3. The activation energy calculated from the rate constant is 12.8 kcal./mole.

4. A simple method for analyzing the reaction mixtures is described.

5. The kinetics of the reaction agree with the generally proposed mechanism for acid-catalyzed *trans*-esterification.

[Contribution from the Propaedeutic-Chemical Laboratory of the University of Helsinki]

The Equilibria of Cupric Hydroxysalts in Mixed Aqueous Solutions of Cupric and Alkali Salts at 25°

By Reino Näsänen and Veikko Tamminen

In a previous paper[1] it was shown that the pH of a cupric salt solution changes on precipitating the cupric ion with alkali hydroxide in a manner as seen in Fig. 3. The titration curve is interpreted as follows. First the trihydroxy salt $(Cu(OH)_{1.5}\cdot Cl_{0.5})$ is precipitated and the course of the titration curve is determined by the solubility product equation

$$[Cu^{2+}][OH^-]^{1.5}[Cl^-]^{0.5} = S_{1.5} \qquad (1)$$

Near the end-point of the titration the product $[Cu^{2+}][OH^-]^2$ reaches the value of the solubility product of cupric oxide

$$[Cu^{2+}][OH^-]^2 = S_2 \qquad (2)$$

and henceforth equations (1) and (2) are both valid. By eliminating $[Cu^{2+}]$ between (1) and (2) we obtain

$$[OH^-] = (S_2/S_{1.5})^2[Cl^-] \qquad (3)$$

Thus the pH of the solution is nearly constant as long as two solid phases are present. When all the trihydroxy salt is turned into oxide an abrupt pH-change again occurs. The course of the curve is then determined by equation (2). The precipitation curve of trihydroxysulfate is similar as that of trihydroxychloride.

In the previous investigation $S_{1.5}$ and S_2 were measured at one ionic strength. These measurements have since been continued in dilute cupric chloride, sulfate, nitrate and perchlorate solutions. The influence of the corresponding alkali salts is especially investigated. In the following, the results of these studies are presented.

Experimental

Materials.—Cupric chloride and sulfate as well as potassium chloride, nitrate and sulfate were of the best qualities obtainable (Kahlbaum, for analysis) and were used without purification. Cupric nitrate and sodium perchlorate were of the quality "purissimum" and were used after a recrystallizing procedure. Cupric perchlorate was prepared from cupric oxide "for analysis" and perchloric acid. Nitrate and perchlorate solutions were standardized gravimetrically with nitron. Sulfate was determined as barium sulfate. Copper was titrated iodometrically. The solution of sodium hydroxide was obtained by dilution of strong carbonate-free solution with carbon dioxide-free water and standardized against potassium biphthalate or bi-iodate.

Procedure.—The experiments were made in conical Pyrex flasks with glass stoppers into which the cupric

salt and corresponding alkali salt solutions as well as the required amount of water and alkali hydroxide solution were measured. Flasks were then kept at 25 ± 0.1° and occasionally stirred. The pH of the solutions became constant after four days at least. In all actual experiments, however, pH is measured at the earliest after one week.

The pH was determined with a "Radiometer, PHM 3" potentiometer using a glass electrode and saturated calomel electrode. The sensitivity of the potentiometer is better than 0.3 mv. The glass electrode was standardized against an acetic acid–acetate buffer[2] pH 4.65 and a phosphate buffer[3] pH 7.54. The temperature of the room where the measurements were made was maintained at 25° to within ±0.2°.

Analysis of Precipitate.—The composition of the precipitate can often be determined from the position of the inflection point of the titration curve and from the slope of the part of the curve which corresponds to the excess of cupric salt.[4] In some cases chemical analysis of the precipitate was required. It was performed as follows. The precipitate was filtered with a glass filter crucible, washed with a small amount of water, dissolved with sulfuric acid and analyzed as regards copper.

Calculation of Solubility Products

A cupric hydroxysalt can be represented by the formulas

$$n\,Cu(OH)_2\cdot Cu(A)_{2/z} \text{ or } Cu(OH)_k(A)_{(2-k)/z}$$
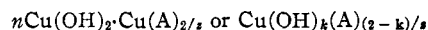
where z is the valence of the ion A^{z-}. The concentration of cupric ion in a solution in equilibrium with this compound can be calculated from

$$[Cu^{2+}] = \tfrac{1}{2}c_{Cu} - (c_B + [H^+])/k \qquad (4)$$

where c_{Cu} is the stoichiometric normality of cupric salt and c_B that of sodium hydroxide. The concentration of the anion A^{z-} is obtained respectively from

$$[A^{z-}] = c + c_{Cu}/z - (c_B + [H^+])(2-k)/kz \qquad (5)$$

where c is the molarity of the added alkali salt. The ionic strength of the solution is obtained from

$$\mu = \mu_0 + c_{Cu}\,(1 + z/2) + 0.5c_B\left(1 - \frac{(2-k)z + 4}{k}\right) \qquad (6)$$

where μ_0 comes from the added alkali salt. By deriving equations (4), (5) and (6) it is supposed that no complex formation occurs. This question

(1) R. Näsänen, *Ann. Acad. Sci. Fennicae*, **A59**, 7 (1942).

(2) S. Kilpi and A. Meretoja, *Suomen Kemistilehti*, **B16**, 23 (1943).

(3) Y. Hentola, *Kemian Keskusliiton Julkaisuja*, **2**, 62 (1946).

(4) *Cf.* R. Näsänen, *Suomen Kemistilehti*, **B21**, 56 (1948).

is discussed later in this paper. The hydrogen ion concentration is small compared with c_{Cu} and can therefore be neglected in calculations. The solubility product is obtained from

$$pS_k = pCu + kpOH + (2 - k)/zpA \qquad (7)$$

where $pS_k = -\log S_k$, $pCu = -\log[Cu^{2+}]$, $pA = -\log[A^{z-}]$ and $pOH = -\log(OH^-) = 13.996 - pH$. In the solubility product so calculated (OH^-) is the activity and therefore the solubility product S_k is a "mixed" one.

Results

The results are listed in Tables I–V. Table I includes the data concerning cupric trihydroxychloride. The concentration of cupric ion lies in these measurements between the values 0.00076 and 0.0056. The concentration of added potassium chloride varies from 0 to somewhat over 1.

TABLE I

SOLUBILITY PRODUCT OF CUPRIC TRIHYDROXY CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS AT 25°

$\sqrt{\mu}$	$c_{Cu} \times 10^3$	$c_B \times 10^2$	c_{KCl}	pH	$pS_{1.5}$
0.145	1.67	0.417	....	4.76	17.02
.132	1.54	.578	....	4.90	17.00
.124	1.31	.433	....	4.89	17.07
.120	1.43	.716	....	5.00	17.08
.118	1.30	.574	....	4.99	17.06
.110	1.29	.713	....	5.12	17.08
.108	1.33	.836	....	5.28	17.04
.215	1.41	.311	0.0282	4.74	16.89
.206	1.39	.614	.0278	4.90	16.90
.231	1.08	.597	.0432	5.07	16.89
.349	1.32	.291	.105	4.74	16.69
.347	1.31	.434	.105	4.80	16.71
.343	1.30	.574	.104	4.90	16.69
.339	1.29	.713	.103	5.04	16.69
.529	1.32	.291	.263	4.72	16.53
.527	1.31	.433	.262	4.79	16.54
.523	1.30	.574	.260	4.89	16.52
.516	1.28	.849	.256	5.24	16.56
.822	1.32	.291	.658	4.63	16.48
.811	1.29	.726	.645	4.95	16.46
.844	1.12	.463	.700	4.84	16.41
1.15	1.32	.291	1.316	4.55	16.44
1.15	1.31	.433	1.310	4.62	16.45
1.15	1.30	.573	1.300	4.70	16.46
1.14	1.29	.713	1.290	4.82	16.44

Thus in these conditions the trihydroxychloride is stable.[5] This can be shown in all the ways mentioned above. The results on trihydroxynitrate are collected in Table II. The solubility of trihydroxynitrate is thus greater than that of trihydroxychloride and therefore trihydroxynitrate precipitated from a dilute cupric nitrate solution turns into cupric oxide before the inflection point of the titration curve as seen for example from the brown color of the precipitate. In this case

(5) In the previous paper[1] it was erroneously concluded that dihydroxychloride is stable when potassium chloride concentration is nearly 1. In these previous experiments, however, the equilibrium was not reached before the pH determination.

chemical analysis was the only way to decide the composition of the precipitate. When potassium nitrate was added, trihydroxynitrate was stable until the corresponding inflection point (cf. Fig. 3).

TABLE II

SOLUBILITY PRODUCT OF CUPRIC TRIHYDROXYNITRATE IN POTASSIUM NITRATE SOLUTIONS AT 25°

$\sqrt{\mu}$	$c_{Cu} \times 10^3$	$c_B \times 10^2$	c_{KNO_3}	pH	$pS_{1.5}$
0.152	1.79	0.362	....	5.33	16.09
.146	1.77	.538	....	5.39	16.08
.139	1.76	.712	....	5.46	16.11
.247	1.95	.394	0.0357	5.24	15.92
.242	1.93	.586	.0354	5.28	15.96
.236	1.91	.775	.0351	5.38	15.94
.232	1.90	.961	.0348	5.48	15.94
.417	1.65	.335	.152	5.21	15.80
.412	1.64	.498	.150	5.29	15.77
.408	1.63	.659	.149	5.38	15.76
.405	1.62	.818	.148	5.48	15.76
.714	1.36	.273	.494	5.23	15.61
.712	1.34	.407	.491	5.31	15.59
.710	1.33	.542	.488	5.36	15.63
.706	1.32	.669	.485	5.44	15.66
1.12	1.79	.362	1.23	5.04	15.58
1.11	1.76	.713	1.21	5.17	15.60
1.10	1.74	.884	1.20	5.29	15.57
1.10	1.73	1.053	1.19	5.45	15.58

The solubility products of cupric trihydroxychloride and nitrate can be presented by equation

$$pS = pS_0 - \frac{2.28\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \qquad (8)$$

For pS_0 and B the values

	pS_0	B
$Cu(OH)_{1.5}Cl_{0.5}$	17.265	0.304
$Cu(OH)_{1.5}(NO_3)_{0.5}$	16.373	.346

are calculated with the aid of the method of least squares.

The results concerning trihydroxysulfate are given in Table III. The solubility product can be presented by means of the equation.

$$pS = pS_0 - \frac{A\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (9)$$

The values

$$pS_0 = 17.115 \text{ and } A = 2.95$$

are obtained by the method of least squares.

According to Beebe and Goldwasser[6] cupric hexahydroxyperchlorate is stable in cupric perchlorate solutions. Our experiments, however, give evidence that in dilute cupric perchlorate solutions with moderate sodium perchlorate concentrations cupric oxide is stable. When the sodium perchlorate concentration is greater than about 0.1 the precipitate remains blue and consists of hexahydroxyperchlorate. Thus here there arises the possibility of determining the solubility product of cupric oxide. Table IV comprises the results

(6) R. A. Beebe and S. Goldwasser, *J. Phys. Chem.*, **39**, 1075 (1935).

TABLE III
SOLUBILITY PRODUCT OF CUPRIC TRIHYDROXYSULFATE IN POTASSIUM SULFATE SOLUTIONS AT 25°

$\sqrt{\mu}$	$c_{Cu} \times 10^2$	$c_B \times 10^2$	$c_{K_2SO_4}$	pH	$pS_{1.4}$
0.122	1.01	0.465	....	4.99	16.81
.117	1.01	.555	....	5.11	16.80
.112	1.00	.645	....	5.30	16.78
.191	2.04	.374	....	4.60	16.72
.183	2.01	.574	....	4.70	16.67
.177	2.00	.733	....	4.75	16.67
.169	1.97	.924	....	4.84	16.69
.159	1.95	1.178	....	5.04	16.69
.151	1.93	1.344	....	5.36	16.67
.332	2.02	0.555	0.0255	4.80	16.35
.322	1.98	.906	.0250	4.97	16.32
.315	1.95	1.161	.0246	5.16	16.33
.310	1.93	1.327	.0244	5.41	16.36
.636	1.98	0.906	.125	5.09	15.99
.628	1.95	1.161	.123	5.28	16.00
.624	1.93	1.327	.122	5.55	16.00
.894	2.01	0.574	.255	5.09	15.71
.881	1.97	0.924	.249	5.21	15.76
.874	1.95	1.178	.246	5.43	15.73
.869	1.93	1.344	.244	5.73	15.72
1.19	2.01	0.574	.458	5.21	15.47
1.17	1.97	.924	.449	5.34	15.49
1.16	1.95	1.178	.443	5.55	15.51
1.16	1.93	1.344	.438	5.85	15.42

concerning cupric oxide. The thermodynamic solubility product is calculated by means of the Debye–Hückel equation

$$pS_0 = pS + \frac{2.02\sqrt{\mu}}{1 + 1.64\sqrt{\mu}} \qquad (10)$$

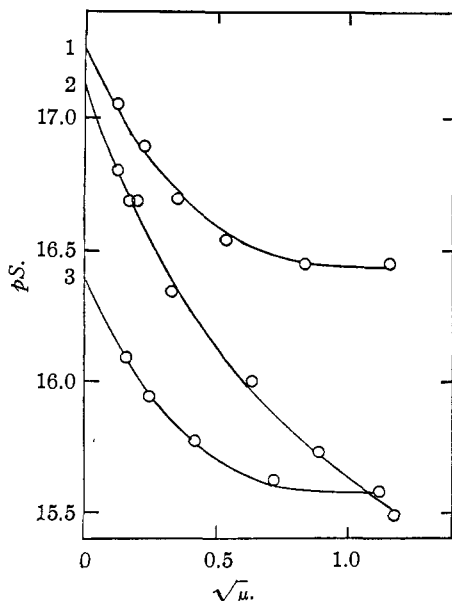by assuming the value 5 Å. for the mean ionic di-

Fig. 1.—Solubility products of cupric hydroxysalts as functions of ionic strength: (1) trihydroxychloride, (2) trihydroxysulfate and (3) trihydroxynitrate.

TABLE IV
SOLUBILITY PRODUCT OF CUPRIC OXIDE AT 25°

$\sqrt{\mu}$	$c_{Cu} \times 10^2$	$c_B \times 10^2$	c_{NaClO_4}	pH	pS_0
0.097	0.694	0.199	....	5.55	19.68
.091	.688	.394	....	5.65	19.69
.085	.683	.587	....	5.87	19.73
.156	1.928	.907	....	5.46	19.62
.151	1.900	1.161	....	5.53	19.61
.147	1.880	1.327	....	5.58	19.64
.145	1.872	1.398	....	5.61	19.63
.138	1.838	1.712	....	5.89	19.66
.137	1.831	1.760	....	6.02	19.63
.135	1.824	1.822	....	6.78	19.66
.247	1.263	0.362	0.0440	5.55	19.60
.242	1.243	.713	.0433	5.63	19.67

ameter. The results in more concentrated sodium perchlorate solutions are given in Table V.

TABLE V
SOLUBILITY PRODUCT OF CUPRIC HEXAHYDROXYPERCHLORATE IN SODIUM PERCHLORATE SOLUTIONS AT 25°

$\sqrt{\mu}$	$c_{Cu} \times 10^2$	$c_B \times 10^2$	c_{NaClO_4}	pH	$pS_{1.714}$
0.444	1.26	0.362	0.176	5.82	16.61
.436	1.25	.539	.175	5.90	16.60
.675	1.26	.362	.440	5.77	16.58
.670	1.24	.712	.433	5.97	16.55
.664	1.23	.883	.429	6.16	16.54
.848	1.26	.362	.703	5.72	16.61
.840	1.24	.713	.693	5.95	16.53
.837	1.23	.884	.688	6.07	16.53
1.346	1.26	.362	1.76	5.43	17.02
1.346	1.26	.362	1.76	5.45	16.96
1.320	1.23	.883	1.72	5.80	16.96

In Fig. 1 and 2 the solubility products are plotted against ionic strength. The points in the figures correspond to mean values of pS at nearly equal ionic strengths.
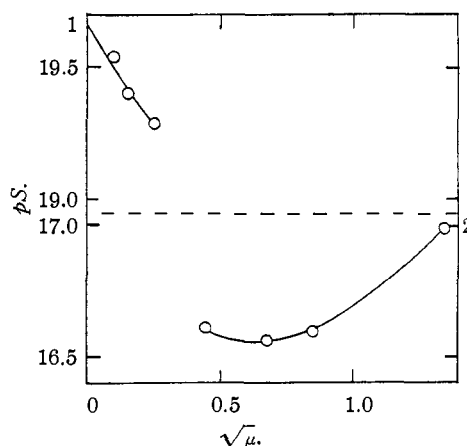

Fig. 2.—Solubility product of cupric oxide (1) and cupric hexahydroxyperchlorate (2) as a function of ionic strength.

Discussion

It is obvious that the treated hydroxy salts are stable when the cupric ion concentration of the

solution is appreciably greater than in the present study. This is in many cases supported by the literature.[7] The equilibrium conditions in these circumstances are under investigation.

The precipitation curve concerning the precipitation of cupric ion from the mixed solution of cupric and potassium nitrate is presented in Fig. 3 in two cases

$$c_{Cu} = 0.01, c_{KNO_3} = 0.01$$
$$c_{Cu} = 0.01, c_{KNO_3} = 0.1$$

Cupric trihydroxynitrate and cupric oxide are the only stable compounds under these conditions. The greater the nitrate ion concentration and the greater the pS of the hydroxysalt when two solid phases exist the greater the pH as seen from equation (3). Therefore this pH value is greater for cupric trihydroxychloride than for cupric trihydroxysulphate and greater for cupric trihydroxysulfate than for cupric trihydroxynitrate at equal anion concentrations. On the other hand equilibrium is often reached very slowly when two solid phases are present and one cannot attain easily reproducible values for the pH of the solution. Therefore it cannot be surely decided from pH values whether still more basic hydroxysalts than trihydroxysalts are stable in these conditions. The brown color of the precipitate when c_B/c_{Cu} is greater than 0.8, however, indicates that more basic salts than tetrahydroxysalt cannot be stable in the above cases except in perchlorate solutions. In fact cupric tetrahydroxysulfate according to Weiser, Milligan and Cook[8] may be stable in these conditions.

The curves representing the relations between the solubility products of cupric trihydroxysalts and the ionic strength are so steep that it is possible that complex formation occurs. The results obtained are in accord in this respect at least qualitatively with the activity coefficient values reported in the literature for the corresponding cupric salt.[9] It is the purpose of the authors to investigate in future whether this deviation is caused in part by complex formation. It may be mentioned that the previous determination shows that the solubility product values of cupric trihydroxychloride and sulfate in sodium perchlorate solutions differ very much from those in potassium chloride and sulfate solutions.

As mentioned above the composition of the precipitate can often be at least roughly determined from the slope of the precipitation curve. A typical case is presented in Table VI. The stoichiometric concentration c_{Cu} is nearly the same

(7) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longman, Green and Co., New York, N. Y., 1928, Vol. 3; R. A. Beebe and A. J. Hopkins, J. Phys. Chem., 34, 570 (1930); R. A. Beebe, ibid., 35, 3677 (1931); O. Binder, Compt. rend., 198, 653, 2167 (1934); 201, 893 (1935); Ann. chim., [11] 5, 337 (1936).

(8) H. B. Weiser, W. O. Milligan and E. L. Cook, THIS JOURNAL, 64, 503 (1942).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 427.
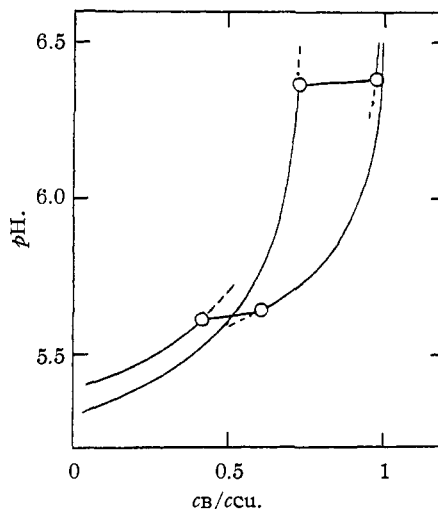
Fig. 3.—Precipitation of cupric ion with alkali hydroxide from a mixed solution of cupric and potassium nitrate: (1) $c_{Cu} = 0.01$, $c_{KNO_3} = 0.01$ and (2) $c_{Cu} = 0.01$, $c_{KNO_3} = 0.1$.

in all experiments while c_B increases. The solubility product is calculated in the cases $k = 1.4$, 1.5 and 1.6. It is evident that the value $k = 1.5$ is the most correct of these three values. A more detailed interpretation of the precipitation curve has been presented by Näsänen.[4]

TABLE VI

THE ESTIMATION OF THE QUANTITY k FROM THE PRECIPITATION CURVE

$c_{Cu} \times 10^2$	$c_B \times 10^2$	pH	$pS_{1.4}$	$pS_{1.5}$	$pS_{1.6}$
1.67	0.417	4.76	16.31	17.02	17.74
1.54	.578	4.90	16.32	17.00	17.69
1.43	.716	5.00	16.46	17.08	17.71
1.33	.836	5.28	16.59	17.04	17.56

The values for the solubility product of cupric oxide reported by various authors differ in part very much from each other. Our value $S_0 = 2.2 \times 10^{-20}$ agrees relatively well with the recent value of Feitknecht[10] 1×10^{-20} and with that of Allmand[11] 1×10^{-19}. The value of Remy and Kuhlmann[12] 1.2×10^{-12} and that of Jellinek and Gordon[13] 1.7×10^{-13} are obviously erroneous. The value obtained in the previous paper[1] 2.6×10^{-19} fits better cupric hydroxide for which Feitknecht[10] has found 1.6×10^{-19}.

The solubility product of cupric trihydroxynitrate and hexahydroxyperchlorate are not earlier determined. The values for cupric trihydroxychloride and sulfate obtained in the previous paper[1] are to some extent greater than those of the present paper. It is obvious that these values do not concern the most stable modifications because pH is measured too early.

(10) W. Feitknecht, Helv. Chim. Acta, 27, 771 (1944).

(11) A. J. Allmand, J. Chem. Soc., 95, 2151 (1909).

(12) H. Remy and A. Kuhlmann, Z. anal. Chem., 65, 178 (1924).

(13) K. Jellinek and H. Gordon, Z. physik. Chem., 112, 214 (1924).

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.

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 $\pm0.005°$, 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).