291. *Heats of Activation in the Mutarotation of Glucose. Part II. Catalysis by Water, Acids, and Bases.*

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The catalytic coefficients and heats of activation have been determined for the catalysis of the mutarotation of glucose by water, by three acids, and by four bases. Slight deviations from the Arrhenius equation have been shown to exist for the water-catalysed reaction, but have not been detected in the case of other catalysts.

The results, together with those recorded in Part I, are examined from the point of view of the kinetic theory of reaction velocity, as expressed by the equation $k = PZe^{-E/RT}$. The heats of activation specific to the various catalysts differ only slightly, and the variations in k are thus due, mainly, to changes in P; P ranges from 10^{-4} for water catalysis to nearly 10^4 for hydroxyl-ion catalysis, and for both acid and basic catalysis can be correlated with the corresponding acid and basic dissociation constants by a relation of the form $P \sim \text{const.} \times K^n$, where n is constant for a series of catalysts.

In view of the fact that values for $P \gg 1$ have been obtained, the question is raised as to the validity of the assumptions made in the computation of P.

THE study of the influence of temperature on the catalysis of prototropic changes, which commenced with an investigation of the acetone–iodine reaction (J., 1934, **1744**; subsequently denoted by *A*), has now been continued with the mutarotation of glucose. The present paper is concerned with the catalysis of this reaction by water, and by a number of acid and basic catalysts chosen so as to include the greatest possible range of acid and basic strengths. The mechanism of the reaction in alkaline solutions, which constituted a separate problem, has already been discussed in Part I (J., 1936, 1824; *B*).

The reaction in pure water was first examined. Although during the past 90 years numerous values for the velocity of mutarotation in water have been recorded for temperatures between 0° and 40°, the reliability of many of these is questionable, and at several temperatures serious discrepancies exist between the individual values. It was, in fact, not possible from the existing data to fix the velocity with certainty for any temperature except perhaps for 20°. A number of measurements have therefore been made at temperatures between 0° and 35°. The velocities obtained, expressed in the units min.$^{-1}$ and logarithms to the base *e*, are given in col. 2 of the foregoing table. For each

The velocity of mutarotation of glucose in water.

Temp.	$10^3 V_{\text{obs.}}$.	$10^3 V_{\text{calc.}}$.	Diff., % (calc. − obs.).
0°	1·715 (1·68,[1] 1·69 [2])	1·74	+1·5
10	5·32	5·24	−1·5
15	8·98	8·85	−1·4
18	12·15 (12·2 [3])	12·0	−1
20	14·7 (15·0,[4] 14·6,[5] 15·2 [2])	14·7	0
25	24·0 (22·1,[1] 23·9,[6] 25·3 [2])	23·9	−0·5
35	59·3	60·0	+1·2

[1] Andrews and Worley, *J. Physical Chem.*, 1928, **32**, 307.
[2] Kilpatrick and Kilpatrick, *J. Amer. Chem. Soc.*, 1931, **53**, 3698.
[3] Brönsted and Guggenheim, *ibid.*, 1927, **49**, 2554.
[4] Riiber, *Ber.*, 1922, **55**, 3132; 1923, **56**, 2185.
[5] Richards, Lowry, and Faulkner, J., 1927, 1733.
[6] Kuhn and Jacob, *Z. physikal. Chem.*, 1924, **113**, 389.

temperature the result given, which is the mean of those obtained in several experiments, was reproducible to about 0·5%. For comparison, there are included in the table velocities recently obtained by other workers, after conversion, where necessary, into the units given above.

It will be seen that for 18°, 20°, and 25° certain previous results are confirmed, but that for 0° the present value is slightly higher than those hitherto recorded. The heat of activation calculated from these figures is not constant over the whole range of temperature, but decreases from 17,160 cals. for the range 18—0° to 16,660 cals. for the range 35—18°. The reaction does not, therefore, conform exactly to the Arrhenius equation, and the extent of the deviations can be seen from the figures given in col. 3 of the table, which are calculated by means of the equation $\log_{10}k = 10{\cdot}785 - 16{,}900/2{\cdot}3026RT$. It will be observed that there is a maximum divergence between the observed and calculated velocities of about ± 1·5%, which is definitely greater than the experimental error. The deviations from the Arrhenius equation, although small, are thus considered to be real.

Previous investigations have failed to detect these slight irregularities, presumably because they were masked by a rather larger experimental error. An exception is the experiments of Hudson and Dale (*J. Amer. Chem. Soc.*, **1917**, **39**, 320). Below are given heats of activation derived from their data for temperatures above and below 20°. These have been calculated, for intervals of not less than 10°, from the mean velocities for α- and β-glucose at each temperature.

Temp.	*E*.	Temp.	*E*.
20°/0·7°	17,900	40°/20°	17,000
20°/5°	16,500	40°/25°	16,700
20°/10°	17,400	40°/30°	16,700
Mean	17,300	Mean	16,800

It is clear that, on the average, *E* is decidedly greater over the lower temperature range, which is in harmony with our own conclusion. On the other hand, this view is at variance with the more recent work of Moelwyn-Hughes, Klar, and Bonhoeffer (*Z. physikal. Chem.*, **1934**, *A*, **169**, 113), who conclude, as the result of measurements at four temperatures between 9·58° and 39·86°, that the reaction follows the Arrhenius equation with an accuracy which is better than 1%, *i.e.*, within the experimental error. This work is, however, open to criticism on experimental grounds. The velocity they obtained for 19·65°, expressed in the units here adopted, is 0·0149, which on the basis of their own results, can be shown to correspond to 0·0154 at 20°. This value is undoubtedly too high, as is shown by the extensive experiments of Lowry (*loc. cit.*) and of Riiber (*loc. cit.*). Lowry, as the result of nine concordant polarimetric determinations, recorded 0·0146, which he regarded as sufficiently accurate to be considered the " standard " value. Riiber's experiments, which were of even greater scope and included polarimetric, dilatometric, and interferometric measurements with both α- and β-glucose and with glucose hydrate, give a mean velocity of 0·0150. Both these results are fairly close to our own, and it can thus be stated with confidence that the correct velocity at 20° is 0·0148 ± 0·0002. The above value of 0·0154, therefore, represents a discrepancy of about 3%, which obviously invalidates the authors' conclusions.

The mean heat of activation resulting from the present measurements, which is about 17,000 cals., is lower than previous estimates, which range from 17,340 (Euler and Ugglas, *Z. physiol. Chem.*, **1910**, **65**, 124) to 17,700 cals. (Hudson and Dale, *loc. cit.*). These differences are, however, more apparent than real, for on the assumption of a constant heat of activation, there is clearly some latitude in fixing its value.

The question which naturally arises is whether the anomalous behaviour observed in the case of the water reaction, persists, or is even accentuated, in the case of other catalysts. A completely unequivocal answer to this question cannot be given. It is found for basic catalysis by hydroxyl ion, glucosate ion (*loc. cit.*, *B*), and phenoxide ion (p. 1417), and for acid catalysis by hydrion (p. 1415) that in each case the reaction conforms to the Arrhenius equation within the limits of experimental uncertainty. This uncertainty is, however, greater than in the case of water, and varies somewhat from catalyst to catalyst. For less efficient catalysts, small irregularities would escape detection entirely, but there is no reason to suspect a behaviour different from that of the catalysts just enumerated.

Acid Catalysis.—(1) *Hydrion.* The velocity of mutarotation in a solution which was 0·0400*M* with respect to hydrochloric acid was measured at five temperatures. The results are given in Table I. In row 2 are given the observed velocities; in row 3 the partial velocities due to hydrion, obtained by subtracting from the total velocity that due to water; and in row 4 are the velocities due to hydrion, calculated from the equation

$$\log_{10}V_h = 12{\cdot}111 - 18{,}600/2{\cdot}3026RT$$

TABLE I.

Mutarotation of glucose in 0·0400M-*hydrochloric acid.*

Temp.	0°	10°	18°	25°	35°
$10^3 V_{\text{obs.}}$	3·33	10·7	25·5	52·8	138·5
$10^3 V_h$	1·615	5·38	13·35	28·8	79·2
$10^3 V_{h,\ \text{calc.}}$	1·610	5·41	13·4	28·5	79·2

This equation is seen to give figures which agree with the experimental values within about 1%, which represents the accuracy with which the partial velocity due to hydrion can be evaluated. The value of 18,600 cals. obtained for the heat of activation is intermediate between those given by Kilpatrick and Kilpatrick (*loc. cit.*) and by Moelwyn-Hughes (*Z. physikal. Chem.*, 1934, *B*, **26**, 272), *viz.*, 19,300 and 18,030 cals. respectively. Confirmation of the present result was sought by making additional measurements at 0° and 25° in solutions in which the concentration of hydrochloric acid was varied. The figures are given in Table II. Following previous procedure (*loc. cit., A*), the temperature coefficient for hydrion catalysis was evaluated from the experimental data by the method of reciprocal ratios, since this method minimises errors due to salt effects. The equations given in the paper referred to may be generalised in the form

$$\frac{1}{R_{\text{obs.}}} = \frac{1}{R_1} + \frac{{}_{25}V_2}{{}_{25}V_{\text{obs.}}}\left\{\frac{1}{R_2} - \frac{1}{R_1}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= \frac{1}{R_2} - \frac{{}_{25}V_1}{{}_{25}V_{\text{obs.}}}\left\{\frac{1}{R_2} - \frac{1}{R_1}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where $V_{\text{obs.}}$ is regarded as the sum of velocities V_1 and V_2 due to catalysts 1 and 2 respectively, and the *R*'s have their previous significance. In the present case 1 is hydrion and 2 is water, and on insertion of the experimental constants (1) reduces to

$$1/R_{\text{obs.}} = 0{\cdot}0566 + 3{\cdot}65 \times 10^{-4}/{}_{25}V_{\text{obs.}}.$$

The values of $1/R_{\text{obs.}}$ obtained by means of this equation are given in the last row of the table.

TABLE II.

Mutarotation of glucose in CM-*hydrochloric acid at* 0° *and* 25°.

C	0	0·01	0·02	0·05	0·10
${}_{25}V_{\text{obs.}} \times 10^2$	2·40	3·13	3·87	5·98	9·53
$1/R_{\text{obs.}}$	0·0714	0·0687	0·0663	0·0624	0·0606
$1/R_{\text{obs.}}$, calc.	0·0718	0·0683	0·0660	0·0627	0·0604

$1/R_h$ is thus 0·0566, which gives $E = 18{,}560$ cals., as compared with 18,600 cals. obtained previously, giving a mean of 18,580 cals.

(2) *Chloroacetic acid.* Kinetic measurements were made at 0° and 25° in solutions of chloroacetic acid varying from 0·10 to 0·60*M*. In such solutions the catalysts are water, undissociated chloroacetic acid, hydrion, and, to a much smaller extent, the chloroacetate ion; thus $V_{\text{obs.}} = V_{\text{H}_2\text{O}} + V_m + V_h + V_a$. In applying (1), catalysts 1 and 2 are regarded as chloroacetic acid and water respectively, and $V_{\text{obs.}}$ is replaced by $V_{\text{corr.}} = V_{\text{obs.}} - V_h - V_a$, and $R_{\text{obs.}} = {}_{25}V_{\text{corr.}}/{}_{0}V_{\text{corr.}}$. The data are given in Table III.

The observed velocities at 25° and 0° are given in rows 2 and 3 respectively, and the values of $V_{\text{corr.}}$ are derived from them by subtracting the partial velocities due to hydrion and

TABLE III.

Mutarotation of glucose in CM-*chloroacetic acid at* 0° *and* 25°.

C	0	0·100	0·200	0·400	0·600
$10^3 \times {}_{25}V_{\text{obs.}}$	24·0	36·6	44·7	58·1	70·8
$10^3 \times {}_{0}V_{\text{obs.}}$	1·715	2·45	2·98	3·82	4·62
$10^3 \times {}_{25}V_{\text{corr.}}$	24·0	27·9	32·45	40·5	49·1
$10^3 \times {}_{0}V_{\text{corr.}}$	1·715	1·97	2·28	2·82	3·39
$1/R_{\text{obs.}}$	0·0714	0·0706	0·0703	0·0696	0·06905
$1/R_{\text{obs.}}$, calc.	0·0715	0·0707	0·0703	0·0696	0·0691

chloroacetate ion, which have been calculated taking by K_a to be $1·5 \times 10^{-3}$, and the respective catalytic coefficients as 0·72 and 0·021 at 25°, and as 0·041 and 0·0012 at 0°. The resulting values of $1/R_{\text{obs.}}$ (row 6) are closely reproduced by those given in row 7, derived from the equation

$$1/R_{\text{obs.}} = 0·0668 + 1·12 \times 10^{-3}/{}_{25}V_{\text{corr.}}$$

hence $1/R_m = 0·0668$, which gives $E = 17{,}500$ cals.

(3) *Acetic acid.* Precisely similar arguments apply to this case. The results of measurements in solutions of acetic acid ranging from 0·5 to 0·2*M* are given in Table IV, the arrangement of which is similar to that of Table III. In the calculation of the partial velocities due to hydrion and acetate ion, K_a has been taken as $1·8 \times 10^{-5}$, the catalytic coefficient for hydrion as before, and that for the acetate ion as 0·133 at 25° and 0·0077 at 0°.

TABLE IV.

Mutarotation of glucose in CM-*acetic acid* 0° *and* 25°.

C	0	0·500	1·000	1·500	2·000
$10^3 \times {}_{25}V_{\text{obs.}}$	24·0	32·6	39·6	46·9	54·6
$10^3 \times {}_{0}V_{\text{obs.}}$	1·715	2·31	2·76	3·27	3·78
$10^3 \times {}_{25}V_{\text{corr.}}$	24·0	30·15	36·0	42·5	49·5
$10^3 \times {}_{0}V_{\text{corr.}}$	1·715	2·15	2·55	3·02	3·49
$1/R_{\text{obs.}}$	0·0714	0·0713	0·0708	0·0710	0·0705
$1/R_{\text{obs.}}$, calc.	0·0715	0·0712	0·0710	0·0708	0·0707

The figures given in the last row are derived from the equation

$$1/R_{\text{obs.}} = 0·0699 + 3·84 \times 10^{-4}/{}_{25}V_{\text{corr.}}$$

from which $1/R_m = 0·0699$, and $E = 17{,}200$ cals.

Basic Catalysis.—(1) *Phenoxide ion.* Aqueous solutions containing appreciable amounts of phenoxide ions are sufficiently alkaline to render perceptible catalytic effects due to hydroxyl and glucosate ions, so that for the observed velocity we have $V_{\text{obs.}} = V_{\text{H}_2\text{O}} + V_{\text{OH}} + V_{\text{G}} + k_{\phi\text{O}}c_{\phi\text{O}}$. Since the partial velocities V_{OH} and V_{G} can be evaluated, a knowledge of $V_{\text{obs.}}$ for a series of solutions in which $c_{\phi\text{O}}$ is varied, allows of the determination of $k_{\phi\text{O}}$. Velocity measurements were made in solutions containing phenol and sodium hydroxide at 0°, 5°, 10°, 15°. Since phenol has an appreciable medium effect on the reaction, its concentration was kept approximately constant throughout. This concentration was made as large as possible in order to diminish catalysis by hydroxyl ions and glucosate ions. The results obtained for 5° are tabulated below.

Mutarotation of glucose in phenol–sodium hydroxide mixtures at 5°.

C_{GH}	$0·715_5$	0·703	0·722	0·733	0·729
$C_{\phi\text{OH}}$	0·466	0·461	0·466	0·464	0·466
10^3C_{NaOH}	2·938	9·30	19·24	28·71	38·51
$10^3C_{\phi\text{O}}$	2·910	9·210	19·05	28·42	38·12
$10^2V_{\text{obs.}}$	1·104	2·69	5·16	7·50	10·0
10^2V_{OH}	0·046	0·15	0·31	0·48	0·65
10^2V_{G}	0·026	0·08	0·17	0·27	0·36
$10^2V_{\text{corr.}}$	1·03	2·46	4·68	6·75	8·99
$10^2V_{\text{corr.}}$, calc.	1·03	2·45	4·68	6·80	8·99

In the first row is given the total concentration of glucose, which to a very close approximation is equal to the concentration of free glucose. In rows **2** and **3** respectively are the total concentrations of phenol and sodium hydroxide. In these solutions the hydrolysis of the sodium phenoxide is very small, and may be neglected in the calculation of the concentration of the phenoxide ion, which thus depends only on the quantities given in rows 1—3 and the ratio of the dissociation constant of glucose to that of phenol, $K_{GH}/K_{\phi OH}$, which has been taken to be $6{\cdot}1 \times 10^{-3}$ at 5°. The value of this ratio, for each of the temperatures employed, has been calculated from the basis that ${}_{20}K_{GH} = 6{\cdot}5 \times 10^{-13}$ (Ölander, *Z. anorg. Chem.*, 1925, **136**, 61) and ${}_{25}K_{\phi OH} = 1{\cdot}1 \times 10^{-10}$ (Lundén, *Z. physikal. Chem.*, 1910, **70**, 249) with respective heats of dissociation of approximately 9500 cals. (*loc. cit.*, *B*) and 7600 cals. (unpublished work). This calculation is sufficiently accurate for the present purpose, since it will be seen that the concentration of phenoxide ion differs from that of the total sodium hydroxide by only about 1%. The partial velocities due to hydroxyl ion and glucosate ion, given in rows 5 and 6, have been obtained by taking the respective catalytic coefficients to be 1,700 and 9·2, and the hydrolysis constant of sodium phenoxide as $4{\cdot}3 \times 10^{-5}$. Values for $V_{\text{obs.}} - V_{OH} - V_{G} = V_{\text{corr.}}$ are given in row 7, and are in close agreement with those given in the last row, derived from the equation $V_{\text{corr.}} = 0{\cdot}37 \times 10^{-2} + 2{\cdot}26\, C_{\phi O}$. The catalytic coefficient for the phenoxide ion at 5° can thus be stated with some confidence to be 2·26, which is about 30 times greater than that for hydrion at this temperature. Precisely similar relations were found to hold at 0°, 10°, 15°. In col. 2 of the following table are given the catalytic coefficients obtained for each temperature, and in col. 3 the values obtained from the equation

$$\log_{10} k_{\phi O} = 14{\cdot}915 - 18{,}500/2{\cdot}3026RT.$$

Temp.	0°	5°	10°	15°
$k_{\phi O}$	1·225	2·26	4·12	7·22
$k_{\phi O}$, calc.	1·23	2·26	4·10	7·26

For catalysis by phenoxide ions, therefore, the heat of activation is 18,500 cals., and there are no obvious deviations from the Arrhenius equation.

(2) *Secondary phosphate ion.* Measurements were made at 0° and 25° in solutions which contained both primary and secondary phosphates, and had the composition $0{\cdot}05M$-KH_2PO_4 + CM-Na_2HPO_4, the values of C being such that catalysis by hydroxyl ions was negligibly small. The observed velocity is given by the expression $V_{\text{obs.}} = V_{H_2O} + V_{H_2PO_4} + V_{HPO_4}$, in which catalysts 1 and 2 of (1) can be regarded as HPO_4'' and $(H_2PO_4' + H_2O)$ respectively. The data are given in the following table, the figures in the last row being calculated from the equation

$$1/R_{\text{obs.}} = 0{\cdot}0620 + 1{\cdot}87 \times 10^{-3}/{}_{25}V_{\text{obs.}}.$$

Mutarotation of glucose in solutions of composition $0{\cdot}05M$-KH_2PO_4 + CM-Na_2HPO_4 *at* 0° *and* 25°.

$C \times 10^3$	0	2·00	3·00	5·00	10·0	15·0
${}_{25}V_{\text{obs.}}$	3·73	4·50	4·88	5·60	7·39	9·07
$1/R_{\text{obs.}}$	0·0672	0·0665	0·0660	0·0657	0·0643	0·0642
$1/R_{\text{obs.}}$, calc.	0·0670	0·0666	0·0658	0·0653	0·0645	0·0641

Hence for catalysis by the secondary phosphate ion $1/R_a$ is 0·0620, which gives $E = 17{,}800$ cals.

(3) *Acetate ion.* Measurements were made at 0° and 25° in solutions of composition $0{\cdot}1M$-acetic acid + CM-sodium acetate. The catalysts are water, acetate ion, and undissociated acetic acid, and similar reasoning applies to that in (2). The results are tabulated below.

Mutarotation of glucose in mixtures of composition 0·1M-*acetic acid* + CM-*sodium acetate at* 0° *and* 25°.

C	0	0·0391	0·0781	0·150	0·250	0·400
$100\,{}_{25}V_{\text{obs.}}$	2·53 *	3·12	3·59	4·59	5·89	7·74
$1/R_{\text{obs.}}$	0·0713 *	0·0686	0·0680	0·0662	0·0644	0·0636
$1/R_{\text{obs.}}$, calc.	0·0716	0·0689	0·0679	0·0660	0·0646	0·0635

* Derived from the data in Table IV.

The numbers in the last row are calculated from the equation

$$1/R_{\text{obs.}} = 0{\cdot}0598 + 2{\cdot}84 \times 10^{-4}/{}_{25}V_{\text{obs.}}$$

thus giving 0·0598 for $1/R_a$, which gives $E = 18{,}200$ cals. This is probably more accurate than the substantially higher value of 19,100 cals. given by Kilpatrick and Kilpatrick.

(4) *Chloroacetate ion.* The procedure was similar to that in (3) above. In this case there is just detectable catalysis by hydrion, but provided $V_{\text{obs.}}$ is replaced by $V_{\text{corr.}} = V_{\text{obs.}} - V_h$, the argument is unchanged. The figures in the last row of the following table are calculated by means of the equation

$$1/R_{\text{obs.}} = 0{\cdot}0578 + 3{\cdot}70 \times 10^{-4}/_{25}V_{\text{corr.}}.$$

Hence for catalysis by the chloroacetate ion $1/R_a = 0{\cdot}0578$ and $E = 18{,}400$ cals.

Mutarotation of glucose in mixtures of composition 0·1M-*chloroacetic acid* + CM-*sodium chloroacetate at* 0° *and* 25°.

C	0	0·300	0·400	0·500	0·700
$100_{25}V_{\text{obs.}}$	—	3·63	3·83	4·06	4·47
$100_0V_{\text{obs.}}$	—	0·247	0·259	0·272	$0{\cdot}292_5$
$100_{25}V_{\text{corr.}}$	2·82 *	3·59	3·80	4·04	4·45
$100_0V_{\text{corr.}}$	0·199 *	0·245	0·257	0·271	0·292
$1/R_{\text{obs.}}$	0·0707 *	0·0682	0·0676	0·0670	0·0657
$1/R_{\text{obs.}}$, calc.	0·0707	0·0682	0·0676	0·0669	0·0661

* Derived from the figures in Table III.

DISCUSSION.

On the evidence available it appears to be legitimate to formulate the chemical reactions giving rise to the mutarotation of glucose in either of two ways, *viz.*, (1) $\alpha \underset{v_\beta}{\overset{v}{\rightleftarrows}} \beta$ in which the two forms of the sugar are directly interconverted, and (2) $\alpha \underset{v_2}{\overset{v_1}{\rightleftarrows}} \mu \underset{v_4}{\overset{v_3}{\leftrightarrows}} \beta$ in which the interconversion takes place *via* an intermediate form, μ, which can be regarded as an open-chain compound. The significance to be attached to the measured unimolecular velocity coefficient, $V_{\text{obs.}}$, differs according to which of these formulations is accepted. It follows from (1) that $V_{\text{obs.}} = V_\alpha + V_\beta$ and the individual velocity coefficients V_α and V_β can be derived from a knowledge of the equilibrium constant, which as deduced from the rotatory powers of the α- and the β-sugar and that of the equilibrium mixture has the value 0·56, independently of temperature (Nelson and Beegle, *J. Amer. Chem. Soc.*, 1919, **41**, 570); hence $V_\alpha = V_{\text{obs.}}/1{\cdot}56$ and $V_\beta = V_{\text{obs.}}/2{\cdot}8$. On the other hand, on the basis of scheme (2), $V_{\text{obs.}} = V_1 = V_3$ (Smith and Lowry, J., 1928, 666), *i.e.*, $V_{\text{obs.}}$ is simply the rate at which either the α- or the β-form undergoes the prototropic change resulting in the production of the intermediate. This is the view adopted in the present paper, but this must not be taken to imply that it is considered possible to decide definitely between the alternative schemes. On the contrary, there is a certain ambiguity in the interpretation of the results, but from the foregoing it will be seen that, in all probability, this can be represented by a numerical factor of not more than about **3**. This uncertainty cannot, therefore, be the reason for the apparently anomalous results obtained for certain catalysts, since, as shown later, the factor involved in these cases is one of several powers of 10, which is of a different order of magnitude.

The results are summarised in the following table, which includes the data given in

	k.	E (cals.).	$Z \times 10^{13}$.	P.	P, calc.	$K_b = 1/K_a$.
Basic catalyst.						
Hydroxyl ion	$9{\cdot}3 \times 10^2$	17,700	1·7	$8{\cdot}2 \times 10^3$	$16{\cdot}0 \times 10^3$	* $1{\cdot}5 \times 10^{16}$
Glucosate ion	5·2	17,000	1·2	$1{\cdot}8 \times 10^1$	42×10^1	$3{\cdot}1 \times 10^{12}$
Phenoxide ion	$1{\cdot}22_5$	18,500	1·4	$5{\cdot}8 \times 10^1$	$4{\cdot}8 \times 10^1$	$1{\cdot}6 \times 10^{10}$
HPO_4'' ion	$2{\cdot}5 \times 10^{-1}$	17,800	1·1	4·1	2·7	$1{\cdot}6_5 \times 10^7$
Acetate ion	$7{\cdot}7 \times 10^{-3}$	18,200	1·4	$2{\cdot}1 \times 10^{-1}$	$2{\cdot}5 \times 10^{-1}$	$5{\cdot}6 \times 10^4$
Chloroacetate ion	$1{\cdot}2 \times 10^{-3}$	18,400	1·2	5×10^{-2}	$3{\cdot}9 \times 10^{-2}$	$6{\cdot}7 \times 10^2$
Water	$3{\cdot}09 \times 10^{-5}$	17·000	1·7	1×10^{-4}	$4{\cdot}7 \times 10^{-4}$	$1{\cdot}8 \times 10^{-2}$
Acid catalyst.						K_a.
Hydrion	$4{\cdot}1 \times 10^{-2}$	18,580	1·7	1·6	1·9	† $5{\cdot}55 \times 10^1$
Chloroacetic acid	$2{\cdot}8 \times 10^{-3}$	17,500	1·2	$2{\cdot}5 \times 10^{-2}$	$2{\cdot}3 \times 10^{-2}$	$1{\cdot}5 \times 10^{-3}$
Acetic acid	$8{\cdot}9 \times 10^{-4}$	17,200	1·4	$3{\cdot}7 \times 10^{-3}$	$3{\cdot}7 \times 10^{-3}$	$1{\cdot}8 \times 10^{-5}$

* Calculated from $P = 2{\cdot}5 \times 10^{-3} \times K_b^{0\cdot42}$.

† Calculated from $P = 0{\cdot}36 \times K_a^{0\cdot42}$.

Part I for hydroxyl-ion and glucosate-ion catalysis. The catalytic coefficients for 0° (col. 2) are derived from the figures given in the tables, and refer to zero salt concentration. The catalytic coefficient for water is taken as $V_{H_2O}/55{\cdot}5$, and should be roughly comparable with the others.

In considering the results from the point of view of the kinetic equation $k = PZe^{-E/RT}$, a complication is apparent in that for one catalyst, and possibly for others, E is not entirely independent of temperature. This, however, is to be anticipated on quantum-mechanical grounds in certain circumstances (Bell, *Proc. Roy. Soc.*, 1936, *A*, **154**, 414), and it is presumably permissible to regard E as representing a mean value for the temperature range considered. On this assumption, the values for P given in col. 5 have been derived, Z being calculated from the formula for binary collisions in a gas. It will be seen that P varies from 10^{-4} for water catalysis to nearly 10^4 for hydroxyl-ion catalysis. Both the absolute magnitudes attributed to P, and the variations in P, represented by a factor of about 10^8, are remarkable.

In this latter connection, it is found that P, for both acid and basic catalysis, is connected with the corresponding acid or basic dissociation constant by an approximate relation of the form previously established in the case of the acetone–iodine reaction (*loc. cit.*; *A*), *viz.*

$$P \sim \text{const.} \times K^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n is constant for a series of catalysts. The calculated values of P are given in col. 6, and have been derived from the equations given at the foot of the table. In applying the equations, it is sufficiently accurate to regard K_a and K_b as independent of temperature, except in the case of the strong bases, for which K_b has been taken for the temperature intermediate between those to which the heat of activation refers. For the basic catalysts, the relation holds within a factor of 5, except in the case of the glucosate ion, where the deviation is much greater. Too much significance should not, however, be attached to this discrepancy for it is by no means certain that the glucosate ion is strictly comparable with the other catalysts, for it obviously occupies a unique position, in that, besides being a base, it is also the ion of the reacting substance. In fact, in this case, it would not be possible to differentiate between the catalytic activity of the ion and its reactivity. For the acid catalysts the series is much less extensive, but is sufficient to establish the relation given above.

The position occupied by water calls for comment. As would be anticipated, water functions as a base, and it is found to have a P value very close to that required by its basic strength. This value is obtained on the assumption that E and Z can be calculated precisely as for the other catalysts, *i.e.*, without the correction for viscosity. On the other hand, if the viscosity correction is applied P becomes approximately unity (Moelwyn-Hughes, " The Kinetics of Reactions in Solution," 1933, p. 233), but this places water in an entirely anomalous position, since it is then quite unrelated to either series of catalysts. In the present case, therefore, the application of the viscosity correction does not appear to be warranted.

It has been pointed out previously that if (2) applies, then $k \sim \text{const.} \times K^nZe^{-E/RT}$. This is clearly not open to question, and in this connection the recent criticism of Moelwyn-Hughes (*Acta Physicochim.*, 1936, **4**, 173) is irrelevant, since it is, in actual fact, directed against an incorrectly quoted version of this expression. The above relation could be interpreted as indicating that for values of $P \lesseqgtr 1$, the probability of an activated collision being effective is limited by the probability of the simultaneous transfer of a proton to, or from, the catalyst molecule. Values of $P \gg 1$, as are obtained in the present instance, cannot, however, have the same significance, and are, indeed, open to suspicion in a reaction considered to be essentially bimolecular. It is therefore necessary to re-examine the bases on which the calculations have been made.

In the first place the question arises as to the validity of applying the gas-collision formula to liquid media. This has been criticised by Bradley (J., 1934, 1910) and by Evans and Polanyi (*Trans. Faraday Soc.*, 1936, **32**, 1333), but the large amount of data now available certainly suggests that the error thereby introduced does not exceed one or two powers of 10, and it would be surprising if it were as large as 10^4. It therefore seems improbable that the large P values are to be attributed entirely to the incorrect computation of Z.

A more likely possibility is that the heat of activation, as evaluated from the temperature coefficient, is not the true value. This could arise through a failure to take cognisance of some temperature-variable factor, thus preventing a complete separation of the two terms of the Arrhenius equation. Such a factor, it might be suggested, is the acid or basic strength of the catalyst, which is related to the catalytic coefficient by the well-known Brönsted equation, $\log k = \log G + n . \log K$, where G and n are constants. It follows that

$$d\log k/dT = d\log G/dT + n . d\log K/dT + dn/dT . \log K,$$

which, if G varies exponentially with temperature, gives

$$E_{\text{obs.}} = E' + nQ + RT^2 . dn/dT . \log K.$$

Provided dn/dT be small, the heat of activation at constant acid or basic strength is then $E_{\text{obs.}} - nQ$ (compare Pedersen, *J. Physical Chem.*, 1934, **38**, 601). This condition holds for the basic catalysis, where n has the values 0·41 at 0° and 0·42 at 25°. The figures are given in the following table, where the values of Q are those given by Harned and Hamer (*J. Amer. Chem. Soc.*, 1933, **55**, 2184) and by Harned and Umbree (*ibid.*, 1934, **56**, 1050) for 10°, except for the glucosate and phenoxide ions, where approximate data are available for 20° only.

Basic catalysis of mutarotation.

Catalyst.	$E_{\text{obs.}}$.	Q.	$E_{\text{obs.}}-nQ$ (cals.).	Catalyst.	$E_{\text{obs.}}$.	Q.	$E_{\text{obs.}}-nQ$ (cals.).
Hydroxyl ion	17,700	14,200	23,400	Acetate ion	18,200	289	18,360
Glucosate ion	17,000	9,500	20,800	Chloroacetate ion	18,400	-593	18,200
Phenoxide ion	18,500	7,600	21,500	Water	17,000	0	17,000
HPO_4'' ion	17,800	1,230	18,290				

The figures in the last col. show that the effect of this correction is to increase materially the heats of activation just for those catalysts for which P is already too large, and the result is thus to accentuate rather than to diminish the existing discrepancy. The preceding argument is therefore of doubtful value, and further, since no simple relation of any sort exists between Q and $E_{\text{obs.}}$, it is very improbable that Q is a quantity of any real significance in this connection.

Finally, it is not impossible that internal degrees of freedom of the glucose molecule are involved in the activation, but there are obvious difficulties in the application of such an hypothesis to account for the results as a whole. We are therefore at present unable to explain our P values in any plausible manner in terms of the kinetic theory of reaction velocity. If the experimental results are accepted, however, they indicate clearly that in a reaction involving solely a prototropic change, either E or Z cannot be evaluated in the customary manner.

Velocity Measurements.—The procedure was as described previously (*loc. cit.*; *B*), except that only in the case of phenoxide-ion catalysis was it necessary to maintain the rigid precautions to exclude atmospheric carbon dioxide from the experimental solutions.

Materials.—With the exception of chloroacetic acid, these were of AnalaR grade, and they were purified either by crystallisation from water, or by fractional freezing to constant f. p.

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