XXXII.—*The Reaction between Ethyl Alcohol and Hydrochloric Acid.*

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VARIOUS chemists have studied the velocity of formation of esters and the equilibrium attained; among them may be mentioned Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, 1862, [iii], 65, 385; 66, 5; 1863, 68, 225); Guldberg and Waage (*J. pr. Chem.*, 1879, [ii], 19, 69); van't Hoff (*Ber.*, 1877, 10, 669); Villiers (*Ann. Chim. Phys.*, 1880, [v], 21, 72); Cain (*Zeit. physikal. Chem.*, 1898, 12, 751); Petersen (*ibid.*, 1895, 16, 385); Tafel (*ibid.*, 1896, 19, 592); Knoblauch (*ibid.*, 1897, 22, 268); and Goldschmidt (*Ber.*, 1895, 28, 3218; 1896, 29, 2208; *Zeit. physikal. Chem.*, 1899, 31, 343).

Berthelot's attempt to apply a mathematical formula to the velocity of reaction was not quite successful, as was also the case with the application of the law of mass action by Guldberg and Waage.

Van't Hoff attacked the question independently of Guldberg and Waage, and on the assumption that the velocity of reaction was proportional to the product of the active quantities of the substances present, he deduced the ordinary velocity equation for a reversible reaction, namely :

$$\frac{dx}{d\theta} = k_1(A-x)(B-x) - k_2(C+x)(D+x) \dots\dots\dots (1),$$

where A , B , C , and D are the concentrations * of the alcohol, acid, ester, and water respectively, at the commencement of the reaction ; x is the quantity of ester formed after the time θ , and k_1 and k_2 are velocity constants.

This gives for the state of equilibrium :

$$\begin{aligned} \frac{dx}{d\theta} &= k_1(A-\xi)(B-\xi) - k_2(C+\xi)(D+\xi) = 0 \\ \therefore \frac{(A-\xi)(B-\xi)}{(C+\xi)(D+\xi)} &= \frac{k_2}{k_1} = a \dots\dots\dots (2), \end{aligned}$$

where ξ = quantity of ester which has been formed in addition to the amount started with.

On applying this equation to the experiments of Berthelot, the agreement between theory and experiment was fairly satisfactory.

Knoblauch (*loc. cit.*) finally proved the complete applicability of this velocity equation in the case of the action of acetic acid on ethyl alcohol. Both the direct and reverse reactions were studied, and the results agreed with theory.

The reaction is, however, always more complicated than is represented by the first equation given above, as other factors have to be taken into account, as, for example, the possible catalytic effect of the hydrogen ions of the acid. Knoblauch got rid of this difficulty by adding a known amount of a strong mineral acid (hydrochloric acid), thus keeping the number of the hydrogen ions constant, as the dissociation of the acetic acid is small, and would be still further reduced by the presence of the hydrochloric acid. The latter, at 25°, does not take any part in the reaction, and simply acts as a catalyser.

* The concentration is assumed to be proportional to the active quantities. This is only strictly true in dilute solution, compare p. 310.

The Case of Equilibrium.

Berthelot and St. Gilles have shown that in the case of organic acids the point of equilibrium is *independent of the temperature*. The value of $1/a = k_1/k_2$ which they found for ethyl alcohol and acetic acid was 4. Knoblauch found for the same 2.74, but his experiments were carried out in aqueous solution, whereas Berthelot and St. Gilles obtained their results by mixing the pure acid and alcohol. He does not give any explanation of this difference, but in a footnote merely says "Durch den Zusatz der Chlorwasserstoffsäure nimmt also k_1/k_2 einen kleineren Wert an."

Goldschmidt has further studied the same reaction and obtained a similar result, using picric acid as a catalyser, the value of the constant ($1/a$) increasing with increase of concentration of the picric acid. He also made an experiment with a normal solution of hydrochloric acid (Knoblauch used acid of a strength less than normal) and found the value 3.46.

In the case of the equilibrium attained when mineral acids act on the alcohols, the effect of temperature is very different from the above. Villiers found in the case of the action of hydrochloric, hydrobromic, and hydriodic acids on alcohol, that the amount of ester formed increases with the temperature, that is, a diminishes as the temperature rises. It can also be shown from his results that a is variable.

Cain applied Guldberg and Waage's law to the equilibrium attained in the reaction between hydrochloric acid and ethyl alcohol, and found that the values of $1/a$ so obtained varied between 7.49 and 8.80.

As the results obtained by former investigators for the equilibrium constant between ethyl alcohol and hydrochloric acid varied so much, it was necessary for me to make some independent determinations.

The method of preparing and storing the reaction mixture was similar to that of Cain (*loc. cit.*), dry hydrogen chloride being passed into the anhydrous alcohol. Drying tubes were always interposed between the stock solution and the outside air.

The reaction tubes were of the shape shown in the diagram. The reservoir *A* had a volume of from 2 to 3 c.c., *B* and *C* were capillary tubes with constrictions at *b* and *c* to facilitate sealing off. The tubes were all thoroughly cleaned with chromic acid mixture, and then steamed out for about 15 minutes each tube. The method of filling from the store flask was as follows. The end *C* was put down into the reaction mixture (compare Cain, *loc. cit.*) and the solution forced

FIG. 1.

up into *A* until the reservoir was nearly full. The tube was then taken from the flask and sealed off at *b* ; this left *C* full and *A* nearly full of the solution. It was allowed to stand until the glass at *b* was cool, then inverted and immersed in broken ice, and after an interval, about half the solution which remained in the capillary tube *C* was drawn into the reservoir *A*. The tube was then taken out of the ice and *A* warmed with the hand until the solution in the capillary was driven past the constriction *c*, where it was then sealed off. By this means any of the solution which had come in contact with the air and could thus have absorbed moisture was rejected, as diffusion through the capillary would take place very slowly. Thus only a reaction mixture which was free from moisture came into use.

The amount of solution in each tube was measured by weighing it before and after filling. The strength of any solution was then found by titrating the contents of any one tube with standard baryta solution. The filled tubes were kept at 0° (at which temperature the reaction does not proceed) until required. Aqueous solutions were prepared by running some of the anhydrous solution into a weighed quantity of cold water. The accuracy of this method is shown by the following figures :

61·2879 grams of a solution of 33 equivalents of hydrogen chloride in 100 equivalents of alcohol were mixed with 20·4669 grams of water. The composition of the mixture (in equivalents) is then calculated to be $100\text{C}_2\text{H}_5\cdot\text{OH} : 33\cdot00\text{HCl} : 107\cdot66\text{H}_2\text{O}$, and in 1 gram of the mixture there should be 0·1554 gram HCl. The HCl found was 0·1553 gram.

A constant temperature was obtained by means of thermostats of the form described in Ostwald's "Hand- und Hilfs-buch," pp. 61—62. Experiments were carried out at 77°, 99°, and 129·5°.

In making a determination of the equilibrium, there are several factors to be taken into account. Berthelot and St. Gilles have shown that pressure has very little influence on the equilibrium, an increase of pressure of 80 to 90 atmospheres scarcely affecting the result. On the other hand, the volume of the space in which the reaction takes place is of great importance, especially at high temperatures, when the constituents can assume the vapour phase, the esterification then tending to become more complete. This effect of volume is clearly shown by the results recorded on p. 307 in which the mixture used contained 100 alcohol : 31·83HCl (equivalents).

Thus, when the tube is two-thirds or more full, the value of *a* remains constant ; otherwise it increases as the volume occupied by the mixture decreases. In all determinations, care was therefore taken that the tubes were about three-quarters full.

In order to be certain that equilibrium had been reached, separate

Temp. = 99°. Time of heating = 5 days.

Weight of mixture in tube.	Vol. of tube occupied.	α (equilib. const.).
1.0963 grams	One-third	0.197
1.6994 "	One-half	0.184
2.2995 "	Two-thirds	0.179
2.8069 "	Four-fifths	0.177

tubes were heated for different lengths of time in order to see if the titre of the acid remained constant. To show the measure of accuracy obtained, one experiment is given in detail :

Weight of mixture.	Time of heating.	Titre in c.c. baryta.	Titre for 1 gram.
2.4620 grams	96 hours	6.20	2.52
1.9837 "	72	5.04	2.54
2.0298 "	72 "	5.02	2.47
1.9627 "	144 "	5.00	2.55

In measuring the strength of the solution, $100\text{C}_2\text{H}_5\text{OH} : 33\text{HCl}$ (equivalents), the following were the figures obtained :

Weight of mixture.	Titre in c.c. baryta.	Titre for 1 gram.
2.1289 grams	78.01	36.64
2.0499 "	75.20	36.69
2.4794 "	90.85	36.66
2.3420 "	86.15	36.78

The accuracy of the measurements is thus all that could be desired.

The following tables give the results of different experiments. The first three columns give the composition of the mixture started with ; the next four give the composition when equilibrium was reached, and the last column gives the values of α so obtained. The compositions are all expressed in equivalents :

Equilibrium at 99°.

$C_2H_5 \cdot OH.$	HCl.	$H_2O.$	$C_2H_5 \cdot OH.$	HCl.	$C_2H_5Cl.$	$H_2O.$	$\alpha.$
100	33·00	—	69·26	2·26	30·74	30·74	0·166
100	33·00	107·66	75·82	8·82	24·18	131·84	0·210*
100	33·00	27·10	71·28	4·28	28·72	55·82	0·190
100	31·16	—	70·95	2·11	29·05	29·05	0·177
100	31·16	22·08	72·23	3·39	27·77	49·85	0·177
100	31·16	31·97	72·60	3·76	27·40	59·37	0·168
100	31·83	—	70·41	2·24	29·59	29·59	0·180
100	31·83	47·89	72·58	4·41	27·42	75·31	0·155*
100	31·83	23·77	71·68	3·51	28·32	52·09	0·171
100	31·83	—	70·39	2·22	29·61	29·61	0·178

Average $\alpha=0\cdot176$, rejecting the results when two layers were formed.

100	23·17	—	78·21	1·88	21·79	21·79	0·227
100	25·74	—	75·99	1·73	24·01	24·01	0·228
100	25·74	19·77	77·09	2·83	22·91	42·68	0·223
100	25·74	38·77	77·90	3·64	22·10	60·87	0·211
100	25·18	—	76·56	1·74	23·44	23·44	0·243
100	24·66	—	77·08	1·74	22·92	22·92	0·255
100	24·66	19·53	78·02	2·68	21·98	41·51	0·229
100	24·66	25·65	78·27	2·93	21·73	47·38	0·223

Average $\alpha=0\cdot230$.

* Two layers formed.

Equilibrium at 77°.

In this case the tubes were heated for five weeks in order to be sure that equilibrium was reached; to make additionally certain, some of the tubes were first heated for a few days at 99° and after that at 77°. The following will indicate the agreement obtained:

Wt. of mixture.	Time of heating.	Titre in c.c. baryta.	Titre for 1 gram.
2·1442 grams	April 13—May 15 April 13—15 at 99° and then until May 15 at 77°	8·62	4·02
2·2207 „		9·01	4·06
2·3375 „		9·40	4·02

$C_2H_5 \cdot OH.$	HCl.	$C_2H_5 \cdot OH.$	HCl.	$C_2H_5Cl.$	$H_2O.$	$\alpha.$
100	23·17	79·34	2·51	20·66	20·66	0·467
100	25·74	76·98	2·72	23·02	23·02	0·395
100	31·16	72·14	3·30	27·86	27·86	0·307

Later on some fresh determinations were made, the temperature in this case being 76.3—76.5°.

Equilibrium at 76.5°.

$C_2H_5 \cdot OH.$	HCl.	$C_2H_5 \cdot OH.$	HCl.	$C_2H_5Cl.$	$H_2O.$	$\alpha.$
100	9.76	91.29	1.05	8.71	8.71	1.263
100	14.26	87.36	1.62	12.64	12.64	0.886
100	16.78	85.12	1.90	14.88	14.88	0.730
100	21.20	81.43	2.63	18.57	18.57	0.620
100	23.45	79.24	2.69	20.76	20.76	0.495
100	27.35	75.91	3.26	24.09	24.09	0.426
100	28.86	74.52	3.38	28.86	28.86	0.302
100	40.84	63.43	4.27	36.57	36.57	0.226

In each case α has been calculated according to the formula

$$\alpha = \frac{\text{alcohol} \times \text{acid}}{\text{ester} \times \text{water}},$$

where alcohol = concentration of alcohol expressed in equivalents, and similarly for acid, ester, and water.

The results at 99° have been arbitrarily divided into two series, for one of which the average of α is 0.176, and for the other 0.230; the concentration of the hydrochloric acid in the reaction mixture used (column 2) remains practically the same throughout each series, but it is different in the two series. Accompanying this difference is a variation of α from 0.176 to 0.230. The variations in each series are irregular, and are probably for the most part within the limit of the error of experiment.

The parallelism between the concentration of the hydrochloric acid (column 2) and the value of α no longer holds if we take the concentrations of the acid when equilibrium was reached, as will be seen by comparing the numbers in the fifth column of the table for 99°. Similar results were obtained at 129.5°, but the figures are not given as they are not so trustworthy, owing to the formation of two layers. This variation of α with the amount of hydrochloric acid present is shown much better by the determinations at 77° and 76.5°, as at these temperatures the value of α is much more sensitive to alterations in the concentration of the hydrochloric acid than is the case at higher temperatures. The curves given in Figs. 2 and 3 illustrate these results, and do not need further explanation. From them we can deduce that "the value of α decreases with increasing concentration of the hydrochloric acid." This is true whether we take the concentrations of the acid at the

beginning of the experiment (Fig. 2), or when equilibrium is reached (Fig. 3).

There are several causes which may bring about this result. The concentrations of the alcohol, acid, &c., have been taken as representing their active quantities, and the equation for the equilibrium constant was developed on this assumption. This is, however, only strictly true in dilute solutions. Arrhenius (*Zeit. physikal. Chem.*, 1899, 28, 317) has shown that better results are obtained when the osmotic pressure is used instead of the concentration; owing to the lack of

FIG. 2.

the necessary data, it is impossible to put this to the test. It is doubtful if this would account for the variations in α , as van't Hoff has shown that in the analogous case of alcohol and acetic acid fairly good constants are obtained.

Alcohol has a tendency to form double molecules; the same is true of water, but to a much greater extent, and this may affect the value of α . In each series at 99°, however, the presence of water does not seem to affect the value of α , as it should do when so many double molecules are calculated as single ones.

The variation of the medium and the catalytic effect of the hydrogen ions will be discussed later on.

The decrease of α as the temperature rises confirms the results of Villiers and Cain :

Ratio of alcohol to acid.	100 : 31.16.	100 : 23.17.	100 : 25.74.
Value of α at 77°	0.307	0.467	0.395
„ „ 99°	0.177	0.227	0.228
„ „ 129.5°	(0.087)	(0.108)	(0.100)*

* The numbers in brackets only denote the approximate value of α , as two layers were formed at the point of equilibrium.

FIG. 3.

The heat of reaction can be calculated in the usual manner from the equation

$$\frac{d}{dT} \log_e \alpha = - \frac{Q}{RT^2}$$

where Q = heat given out during the reaction when no external work is done.

Integrating this on the assumption that the heat of reaction is independent of the temperature, we have for the temperatures T_1 and T_2

$$Q = - \frac{4.584(\log a_1 - \log a_2)T_1T_2}{T_1 - T_2} \text{ calories,}$$

when the calculations are made with ordinary logarithms, and R is expressed in heat units ($= 1.991$). On calculating Q from the values of a obtained at 77° and 99° , we have

From 100 C_2H_5OH : 31.16 HCl . $Q = +6489$ calories.

„ 100 C_2H_5OH : 25.74 HCl . $Q = +6475$ „

„ 100 C_2H_5OH : 23.17 HCl . $Q = +8500$ „

The first two values of Q agree very well, although the constants are taken from two different series, but the third value is altogether different.

Using the data given in Berthelot's "Thermochimie," Q is calculated to be 6750 Calories, but the figures are not very satisfactory.

Velocity of Esterification.

Villiers and Cain both measured the velocity of esterification, but their experiments were more of a qualitative than a quantitative nature.

Goldschmidt (*loc. cit.*) has shown that in the reaction between benzoic acid and ethyl alcohol, hydrochloric acid acts catalytically, the velocity of esterification being proportional to the amount of hydrochloric acid present. In the case of the action of alcohol on trichloroacetic acid (alcohol in excess and no other acid present), he shows that the trichloroacetic acid acts autocatalytically. The reverse reaction was considered to be negligible.

In the case of the action of hydrochloric acid on ethyl alcohol we have

and this gives us $\frac{dx}{d\theta} = k_1(A-x)(B-x) - k_2(C+x)(D+x)$

$$\text{and } a = \frac{k_2}{k_1} = \frac{(A-x)(B-x)}{(C+x)(D+x)}$$

as used in the first part of the paper.

On calculating the constants from Cain's numbers (*loc. cit.*) according to the above equation, the results showed plainly that it did not represent the true course of the reaction as the "constants" decreased very

rapidly. The probable reason of this is that the acid acts autocatalytically, and this action must be taken into account.

Ostwald (*Lehrbuch der allgem. Chemie*, 2 Aufl., 2², 263) represents the acceleration due to a catalyser by an additive term in the velocity equation. In the case of a single substance which acts on itself catalytically, he writes the equation as

$$\frac{dx}{d\theta} = \{k_1 + k_2(A - x)\}(A - x),$$

where k_1 = velocity coefficient if no catalyser is present,

k_2 = „ „ due to catalyser.

Now, in most cases of autocatalysis, the constant k_1 becomes indefinitely small in comparison with k_2 , and can be neglected. The above equation then becomes

$$\frac{dx}{d\theta} = k_2(A - x)^2.$$

In the reaction between hydrochloric acid and ethyl alcohol, the hydrogen ions only act autocatalytically in the direct reaction; the reverse reaction would take place very slowly, however, if it were not catalytically influenced by the acid present (compare the rate of catalysis of methyl acetate by water alone and in the presence of hydrochloric acid), and in this case also we can neglect the amount of ester which would be formed if no catalyser were present. We may therefore write the velocity equation as

$$\frac{dx}{d\theta} = k'p(A - x)(B - x)^2 - k''p(B - x)(C + x)(D + x),$$

since the concentration of the hydrogen ions is given by that of the dissociated part of the acid, that is, by $p(B - x)$ where p is a function of the concentration $(B - x)$. This function would generally be re-

presented by Ostwald's dilution law $\frac{p^2}{1 - p} = \beta v = \frac{\beta}{B - x}$ where β is the

conductivity constant, or by some such formula as that of Rudolphi (*Zeit. physikal. Chem.*, 1895, 17, 385) or Bancroft (*ibid.*, 1899, 31, 188), but in the present case it is almost impossible to find an equation for it, as the composition of the medium is continually changing. We can, however, assume that the concentration of the hydrogen ions is proportional to the amount of acid present, that is, the dissociation of the hydrochloric acid is considered to be constant during the time of experiment. The reaction equation then becomes

$$\frac{dx}{d\theta} = k_1(A - x)(B - x)^2 - k_2(C + x)(D + x)(B - x).$$

If no ester is present to begin with, $D = 0$ and

$$\frac{dx}{d\theta} = k_1 \{ (A - x)(B - x)^2 - ax(C + x)(B - x) \} \text{ where } k_2 = ak_1.$$

Integrating this on the assumption that when $x = 0$, $\theta = 0$, we have

$$\begin{aligned} & \frac{A + aC - B(1 - 2a)}{\sqrt{P}} \log_e x \{ A + B + aC - \sqrt{P} \} - 2AB \\ & - \log_e \frac{1}{AB} \{ x^2(1 - a) - x(A + B + aC) + AB \} + 2 \log_e \frac{B - x}{B} \\ & = 2aB(B + C)k_1\theta \dots \dots \dots (3) \end{aligned}$$

where $P = (A + B + aC)^2 - 4AB(1 - a)$.

Goldschmidt (*loc. cit.*) found that satisfactory constants were obtained if the reverse reaction were neglected. In the present case, the value of k_2 is only about one-fifth of k_1 ($a = 0.176$ or 0.230), so that the reverse reaction will have a much less velocity than the direct one, and when it is in its first stages and x and $(C + x)$ are very small, it is probable that the term due to the reverse reaction can be neglected. We then have for the velocity equation

$$\frac{dx}{d\theta} = k(A - x)(B - x)^2,$$

or on integration,

$$\frac{(A - B)x}{B(B - x)} + \log_e \frac{A(B - x)}{B(A - x)} = (A - B)^2 k \theta \dots \dots \dots (4)$$

Donnan (*Ber.*, 1896, 29, 2422) has shown that the same form of reaction equation as Goldschmidt used for the reaction between trichloroacetic acid and alcohol is obtained on the assumption that the reaction takes place between the alcohol and the ions of the acid; that is to say, there is no need to assume that the acid acts autocatalytically. However, the experiments of Knoblauch on the reaction between ethyl alcohol and acetic acid in the presence of hydrochloric acid, and of Goldschmidt on the reactions between (1) ethyl alcohol and benzoic acid in the presence of hydrochloric acid, (2) ethyl alcohol and phenylacetic acid in the presence of picric acid and the *p*-toluidine salt of picric acid, seem to show that the foreign acid acts catalytically. Goldschmidt has also shown that the equilibrium between ethyl alcohol and acetic acid is affected by picric acid (which is a foreign acid and acts catalytically) in the same way as the equilibrium between hydrochloric acid and ethyl alcohol is affected by the acid.* We may

* Where picric acid is the catalyser, this variation of the equilibrium may be due to the alteration in the medium (compare Koelichen, *Zeit. physikal. Chem.*, 1900, 33, 129) but with hydrochloric acid, this explanation would not seem to hold, both

therefore assume for the present that the hydrochloric acid in the latter reaction acts autocatalytically.

From the first form of the velocity equation we again get

$$\alpha = (A - x)(B - x)/(C + x)(D + x).$$

Zaitschek (*Zeit. physikal. Chem.*, 1897, 24, 1), in the course of his investigations on the equilibrium between sulphuric acid and alcohol, has also found that the equilibrium constant α (calculated as above) depends on the amount of acid present. He explains it on the assumption that the hydrogen ions act catalytically, but that their influence is greater in the direct than in the reverse reaction. The decrease of α with the increase of the amount of acid then follows as a matter of necessity, because the value of α is simply the ratio of the velocity constants of the reverse and direct reactions ($k_2 = \alpha k_1$).

According to the second law of thermodynamics, we can prove that "if a reaction which proceeds to a state of equilibrium is catalytically influenced, the reverse reaction must also be influenced to the same extent, and therefore the value of α will not alter"* (Ostwald, *Grundriss*, 2^{te} Aufl., p. 519). This only holds for the extreme case when we can (theoretically) introduce the catalyser at the beginning of the reaction and take it out again at the end, so that the sum of the work done is zero. In the present case ($C_2H_5 \cdot OH$ and HCl), it is doubtful if this condition is fulfilled, because the catalyser is an auto-one, and one of the components of a system which is in equilibrium cannot be added or taken away without disturbing it.

Zaitschek's explanation is really as follows: the velocity equation can be written as

$$\frac{dx}{d\theta} = k'(A - x)(B - x)k_3(B - x) - k''(C + x)(D + x)k_4(B - x),$$

k_3 and k_4 representing the catalytic coefficients in the direct and reverse reactions respectively. For equilibrium, we then have

$$\frac{dx}{d\theta} = 0 \text{ and } \frac{(A - x)(B - x)}{(C + x)(D + x)} = \frac{k''k_4}{k'k_3} = \alpha = \frac{k_2}{k_1};$$

k' and k'' are constants; α , we know, diminishes as the amount of hydrochloric acid increases, that is, the ratio of $k_4 : k_3$ does not remain constant, but decreases as $(B - x)$ increases; in other words, the law

Goldschmidt and Knoblauch finding that the equilibrium in aqueous solution alters with the concentration of the acid (catalyser) present, although the variation in the amount of the same would not affect the medium very much. Similarly, in the reaction between ethyl alcohol and hydrochloric acid, we may assume that the variation in α is not *primarily* caused by the variation in the medium.

* Koelichen has shown this to be the case in the condensation of acetone to diacetonealcohol by means of sodium hydroxide (*Zeit. physikal. Chem.*, 1900, 33, 129).

which connects the concentration and catalytic effect of the hydrogen ions is different in the direct and reverse reactions. This may very well be the case, as in the direct reaction the acid acts auto-catalytically, and in the reverse reaction as an ordinary catalyser.

Measurements of Velocity.

Owing to the conditions of experiment, the reaction mixture cannot be warmed up to the required temperature before the reaction is allowed to begin. The measurement of the time (θ) is thus subject to an error due to the warming and cooling of the tubes at the beginning and end of the experiment. This error can be obviated by reckoning θ from the time when the first tube is taken out of the thermostat.*

Then, if the value of $k\theta_0$ for the first tube is V_0 , and the value of $k\theta_1$ for the second tube is V_1 , the true value of k is given by $\frac{V_1 - V_0}{\theta_1 - \theta_0}$.

In the following tables,

A = amount of alcohol used, expressed in equivalents.

B = " hydrochloric acid used, expressed in equivalents.

C = " water " " "

x = " ester formed " " "

θ = time in minutes, reckoned from when tubes were immersed.

α = equilibrium constant.

$\kappa_1 = 2\alpha B(B+C)k_1$ = constant calculated according to equation (3), page 314. } taking first measurement

$\kappa = (A-B)^2k$ = constant calculated according to equation (4), page 314. } as starting point.

All the calculations have been made with Briggs' logarithms, and are expressed accordingly.

* To obtain the greatest degree of accuracy, each value of θ should separately be taken as the starting point for succeeding measurements; this does not affect the results, however, except in the cases where C has a value different from zero. It will be seen that in these cases the values of the constants vary, and can only be used for qualitative comparison, so that the extra calculation is unnecessary.

Results at 99°.

$$A=100. \quad B=33.00. \quad C=0. \quad \alpha=0.176.$$

$\theta.$	$x.$	$\kappa_1 \times 10^6.$	$\kappa \times 10^4.$	$k_3 \times 10^{7*}.$
35	10.34	—	—	—
60	14.51	771	204	410
85	17.25	761	203	376
110	19.25	777	203	352
138	20.77	763	197	322
174	22.56	787	203	309
214	23.62	772	193	278

$$\therefore \kappa_1 \times 10^6 = 774\ddagger.$$

$$\therefore \kappa \times 10^4 = 201\ddagger.$$

$$\therefore k_1 \times 10^9 = 2019.$$

$$\therefore k \times 10^8 = 448.$$

$$A=100. \quad B=41.33. \quad C=0. \quad \alpha=0.103\ddagger.$$

$\theta.$	$x.$	$\kappa_1 \times 10^6.$	$\kappa \times 10^4.$
16	8.26	—	—
33	14.29	689	154
49	18.12	697	156
62	20.45	703	154
77	22.47	698	154
96	24.41	691	152
120	26.53	708	154

$$\therefore \kappa_1 \times 10^6 = 698.$$

$$\therefore \kappa \times 10^4 = 154.$$

$$\therefore k_1 \times 10^9 = 1984.$$

$$\therefore k \times 10^8 = 447.$$

* For the sake of comparison, the constants have also been calculated (in this case only) according to the formula

$$\frac{dx}{d\theta} = k_3 \{ (A-x)(B-x) - \alpha(C+x)(D+x) \}.$$

It will be seen that the so-called constants are not by any means constant, but diminish rapidly, thus showing that the action of the hydrochloric acid as a catalytic agent cannot be neglected.

† Mean of the values under κ_1 and κ respectively.

‡ The value of α has been calculated from the known results on the assumption that it is proportional to the amount of hydrochloric acid present.

$A=100, B=31.83, C=0, \alpha=0.176.$				$A=100, B=24.66, C=0, \alpha=0.230.$			
$\theta.$	$x.$	$\kappa_1 \times 10^8.$	$\kappa \times 10^4.$	$\theta.$	$x.$	$\kappa_1 \times 10^8.$	$\kappa \times 10^4.$
15	5.56	—	—	15	3.85	—	—
30	9.85	785	248	30	7.08	774	353
45	12.67	787	242	45	9.46	777	361
60	15.03	823	249	60	11.21	782	361
75	16.60	812	243	75	12.42	760	349
90	18.08	834	247	90	13.55	769	352
105	19.08	822	243	107	14.62	783	355
128	20.35	814	237	121	15.16	760	344
$\therefore \kappa_1 \times 10^8 = 811$ and $\kappa \times 10^4 = 244$				$\therefore \kappa_1 \times 10^8 = 772$ and $\kappa \times 10^4 = 354$			
$\therefore k_1 \times 10^9 = 2274$ and $k \times 10^8 = 525$				$\therefore k_1 \times 10^9 = 2760$ and $k \times 10^8 = 624$			

$A=100, B=23.17, C=0, \alpha=0.230.$				$A=100, B=33.00, C=107.66, \alpha=0.176.$			
18	4.58	—	—	35	3.55	—	—
30	6.68	651	357	78	6.61	713	43.3
61	10.41	673	366	147	10.02	695	41.2
62	10.57	685	373	193	11.54	668	39.0
77	11.77	686	372	246	13.11	665	38.1
90	12.58	681	368				
92	12.76	690	372	369	15.35	(616)	(34.1)
107	13.51	683	367	474	16.90	(609)	(32.6)
$\therefore \kappa_1 \times 10^8 = 678$ and $\kappa \times 10^4 = 369$				$\therefore \kappa_1 \times 10^8 + 685$ and $\kappa \times 10^4 = 40.4^*$			
$\therefore k \times 10^9 = 2746$ and $k \times 10^8 = 625$				$\therefore k \times 10^9 = 419$ and $k \times 10^8 = 90$			

* Results below the dotted line are not included in the average.

$A=100, B=33.00, C=27.10, \alpha=0.176.$				$A=100, B=24.66, C=25.65, \alpha=0.230.$			
30	7.84	—	—	15	2.41	—	—
69	13.06	940	134	30	4.80	940	212
102	15.73	918	129	46	6.71	920	207
130	17.14	867	121	60	8.02	904	202
169	18.90	861	118	76	9.39	922	204
207	20.04	832	112	90	10.17	885	195
246	20.89	797	106	105	10.97	871	191
				120	11.68	862	188
$\therefore \kappa_1 \times 10^8 = 869$ and $\kappa \times 10^4 = 120$				$\therefore \kappa_1 \times 10^8 = 901$ and $\kappa \times 10^4 = 199$			
$\therefore k_1 \times 10^9 = 1245$ and $k \times 10^8 = 267$				$\therefore k_1 \times 10^9 = 1579$ and $k \times 10^8 = 351$			

These results are summarised in the following table :

A.	B.	C.	$k_1 \times 10^3$.	$k \times 10^3$.
100	33.00	—	202	448
100	41.33	—	198	447
100	31.83	—	227	525
100	33.00	107.66	42	90
100	33.00	27.10	125	267
100	23.17	—	275	625
100	24.66	—	276	624
100	24.66	25.65	158	351

In those experiments where no water was present to start with, the constants are very satisfactory, indeed, better than would be expected when the change which takes place in the medium during the progress of the reaction is taken into account. The constants calculated with the formula (4) are quite as good as those calculated according to the equation (3).

The case is different, however, when water takes part in the reaction from the beginning (compare Goldschmidt, *loc. cit.*). The constants then diminish as the time increases, and although there is not much difference as regards the application of the two formulæ, the first one gives a slightly better result.

On comparison of the constants of one series with those of another (compare summarised table), the action of water in retarding the reaction is very apparent; the greater the amount of water present, the greater the retardation, although the results are not proportional. This retardation is most probably due to the alteration in the medium, as this has a great effect on reaction velocity, as shown by Menschutkin (*Zeit. physikal. Chem.*, 1890, 5, 589), Hemptinne (*ibid.*, 1899, 23, 225), and others.

The velocity constants fall into two divisions, corresponding to the two values of the equilibrium constant, excluding the cases where aqueous alcoholic solutions were used. They also diminish as the proportion of acid to alcohol increases; this may be due to an alteration in the medium, but can also be deduced as follows :

The constant k_1 is really the product of two factors, namely, k , the true velocity constant, and a factor depending on the dissociation of the acid. In writing down the velocity equation, the concentration of the hydrogen ions has been taken as being simply proportional to the amount of acid present, that is, proportional to $(B - x)$, so that we may write the concentration as $c(B - x)$, where c^* is a constant. The

* This c is a true constant and not a function of the concentration as in Ostwald's dilution law. It varies with each experiment, but during each one is taken as constant, this being the assumption on which the velocity equation was formulated.

velocity equation is then

$$\begin{aligned}\frac{dx}{d\theta} &= kc(A-x)(B-x)^2 - k'cx(C+x)(B-x) \\ &= k_1(A-x)(B-x)^2 - k_2x(C+x)(B-x),\end{aligned}$$

where $k_1 = kc$, and $k_2 = k'c$.

Now, for two different solutions, k and k' will remain the same, but c will vary. If the values of k_1 for these two solutions are $(k_1)_a$ and $(k_1)_b$, and of c are $(c)_a$ and $(c)_b$, we have $(k_1)_a = k(c)_a$, and $(k_1)_b = k(c)_b$; therefore, if $(c)_a > (c)_b$, then $(k_1)_a > (k_1)_b$. Similarly for k_2 . Now the more dilute the solution of hydrochloric acid in alcohol is, the more the dissociation increases, that is, the value of c increases as the proportion of acid diminishes, and therefore the value of k_1 must act similarly, as shown by the table. Thus, only constants can be compared with each other in those experiments in which the proportion of acid present is the same or approximately the same. Since the two formulæ give equally good constants, it follows that the reverse reaction takes place so slowly (at least during the time of experiment) that it may be neglected.

Velocity at 77°.

The equilibrium constants in the particular mixtures used were not determined directly, owing either to the breaking of the tubes before equilibrium was reached, or to the formation of two layers. They have been calculated from the constants of the mixtures with 31.16 and 25.74 equivalents of HCl respectively, and cannot be far from correct, as may be seen by comparison with the values obtained at 76.5°.

$A=100. \quad B=33.00. \quad \alpha=0.28.$				$A=100. \quad B=41.33. \quad \alpha=0.18.$			
$\theta.$	$x.$	$\kappa_1 \times 10^6.$	$\kappa \times 10^5.$	$\theta.$	$x.$	$\kappa_1 \times 10^6.$	$\kappa \times 10^5.$
60	3.20	—	—	20	6.76	—	—
146	7.12	172	280	50	8.73	169	217
248	10.09	153	259	90	10.93	174	214
412	13.61	151	253	137	13.19	169	216
				196	15.68	174	223
				238	17.03	173	220
				282	18.32	173	220
$\therefore \kappa_1 \times 10^6 = 159$ and $\kappa \times 10^5 = 264.$				$\therefore \kappa_1 \times 10^6 = 172$ and $\kappa \times 10^5 = 218.$			
$\therefore k_1 \times 10^9 = 261$ and $k \times 10^8 = 59.$				$\therefore k_1 \times 10^9 = 280$ and $k \times 10^8 = 63.$			

The following table gives a comparison of the results at 99° and 77°:

Temperature.	<i>A</i> .	<i>B</i> .	$k_1 \times 10^8$.	$k \times 10^8$.
99°	100	33	202	448
77	100	33	26	59
99	100	41·33	198	447
77	100	41·33	28	63

The influence of temperature on the reaction velocity is thus very great, a rise in the former of 22° increasing the latter to between seven and eight times its former value. According to Arrhenius (*Zeit. physikal. Chem.*, 1889, 4, 226), the influence of temperature on the velocity of reaction may be represented by the equation

$$\frac{d}{dT} \log_e k = \frac{A}{T^2},$$

or, integrated on the assumption that *A* is independent of the temperature $\log_e k = -\frac{A}{T} + B$, where *A* and *B* are constants.

On calculating the value of *A* from the results given above we find :

Mixture.	From k_1 .	From <i>k</i> .
100 : 33	12134	11998
100 : 41·33	11576	11596

The values agree as closely as could be expected. In the case of the simple esters of organic acids, *A* has been found to be about 8670 (compare Price, *Öfvers. Kongl. Vet.-Ak. Förhand.*, 1899, No. 9, 932), so that the influence of temperature is much greater in the present case.

So far it has not been found practicable to measure the velocity of the reverse reaction. That the same equilibrium constant is obtained has already been shown by Villiers and Cain.

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