nia-insoluble dipotassium salt of guanidine during the course of the potentiometric titrations. Furthermore, it is significant that neither carbon(IV) iodide nor iodoform was present at the end of the titration; this is shown by the fact that the gross product was water-soluble. Accordingly, one may postulate either a metathesis resulting in the formation of H_2NCI_3 and KI or a base-catalyzed ammonolysis yielding HCI_3 and NH_2I. The latter product would undoubtedly react with potassium amide to form hydrazine, which has been shown to react with carbon(IV) iodide as

$$2CI_4 + N_2H_4 + 2NH_3 \longrightarrow N_2 + 2NH_4I + 2HCI_3 \quad (1)$$

Iodoform so produced should be expected to be consumed in a reaction analogous to that reported[11] for chloroform.

$$CHCl_3 + 4KNH_2 \longrightarrow KCN + 3KCl + 3NH_3 \quad (2)$$

This would account for the consumption of four equivalents of potassium amide in addition to the one equivalent required for the formation of iodoamide, and the assumption of the base-catalyzed ammonolysis followed by the indicated secondary reactions is therefore consistent with the results of the potentiometric titrations. Apparently the only alternative is to consider that carbon(IV) amide is formed and undergoes ultimate deammoniation to form cyanamide. However, this product should form an ammonia-insoluble dipotassium salt,[11] and no such product was obtained.

As shown by equation 1, carbon(IV) iodide acts as an oxidizing agent toward hydrazine in liquid ammonia in a manner apparently strictly analogous to that previously reported for the reactions between hydrazine and carbon(IV) chloride[12] and bromide.[13] Moreover, all of the hydrazine lost from the system appears quantitatively as elemental nitrogen, and it is suggested that this reaction might be employed for the analytical estimation of hydrazine in liquid ammonia solutions. The occurrence of the secondary reaction

$$HCI_3 + N_2H_4 + 2NH_3 \longrightarrow N_2 + CH_3I + 2NH_4I \quad (3)$$

is indicated by the fact that the iodate titrations gave a titer value about 2% greater than expected solely on the basis of equation 1, and the loss of carbon-containing substances amounting to about 10%. The over-all consumption of hydrazine is sufficient to account for the utilization in reaction (3) of about 10% of the iodoform resulting from reaction (1). Finally, the methyl iodide formed in (3) would probably react with the solvent to form a mixture of the corresponding primary, secondary, and tertiary amines.[14]

[11] E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publ. Corp., New York, N. Y., 1935, pp. 207, 95.

[12] S. H. Patinkin and E. Lieber, This Journal, **72**, 2778 (1950).

[13] A. K. Macbeth and D. Traill, *J. Chem. Soc.*, **127**, 894 (1925).

[14] G. W. Watt and J. B. Otto, Jr., This Journal, **69**, 836 (1947).

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The Kinetics of Mutarotation of D-Glucose with Consideration of an Intermediate Free-aldehyde Form

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The rate constants of the mutarotation equilibrium $\alpha \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \gamma \underset{k_2}{\overset{k_2'}{\rightleftarrows}} \beta$ as applied to D-glucose have been measured by a polarographic method in phosphate buffer solutions (*p*H about 6.9) for different buffer concentrations and ionic strengths, but constant buffer ratio. The rate constants are shown to be a linear function of the buffer concentration and independent of the ionic strength within experimental error. The concentration of intermediate free aldehyde (γ) has been determined from the rate constants and was found to be (0.0026 ± 0.0002%) of the total glucose concentration (0.655 mole/l.). Its value showed a small trend of decreasing with increasing buffer concentration. Possible reasons for this trend have been discussed.

Under the tacit assumption that diffusion is the only process determining the limiting current in the reduction of a number of aldose sugars at the dropping mercury electrode (d.m.e.), Cantor and Peniston[2] were led to calculate the free aldehyde concentration of these sugars from the Ilkovic equation. However, it was pointed out by Wiesner[3] that the polarographic waves observed behave quite differently from waves controlled by diffusion. Their limiting currents show an unusually great dependence on temperature and *p*H and in certain instances (*e.g.*, for glucose, galactose and xylose) they are practically independent of the head of mercury. These phenomena have been interpreted through the concept of kinetic waves.[3] The cyclic hemiacetal form of the aldose—itself non-reducible—produces a reducible form, presumably the free aldehyde, in a very fast chemical reaction at the electrode surface. If the concentration of the non-reducible substance at the electrode surface in the potential range of the limiting current is practically the same as that in the bulk of the solution, the current is said to be completely rate controlled.

Complete rate control requires that i_k, the kinetic limiting current, be very small as compared to i_{hd}, the hypothetical diffusion current (*i.e.*, the current in case the non-reducible component were reducible as well), or, consequently, that i_k be independent of the head of mercury.[4] Using the latter criterion Wiesner also found that D-glucose gives a completely rate-controlled wave.

[1] Holder of a National Research Council of Canada Studentship.

[2] S. M. Cantor and Q. M. Peniston, This Journal, **62**, 2113 (1940).

[3] K. Wiesner, *Collection Czechoslov. Chem. Commun.*, **12**, 64 (1947).

[4] K. Wiesner, *Z. Elektrochem.*, **49**, 163 (1943).

Delahay and Strassner[5] measured the polarographic waves of equilibrium mixtures of α- and β-pentoses and hexoses as a function of *p*H and temperature and adopting the scheme $(\alpha,\beta) \underset{k_s'}{\overset{k_s}{\rightleftarrows}} \gamma$ (where γ is the free aldehyde), they obtained from their data values of a first-order surface rate constant k (in cm. sec.$^{-1}$) which they related to k_s, the first-order rate constant in solution (in sec.$^{-1}$) by the quite arbitrary relationship $k_s = k/\delta$, δ being the average distance between two molecules of aldose in solution. Their values of k_s, thus calculated, are 2 to 3 orders of magnitude higher than the data presented in this paper. The equilibrium constants k_s/k_s' being unknown, the authors were unable to calculate the rate of the reverse reaction. In fact, it is even impossible to calculate k_s from the magnitude of the kinetic limiting current without simultaneously taking into account the rate of the reverse reaction, k_s'. Moreover, the authors do not mention the buffer concentrations which they used. Since mutarotation of aldoses is subject to general acid–base catalysis, this omission would render the values of any measured rate constant rather meaningless, particularly in the region around *p*H 7.

In a preliminary communication[6] by two of the present authors it has been shown that it is possible to evaluate the four rate constants—and therefore the equilibrium concentration of the free aldehyde (γ)—of the mutarotation equilibrium of D-glucose

$$\alpha \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \gamma \underset{k_2}{\overset{k_2'}{\rightleftarrows}} \beta \qquad (1)$$

by methods of polarography (α and β are the cyclic hemiacetal forms). Three of the four necessary equations could be obtained from polarographic current–time and current–voltage curves and the fourth from the over-all equilibrium constant. The equation relating the kinetic limiting current to a function of the rate constants was derived on the basis of the reaction volume concept.[7]

The thickness of the reaction layer, μ, for the reaction

$$\mathrm{A} \underset{k'}{\overset{k}{\rightleftarrows}} \mathrm{B} \qquad (2)$$

where only B is reducible at a certain potential, is given by $\mu = \sqrt{D/2k'}$, $1/k'$ being the average life time and D the diffusion coefficient of the species B. However, Koutecky and Brdicka[8] showed for the case of plane electrodes that, if the reaction volume concept is to be maintained, its thickness should be $\mu = \sqrt{D/k'}$ and this again would only hold true if $k << k'$. The latter expression for μ was the one actually used in the original work[6] for the evaluation of the rate constants in equation 1, with the exception that the average life time of γ-molecules is now given by $1/(k_1' + k_2')$, thus rendering $\mu = \sqrt{D/(k_1' + k_2')}$.

In 1953 Koutecky[9] gave a rigorous solution for the problem of the fast reaction (2) producing a kinetic wave at an expanding spherical electrode. Provided that $l = k(1 + K) >> 1$, $(K = k'/k)$, Koutecky could show that the thickness of the reaction layer is correctly expressed by $\mu = \sqrt{D(1+K)/kK^2}$ which approximates the expression $\mu = \sqrt{D/k'}$ for $K >> 1$ or $k' >> k$. Though no definite proof of the point is available as yet, in such cases of reaction scheme (1) where analogous conditions are fulfilled, it seems obvious that the reaction volume treatment represents the kinetic phenomena at the d.m.e. sufficiently well if only μ is given by $\sqrt{D/(k_1' + k_2')}$. For each of the two equilibria involved in scheme (1) and applied to D-glucose, the conditions $l >> 1$, $k' >> k$ are satisfied, as will be demonstrated, *a posteriori*, by the results of the present investigation. An obvious test for the correctness of this treatment and of the assumption that equation 1 is a fair representation of the mutarotation equilibrium, is the verification of the requirement that the concentration of free aldehyde must be independent of the rate constants obtained under different circumstances at any given temperature.

The Basic Equations.—On the basis of the reaction volume concept, one has for the rate-controlled limiting current of the α isomer only

$$i_{\mathrm{k},\alpha} = 493n(mt_{\mathrm{d}})^{2/3}\mu k_1 C_\alpha \qquad (3)$$

with i_{k} in μa., C_α in mmoles liter^{-1}, m in mg. sec.$^{-1}$, t_{d} (= drop time) in sec., μ in cm. and k in sec.$^{-1}$, conforming with the units used by Kolthoff and Lingane.[10] The numerical factor (493) in equation 3 holds for 25°, but it has a very small temperature coefficient, *viz.*, the same as the constant 607 in the Ilkovic equation,[10] *i.e.*, +0.00012 deg.$^{-1}$.

If now the equation

$$\mu = \sqrt{D/(k_1' + k_2')} \qquad (4)$$

analogous to the relationship of Wiesner,[7] is introduced into equation 3, one obtains

$$i_{\mathrm{k},\alpha} = 493n(mt_{\mathrm{d}})^{2/3}(D)^{1/2}\frac{k_1}{(k_1' + k_2')^{1/2}}C_\alpha$$

A corresponding expression is valid for $i_{\mathrm{k},\beta}$

$$i_{\mathrm{k}.\beta} = 493n(mt_{\mathrm{d}})^{2/3}(D)^{1/2}\frac{k_2}{(k_1' + k_2')^{1/2}}C_\beta$$

The total limiting current is

$$i_{\mathrm{k}} = i_{\mathrm{k},\alpha} + i_{\mathrm{k},\beta}$$

so that, at 25°

$$i_{\mathrm{k}} = 493n(mt_{\mathrm{d}})^{2/3}(D)^{1/2}\frac{1}{(k_1' + k_2')^{1/2}}(k_1C_\alpha + k_2C_\beta) \qquad (5)$$

The mutarotation reaction is first order in α and β, so that

$$C_\beta = x = x_\infty(1 - e^{-kt}) \qquad (6)$$

where the subscript ∞ indicates the equilibrium state and k = conventional first-order rate constant of mutarotation. If now a represents the total concentration of glucose, then, because C_γ is very small, $C_\alpha = a - x$, and substituting this equality,

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[5] P. Delahay and J. E. Strassner, THIS JOURNAL, **74**, 893 (1952).

[6] J. M. Los and K. Wiesner, *ibid.*, **75**, 6346 (1953).

[7] K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

[8] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 337 (1947).

[9] J. Koutecky, *ibid.*, **18**, 597 (1953).

[10] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Chapter IV, Interscience Publishers, New York, N. Y., 1952.

together with equation 6, into equation 5, it follows for the kinetic current at time t that

$$i_k(t) = 493n(mt_d)^{2/3}(D)^{1/2}\frac{1}{(k_1' + k_2')^{1/2}}[k_1a - (k_1 - k_2)x_\infty + (k_1 - k_2)x_\infty e^{-kt}] \quad (7)$$

Subtracting from this the corresponding equation at time t', where $t' - t = \Delta > 0$ and taking logarithms, it follows that

$$\ln [i_k(t) - i_k(t')] = \ln 493n(mt_d)^{2/3}(D)^{1/2}\frac{k_1 - k_2}{(k_1' + k_2')^{1/2}}x_\infty(1 - e^{-k\Delta}) - kt \quad (8)$$

Taking Δ = constant, in accordance with the method of Guggenheim[11] and plotting $\ln [i_k(t) - i_k(t')]$ *vs.* t, we should obtain a straight line with slope $= -k$ and

$$\text{intercept} = \ln 493n(mt_d)^{2/3}(D)^{1/2}\frac{k_1 - k_2}{(k_1' - k_2')^{1/2}}x_\infty(1 - e^{-k\Delta}) \quad (9)$$

Now k may be expressed in the rate constants of equation 1[12]

$$k = {}^1/_2[k_1 + k_1' + k_2 + k_2' - \sqrt{(k_1 + k_1' - k_2 - k_2')^2 + 4k_1'k_2'}]$$

or, if $k_1', k_2' >> k_1, k_2$—which holds in the case of D-glucose as shown below—this equation will simplify to

$$k = \frac{k_1k_2' + k_1'k_2}{k_1' + k_2'} \quad (10)$$

The latter equation may also be derived by applying the steady-state assumption to the very small concentration of γ.

A further relationship among the four rate constants may be obtained from equation 7 at $t = \infty$

$$i_k(\infty) = 493n(mt_d)^{2/3}(D)^{1/2}\frac{1}{(k_1' + k_2')^{1/2}}[k_1a - (k_1 - k_2)x_\infty] \quad (11)$$

Finally, the over-all equilibrium constant at 25° is known to be[13]

$$\frac{x_\infty}{a - x_\infty} = \frac{k_1k_2'}{k_1'k_2} = 1.740 \quad (12)$$

The four equations 9, 10, 11 and 12 should provide a solution for all four rate constants.

It should be mentioned that $C_\gamma = y(t)$ may be obtained at any time in a simple way from the steady-state treatment

$$y(t) = \frac{k_1(a - x_\infty) + k_2x_\infty}{k_1' + k_2'} - \frac{k_2 - k_1}{k_1' + k_2'}x_\infty e^{-kt} \quad (13)$$

and

$$y_\infty = \frac{k_1(a - x_\infty) + k_2x_\infty}{k_1' + k_2'} = \frac{k_1(a - x_\infty)}{k'} = \frac{k_2x_\infty}{k_2'}$$

Experimental

Materials.—The glucose used in the experiments was "Analar" grade (B.D.H.), which is pure α-D-glucose, free from catalytically active impurities. The glucose was stored in a vacuum desiccator over $Mg(ClO_4)_2$. The buffer components, NaH_2PO_4 and Na_2HPO_4, were "Reagent" grade and so was the KCl, added in some experiments to bring the solutions to the desired ionic strength.

Equipment.—A Leeds and Northrup (pen-recording) Electro-Chemograph type E was used for all polarographic work and the electrolysis vessel was an H-type Lingane cell with a saturated calomel electrode. *p*H values were measured with a Beckman Model G *p*H meter with a large electrode. All experiments were carried out in a water thermostat at 25 ± 0.05°.

Method.—In this investigation two types of polarographic curves were recorded: current–time and current–voltage curves.

The current–time curves, at the constant potential of −1.75 volts with respect to the S.C.E., were obtained by dissolving 1.28 g. of α-D-glucose in 10 ml. of buffer solution, previously brought to bath temperature in the electrolysis cell. A rather vigorous stream of nitrogen, passed through this solution, was used for making it oxygen-free and also for rapidly dissolving the glucose. Complete dissolving took about 45 seconds and *zero*-time was taken at the moment of adding the glucose. Recording could usually be started at about 60 seconds. Damping 1 was generally used (corresponding to critical galvanometer damping), but damping 3 gave the same results within experimental error. Damping 1 was more convenient, since the curves usually were not free from irregularities (probably due to the close proximity of the recording potential to the deposition potential of hydrogen) and damping 1 caused the current to return to its proper value considerably faster than damping 3. (Damping 0 was out of the question, since the amplitude of the pen would be much too large). A current range of 3 (10″ = 3 μa.) was found to be most satisfactory. The recorder zero had to be turned off the chart in order to register the current–time curve. Current–time curves were always recorded continuously for the first 20 minutes and thereafter for periods of 1 minute each, at 20-minute intervals. If a run was made to last quite long (more than 40 minutes), the current would show a tendency to increase slightly after the minimum current, corresponding to the mutarotation equilibrium, had been reached. The effect was not reproducible and might be due to some hysteresis in the recording system. The precision of the measurements could well be determined by it. All current–time curves were recorded with the same head of mercury (55.8 cm.).

A series of current–voltage curves with different heads of mercury was recorded after each current–time curve, using the equilibrium solution obtained upon the completion of the latter. A current range of 5 (10″ = 5 μa.) was always applied for these waves. For each of the polarographic waves a residual current–voltage curve was recorded. The difference curve should represent the current–voltage wave due to the reduction of equilibrium D-glucose alone. A representative set of the latter is given in Fig. 1.

Results

The experiments performed (at 25°) are listed in Table I.

TABLE I

Expt.	Total buffer concn., moles/l.	KCl concn., moles/l.	Ionic strength	*p*H
A1	0.070	0.100	0.27	6.92
B1	.112	...	.27	6.95
B2	.112	.200	.47	6.85
C2	.153	.100	.47	6.87
D2	.194	...	.47	6.91

The glucose concentration in all cases was 0.655 mole/liter. The *p*H values listed in the last column were those measured after mutarotation equilibrium of the added glucose had been reached. The buffer ratio in all experiments was $[NaH_2PO_4]/[Na_2HPO_4] = {}^2/_5$. Each experiment listed in Table I was repeated 2 to 4 times.

Since the mutarotation of D-glucose is an acid-base catalyzed process, it must be expected that the rate constants involved in equation 1 will be quite dependent on the buffer concentration. In the *p*H region of Table I they should be a linear function of the buffer concentration (not proportional, because of the catalysis by the water me-

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[11] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[12] T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1910).

[13] J. C. Kendrew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A176**, 352 (1940).

dium). Since H^+ and OH^- catalysis is negligible in the *p*H region of 4 to 7, the small *p*H differences are of no importance.

On the other hand, the equilibrium constants involved in equation 1, or the relative concentration of free aldehyde, should be independent of the buffer concentration and, at best, only slightly dependent on the ionic strength. Experimental confirmation of these points should be admitted as a strong support for the ideas advanced.

A set of current–voltage curves for experiment D2 and corrected for residual current is demonstrated in Fig. 1. It is seen that for the longer drop times (smaller heads of mercury) the limiting current at the points indicated (−1.75 v.) is higher than for shorter drop times and, moreover, there is no horizontal plateau as in the last two curves shown. The same phenomenon has been observed by Delahay and Strassner.[5] The cause might be a small catalytic hydrogen wave superimposed on the kinetic wave of D-glucose and analogous to the very large catalytic hydrogen waves described by Vojir.[14] The latter are observed in the polarography of certain dyes in a buffer solution and also have the characteristic of decreasing with increasing head of mercury, contrary to the behavior of a diffusion current. In order to avoid this effect as much as possible, we have chosen for the current–time curves an optimum head of mercury of 55.8 cm. which gives a horizontal plateau while still permitting a reasonable drop time (2.47 sec. at −1.75 v.; m = 2.390 mg./sec.). Because of this effect, the criterion of absolute rate control, *viz.*, that the limiting current is independent of the head of mercury, has become of little use in this case. However, absolute rate control of the kinetic part of the current (see below) is still guaranteed by the ultimate results, which ascertain that $i_k << i_{hd}$, while the glucose concentration on the electrode surface is approximately given by $(i_{hd} - i_k)/\kappa$ (κ = Ilkovic factor), from which it follows that the latter concentration is the same as that in the bulk of the solution (i_{hd}/κ), within experimental error.

Plotting $\log_{10} [i_k(t) - i_k(t')]$ *vs.* t with $\Delta = t' - t$ some 2 to 3 times the half-life time of mutarotation and computing the values of the rate constants, it was found that the concentration of free aldehyde, y_∞, was about 0.003% of the total glucose concentration, as had been obtained previously.[6] These values have been entered in the second column of Table II. The diffusion coefficient, D, was taken from the measurements of Friedman and Carpenter[15] who obtained D as a function of the glucose concentration in water. For the glucose concentration used in our experiments, $D = 6.16 \times 10^{-6}$ cm.²/sec.

With the aid of the Ilkovic equation it was next calculated that the y_∞ values obtained in the first approximation correspond to a diffusion current with a magnitude of 4 to 7% of the total current (the largest value for the smallest buffer concentration). Since this cannot be neglected, a correction must be made.

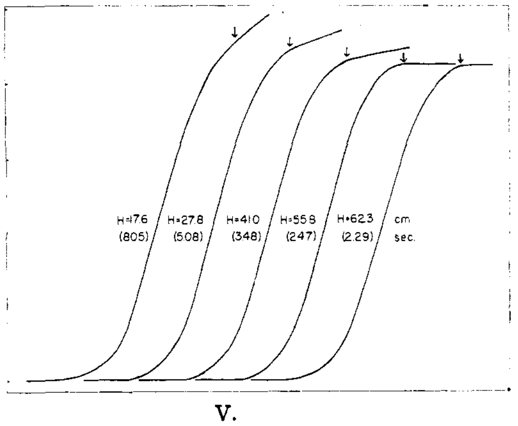

Fig. 1.—Current–voltage curves of equilibrium D-glucose after subtraction of residual currents for different heads of mercury H (expt. D2). The values in brackets are the corresponding drop times at −1.75 v. (these potentials are indicated by an arrow). Waves start at −1.30 v., with respect to the S.C.E.

The actual kinetic current is given by

$$i_k(t) = i - i_d = i - \kappa y(t)$$

where $y(t)$ is the function represented by equation 13. Therefore

$$i_k(t) - i_k(t + \Delta) = i(t) - i(t + \Delta) - \kappa \frac{k_1 - k_2}{k_1' + k_2'} x_\infty (1 - e^{-k\Delta}) e^{-kt}$$

so that the final results may be obtained by a series of successive approximations till the values of the rate constants—and of y_∞—do not change any further. A Guggenheim plot for these final calculations is demonstrated in Fig. 2 for one representative run in each of the series mentioned in Table I. The larger scatter of the experimental points as compared to the less accurate method of employing the infinite value is well known for this method of plotting.

The results finally obtained for the averages of all runs made are listed in Table II. The figures in brackets for the first column indicate the number of runs made in each series and for the other columns are the percentage deviations from the average values. The average of the y_∞ values in the last column is 0.0026% of a with a percentage deviation of the individual values from this average of almost 9%.

TABLE II

Expt.	y_∞[a] $\times 10^4$ % of a	$k \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$	k_1'	k_2'	$y_\infty \times 10^4$ % of a
A1(3)	49	3.1(3)	5.5(3)	1.8(4)	64(5)	37(5)	31(2)
B1(2)	31	4.0(1)	7.3(2)	2.2(2)	96(3)	51(1)	28(1)
B2(2)	29	4.6(5)	7.6(3)	2.7(6)	108(8)	66(11)	26(5)
C2(3)	29	5.6(4)	9.8(2)	3.2(5)	139(5)	78(9)	26(3)
D2(4)	24	6.8(3)	12.7(8)	3.8(2)	212(11)	110(4)	22(3)

[a] No diffusion corrections made.

Discussion

The values of the several rate constants have been plotted in Fig. 3 as a function of the buffer concentration. It is seen that deviations from the expected straight line relationships are not very great. Only for k, the over-all rate constant, an exact extrapolation to zero buffer concentration

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[14] V. Vojir, *Collection Czechoslov. Chem. Commun.*, **18**, 629 (1953).

[15] L. Friedman and P. G. Carpenter, THIS JOURNAL, **61**, 1745 (1939).

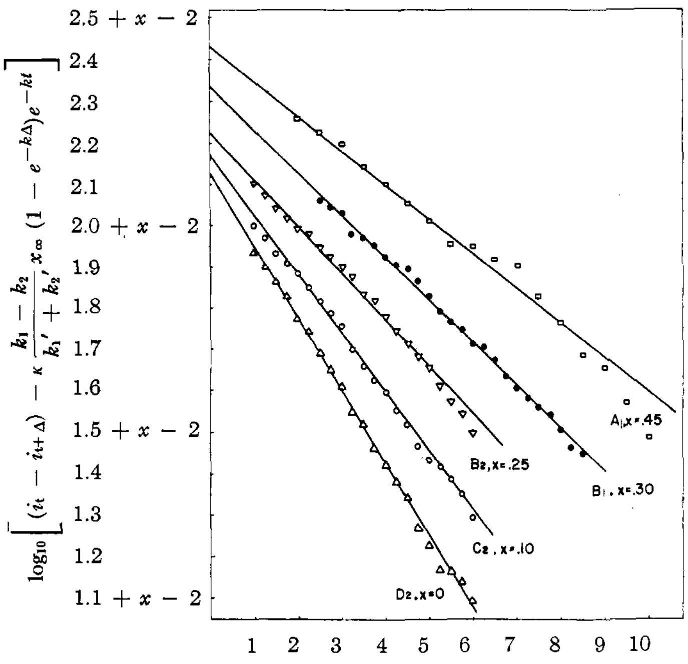

Fig. 2.—Guggenheim plots of D-glucose with final correction for diffusion current. Δ = 8 min. for A1, 6 min. for B1, 5 min. for B2, C2 and D2. In order to facilitate the plotting in this figure, each line is shifted by a convenient amount x along the ordinate.

was feasible, since the catalytic coefficient in water is accurately known (see, *e.g.*, ref. 13), namely, 0.40 × 10^{-3} sec.$^{-1}$.

Comparison of experiments B1 and B2 shows that ionic strength does not have any effect on the y_∞ value within experimental error. Ionic strength might have some effect on the rate constants. However, the data in Table II do not quite warrant such a conclusion and in view of the straight line relationships in Fig. 3, particularly that of k, it seems that the percentage deviations of Table II give a somewhat too flattering idea of the precision attained.

Whether or not the latter point of view is also relevant with respect to the percentage deviation of the y_∞ values of Table II remains to be seen. Certainly the conclusion is justified that the method applied is correct in the first analysis, in so far as the particular test for constancy of y_∞ with respect to changes in buffer concentration and ionic strength is concerned. On the other hand, the relative deviation of 9% among the values in Table II is rather high. Moreover, there is a definite downward trend in the y_∞ values. As this is also the direction of increasing buffer concentration, it may be thought that insufficient buffer capacity is the cause for the presumably too high values of y_∞ at the lower buffer concentrations. Indeed, insufficient buffering should lead to higher values of i_k, since this produces more of the powerful catalytic ion $HPO_4^=$ around the electrode during the H^+-consuming reduction and this, in turn, would yield y_∞ values that appear high. However, low buffer capacity could hardly be the real cause of the downward trend. Brdicka, who recently published new data[16] on the kinetic formaldehyde waves, found no deviations from theoretically expected values for buffer concentrations as low as 0.01 molar (NaOH and borate).

The fact that a diffusion current correction was necessary may be thought of as being caused by the rather small values of k_1 and k_2, which made a large glucose concentration imperative. The procedure of subtracting a diffusion current contribution of the depolarizer itself, in conjunction with the reaction volume theory, has been criticized by Kern,[17] and it may be that the more rigorous theory of Koutecky could obviate the small discrepancy.

Finally, there is the possibility that reaction scheme (1) is not quite complete. The possibility of hydration of the free aldehyde might have to be considered as well.

The latter two points will be further investigated.

Acknowledgment.—The authors are indebted to the National Research Council of Canada for financial support of this work and to the Leeds and Northrup Company (Philadelphia, Penna.) for the loan of an Electro-Chemograph.

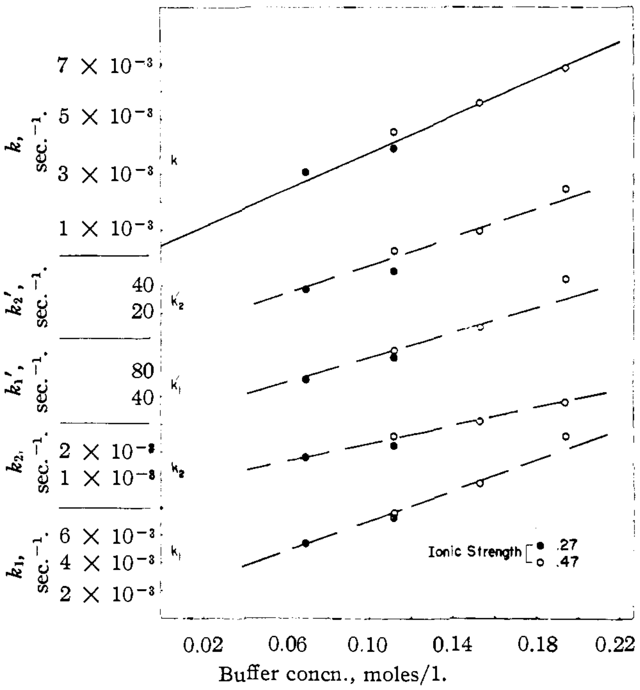

Fig. 3.—The rate constants as a function of the buffer concentration.

Fredericton (N.B.), Canada

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[16] R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **20**, 387 (1955).

[17] D. M. H. Kern, This Journal, **75**, 2473 (1953).