[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE MEASUREMENT OF REACTION VELOCITY AND THE TEMPERATURE COEFFICIENT OF REACTION VELOCITY[1]

BY F. O. RICE AND MARTIN KILPATRICK, JR.

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Introduction

The reaction selected for investigation was that between acetone and iodine in dilute aqueous solution. In neutral solution this reaction is exceedingly slow, but is catalyzed by acids, the resulting accelerations being approximately proportional to the strength of the acid. The stoichiometric equation representing the change is, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$. The reaction is, therefore, autocatalytic.

Lapworth[2] using bromine instead of iodine was the first to make a quantitative study of this type of reaction. In outline, his method was to prepare an aqueous solution of acetone, acid and bromine, the concentrations of the acetone and acid being at least 10 times that of the bromine so that bromine was disappearing from a solution of acetone and acid of fixed concentration. "These solutions were kept at constant temperature, the concentration of bromine being determined from time to time by withdrawing aliquot portions of the solution by means of a pipet, and running them directly into a solution of potassium iodide; the amount of iodine liberated was ascertained by titration with 0.05 *N* sodium thiosulfate, the exact value of which was checked from time to time."

The velocity constant, k, was calculated by means of the formula $k = 10^4 \times v/c_1 \times c_2$, where v is the number of moles of bromine reacting per minute per liter, in a solution containing c_1 *M* acetone and c_2 *N* acid. Lapworth found that the velocity v was proportional to c_1 and c_2 but was independent of the concentration of the bromine. From these results he concluded that (1) the reaction takes place in at least two stages, in one of which the bromine is not involved; (2) in the stage or stages in which the bromine takes part, the velocity of reaction is so great that the time occupied is not measurable.

He advanced the hypothesis that the bromination of the acetone is best regarded as the result of a slow reversible change effected in the acetone by the hydrogen ions, followed by an almost instantaneous bromination of the product, a change which is not appreciably reversible. The intermediate product is perhaps the enolic form of the ketone.

$$CH_3COCH_3 \overset{H^+}{\rightleftarrows} CH_3C(OH){=}CH_2. \qquad (1)$$

$$CH_3C(OH){=}CH_2 + Br_2{=}CH_3COCH_2Br + HBr \qquad (2)$$

Dawson[3] and his co-workers using iodine instead of bromine repeated and extended Lapworth's work and endorsed the keto-enol transformation theory.

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[1] The work included in this paper is from the thesis presented by Martin Kilpatrick, Jr., as part of the requirement for the degree of Doctor of Philosophy in New York University.

[2] Lapworth, *J. Chem. Soc.*, **85**, 30 (1904).

[3] Dawson and Leslie, *ibid.*, **96**, 1860 (1909). Dawson and Wheatley, **98**, 2048 (1910).

We intended to use this reaction in an investigation of some of the problems of homogeneous solution and our experimental procedure was similar to that followed by Dawson. We first added 25 cc. of approximately 0.1 N iodine solution in 4% potassium iodide solution to a 250 cc. stoppered graduated flask and then 25 cc. of standard hydrochloric acid (about 1.0 N). The flask was then made up with distilled water to within a few cubic centimeters of the mark and placed in a thermostat at 25° ± 0.01°. When the contents of the flask had attained 25°, we noted the time and added a known amount of acetone from a calibrated pipet, made up to the mark with water and mixed the contents thoroughly by shaking. From time to time we withdrew 25cc. portions from the flask, ran them into sodium bicarbonate solution and determined the iodine by means of standard thiosulfate solution. The iodine titrations gave us a value for v, the rate of disappearance of iodine in moles per liter of solution and by dividing this by the molarity of acetone and the normality of acid, and multiplying by 10^4 we obtained the value of k, the velocity constant. We performed 10 experiments using solutions having approximately 0.1 M acetone, 0.1 N hydrochloric acid and 0.01 N iodine initially and obtained a value for k of 16.48, av. dev. 3.9%. Since this high deviation might be due to opening the flask when withdrawing the 25cc. samples, we performed another series of 10 experiments in which the flasks were opened only twice when the experiment was nearing completion. These gave a value for k of 17.08, av. dev. 0.81%. We did the analytical part of the work with great care and the error here did not exceed 0.1%, yet the error in k was more than 8 times this amount. We decided, therefore, to make a careful study of all the errors that might enter into the measurement of k and eliminate them as far as possible. Our aim was to measure velocity of reaction with a degree of precision such that the error would be less than 0.1%.

Measurement of Reaction Velocity

Suppose we have an aqueous solution containing initially b moles of acetone, a moles of acid per liter and some iodine. Since the velocity is independent of the iodine concentration it is not necessary to take it into account at this point.

Suppose that after t minutes x moles of acetone react with iodine. The concentration of acetone then is $(b-x)$ moles per liter, and that of the acid is $(a+x)$ moles per liter. Therefore, $dx/dt = k(a+x)(b-x)$. Integrating: $k = \frac{1}{t(a+b)} \log \frac{b(a+x)}{a(b-x)}$. The measured quantities from which we calculate k are t, a, b, and x.

To find the error in k caused by a deviation in one of the directly measured quantities we must take the partial differential of k with respect to the quantity and multiply by its deviation.[4]

$$\frac{\partial k}{\partial t} = -\frac{1}{a+b}\left[\log\frac{b(a+x)}{a(b-x)}\right]\frac{1}{t^2} = -\frac{k}{t}.$$

$$\frac{\partial k}{\partial a} = -\frac{k}{(a+b)}\left[1+\frac{x}{akt(a+x)}\right] - \frac{k}{a}\text{ approximately.}$$

$$\frac{\partial k}{\partial b} = -\frac{k}{(a+b)}\left[1+\frac{x}{bkt(b-x)}\right] - \frac{k}{b}\text{ approximately.}$$

$$\frac{\partial k}{\partial x} = \frac{1}{t(a+x)\,(b-x)}.$$

These approximations hold because in our experiments a approximates b, and $x/a^2kt = 1$ approximately. Hence the deviation in k caused by a deviation δ_t in t is

$${}_k\Delta_t = \frac{k}{t}\delta_t.$$

Similarly for the other quantities

$${}_k\Delta_a = \frac{k}{a}\delta_a;\ {}_k\Delta_b = \frac{k}{b}\delta_b;\ {}_k\Delta_x = \frac{\delta_x}{a\,b\,t}.$$

Hence;

$${}_k\Delta_t/k = \delta_t/t;\ {}_k\Delta_a/k = \delta_a/a;\ {}_k\Delta_b/k = \delta_b/b;$$

$$\frac{{}_k\Delta_x}{k} = \delta_x/x\left(\frac{x}{a\,b\,k\,t}\right)\delta_x/x\text{ approximately.}$$

From this we conclude that a percentage error in any one of the quantities t, a, b, and x, produces the same percentage error in the final result k.

Determinate Errors

The precision of k, the final result, depends upon the errors of certain direct measurements, which are in this case (1) two titrations of iodine from which the value of x is obtained, (2) measurement of the time t during which x molecules of iodine reacted per liter, (3) measurement of a the initial concentration of acid, (4) measurement of b the initial concentration of acetone, (5) measurement of the temperature of the reaction. We shall now give a preliminary discussion of these errors taking them in this order.

1. We estimated the iodine by a weight-volumetric method described in a previous paper.[5]

We could estimate the iodine with an error of about 0.05%, and we allowed sufficient iodine to react so that the error in x was about 0.15%.

We did not purify the iodine but purchased the highest grades and used them directly. Different specimens gave identical results, and from the work of Foulk and Morris[6] it is unlikely that iodine contains anything that would affect the velocity.

Another determinate error which we should consider here is the possibility of loss of iodine from the solution by volatilization. Any careless-

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[4] See Goodwin, "Precision of Measurements and Graphical Methods," McGraw-Hill Book Co., **1917,** for the definition of terms and symbols used in this paper.

[5] Rice, Kilpatrick and Lemkin; THIS JOURNAL, **45,** 1361 (1923).

[6] Foulk and Morris, *ibid.*, **44,** 221 (1922).

ness in handling or transfering such a solution would mean a large loss of iodine. The methods used for avoiding this loss are described under experimental procedure.

2. To measure the time with an error of about 0.1%, the variation of the watch should not be greater than 0.03%, an error which can be neglected. Since our experiments extended over 2–4 hours the watch should not vary by more than ± 1 second per hour. Ordinary watches containing 9 jewels or less do not have this degree of precision, and for the earlier part of the work we used two 19-jewel watches which we found satisfactory; for the later part of the work we obtained an astronomical watch, the variation of which was very much less than the other errors in measuring t. Throughout the work we checked the watches against time signals from the Washington Observatory.

In measuring the time t there are two errors, one in measuring the initial time and one in measuring the final time. We estimate these to be not greater than ± 5 seconds in each case so that the total error in t is ± 7 seconds. Therefore, if the error in t is to be less than 0.1% an experiment should extend over a minimum time of 2 hours.

3. The estimation of a, the initial concentration of acid, was fairly easy, and the error was probably not greater than 0.03%. Hulett's method[7] was used for preparing standard hydrochloric acid, and as an additional check the chlorine was determined gravimetrically as silver chloride.

4. The initial concentration b of the acetone was determined by weighing the acetone in a small, stoppered weighing bottle, and adding this to a weighed quantity of solution. The weight of acetone added was usually 2–4 g. so that this weight could easily be determined to 0.03%. Since acetone is very volatile there is the possibility of loss of acetone vapor when the weighing bottle is opened at the moment it is dropped into the solution. The vapor pressure of pure acetone is 230 mm. at 25°, so that an air space of 1 cc. saturated with the vapor would contain 0.0026 g. of acetone. If this were lost during transference it would mean an error of 0.03% for a weight of 1 g. of acetone. The weights of acetone used varied from 2 to 5 g. and the weighing bottles used varied in size according to the amount of acetone, the air space in all cases being 1–2 cc. If there had been any appreciable loss of acetone we should have detected it, for the percentage error varies with the quantity of acetone weighed. Also, we made a further test by weighing acetone, removing the stopper from the weighing bottle for a moment, replacing the stopper and weighing the bottle again. The maximum loss was 0.0007 g. We conclude, therefore, that the error due to loss of acetone when transferring it from the balance to the solution is negligible.

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[7] Hulett and Bonner, THIS JOURNAL, **31,** 390 (1909).

We purified the acetone by two methods. The first was the well-known bisulfite method, the final treatment of the acetone being drying with calcium chloride for 24 hours and distillation through a 5-section evaporator still-head. The second method was that described by Shipsey and Werner[8] the final treatment being the same as in the first method. We used acetone from different sources, and since many different specimens of acetone gave the same value for the velocity it is unlikely that there is any appreciable error due to impurity in the acetone used.

5. A preliminary measurement of the temperature coefficient of the reaction showed that an error of 0.01° for the whole time of the reaction caused an error of 0.13% in the velocity constant. Therefore, we regulated our thermometers to ± 0.003° of the required temperature. The thermometers used were checked at intervals against thermometers certified by the Bureau of Standards. From this discussion of errors it will be readily seen that our aim was wherever possible to measure a quantity to ± 0.03% if this could be accomplished without too great difficulty. This seemed possible except in the case of the iodine estimation (error ± 0.15%) and the time (error ± 0.1%). We believe, therefore, that we have reduced all other determinate, indeterminate and residual errors so that they are negligible in comparison with these two errors. Therefore, the precision measure of a single experiment should be, $\sqrt{(0.15)^2 + (0.1)^2} = 0.18\%$.

Experimental Procedure

We shall now describe our final method, and illustrate it by reference to Table I which contains the complete data of Expt. 210.

A dry, stoppered, liter bottle was weighed, and about 102 g. of 0.1 *N* iodine in 0.25 *N* potassium iodide added. Some 300–400 cc. of water was next added, followed by a known weight of standard hydrochloric acid. The acid was contained in a weight buret, that the amount added might be determined accurately. The bottle was then filled to the neck with water and weighed again.

The solution was shaken and by means of a fast running siphon 3 reaction tubes were filled with the solution. These reaction tubes were glass-stoppered tubes of thin blown glass, about 5 cm. diameter, and of 300 cc. capacity. Two of the tubes were weighed empty and when filled with solution were weighed again so that the weight of the solution was known. These two tubes were then placed in the thermostat.

The third tube was retained as a blank and the iodine was estimated by the siphon method described in a previous paper.[5] The iodine concentration was expressed in terms of "g. of thiosulfate solution per g. of the iodine solution" abbreviated to "T/I." This value will be referred to as the "pre-initial T/I" since in order to obtain the true initial concentration a small correction must be made for the weight of acetone added at the time of starting the experiment. From the weights of acid and solution the "pre-initial" normality of the acid may also be calculated. It is to be noted that all concentrations are given in terms of weight normality.

The acetone was weighed in a weighing bottle, the reaction tube removed from the

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[8] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

thermostat and the acetone introduced by holding the weighing bottle by the stopper over the mouth of the tube, allowing the bottle to fall into the solution, and then dropping in the stopper. The reaction tube was immediately stoppered and shaken, the time being recorded at the moment of shaking. Acetone was added to the other tube in the same way. When approximately $^1/_3$ of the iodine had disappeared, that is to say about 200 minutes after the start of the reaction, a tube was removed to a Dewar flask containing water taken from the thermostat at the same time. The method of estimating the iodine was similar to that described in the previous paper.[6] The reaction tube was fitted with a titrating siphon, and the tube was connected with a pressure reservoir under 5–8 cm. of mercury. The iodine was estimated by opening the siphon fully and running the solution into a weighed quantity of standard thiosulfate solution in a conical flask which contained also an excess of borax-boric acid buffer solution. After practice we could allow the iodine solution to run at full rate until about 95% of the thiosulfate had reacted. The iodine solution was then added slowly until a faint blue color persisted. By weighing the flask again we obtained the weight of reacting solution added and hence could calculate the final "T/I." We made 3 titrations, at minute intervals as a rule, the times of opening the stopcock, of slowing down the flow, and of completing the titration being recorded. From these data we could determine the final time.

A portion of the remaining solution was drawn into a pycnometer and the density determined. Previous experiments had shown that the reacting solution did not change appreciably during the course of the reaction.

The method of calculation is shown in Table I. The initial normality of the acid and the initial molality of the acetone were calculated, supplying the *a* and *b* terms of the equation. The fall in "T/I" multiplied by the weight normality of the thiosulfate and divided by 2 gave the number of

TABLE I

DATA FOR EXPT. 210

Aug. 12, 1922 Temperature 25°

Wt. of bottle, 446.1 g. Wt. of 5.552 *N* HCl, 17.0495 g. Wt. of bottle + $H_2O + I_2$, 1414.8 g. Total wt. of solution, 985.7 g. Wt. of 0.1 *N* I_2 containing 0.25 *N* KI, 102 g. (approx.).

Solution titrated with 0.01256 *N* $Na_2S_2O_3$. Analysis of solution before addition of acetone (wt. normality): acid, 0.09603; iodine as T/I, 0.9684; KI, 0.027 *M*.

	Expt. a. Bottle 1			Expt. b. Bottle 2		
Wt. of solution	290.1	.....	.....	299.1	.....	.....
Wt. of acetone added (NaI)	1.4394	.....	.....	1.4962	.....	.....
Time of starting	10:38:00	.....	.....	10:51:00	.....	.....
Wt. of thiosulfate	20.02	20.23	20.14	19.73	20.28	19.99
Wt. of reacting soln. (uncorr.)	30.43	30.95	30.85	32.58	33.60	33.27
Correction	0.08	0.16	0.12	0.08	0.12	0.16
Wt. of reacting soln. (corr.)	30.34	30.79	30.73	32.50	33.48	33.11
Time of starting titration	12:56:00	12:57:00	12:58:00	1:31:00	1:33:00	1:33:00
Fully open (seconds later)	15	15	15	18	20	22
Finished (seconds later)	45	45	45	45	45	45
Final time	12:56:08	12:57:08	12:58:08	1:31:09	1:32:10	1:33:11
Number of minutes *t*	138.1	139.1	140.1	160.2	161.2	162.2
Final T/I	0.6599	0.6580	0.6554	0.6071	0.6057	0.6037
Initial T/I (corr. for acetone)	0.9638	.....	.....	0.9638	.....	.....
T/I reacted	0.3039	0.3068	0.3084	0.3565	0.3579	0.3599
Moles of I_2 reacted per 1000 grams, *x*	0.001908	0.001927	0.001937	0.002239	0.002248	0.002260
Initial normality iodine	0.01211	.....	.....	0.01210	.....	.....
Initial normality acid *a*	0.09557	.....	.....	0.09555	.....	.....
Initial molality acetone *b*	0.08505	.....	.....	0.08573	.....	.....
K per 1000 × 10^4	17.02	17.06	17.03	17.08	17.05	17.04

moles of iodine used for 1000 g. of solution, or x. From the initial and final times, t was determined in minutes. Substituting these values in the equation, the constant k was computed for 1000 g. of solution. The value of k per liter of solution was obtained by multiplying the value for 1000 g. by the density of the solution.

Table II

Experiments at 25° with Hydrochloric Acid

Initial normality iodine	Initial normality HCl a	Initial molality acetone b	Moles of I_2 used per 1000 g. x	Time in min. t	Constant per liter k_{25}
0.01391	0.11525	0.07585[a]	0.002467	166.5	17.12
.....	.....	......	2479	167.5	17.10
.....	.....	......	2490	168.5	17.07
			Av.		17.097
.01356	.08267	.08549[a]	2490	206.6	17.12
.....	.....	......	2498	207.6	17.09
.....	.....	......	2520	208.6	17.16
			Av.		17.123
.01211	.09557	.08505[a]	1908	138.1	17.09
.....	.....	......	1927	139.1	17.13
.....	.....	......	1937	140.1	17.10
			Av.		17.103
.01210	.09555	.08573[a]	2239	160.2	17.15
.....	.....	......	2248	161.2	17.12
.....	.....	......	2260	162.2	17.11
			Av.		17.127
.01274	.06711	.08246[a]	1717	181.6	17.12
.....	.....	......	1723	182.6	17.19
.....	.....	......	1784	183.6	17.23
			Av.		17.180
.01275	.06715	.07124[a]	1817	222.1	17.16
.....	.....	......	1833	223.1	17.23
.....	.....	......	1840	224.1	17.23
			Av.		17.207
.01208	.09238	.07566[b]	1789	150.1	17.18
.....	.....	......	1802	151.2	17.22
.....	.....	......	1816	152.2	17.19
			Av.		17.197
.01208	.09235	.08105[b]	2246	176.2	17.14
.....	.....	......	2261	177.2	17.15
.....	.....	......	2268	178.2	17.10
			Av.		17.130
.01278	.08535	.07365[b]	2371	221.7	17.13
.....	.....	......	2381	222.7	17.14
.....	.....	......	2409	223.7	17.24
			Av.		17.170

Final av., 17.148, av. dev. 0.21%, deviation of the mean 0.070%.

[a] Acetone purified by NaI method.

[b] Acetone purified by bisulfite method.

Table II contains a summary of our experiments at 25° with hydrochloric acid. In all of our experiments the solution contained 0.027 *M* potassium iodide to keep the iodine in solution.

From the results at 25° it will be seen that the average deviation of a single experiment was 0.21% which is very near to the value 0.18% predicted from the discussion of errors. In calculating the precision measure of our results we have, therefore, taken the average deviation of a single experiment to be 0.21% in all cases. For the experiments at 0° the error in measuring *t* was probably negligible, but due to the difference in temperature from the room there would probably be slight temperature errors not occurring in the experiments performed nearer room temperature, which would compensate for the increased precision in measuring the time.

Table III contains experiments at 25° using nitric and sulfuric acids as catalysts. Nitric acid gives the same result as hydrochloric within the limits of experimental error. Sulfuric acid is about 10% weaker than either hydrochloric or nitric acid. Table III also contains the experiments at 27°, 35° and 0°, respectively, using hydrochloric acid as catalyst. We made one experiment at 24° and obtained a value of 15.187. Acetone purified by sodium iodide was used in all of these experiments.

TABLE III

EXPERIMENTS AT 25° WITH NITRIC AND SULFURIC ACIDS

Initial normality iodine	Initial normality acid a	Initial molality acetone b	Moles of I_2 used per 1000 g. x	Time in min. t	Constant per liter
0.01270	0.06261	0.08277	0.001612	182.1	17.10
.....	nitric	......	1621	183.1	17.10
.....	.....	......	1636	184.1	17.16
			Av.		17.120
.01271	.06262	.07718	1686	203.4	17.18
.....	nitric	......	1692	204.4	17.15
.....	.....	......	1698	205.4	17.13
			Av.		17.153
.01388	.08063	.08140	2570	253.4	15.55
.....	sulfuric	......	2580	254.4	15.55
.....	.....	......	2587	255.4	15.53
			Av.		15.543
EXPERIMENTS AT 27° WITH HYDROCHLORIC ACID					
0.01341	0.07428	0.07935	0.002228	175.3	21.62
.....	.....	......	2249	177.3	21.58
			Av.		21.600
.01341	.07428	.07936	2811	202.5	21.71
.....	.....	......	2812	203.5	21.61
.....	.....	......	2816	204.6	21.53
			Av.		21.617

EXPERIMENTS AT 35° WITH HYDROCHLORIC ACID

0.01188	0.03479	0.03371	0.001418	228.6	52.83
.....	.....	......	1431	230.6	52.86
.....	.....	......	1441	232.6	52.76
			Av.	52.817	
.01188	.03479	.03329	1631	267.1	52.72
.....	.....	......	1644	268.1	52.93
.....	.....	......	1644	269.1	52.89
			Av.		52.847
.01113	.03258	.02684	1368	297.1	52.64
.....	.....	......	1371	298.1	52.76
.....	.....	......	1377	299.2	52.81
			Av.		52.737
.001113	.03258	.02699	1455	313.6	52.76
.....	.....	......	1464	314.6	53.18
.....	.....	......	1464	315.6	52.93
			Av.		52.957
			Final Av., k_{35}		52.840

EXPERIMENTS AT 0° WITH HYDROCHLORIC ACID

0.009767	0.09696	0.08176	0.001675	3045.2	0.6976
.....	.....	......	1679	3046.2	.6994
			Av.		.69850
.009753	.09683	.1054	2109	2963.3	.6995
.....	.....	......	2119	2964.4	.7027
			Av.		.70110
.009754	.09684	.1039	2046	2918.2	.6994
.....	.....	......	2041	2919.7	.6991
			Av.		.69925
.009766	.09694	.08524	1704	2967.2	.69890
			Final Av., k_0		.69944

Measurement of Temperature Coefficients

This is usually done by measuring the velocity at two temperatures, the ratio giving a measure of the effect of temperature on the velocity. Table IV contains these ratios for various temperature limits, and also values of Q calculated from the Arrhenius formula, $2.3026 \log k_1/k_2 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_1}\right)$. The value of R was taken as 1.9864 cal./degree, and 0° = 273.09° K. This equation reproduces the experimental results fairly well, the maximum variation from the mean value being only 0.4%. This is, however, much greater than our experimental error and the results show that Q diminishes slightly with rise in temperature. For the range 0° – 25°, Q = 20,695.1; and for the range 25° – 35°, Q = 20,431.

This method of measuring temperature coefficients is laborious and time-consuming, for it requires two separate exact experiments. Accordingly, we devised a method for measuring temperature coefficients that required only one experiment and gave a high degree of precision in the result.

Table IV

Temperature Coefficients between 0° and 35°

Ratio k_1/k_2	Precision measure of k_1/k_2 %	Q	Precision measure of Q %
$k_{35}/k_0 = 75.546$	0.14	20,652.1	0.032
$k_{27}/k_0 = 30.895$	.17	20,684.9	.049
$k_{25}/k_0 = 24.517$	.12	20,695.1	.038
$k_{24}/k_0 = 21.713$	.22	20,669	.073
$k_{35}/k_{27} = 2.4453$	.17	20,528	.19
$k_{35}/k_{25} = 3.0814$	.12	20,531	.11
$k_{27}/k_{25} = 1.2601$	.16	20,540	.70

We had two thermostats working side by side, one at t_1 and the other at t_2, and each regulated to ± 0.003°. We filled a liter bottle with a solution of acid and iodine of approximately the strengths used in a velocity determination. The bottle was then fitted with a titrating siphon and the iodine accurately estimated in the usual manner with thiosulfate. After removing the siphon, we weighed the bottle and contents and by subtracting the weight of the empty bottle we obtained the weight of the solution. We then placed the bottle in the thermostat of lower temperature (t_1), and when it had attained this temperature we started the reaction by running in the required quantity of acetone from a pipet, immediately agitated the bottle, fitted it with a quick-running siphon and filled four 100 cc. glass-stoppered reaction tubes with the solution. Two of the tubes were placed in the thermostat at t_1, and 2 in the other thermostat. We noted carefully the time at which we added the acetone and also the time at which the 2 tubes were placed in the thermostat at t_2. After a suitable time, usually 3–4 hours, we fitted the tubes with a titrating siphon and determined the iodine as in a velocity experiment. From these data we could obtain the rate of loss of iodine in each set of tubes expressed in terms of cubic centimeters of thiosulfate per minute. No correction is necessary for the results at t_1, since the tubes were at this temperature all the time. A small correction is necessary for the results obtained at t_2, since the reacting solution was at t_1 for a short time (usually 2 minutes) and also the solution took some time to attain the temperature t_2 after being transferred to the bath of higher temperature. A further correction is necessary because the solution diminished in density when raised to the higher temperature. The total of these corrections, however, is very small and amounts usually to less than 1%.

Therefore, after applying these corrections we need only divide the rates of loss of iodine at the two temperatures to obtain the temperature coefficient. The rates may be expressed in terms of cubic centimeters of thiosulfate per minute so that it is not necessary even to standardize the thiosulfate.

The main advantages of this method are that it is not necessary to prepare accurately standardized solutions of acid and acetone, and a single experiment gives the temperature-coefficient. The two temperatures which we selected for our experiments to test this method were 25° and 27°. From Table IV it will be seen that we sacrificed the degree of precision to some extent, but on the other hand these temperature limits had the great advantage that an experiment could be completed in one day. Four experiments by this method gave $k_{27}/k_{25} = 1.2613$; av. dev., 0.20%; deviation of the mean, 0.10%, which compares very favorably with the value of 1.2601 calculated from the absolute determinations of the constant at 27° and 25°.

Our experience with this method has been very satisfactory and we consider that the method could be developed to give results to 0.01% if this should be desirable at any time.

The Effect of Non-electrolytes on the Temperature Coefficient.—Having thus developed a method for measuring temperature coefficients we have applied it in this section to measuring the effect of certain non-electrolytes on the temperature coefficient. Sucrose, glycerol, methyl acetate and methyl alcohol in concentrations varying from 5% to 30% were used. Acetic acid (0.9 *N*) was also used, since its dissociation in presence of the hydrochloric acid used as catalyst was so slight that it behaved like a non-electrolyte. We purchased the highest grades of the non-electrolytes and used them without further purification. Preliminary blank experiments showed that the absorption of iodine by the non-electrolytes was negligible over the period of an experiment.

TABLE V

EFFECT OF NON-ELECTROLYTES ON THE TEMPERATURE COEFFICIENT

Non-electrolyte		$k_{25} \times 10^4$	k_{27}/k_{25}	k_{27}/k_{25} Av.	Precision measure %
		17	1.265	1.2613	0.09
		17	1.260		
		17	1.259		
		17	1.261		
Sucrose	20.6%	24	1.260	1.2610	.13
	17.8%	21	1.262		
Glycerol	17.9%	24	1.266	1.2645	.13
	19.2%	25	1.268		
	30.0%	30	1.260		
	28.6%	28	1.264		
Acetic acid	0.92 *N*	17	1.262	1.2620	.13
	0.90 *N*	18	1.262		
Methyl acetate	6.8%	15	1.264	1.2660	.13
	7.2%	17	1.268		
Methyl alcohol	10.7%	19	1.260	1.2570	.13
	11.1%	21	1.254		

The velocity at 25° ($k_{25} \times 10^4$) was roughly determined. The error is about ±7%.

In our experiments the concentrations of acid and acetone were similar to those used in the previous part of the work, and the experimental procedure was similar to that described in the previous section.

Table V contains a summary of our results. With the more concentrated solutions of non-electrolyte we had difficulties in the titrations due to precipitation of the buffer, so that the degree of precision is not quite so high as in the absence of non-electrolyte. It will be seen from the table that non-electrolytes have no effect on the temperature coefficient. The mean of all the results for k_{27}/k_{25} is 1.2620, and the maximum variation is only 0.32% which is not much greater than the experimental error. It is noteworthy that although the velocity undergoes wide variations, in some cases almost 100%, the temperature coefficient remains unaffected.

A theoretical discussion of the results obtained in this paper will be given in a succeeding communication.

Summary

1. We have made a study of the errors occuring in the measurement of reaction velocity, and have shown how they may be diminished so that the precision measure of a single experiment is 0.20%. The reaction which we selected for investigation was that between acetone and iodine in dilute aqueous solution catalyzed by hydrochloric acid.

TABLE VI

SUMMARY

° C.	0	24	25	27	35
Velocity constant k	0.69944	15.187	17.148	21.609	52.840
Precision measure, %	0.10	0.20	0.070	0.14	0.10

The velocity constant k is the (calculated) rate of disappearance of iodine in moles from a liter of solution containing 1 mole of acetone, 1 g. eq. of HCl, about 0.01 g. eq. of iodine, and 0.025 M KI.

2. Using nitric acid as catalyst we obtained k_{25}, 17.137; precision measure, 0.14%, which is the same as that given by hydrochloric acid within experimental error. With sulfuric acid we obtained k_{25}, 15.543; precision measure, 0.21%.

3. We have developed a method for determining the temperature coefficient of a reaction with a high degree of precision by a single experiment. For the above reaction k_{25}/k_0, 24.517; precision measure, 0.12%; and k_{35}/k_{25}, 3.0814; precision measure, 0.12%. Substituting these values in the Arrhenius formula gives Q equal to 20,695.1; precision measure, 0.038%, and 20,431; precision measure 0.11, respectively. The value of Q, therefore, diminishes slightly with rise in temperature.

4. We have shown that non-electrolytes have no effect on the temperature coefficient up to concentrations of 30%.

UNIVERSITY HEIGHTS, NEW YORK, N. Y.