[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, STANFORD UNIVERSITY SCHOOL OF MEDICINE, PALO ALTO, CALIF.]

The Sedimentation Coefficient of Sucrose[1]

BY F. E. LABAR AND R. L. BALDWIN

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A new method is presented for measuring sedimentation coefficients of small molecules. It is well suited for use with interference optics because it requires only the difference in concentration between the meniscus and the base of the column. In this way the sedimentation coefficient of sucrose has been measured at several concentrations with a precision of 0.5%. The results confirm the extended Svedberg equation, showing that the frictional coefficient is the same in sedimentation as in diffusion, even at finite concentrations. The experimental data could be used in another way, to measure the molecular weight, when the sedimentation coefficient is known.

Introduction

In view of the gain in accuracy obtained when Rayleigh interference optics are used to determine molecular weights at sedimentation equilibrium,[2-4] it seems advantageous to apply this optical system in determining sedimentation coefficients. However, none of the present theoretical methods[5,6] makes good use of the results which interference optics can best supply, namely the total fringe count between ends of the solution column. A method presented here overcomes this difficulty and allows us to examine the transport properties of a very small molecule, sucrose, which has a sedimentation coefficient of less than 0.3 S.

Precise measurements of the sedimentation coefficient of sucrose ought to provide a good test for the extended Svedberg equation at finite concentrations, since accurate data for the other quantities needed are already available: cf. Gosting and Morris.[7] The predicted value of the sedimentation coefficient is

$$s_1 = \frac{DM_1(1 - \bar{v}_1\rho)}{RT(1 + c_1\partial \ln y_1/\partial c_1)} \tag{1}$$

This equation applies to two-component systems (e.g., solute + solvent) and the subscript 1 refers to one component, usually the solute; for a solute which ionizes, M_1 should be replaced by M_1/ν where ν is the number of ions per molecule. Here R is the gas constant and D is the mutual diffusion coefficient, ρ the density, and T the temperature of the solution; s_1 is the sedimentation coefficient, $\bar{v}_1$ the partial specific volume (ml./g.), c_1 the concentration (g./ml. or g./dl.), and y_1 is the activity coefficient (on the c-scale) of the solute. (The subscript 1 will be omitted in later equations.)

Equation 1 has been derived rigorously from the principles of thermodynamics of irreversible processes[8,9] (for a summary see Fujita[10] and Williams, et al.[11]) as well as from expressions for the frictional coefficients of sedimentation and diffusion.[12] There has been criticism of the latter derivation of eq. 1 and the question of a "backward flow" which is supposed to occur in sedimentation but not diffusion, has been raised.[13,14] The data presented here for the sedimentation of sucrose provide an experimental answer to this question. The results confirm eq. 1, in agreement with an earlier investigation by Creeth[15] of the transport properties of thallous sulfate, which has a larger sedimentation coefficient (ca. 1 S.). His sedimentation measurements were made by the method of Gutfreund and Ogston[5] and have a precision of 2–4%; the ones reported here for sucrose, based on the new method, have a precision of 0.5%.

Experimental

Materials.—Sucrose from the National Bureau of Standards (Sample 17, Lot No. 6004) was used for the experiments; the concentrations were determined by weight, corrected to weight in vacuo. 1,3-Butanediol was purchased from Eastman Organic Chemicals and redistilled before use. Fluorochemical FC 43 was obtained from Spinco Division, Beckman Instruments.

Sedimentation Experiments.—A Spinco Model E ultracentrifuge with temperature control was used. The Rayleigh interference optical system was modified by the addition of a Bausch and Lomb second-order interference filter to the conventional Wratten 77A filter in order to isolate the 546 mμ Hg line. Eastman Spectroscopic IIG plates were used for the photography and they were read on a Gaertner microcomparator (M2001RS).

All sedimentation experiments were carried out at 42,040 r.p.m. and at 25°. Corrections of the fringe interval recorded on the photographic plate were made for the reference base line and for the sedimentation of 1,3-butanediol on the reference side of the cell. Focusing of the optics, evaluation of the fractional fringe difference at each end of the column, and other particulars regarding the experiments have been reported earlier.[4]

Theory

In considering the sedimentation of small molecules, or large molecules at low rotor speeds, one can obtain the concentration at the meniscus from the equation of Fujita and MacCosham,[16,17] who solved the Lamm differential equation of the ultracentrifuge for the case of a semi-infinite cell. The effect of the meniscus in causing restricted diffusion is taken explicitly into account in their solution, which assumes that a "plateau region" $(\partial c/\partial r = 0)$ exists ahead of the boundary and that the sedimentation and diffusion coefficients are constant. An approximation is made which is exact at the meniscus; Fujita and MacCosham conclude that it is a good approximation so long as $2\omega^2 st$ is small compared to unity. A study by Yphantis[18] of numerical solutions to the Lamm equation also indicates that the approximation is satisfactory; furthermore, he finds that this equation for the concentration at the meniscus holds long after the plateau region has vanished.

(1) This work was supported by a research grant from the National Institutes of Health, PHS AM 04763-03.

(2) J. S. Johnson, G. Scatchard, and K. A. Kraus, J. Phys. Chem., 63, 787 (1959).

(3) E. G. Richards and H. K. Schachman, ibid., 63, 1578 (1959).

(4) F. E. LaBar and R. L. Baldwin, ibid., 66, 1952 (1962).

(5) H. Gutfreund and A. G. Ogston, Biochem. J., 44, 163 (1949).

(6) R. J. Goldberg, J. Phys. Chem., 57, 194 (1953).

(7) L. J. Gosting and M. S. Morris, J. Am. Chem. Soc., 71, 1998 (1949).

(8) G. J. Hooyman, Dissertation, Leiden University, Netherlands, 1955.

(9) The chief assumption made in deriving eq. 1 is that the partial specific volumes are constant, independent of concentration and pressure. Then the sedimentation and diffusion coefficients measured with the cell as a frame of reference are identical with those referred to a volume-fixed reference frame.

(10) H. Fujita, "Mathematical Theory of Sedimentation Analysis," Academic Press, Inc., New York, N. Y., 1962, p. 25.

(11) J. W. Williams, K. E. Van Holde, R. L. Baldwin, and H. Fujita, Chem. Rev., 58, 715 (1958).

(12) R. L. Baldwin and A. G. Ogston, Trans. Faraday Soc., 50, 749 (1954); see also O. Lamm, Acta Chem. Scand., 7, 173 (1953).

(13) G. Kegeles, S. M. Klainer, and W. J. Salem, J. Phys. Chem., 61, 1286 (1957).

(14) H. K. Schachman, "Ultracentrifugation in Biochemistry," Academic Press, Inc., New York, N. Y., 1959, p. 222.

(15) J. M. Creeth, J. Phys. Chem., 66, 1228 (1962).

(16) H. Fujita and V. J. MacCosham, J. Chem. Phys., 30, 291 (1959).

(17) Reference 10, p. 82.

(18) D. A. Yphantis, J. Phys. Chem., 63, 1742 (1959).

$$(c_a/c^0) = \exp(-\tau)\{[1 + 2V_a{}^2][1 - \Phi(V_a)] - (2V_a/\sqrt{\pi})\exp(- V_a{}^2)\} \quad (2)$$

$$\tau = 2\omega^2 st \quad (2a)$$

$$V_a = ({}^1/_2)\omega^2 s r_a(t/D)^{1/2} \quad (2b)$$

$$\Phi(x) = (2/\sqrt{\pi}) \int_0^x \exp(-z^2)dz \quad (2c)$$

On carrying out a similar analysis for the base, subject to the analogous approximation, one obtains

$$(c_b/c^0) = \exp(-\tau)\{[1 + 2V_b{}^2][1 + \Phi(V_b)] + (2V_b/\sqrt{\pi})\exp(- V_b{}^2)\} \quad (3)$$

$$V_b = ({}^1/_2)\omega^2 s r_b(t/D)^{1/2} \quad (3a)$$

In these equations c^0 is the initial uniform concentration, b and a denote the base and meniscus of the solution column, r is radial distance measured from the center rotation, t is time, and ω is the angular velocity (rad./sec). The following series expansions

$$\exp(-x^2) = 1 - x^2 + \ldots \quad (4a)$$

$$\Phi(x) = (2/\sqrt{\pi})[x - ({}^1/_3)x^3 + \ldots] \quad (4b)$$

allow one to express c_a/c^0 and c_b/c^0 in convenient series form since $(x = V_b$ or $V_a)$ is of the order of 10^{-2} in these experiments.

$$(c_a/c^0) = \exp(-\tau)\{1 - 4V_a/\sqrt{\pi} + 2V_a{}^2 - 4V_a{}^3/3\sqrt{\pi} + O(V_a{}^4)\} \quad (5a)$$

$$(c_b/c^0) = \exp(-\tau)\{1 + 4V_b/\sqrt{\pi} + 2V_b{}^2 + 4V_b{}^3/3\sqrt{\pi} + O(V_b{}^4)\} \quad (5b)$$

Then the difference in concentration across the column is given by subtracting eq. 5a from eq. 5b.

$$(\Delta c/c^0) = \exp(- \tau)\{(4/\sqrt{\pi})(V_b + V_a) + 2(V_b{}^2 - V_a{}^2) + ({}^4/_3\sqrt{\pi})(V_b{}^3 + V_a{}^3) + O(V_a{}^4, V_b{}^4)\} \quad (6)$$

$$\Delta c = c_b - c_a \quad (6a)$$

For convenience in computing the results, eq. 6 can be squared to give

$$\frac{(\Delta c/c^0)^2}{(1 + \delta)} = \frac{(4\omega^2 s \bar{r})^2}{\pi D} t \quad (7)$$

$$\bar{r} = (r_b + r_a)/2 \quad (7a)$$

$$\delta = H\omega^2 s \sqrt{\pi t/4D} - 4\omega^2 st + (\omega^2 s)^2(r_b{}^3 + r_a{}^3)t/12\bar{r}D \quad (7b)$$

$$H = (r_b - r_a)$$

Terms contributing less than 0.05% have been dropped from this equation; for an accuracy of 1%, the term δ can also be dropped.

Except for the factor $\exp(-\tau)$, eq. 6 can be readily derived from the equations of Yphantis[18] for the concentration at the meniscus and base of a rectangular cell when sedimentation takes place in a constant field. Yphantis used them to study the nature of the average molecular weights obtained by the Archibald method. His equations are series expansions of the classical Mason–Weaver solutions[19] for sedimentation in a semi-infinite rectangular cell subjected to a uniform field. The physical meaning of combining two semi-infinite solutions, one for the base and one for the meniscus, is that sedimentation at each is not influenced by changes at the other end so long as a plateau region separates the two.[17]

Results

Measurement of s.—The sedimentation coefficient is measured from eq. 7, which predicts that for a well-behaved system the plot of $(\Delta c/c^0)^2/(1 + \delta)$ vs. t is linear, with a slope proportional to s^2. Since s is found from the *slope* of this plot, it is not necessary to know accurately the time at which sedimentation begins. Considering the assumptions made in its derivation, one should use the equation only so long as the plateau region lasts; however, the numerical results of Yphantis[18] indicate that it actually will hold for a

(19) M. Mason and W. Weaver. *Phys. Rev.*, **23**, 412 (1924).

much longer period. The slope of this plot gives s^2/D; s can be found with the aid of independent diffusion measurements (method I). Fortunately, in the case of sucrose accurate data for D are available[7] in this range of concentration.

Alternatively s can be found by continuing the experiment to equilibrium and measuring s/D from an equilibrium photograph (method II). Unlike method I this requires that the extended Svedberg equation be valid. At equilibrium $\Delta c/c^0$ gives the apparent molecular weight evaluated[20] at the concentration $(c_a + c_b)/2$

$$(\Delta c(eq)/c^0) = \frac{M(1 - \bar{v}\rho)\omega^2 \bar{r}H}{RT(1 + c\partial \ln y/\partial c)}\bigg|_{c = (c_a + c_b)/2} \quad (8)$$

and substitution of this into eq. 1 gives

$$(\bar{r}\omega^2 s/D)\bigg|_{c = (c_a + c_b)/2} = \Delta c(eq)/Hc^0 \quad (9)$$

We assume that eq. 7 gives s^2/D at c^0 whereas eq. 9 gives s/D at $(c_a + c_b)/2$; however, the difference between c^0 and $(c_a + c_b)/2$ is small under the conditions in which these sedimentation experiments are carried out. To determine s/D it may be advantageous to set up a separate experiment with a short column of solution, to reduce the time needed to reach equilibrium.[4,20]

One can compute δ (eq. 7b) with satisfactory accuracy after plotting $(\Delta c/c^0)^2$ against t, and knowing either D or s/D. In these experiments the largest value of δ was only 0.005.

Precision.—Figure 1 shows a plot of $(\Delta c/c^0)^2/(1 + \delta)$ for one of the experiments. The data fall on a good straight line. For each experiment the slope of this line, and also the variance of the slope,[21] was found by least squares. These data are given in Table I in the form of the observed sedimentation coefficient divided by the value predicted from eq. 1. (The actual values of s are shown in Fig. 2.) The precision of these measurements, computed from the standard error of the slope, is at least 0.5%. In a typical experiment the last point on the plot has a Δc of 25 fringes (with $c^0 =$

TABLE I

COMPARISON OF OBSERVED WITH PREDICTED VALUES FOR THE SEDIMENTATION COEFFICIENT OF SUCROSE AT 25°

	s (obsd.)/s (theor.)	
c^0, g./100 ml.	Method I[a]	Method II[b]
3.619	1.002 ± 0.002	...
4.498	1.002 ± .004	0.995 ± 0.009
5.420	0.998 ± .002	.991 ± .004
5.579	0.994 ± .003	.994 ± .007

[a] To find s by method I, independent measurements of the diffusion coefficient (in this case, the data of Gosting and Morris[7]) are used together with a plot of eq. 7. Least squares was used to find the slope of this plot and also the variance of the slope[21]; the square root of the variance was used to estimate the uncertainty in s (obsd.). The predicted value of s is given by eq. 1 and can be represented by the empirical equation $s_{25} = 0.2770/[1 + 0.0312c + 0.0008c^2]S$, where c is in g./100 ml. [b] In finding s by method II the experiment is continued to equilibrium and then $\Delta c(eq)$ is used to give s/D (eq. 9). This is then combined with the slope from a plot of eq. 7. Considering only the uncertainty connected with reading the photographs, the experimental error in finding s by method II is twice that of method I since eq. 7 yields s^2 with method I but s with method II. Of course, other factors would enter in a complete analysis of error. The experiment at 3.619 g./100 ml. was not continued to equilibrium, and so s could not be found by method II.

(20) K. E. Van Holde and R. L. Baldwin, *J. Phys. Chem.*, **62**, 734 (1958).

(21) J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," 4th Ed., 1955, p. 557. The actual equations used are:

(1) $y = a + bx$, with n values of (x, y); then

(2) $b = [\Sigma xy - \bar{x}\Sigma y]/[\Sigma x^2 - n\bar{x}^2]$ with $\bar{x} = (1/n)\Sigma x$, $\bar{y} = (1/n)\Sigma y$; and

(3) $\sigma^2(b) = \left(\frac{1}{n - 2}\right)\{-b^2 + [\Sigma y^2 - n\bar{y}^2]/[\Sigma x^2 - n\bar{x}^2]\}$
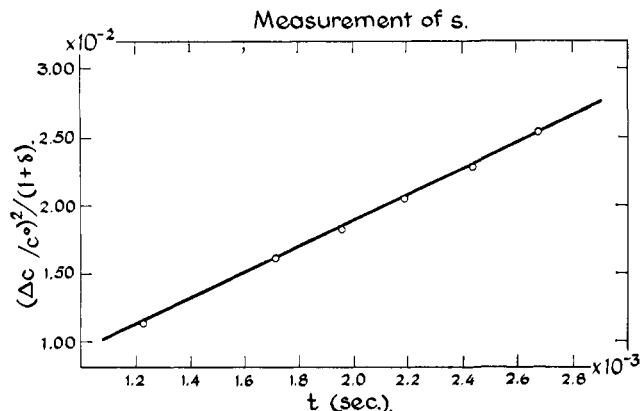
Fig. 1.—A plot of eq. 7 for an experiment with sucrose at an initial concentration of 5.579 g./100 ml. From the slope of this plot s can be obtained if D is known (method I) or if s/D is known (method II). Alternatively the molecular weight can be found if s is known.

140 fringes); an error of 0.5% in measuring $\Delta c = 25$ fringes is an error of 0.12 fringe. Put another way, if only the first and last photographs were used to compute s and if $\Delta c = 5$ fringes in the first photograph, then an error of 0.5% in s would correspond to an error (of opposite sign) of 0.05 fringe in each photograph.

Discussion

Validity of the Extended Svedberg Equation.—The sedimentation coefficients measured with eq. 7, by both methods I and II, agree with those predicted from the extended Svedberg equation (Table I). Only the results obtained with method I can be used to test this point since eq. 1 was used in deriving method II. The experimental sedimentation coefficients found by method I are shown as a function of concentration in Fig. 2. One can see a pronounced dependence of s on concentration, and also that the agreement between experimental and predicted values is very good. Thus the frictional coefficient of sucrose is the same in sedimentation as in diffusion at these concentrations. The frictional coefficient f is related to s and D by (cf. Williams, et al.[11])

$$s = M(1 - \bar{v}\rho)/Nf \tag{10a}$$

$$D = RT(1 + c\partial \ln y/\partial c)/Nf \tag{10b}$$

where N is the Avogadro number. Since the two frictional coefficients are identical, any "backward flow" in sedimentation has its exact counterpart in diffusion. Of course, this is the conclusion expected from considerations of thermodynamics of irreversible processes[8] so long as the system contains only two components and s is independent of rotor speed.

Creeth[15] has previously confirmed eq. 1 with the results of his study of thallous sulfate. He pointed out that his sedimentation measurements were not very accurate and suggested that whenever a homogeneous solute was found for which one could determine s accurately, that this type of study should be repeated. Rather than finding a new test system, we have worked out a new method for measuring sedimentation coefficients of small molecules.

Although there has been no reason to doubt the validity of the Svedberg equation at zero concentration, there have been few attempts to test the equation directly. As Creeth points out,[15] his data for thallous sulfate seem to provide the first direct test with a two-component system. Accurate studies have been made of the sedimentation and diffusion behavior of silicotungstic and phosphotungstic acids[22] and the results,

(22) M. C. Baker, P. A. Lyons, and S. J. Singer, J. Am. Chem. Soc., 77, 2011 (1955); J. Phys. Chem., 59, 1074 (1955).
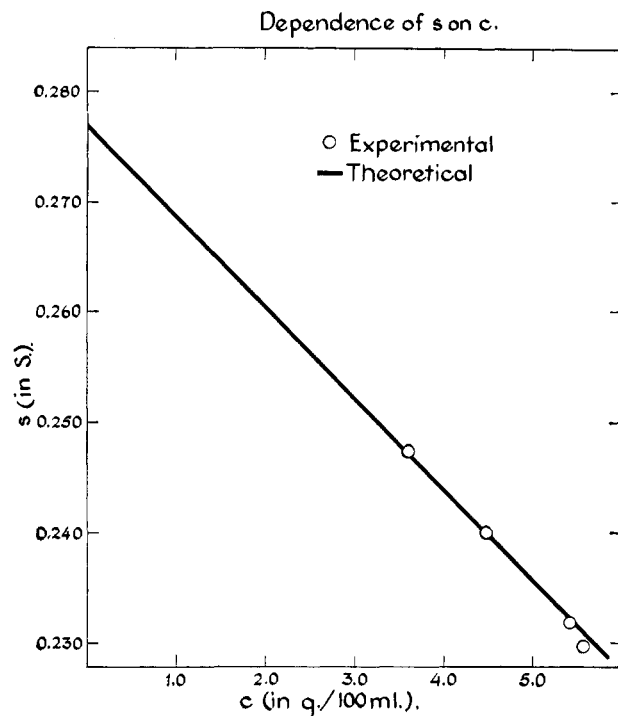

Fig. 2.—The sedimentation coefficient of sucrose at 25° as a function of concentration (values found by method I). The solid line shows the values predicted from the extended Svedberg equation and the diffusion data of Gosting and Morris.[7]

extrapolated to zero concentration, seemed to fit the Svedberg equation. However these measurements were made on three-component systems, in the days before the complications inherent in studying three-component systems were appreciated. The work of Gosting[23] and his collaborators has shown that four diffusion coefficients are needed to describe the diffusion of a three-component system, and although the sedimentation coefficient of one component in a three-component system can be predicted from other measurements,[11,24] the relation is more complex than eq. 1.

Methods of Measuring Sedimentation Coefficients of Small Molecules.—In the present experiments a freely sedimenting boundary is never formed and instead one measures the changes in concentration at the base and the meniscus. The usual method of measuring sedimentation coefficients is to follow the movement of a boundary. With schlieren optics it is easy to measure the position (r_H) of the maximum gradient in the boundary, and for large molecules one can find s from dr_H/dt. However, the boundary position is given, strictly, not by r_H but by the square root of a second moment of the boundary gradient curve.[6] The error in using r_H is very small for large molecules, which form sharp boundaries and move rapidly, but becomes substantial for molecules as small as sucrose where the error is of the order of 10% (see eq. 56 b, p. 759 of the review by Williams, et al.[11]). Actually this source of error was noted by Lamm,[25] in 1929, from his study of Faxén's equation. Thus for very small molecules there is little advantage in forming a synthetic boundary by means of a boundary-forming cell.

Gutfreund and Ogston[5] have derived an equation for measuring s from experiments with a standard cell, and this has been modified for use with schlieren optics.[26] Their method is analogous to the moving-boundary

(23) L. J. Gosting, Advan. Protein Chem., 11, 429 (1956).
(24) R. L. Baldwin, J. Am. Chem. Soc., 80, 496 (1958).
(25) O. Lamm, Z. physik. Chem., 143A, 177 (1929).
(26) R. L. Baldwin, Biochem. J., 55, 644 (1953).

method in being applicable only so long as the plateau region lasts: both are based on the conservation of mass and the fact that transport occurs only by sedimentation in a region where $\partial c/\partial r = 0$. Unfortunately there seems to be little gain in accuracy when it is used with interference[15] rather than schlieren optics.[26,27]

In addition to being precise, the present method has the advantage that the measurements and computations are simple. To find Δc it is necessary only to record the positions of a few fringes at either end of the column and then to count the fringes in between.[4]

A New Method for Measuring Molecular Weights during the Transient Period.—Since the slope of the plot in Fig. 1 gives s^2/D, it could be used to find s/D (and therefore M) if s were known. This is illustrated in Table II, where predicted values of s (eq. 1) and known values of $\bar{v}$, ρ, and $\partial \ln y/\partial c$ have been combined with the present measurements of s^2/D to give M. The

TABLE II

VALUES FOR THE MOLECULAR WEIGHT OF SUCROSE OBTAINED BY A NEW METHOD

c^0, g./100 ml.	M (obsd.)$/M^a$
3.619	0.994 ± 0.004
4.498	$0.998 \pm .009$
5.420	$1.003 \pm .004$
5.579	$1.001 \pm .007$

^{a} Calculated from eq. 7 using known values for the sedimentation coefficient: in this case, the ones given by the extended Svedberg equation and the diffusion data of Gosting and Morris.[7] The experimental uncertainty indicated for M (obsd.) is that of finding the slope of eq. 7.[21]

agreement is quite good. This new method might be a good way of making use of the potential accuracy of interference optics in finding molecular weights from the transient period, something which has not yet been accomplished with the Archibald method (cf. Richards and Schachman[3]). It could be useful with proteins of large molecular weight which take a long time to reach sedimentation equilibrium because of low diffusion coefficients.[20] The procedure would be to find s from the rate of movement of a boundary at high rotor speed

(27) K. E. Van Holde, *J. Phys. Chem.*, **63**, 1574 (1959).

(inspection of the boundary shape also provides a check on the homogeneity of the material) and then to measure $(\Delta c/c^0)$ vs. t in experiments at lower rotor speed where a freely sedimenting boundary is not formed. Then the results from the two experiments are combined to give the molecular weight.

Factors Controlling the Time Needed to Reach Equilibrium.—With the aid of eq. 6 we can now derive expressions for two effects noted experimentally in an earlier study[4] of the approach to sedimentation equilibrium. First $\Delta c/c^0$ is almost independent of column height while the plateau region lasts. When we compare two experiments (1 and 2) at the same time and rotor speed but with different column heights, we find from eq. 6

$$\frac{\Delta c_1}{\Delta c_2} = \frac{\bar{r}_1}{\bar{r}_2} \frac{[1 + H_1(\omega^2 s/4)(\pi t/D)^{1/2} + \ldots]}{[1 + H_2(\omega^2 s/4)(\pi t/D)^{1/2} + \ldots]} \quad (11)$$

The column height H enters only in a small correction term. There is however a definite dependence of Δc on the position of the mid-point $\bar{r}$. In principle one could hold $\bar{r}$ constant while varying H, but in routine experiments $\bar{r}$ would be likely to change when H is changed.

Secondly it was noted[4] that the rate of approach to sedimentation equilibrium is nearly independent of ω^2 during the existence of the plateau region as well as in later stages of the experiment. The departure from equilibrium may be measured by the parameter ϵ,[4,20] which is defined as

$$\epsilon \equiv 1 - \Delta c/\Delta c(\text{eq}) \quad (12)$$

When $\Delta c(\text{eq})$ is expressed by eq. 9 and Δc by eq. 6, and these are substituted into eq. 11, one obtains a simple expression for ϵ which is valid in the first part of the experiment, while the plateau region lasts. Here

$$\epsilon = 1 - 4(Dt/\pi H^2)^{1/2}[1 + (H\omega^2 s/4)(\pi t/D)^{1/2} + \ldots] \quad (13)$$

ω^2 appears only in the minor correction term and ϵ depends chiefly on (D/H^2), as is also true after the plateau region vanishes.[4,20]

Acknowledgment.—We wish to thank Dr. T. Kotaka for his discussions of the theory.

The Reactions of Iodopentaamminecobalt(III) with Various "Two-Electron" Oxidizing Agents

BY ALBERT HAIM[1] AND HENRY TAUBE

The reactions of $Co(NH_3)_5I^{++}$ with Cl_2 and Br_2 result in quantitative yields of $Co(NH_3)_5Cl^{++}$ and $Co(NH_3)_5Br^{++}$, respectively. Similarly, the reactions of $Co(NH_3)_5Br^{++}$ and $Cr(NH_3)_5Br^{++}$ (in 0.10 M Cl^-) with Cl_2 produce quantitative yields of $Co(NH_3)_5Cl^{++}$ and $Cr(NH_3)_5Cl^{++}$, respectively. The reactions of $Co(NH_3)_5Br^{++}$ with HOBr and HOCl and of $Co(NH_3)_5I^{++}$ with HOBr, ICl, O_3, CH_3CO_3H, $S_2O_8^{-2}$, HSO_5^-, and H_2O_2 yield $Co(NH_3)_5OH_2^{+3}$ quantitatively. O^{18} tracer studies on the reactions of $Co(NH_3)_5I^{++}$ with H_2O_2 and O_3 indicate that 31 and 5.5%, respectively, of the oxygen in the $Co(NH_3)_5OH_2^{+3}$ product is derived from the oxidizing agent. The reaction of $Co(NH_3)_5I^{++}$ with H_2O_2 when H^+ and H_2O_2 are in excess obeys the rate law $k_3(Co(NH_3)_5I^{++})(H_2O_2)(H^+)$ during approximately the first two half-lives, but this phase is terminated by a sharp decrease in $(Co(NH_3)_5I^{++})$. Iodine and iodate ion strongly accelerate the rate of disappearance of $Co(NH_3)_5I^{++}$. The rate of reaction of $Co(NH_3)_5I^{++}$ and H_2O_2 is independent of (Cl^-) but as (Cl^-) is increased $Co(NH_3)_5Cl^{++}$ becomes an increasingly important product. $Co(NH_3)_5Cl^{++}$ is also formed in high yields when $Co(NH_3)_5I^{++}$ reacts with O_3 or $S_2O_8^{-2}$ in the presence of Cl^-. The mechanisms of the reactions are discussed, and they feature rearrangements of the type $(NH_3)_5CoIOH^{+3}$ to $(NH_3)_5Co\overset{H}{O}I^{+3}$ and $(NH_3)_5CoICl^{+3}$ to $(NH_3)_5CoClI^{+3}$, followed in each case by loss of $I(I)$ (as HOI, for example).

The behavior of the iodopentaamminecobalt(III) ion toward various "one-electron" oxidation–reduction reagents has been reported recently.[1] It was demonstrated that with some of these reagents (hydroxyl and

(1) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 495 (1963).

methyl radicals, iodine atoms) reduction of the Co(III) center occurs, whereas with other reagents (ceric and cobaltic ions) the oxidation state of the Co(III) center is preserved. In the present paper we report the results obtained in a study of the reactions of $Co(NH_3)_5$-