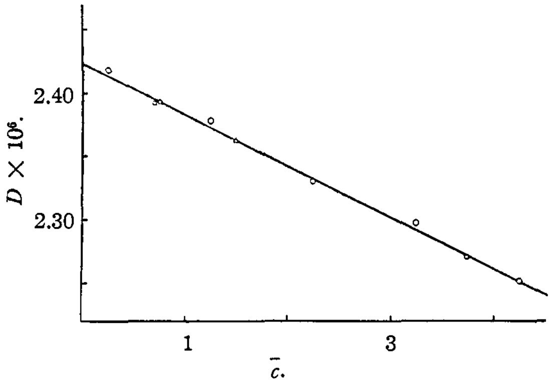

Fig. 4.—D at 1.00° as a function of the average sucrose concentration of each experiment: ○, $\Delta c \cong 0.5$; □, $\Delta c \cong 1.5$; Δ, $\Delta c \cong 3.0$.

A plot of the values of D at 1° against the average concentration, $\bar{c} = (c_0 + c_s)/2$, is shown in Fig. 4. It is of interest that these 1° data corresponding to concentration increments of approximately 1.5 and 3.0 lie on the line determined by 0.5-increment experiments within the experimen-

TABLE III

DIFFUSION COEFFICIENTS AND SPECIFIC REFRACTIVE INCREMENTS FOR SUCROSE AT 1.00°

1 Δc[a]	2 $\bar{c}$[b]	3 j_m	4 $(\Delta n/\Delta c) \times 10^6$	5 Δt, sec.	6 No. of photos	7 $D \times 10^6$ sq. cm./sec.	8 Av. dev., %
0.5004_2	0.2502_1	33.44	1468.9 ± 1.4	19	15	2.418	0.10
$.5004_6$	1.2513	33.44	1468.8 ± 2.0	21	21	2.378	.10
.5008	2.2521	33.41	1466.5 ± 2.6	30	20	2.330	.08
.5012	3.2539	33.46	1467.5 ± 3.2	17	21	2.297	.08
.5011	4.2551	33.40	1465.1 ± 3.8	24	21	2.251	.08
1.4017	0.7008_6	93.64	1468.5 ± 0.8 (1468.6 ± 0.6)[c]	26	18	2.392_0	.023
1.5009	0.7504_7	100.26	1468.4 ± 0.8 (1468.1 ± 0.6)[c]	24	14	2.392_8	.029
1.5020	0.7509_8	100.33	1468.4 ± 0.8	30	11	2.393_7	.046
1.5018	3.7543	100.21	1466.8 ± 1.4 (1465.8 ± 1.2)[c]	35	13	2.270_4	.023
3.0037	1.5018	200.64	1468.3 ± 0.7 (1468.2 ± 0.5)[c]	29	9	2.362_0	.014

[a] $\Delta c = c_s - c_0$. [b] $\bar{c} = (c_s + c_0)/2$. [c] Data from the refractometer cell.

TABLE IV

DIFFUSION COEFFICIENTS AND SPECIFIC REFRACTIVE INCREMENTS FOR SUCROSE AT 24.95°

1 Δc	2 $\bar{c}$	3 j_m	4 $(\Delta n/\Delta c) \times 10^6$	5 Δt, sec.	6 No. of photos	7 $D \times 10^6$ sq. cm./sec.	8 Av. dev., %
1.5014	0.7506_8	97.74	1430.7 ± 0.8	22	10	5.170	0.040
1.5016	1.0011	97.76	1430.8 ± 0.9	15	11	5.148	.045
1.5016	2.2521	97.69	1429.8 ± 1.1	21	10	5.049	.049
1.5018	3.7535	97.68	1429.4 ± 1.3	17	9	4.934	.043
1.5025	5.2546	97.72	1429.3 ± 1.5	18	11	4.821	.044

TABLE V

AVERAGE VALUES OF $C_t\sqrt{t' + \Delta t}$[a] FOR 1° EXPERIMENTS WITH THE GREATEST DEVIATION FROM IDEALITY

	$\Delta c = 0.5012$ $\bar{c} = 3.2539$			$\Delta c = 1.5009$ $\bar{c} = 0.7504_7$		
1 j	2 δ[b] $= 0.0007$ $j_m = 33.46$	3 $\delta = 0.0007$ $j_m = 33.44$	4 $\delta = 0.0010$ $j_m = 33.44$	5 $\delta = 0.0010$ $j_m = 100.26$	6 $\delta = 0.0010$ $j_m = 100.24$	7 $\delta = 0.0013$ $j_m = 100.24$
0	104.28 ± 0.05	104.28	104.32	306.17 ± 0.06	306.17	306.21
1	104.25 ± 0.04	104.25	104.29	306.11 ± 0.06	306.11	306.15
2	104.25 ± 0.05	104.26	104.31	306.12 ± 0.06	306.12	306.16
4	104.27 ± 0.05	104.29	104.35	306.09 ± 0.05	306.09	306.14
6	104.25 ± 0.06	104.27	104.33	306.05 ± 0.05	306.05	306.10
8	104.21 ± 0.06	104.24	104.31	306.04 ± 0.10	306.05	306.10
10	104.19 ± 0.06	104.23	104.31	306.05 ± 0.08	306.06	306.11
12	104.19 ± 0.06	104.25	104.34	306.06 ± 0.10	306.07	306.13
14	104.16 ± 0.08	104.22	104.33	306.03 ± 0.08	306.04	306.10
16	104.10 ± 0.06	104.18	104.30	306.02 ± 0.06	306.04	306.10
18	104.04 ± 0.08	104.14	104.29	305.98 ± 0.06	306.00	306.06
20	103.99 ± 0.12	104.11	104.29	305.99 ± 0.07	306.03	306.10
24	103.73 ± 0.21	103.95	104.23			
28	102.7 ± 0.47	103.5	104.1			
30				305.97 ± 0.10	306.02	306.10
40				305.89 ± 0.13	305.95	306.05
50				305.93 ± 0.20	305.99	306.12
60				305.79 ± 0.18	305.90	306.09
70				305.71 ± 0.25	305.81	306.06
80				305.5 ± 0.39	305.8	306.2
90				304.4 ± 1.13	305.1	306.1

[a] Abbreviated in text to $C_t\sqrt{t}$. [b] δ values are given in cm.

tal error of the latter. Therefore, it appears that no detectable errors due to boundary skewness have occurred and the higher precision of the former experiments may be utilized. The equation

$$D = 2.423_4(1 - 0.0167_1c) \times 10^{-6} \qquad (16)$$

was found by the method of least squares to represent the best straight line through these 1.00° data after weight factors of 1, 3 and 6 were assigned to data from experiments with Δc in the neighborhood of 0.5, 1.5 and 3, respectively. The average deviation of all experimental points from this line is 0.10%. The corresponding equation for the 24.95° experiments is

$$D = 5.226(1 - 0.0148_0c) \times 10^{-6} \qquad (17)$$

with an average deviation of 0.04%.

Specific refractive increments, $\Delta n/\Delta c$, were calculated from equation (2) after setting $n_s - n_0 = \Delta n$ and finding $a = 2.4854 \pm 0.0007$ cm. at 25° by using a bar and microscope as described by Longsworth.[20] The value of a at 1° was computed to be 2.4849 cm. Estimates of the *maximum* error of these values of $\Delta n/\Delta c$, given in columns 4, were made by assuming an error of 0.02 fringe in j_m, 0.01% in each volume measurement, and 0.03% in a. It should be noted that within the range of concentration studied $\Delta n/\Delta c$ is quite constant, so the refractive index of sucrose solutions at both temperatures is very nearly a linear function of solute concentration expressed as weight per unit volume of solution.

Confirmation of the Theory.—The work of Longsworth provided the first confirmation of the theory of this method for studying diffusion by showing that C_t calculated from equation (4) was constant for each fringe of a given picture after j_m and the undeviated slit image position had been suitably adjusted within reasonable limits. Since the present apparatus[7] allows direct measurement of these two quantities to within 0.02 fringe and 0.003 cm., or better, respectively, the data from the 1° experiments were carefully analyzed and provide even more conclusive confirmation of the theory.

It is seen from equation (3) that the product, $C_t\sqrt{t}$, should be constant for all fringes throughout an experiment. Thus as soon as the zero time correction, Δt, was determined for a diffusion, the values of $C_t\sqrt{t' + \Delta t}$ (henceforth denoted simply as $C_t\sqrt{t}$) for a given fringe in all the pictures could be averaged to eliminate random errors, and the constancy of these averages, *i. e.*, $\overline{C_t\sqrt{t}}$, for representative fringes could be investigated. Compared with the figures for $\overline{C_t\sqrt{t}}$ at $j = 0.06j_m$, the $\overline{C_t\sqrt{t}}$ values at $j = 0.5j_m$, $0.6j_m$, $0.7j_m$, and $0.8j_m$ were lower by 0.05 ± 0.04%, 0.11 ± 0.07%, 0.21 ± 0.13%, and 0.40 ± 0.26%, respectively. These percentage decreases are unweighted averages of all the 1° experiments.

Table V has been compiled to provide another estimate of the precision within which these data

---

(20) Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

conform to the theory and also to emphasize the importance of accurate experimental measurements of j_m and the undeviated slit image position. Those experiments showing the strongest $\overline{C_t\sqrt{t}}$ drifts encountered in the concentration increment ranges $\Delta c = 0.5$ and $\Delta c = 1.5$ were chosen for this table. The $\overline{C_t\sqrt{t}}$ values for selected fringes are presented in columns 2 and 5, together with the corresponding average deviations from the mean. Columns 3 and 6 list these data recalculated with $j_m = 0.02$ fringe lower than the experimentally measured values. It is seen that this adjustment makes the $\overline{C_t\sqrt{t}}$ values nearly constant within the calculated average deviations from the mean. On again recalculating the data, using $j_m = 0.02$ fringe lower than the experimentally measured value and in addition adjusting each undeviated slit image position upward by 0.0003 cm. as indicated by increasing δ by this amount, the data in columns 4 and 7 were obtained. These values for all fringes of the experiments are seen to be constant well within the average deviations previously given. Corresponding calculations for the experiment with $\Delta c = 3.0037$ yielded similar results, with a slightly greater downward drift in $\overline{C_t\sqrt{t}}$. It should be emphasized that adjustments of 0.02 fringe and 0.0003 cm. in the undeviated slit image position are necessary to bring only the poorest experiments of this research into agreement with the theory. If corrections half this large are applied to all experiments, the $\overline{C_t\sqrt{t}}$ values for the average experiment will be essentially constant.

Although the estimated maximum errors in j_m and δ for an individual experiment are of this magnitude, it is believed that random errors in j_m, δ, and the Y_j values do not account for the small consistent downward drift of the $\overline{C_t\sqrt{t}}$ values with increasing j. It is to be noted that the deviations of $\overline{C_t\sqrt{t}}$ occur at the highest fringes, within the region of the pattern most susceptible to theoretical and experimental errors. The "quarter wave" interference conditions may be expected to lose some exactness at these fringes. In addition, the experimental masking[7] of the diffusion cell is only an approximation to the conditions that are assumed in the theory. Furthermore, during these diffusions the photographic exposures have been adjusted to yield optimal definition of the pattern at the lower fringes, and the consequent overexposure of the region near the slit image may lead to erroneous Y_j readings.

Very good experimental data for the lower fringes of experiments with low values of j_m would be required to prove the superiority of the Airy integral interference conditions given by equations (11) and (12) over the "quarter wave" relations derived previously[5] as expressed by equations (5) and (6). However, some experimental indication of the superiority of the Airy integral results is obtained by comparing the $\overline{C_t\sqrt{t}}$ values of minima 0, 1, 2 and 4 in column 2 of Table V with the values 104.20, 104.22, 104.23 and 104.26 calculated for these fringes, respectively, by means of equation (5).

The fact that values of $\overline{C_t\sqrt{t}}$ for a given fringe at a reasonable distance from the slit image showed no drift with time is good evidence that the cell and bath windows are of satisfactory quality.

Refractometer Cell Results.—It is evident that equation (2) applies to the refractometer cell as well as to the diffusion cell and that for a given set of liquids

$$j'_m = (a'/a)j_m$$

in which the primed and unprimed letters refer to the refractometer and diffusion cells, respectively. The cell thickness, a', was found to equal 5.366 ± 0.001 cm. after correcting to 1°. Therefore $a'/a = 2.1594$ and may be used to calculate j'_m from j_m. That is

$$2.1594 \times j_m = j'_m = I' + F' \qquad (18)$$

where I' is an integer and F' the remaining fraction comprising j'_m. Only F' is determined through the use of the refractometer cell. However, the refractive index increment computed from the calculated I' and the experimental F' should be more precise than that from j_m, if F, the fractional part of j_m, and F' are known with the same precision, *e. g.*, within ± 0.02 fringe, because a' is larger and more precise than a.

Specific refractive increments for sucrose based on refractometer cell data are included in Table III together with the errors calculated from estimated maximum uncertainties of 0.02 in j_m and 0.02% in a', and the volume error in Δc assumed for the other data. The close checks between the refractometer and diffusion cell data are interpreted as confirmation of the F determinations in the diffusion cell.

In addition the refractometer cell has been used to compare air-saturated with air-free water at 1°. The minimum difference in their refractive indices was found from measurements of F' to correspond to about 0.14 in j_m for the diffusion cell. As a difference in air content of solution and solvent might therefore lead to erratic diffusion results, the procedure mentioned previously, of air-saturating all water used, was adopted as a means of standardizing experimental conditions in this respect.

Density and Viscosity Data.—Since insufficient viscosity and density data on sucrose solutions were available for the quantitative interpretation of our diffusion results, these data were obtained as described under Experimental. The dependence of the density, d, upon the sucrose concentration, c, expressed in g. per 100 ml. of solution, can be adequately represented at 24.95° by the relation

$$d = 0.99708 + 0.00384c \quad c < 6 \qquad (19)$$

and at 1.00° by

$$d = 0.99993 + 0.00393c \quad c < 6 \qquad (20)$$

with average deviations of about 0.01%. Where these results overlap data reported in the literature,[21,22] they are substantially in agreement with the previous values. Equations (19) and (20) correspond to partial specific volumes for the sucrose of 0.618 cc./g. and 0.607 cc./g. at 25 and 1°, respectively.

Using the method of least squares to determine coefficients, the relative viscosity, η/η_0, of sucrose solutions may be represented by the quadratic expression

$$\eta/\eta_0 = 1 + 0.0250_0c + 0.00058c^2 \quad c < 6 \quad (21)$$

at 24.95° and by

$$\eta/\eta_0 = 1 + 0.0278_3c + 0.00085c^2 \quad c < 6 \; (22)$$

at 1.00° with average deviations of less than 0.05%. Water saturated with air had the same flow time at 1°, within experimental error, as unsaturated water, so the effect of air-saturation on the viscosity was assumed to be negligible.

Discussion

Gordon[23,24] had proposed a relation expressing the concentration dependence of the diffusion coefficient in terms of the activity coefficient, f, of the solute and the viscosities, η_0 and η, of the water and of the solution. For non-electrolytes his relation is

$$D = D_0 \left[1 + c\,\frac{\mathrm{d}\ln f}{\mathrm{d}c}\right] \eta_0/\eta \qquad (23)$$

where D_0 is the limiting value of D as $c \rightarrow 0$. It should be noted that the only difference between this relation and that proposed by Onsager and Fuoss[25] is the use of the macroscopic relative viscosity to express the variation with concentration of the diffusion mobility, *i. e.*, Ω/c in their notation.

It is of interest that equation (23) describes accurately the dependence that we have observed of the diffusion coefficient upon the concentration. This is shown in Table VI for the data at 25° and in Table VII for those at 1°. In Table VI the mean concentration of each diffusion experiment and the corresponding observed value of D are given in the first two columns, respectively. The third column contains values of η/η_0 given by equation (21) and corresponding to the mean concentration of column 1. The values of $[1 + c(\mathrm{d}\ln f/\mathrm{d}c)]$, column 4, were computed with the aid of the isopiestic data of Scatchard, Hamer and Wood[26] and equation (19). Substitution of these values of D, η/η_0 and $[1 + c(\mathrm{d}\ln f/\mathrm{d}c)]$ into equation (23) then gives the values of D_0 reported in the last column of Table VI. The constancy of the values of D_0 thus computed is good evidence for the validity of Gordon's relation as applied to this non-electrolyte.

TABLE VI

AN EXPERIMENTAL TEST OF GORDON'S RELATION AT 24.95°

1 $\bar{c}$	2 $D \times 10^6$ sq. cm./sec.	3 η/η_0 (eqn. 21)	4 $\left[1 + c\frac{\mathrm{d}\ln f}{\mathrm{d}c}\right]$	5 $D_0 \times 10^6$ sq. cm./sec.
0.7507	5.170	1.019_1	1.007_9	5.227
1.0011	5.148	1.025_6	1.010_6	5.224
2.2521	5.049	1.059_2	1.024_3	5.221
3.7535	4.934	1.102_0	1.041_2	5.222
5.2546	4.821	1.147_4	1.058_8	5.224

TABLE VII

AN EXPERIMENTAL TEST OF GORDON'S RELATION AT 1.00°

1 $\bar{c}$	2 Δc	3 $D \times 10^6$ sq. cm./sec.	4 η/η_0 (eqn. 22)	5 $\left[1 + c\frac{\mathrm{d}\ln f}{\mathrm{d}c}\right]$	6 $D_0 \times 10^6$ sq. cm./sec.
0.2502	0.5004	2.418	1.007_0	1.002_9	2.428
1.2513	.5005	2.378	1.036_2	1.014_5	2.429
2.2521	.5008	2.330	1.067_0	1.026_4	2.422
3.2539	.5012	2.297	1.099_6	1.038_6	2.432
4.2551	.5011	2.251	1.133_8	1.051_1	2.428
0.7009	1.4017	2.392_0	1.019_9	1.008_0	2.420_2
0.7505	1.5009	2.392_8	1.021_4	1.008_6	2.423_2
0.7510	1.5020	2.393_7	1.021_4	1.008_6	2.424_1
1.5018	3.0037	2.362_0	1.043_7	1.017_4	2.423_1
3.7543	1.5018	2.270_4	1.116_5	1.044_8	2.426_2

The arrangement of Table VII, containing the data at 1°, is similar to that of Table VI except that an additional column, 2, has been added to indicate that the concentration interval varied considerably among the experiments. In computing the values of $[1 + c(\mathrm{d}\ln f/\mathrm{d}c)]$, column 5 of Table VII, the values at 25° have been corrected to 1° with the aid of the heat of dilution data of Gucker, Pickard and Planck[27] and the assumption that the partial molal heat capacity of the solvent is independent of the temperature over the interval from 25° to 1°. Although the constancy of D_0 at 1°, column 6 of Table VII, is not as good as at 25°, due in part to the somewhat lower precision of the values of D from experiments in which $\Delta c \cong 0.5$, it nevertheless gives added support to the validity of equation (23) for this system.

It is also of interest that our values of D_0 at the two temperatures are in fair, but not exact, agreement with the Stokes–Einstein relation

$$D_0\eta_0/T = D_0'\eta_0'/T' \qquad (24)$$

Using our extrapolated value of 5.226×10^{-6} from equation (17) for D_0 at 24.95°, and 0.896_0 centipoises for the viscosity of water at this temperature,[28] a value of 2.486×10^{-6} was computed, from equation (24), for D_0' at 1.00° where η_0' is 1.732 centipoises.[28] This may be compared with

---

[21] Landolt-Börnstein, Fourth Edition, Julius Springer, Berlin, 1912, p. 311.

[22] Butler, *J. Chem. Soc.*, **123**, 2060 (1923).

[23] Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

[24] James, Hollingshead and Gordon, *ibid.*, **7**, 89 (1939).

[25] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[26] Scatchard, Hamer and Wood, THIS JOURNAL, **60**, 3061 (1938).

[27] Gucker, Pickard and Planck, *ibid.*, **61**, 459 (1939).

[28] "International Critical Tables," Vol. V, 1929, p. 10.

our extrapolated value of 2.423×10^{-6}, equation (16), at the lower temperature. Although the difference is small in view of the variation of D_0 over this temperature interval, the direction is that which would be anticipated from increased hydration at the lower temperature.

Acknowledgments.—The authors are deeply appreciative of the interest and suggestions of Dr. J. W. Williams throughout the progress of this research. They are also much indebted to Miss Ruth Christofferson, Miss Jean V. Thomas and Mrs. Dorothy C. Gosting for aid in performing calculations. The coöperation of Mr. Edwin Hanson in the design of the refractometer cell and the construction of the cell by him are gratefully acknowledged.

This work was supported in part by grants from the Wisconsin Alumni Research Foundation and the United States Public Health Service.

Summary

Diffusion results obtained at 1 and at 25° using the Gouy interference method are reported for aqueous sucrose solutions at concentrations below 6 g./100 ml. These data provide further confirmation of the theory of this method. Specific gravities and relative viscosities were determined over the same concentration range so that tests of equations relating the concentration dependence of the diffusion coefficient to viscosity and thermodynamic factors might be made. Gordon's relation was found to hold with high precision for this system. Specific refractive increments for sucrose have been derived from the diffusion experiments and from a separate refractometer cell.

Additional theory utilizing the Airy integral has been presented as an improvement over the previous theory of Kegeles and Gosting for fringes farthest from the slit image.

MADISON 6, WISCONSIN RECEIVED JANUARY 18, 1949

[CONTRIBUTION FROM THE GIBBS LABORATORY, HARVARD UNIVERSITY]

Anomalous Temperature Effects in the Hydrolysis of Urea by Urease

BY G. B. KISTIAKOWSKY AND RUFUS LUMRY

Several investigations of the rates of biochemical processes have shown the effect of temperature to be more complex than would be expected on the basis of simple Arrhenius hypothesis. In particular, it has been claimed[1] that joined segments of straight lines are observed on plotting the logarithm of the rate constant against inverse temperature, with sharp breaks at "critical" temperatures. Crozier[1] has proposed the theory of "Master" or "Pacemaker" reactions which are supposed to account for the sudden changes in activation energy. This theory has been repeatedly discussed[2] but a brief analysis from the point of view of chemical kinetics will further clarify the situation.

A curvature in the line of an Arrhenius plot, providing it does not exceed, say, 100 cal./degree, finds ready kinetic or statistical interpretation,[3] but discontinuous changes in activation energy do not unless a first order phase transition of at least one of the reactants is assumed to occur. While such cannot be denied *a priori* for processes in living cells, they are inconceivable in homogeneous solutions of enzymes *in vitro*. Actually it is impossible to prove a discontinuity in activation energy from *rate measurements alone;* such measurements can at most establish that two straight segments of an Arrhenius plot are joined by a curve extending over a finite temperature range. In fact, experimental precision must rise to rather unusual heights in kinetic work to limit a suspected range of curvature to only a few degrees. For instance, if the two activation energies differ by 3,000 cal./mole, an extensive and statistically well planned series of tests, with a standard deviation of 1%, could restrict the curved region to within 2°, with a level of confidence somewhat greater than 90%. Contrasting these considerations with the precision and extent of published data, one begins to doubt altogether the reality of the majority of claimed anomalies. A few, however, do appear to be genuine and call for a kinetic interpretation.

Consider first the proposition that two competing mutually non-exclusive elementary reactions are involved. For instance, that what was thought to be a pure molecular species is in reality a mixture of two enzymes; or that each enzyme molecule has several active centers which catalyse the reaction with different activation energies; or that the reaction may proceed through the intermediate formation of two different "critical complexes." Any such mechanism may be readily ruled out because it demands that the activation energy increase with rising temperature, whereas in cited instances just the reverse is observed. Furthermore the curved region of the Ar-

---

(1) W. J. Crozier, *J. Gen. Physiol.*, **7**, 189 (1924), and other publications; I. W. Sizer, *ibid.*, **22**, 719 (1939); I. W. Sizer and B. S. Gould, *Enzymologia*, **8**, 75 (1940); I. W. Sizer and E. S. Josephson, *Food Research*, **7**, 201 (1943); I. W. Sizer, *Annals of Surgery*, **121**, 231 (1945); S. Darling, *Nature*, **160**, 838 (1947).

(2) W. J. Crozier, *J. Gen. Physiol.*, **7**, 189 (1924); A. C. Burton, *J. Cell. and Comp. Physiol.*, **9**, 1 (1937); M. F. Morales, *ibid.*, **30**, 303 (1947).

(3) V. K. La Mer, *J. Chem. Phys.*, **1**, 289 (1933). S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941.