CCXVI.—*Ester Catalysis and a Modification of the Theory of Acids.*

By EDWARD FITZGERALD and ARTHUR LAPWORTH.

THE main facts relating to the phenomena of catalysis by acids are well known. They have been studied in the main with reference to esterification and ester and sucrose hydrolyses. The influence of acids as catalysts is known to be exerted in many other types of reaction, as,

for example, in the bromination of carbonyl compounds, the decomposition of diazoacetic ester (Bredig and Fraenkel, *Ber.*, 1906, **39**, 1756), and the transformation of hydrazobenzene into benzidine. The numerous theories which have been devised to explain the catalytic influence of acids on esterification and ester hydrolysis have recently been dealt with in a fairly complete manner by Acree (*Amer. Chem. J.*, 1908, **39**, 145), and therefore it is not necessary fully to review the question here from the historical standpoint. It is sufficient to say that Kastle appears to have been the first (*Amer. Chem. J.*, 1897, **19**, 894) to have suggested the view now most generally held, namely, that the ions of the acid acting catalytically react with the substance undergoing change, forming an unstable addition product which subsequently yields the final products; it is evident, however, that the same natural idea has occurred independently to other chemists. The view now most generally held in reference to ester catalysis, is that the carbonyl compound forms a complex with the hydrogen ions. On the other hand, Goldschmidt and Udby (*Zeitsch. physikal. Chem.*, 1907, **60**, 728) claim to have established that it is the alcohol which mainly forms the reacting initial addition compound or complex hydron, but this claim cannot be accepted.

The facts on which a recent discussion of the mechanism of esterification and ester hydrolysis have been based (Acree and Johnson, *Amer. Chem. J.*, 1907, **38**, 301) are: that the velocity of catalysed esterification and ester hydrolysis are usually nearly proportional to the concentration of catalyst, where the latter is a powerful acid, and to the concentration of the carbonyl compound (ester or carboxylic acid); and further, that the activity of the catalyst is roughly proportional to its so-called degree of dissociation as given by conductivity measurements.

A slight lowering of the conductivity of acids was found by these authors to be produced by the addition of carboxylic ester. But their subsequent discussion of the question is based on the assumption that the velocity of esterification and ester hydrolysis is intrinsically proportional to the concentration of the alcohol and water respectively. This assumption is one which is made in most text-books on Physical Chemistry, but was not sufficiently well justified to warrant the rejection of any theory of esterification which did not fulfil this condition.

It must be pointed out that the classical experiments of Berthelot and Péan de Saint-Gilles do not throw any light on the question. Further the condition at equilibrium in a mixture of alcohol, carboxylic acid, ester, and water is determined by thermodynamic laws and must be the same whatever the path by which it is attained. The mechanism can only be decided after a study of the conditions

affecting the initial rate of change in the absence of the products of change.

A theory put forward by one of us having been assailed on the above ground, experiments were made showing that, in point of fact, the initial velocity of hydrolysis of an ester in acetone is nearly independent of the water concentration over a wide range (Proc., 1908, **24**, 101, 152), but the erroneous conclusion was drawn that, on this account, theories demanding a proportionality between the velocity and water concentration were wrong. The equivocal character of the results was clear from the fact that, within the same range of water concentration in acetone, the initial velocity of catalytic esterification is roughly inversely proportional to the concentration of the water, but proportional to the concentration of the alcohol, which is its analogue in the reverse reaction. The numbers obtained by Kistiakowsky (*Zeitsch. physikal. Chem.*, 1898, **27**, 253 *et seq.*) also show that, within similar limits, similar relations obtain, whilst Goldschmidt (*Ber.*, 1896, **29**, 2208 *et seq.*) was the first to draw attention to the very great depression produced by small quantities of water on the velocity of esterification in alcoholic solution.

In addition to the points above referred to, it was found by Fitzgerald and Lapworth (*loc. cit.*) that alcohol produced a very slight lowering only on the velocity of catalytic hydrolysis in acetone, and that the initial velocity of esterification is roughly proportional to the alcohol concentration.

The solution of the question whether the initial velocity of hydrolysis of esters by acids and water is proportional to, or independent of, the concentration of the water was evidently necessary for the final determination of the question of the mechanism of ester catalysis. During the interval since the publication of the preliminary notes, the authors have been engaged in experiments on the velocity of esterification of acetic acid under varying conditions, but have come to the conclusion that rapid progress towards the solution of the problem is to be made along different lines, and after a due consideration of the facts referred to above.

Their reasoning has been based on the belief that the alcohol and the water, so far as they take part in the esterification or ester hydrolysis, play similar parts. Now the velocity of esterification appears to be at the very first moment nearly proportional to the concentration of the alcohol, and therefore it seems impossible to avoid the conclusion that this is really also the case with the water, and that the general depressant effect of the increased concentration of water exactly neutralises the acceleration which would otherwise be observed. The most obvious view of the respective effects of alcohol

and water on ester catalysis is that, in solutions containing both, the two substances in question share between them some intermediate product, but on careful examination this fails to meet the case.

No consistent hypothesis can be advanced until the possibility of combination of the catalyst itself with the water is considered.

The theory advocated by the school of Arrhenius in the case of the hydrolysis of, say, aniline hydrochloride by water, is that, as the result of the dissociation of water in hydrogen and hydroxyl ions, the phenylammonium ions unite with hydroxyl ions from the water to form feebly dissociated phenylammonium hydroxide, and this, in turn, yields aniline and water. Further examination shows that this really explains hydrolysis by assuming the base to be converted into a relatively inactive hydrate. This is easily seen on considering the following expressions.

Let a small quantity of a weak base in a solvent containing hydrogen chloride and water be considered. The following equations represent the relations usually supposed to obtain, where B = free base, BH_2O the undissociated hydrate (ionisable + non-ionisable), $\dot{B}H$ the cation, $BHCl$ the undissociated hydrochloride of the base. The equations are :

To these may be added a seventh, which is not so frequently introduced, but which is mathematically consequent on the others, namely,

Expressing concentrations by bracketing the symbols, the law of mass action leads to the following expressions, most of which are in general use :

$$K_1 = \frac{(\dot{H})(\dot{Cl})}{(HCl)}, \quad K_3 = \frac{(\dot{B}H)(Cl)}{(BHCl)}, \quad K_4 = \frac{(\dot{B}H)(\dot{OH})}{(BH_2O)}, \quad K_5 = \frac{(\dot{H})(\dot{OH})}{H_2O},$$

$$K_6 = \frac{(BHCl)}{(B)(HCl)}, \quad K_7 = \frac{(B)(H_2O)}{(BH_2O)}, \quad \text{and} \quad K_2 = \frac{(B)(\dot{H})}{(\dot{B}H)}.$$

Two of these being redundant, K_6 and K_7 may be conveniently expressed in terms of the others ;

$$\text{hence} \quad K_6 = \frac{K_1}{K_2 K_3} \quad \text{and} \quad K_7 = \frac{K_2 K_4}{K_5}.$$

The following relations also result :

$$\begin{aligned}(\text{BH}_2\text{O}) &= \frac{1}{K_7}(\text{B})(\text{H}_2\text{O}) = \frac{K_5}{K_2 K_4}(\text{B})(\text{H}_2\text{O}), \\(\dot{\text{B}}\text{H}) &= K_4 \frac{(\text{BH}_2\text{O})}{(\text{OH})} = \frac{1}{K_2}(\text{B})(\dot{\text{H}}), \\(\text{BHCl}) &= \frac{1}{K_3}(\dot{\text{B}}\text{H})(\text{Cl}) = \frac{1}{K_2 K_3}(\text{B})(\dot{\text{H}})(\text{Cl}),\end{aligned}$$

which express the relationships between the concentrations of the compounds of B with the active masses of the hydrogen ions, the chlorine ions, and the water.

Whence it follows that if the hydrogen and chlorine ions remain nearly constant in amount or increase on addition of water,* the only way in which the salt and its cation can disappear is by conversion into undissociated BH_2O , as they are otherwise nearly independent of the amount of water present.

The application of the Arrhenius view, then, to the case of catalysis involves the assumption that the water combines with the substance affected, thus rendering it inactive. If so, when esterification in alcohol is considered, it must be the carboxylic acid which forms an inactive hydrate, as the alcohol is in enormous excess. This, apart from its inherent improbability, is not capable of explaining the depressions which are observed, and when the influence of water on the bromination of acetone, referred to in another paper, is considered, the explanation is totally inadequate and must be rejected.

The Hydrogen Ions of the Catalyst are Hydrated?—Inspecting the expressions above given for the equilibrium of a base in presence of an acid and water, it is seen that the only other explanation of the reduction in concentration of the salt or its cation is that the hydrogen ions disappear, that is, that water acts on them in virtue of its power of forming oxonium salts. The assumption that such complexes may be formed is in no way novel, and has been used by many chemists. What is novel in the present conception is that *the introduction of water into alcohol containing hydrogen chloride must necessarily reduce the number of hydrogen ions, or, in other words, of the amount of available hydrochloric acid*. Further, as acid catalysis, unless hydrolytic, occurs enormously faster in alcohol than in water, the number of hydrogen ions in an aqueous solution of hydrogen chloride must be extremely small, even compared with one in alcohol, which itself must be regarded as a base.

The mechanism of esterification in this view is intrinsically

* The increase in conductivity of hydrogen chloride dissolved in alcohol consequent on the replacement of alcohol by water is usually attributed to a greater degree of dissociation of the acids into H and Cl ions.

proportional to (alcohol) $\times$ (carboxylic acid) $\times$ (hydrion); that of hydrolysis to (water) $\times$ (ester) $\times$ (hydrion), and the apparent discrepancies between this, the usually accepted view, and experiment is due to alterations in the hydrion concentration which have not been foreseen. It is not yet possible to ascertain whether the alcohol and the water, on the one hand, or the ester and carboxylic acid, on the other, form the reactive complex ions, as the same results will be obtained in either case. The important work of Stieglitz on the hydrolysis of imino-ester ions and the properties of carbonyl compounds as a whole render the latter, and usual, view by far the more probable one.

This question, however, assumes a secondary importance as compared with the broader reflections to which its study has given rise. The proposition that free hydrogen ions are responsible for the catalytic activity of acids leads to the conclusion that they must be relatively few in number in aqueous solution. On the other hand, the original conception of hydrogen ions was applied to explain the conductivity of acids in aqueous solution, so that the terms are not synonymous.

In the latter case, they must be complex ions, probably of the form $\dot{\text{H}}_2\text{OH}$, if the analogy between water and ammonia is complete; the catalytically active hydrogen ions, if they have a real existence, are simpler than these, probably $\dot{\text{H}}$.

The view that both types exist will perhaps prove useful in the theoretical treatment of certain questions, but the alternative must be considered, for it has long been entertained in one form or another by a school of chemists, including Armstrong and Lowry.

The Velocity of Esterification when no Water is Present.

The velocity of esterification having been found to be over a wide range nearly inversely as the amount of water present, it was obvious that the form of the curve expressing the variation of velocity with the amount of water was roughly of the form of a rectangular hyperbola, but that the hyperbola would cut the velocity axis was tolerably certain, otherwise esterification with no water present would be instantaneous. This being highly improbable, it was clear that the curve near this point would have the form :

$$\frac{dx}{dt} \times [\text{H}_2\text{O} + b] = a,$$

when b and a were constants. The constant b was termed by the authors the water value of the solvent long before its true significance was understood.

The Theory of Goldschmidt and Udby.

Goldschmidt and Udby have discussed the question of the retarding effect of water on the catalytic esterification of carboxylic acids in alcohol (*Zeitsch. physikal. Chem.*, 1907, **60**, 728). These authors accept, without discussing the view of Arrhenius, the idea that the process of catalytic esterification depends on the intermediate formation of complex hydrions by one of the substances taking part in the change. They claim to prove that the alcohol must be the substance which mainly forms the reactive complex ions, but their process of reasoning would indicate that when the initial concentration of alcohol varied, the velocity would be unaltered, and this is contrary to experience.

They adopt the view that the complex water ions, H_3O , are the carriers of catalytic activity of acids in aqueous solution, and their views are thus essentially opposed to that advanced in the present papers, which is that these are usually, if not always, ineffective as catalysts.

Had these authors but perceived that the hydrogen ions, or the available hydrochloric acid, diminish in amount when water is added to alcoholic hydrogen chloride, they could not have formed the main conclusion which is put forward in their communication. Nevertheless, they must be credited with the first attempt to explain the anticatalytic effect of water on esterification in alcohol as the result of complex ion hydrolysis.

EXPERIMENTAL.

The experiments described were all carried out at $25 \pm 0.02^\circ$, using flasks which had been steamed and then dried by a current of hot air.

Except where a definite statement is made to the contrary, the total volume of solution was made up with pure acetone to a total volume of 25 c.c. The catalyst used throughout was hydrogen chloride, and during the reactions had the concentration 0.0123 *N*. It was found undesirable to prepare the preliminary solutions of the catalyst by passing hydrogen chloride into acetone, as evidence was obtained that interaction occurred under these conditions; for this reason the solution of the catalyst was prepared by adding aqueous hydrogen chloride of known strength to dry acetone. This necessarily introduced a small quantity of water, but it was never found possible to work with less water than this, for the results were then discordant, owing, doubtless, to changes resulting in condensation of the acetone. Separate tests showed that the concentration of the hydrogen chloride

in the solution used did not change appreciably during the time occupied by an experiment.

The quality of the acetone was found to make an appreciable difference, and it proved necessary to use highly purified material. Concordant results were obtained from acetone, from the bisulphite compound obtained from Kahlbaum (*A*), or prepared and dried by us (*B*); good results attended the use of acetone (*C*) which had been prepared from commercial purified acetone by boiling it with about 3 per cent. of its weight of metallic calcium for some hours, and afterwards fractionating by means of an eight-section Young's dephlegmating column.

The following represent a comparative experiment with the three specimens: water (0.253), alcohol (0.873), and acetic acid (1.143) grams, and the same amount of catalyst being added to three 25 c.c. flasks, which were then filled with acetone at 25°, quantities of 2 c.c. being removed from each and titrated from time to time; x is the titre of the free acetic acid in c.c. of $N/10$ alkali.

<i>A.</i>	$t = 12$	65	107	135	285	$k = 0.0230$
	$x = 14.33$	13.30	12.49	12.00	10.20	
<i>B.</i>	$t = 24$	74	115	142	292	$k = 0.0233$
	$x = 14.33$	13.30	12.59	12.16	10.40	
<i>C.</i>	$t = 30$	80	121	148	302	$k = 0.0243$
	$x = 14.02$	12.86	12.11	11.71	9.80	

It is seen that the results are not completely concordant; for this and similar reasons the authors have not attempted to express all the velocity constants obtained in exactly the same measure. The constants for any one series, however, are strictly intercomparable, the individual experiments being made under identical conditions with only one variant. The different series in acetone are to be regarded as corresponding within a few per cents. only. It would be possible, if it served any really useful purpose, to pass from one series to another by fixing the point at which the conditions of the series in pairs correspond. The interest lies principally in the consideration of the influence of one variant at a time.

The alcohol and acetic acid, which were as nearly as possible anhydrous, were introduced in equimolecular quantities at 25° by carefully standardised pipettes, except when either was a variable in a series, when it was accurately weighed. In all other cases, too, the quantities of the reacting substance were weighed in the flasks, partly filled with acetone, then placed in the thermostat for some time, after which the catalyst in acetone was introduced, and the volume at once made up with pure acetone to 25 c.c., all the liquids having previously attained the temperature of the thermostat. At measured intervals of time, portions of 2 c.c. were withdrawn by means of a carefully

standardised pipette, and titrated with $N/10$ alkali, free from carbonate. In tabulating the titres in each case, that part due to the catalyst was first subtracted. It was ascertained that in the absence of alcohol no measurable diminution in the titre of acetic acid and hydrogen chloride occurred in wet acetone under the experimental condition.

A word must be added with reference to the mode of estimating the initial velocities of change. The titres plotted against time give curves which are not easily expressed by a simple mathematical relationship, so that other methods than the use of formulæ had to be adopted. In the case of the esterification numbers, the curves at first are nearly of the bimolecular form, so that by plotting the reciprocals of the titres against the time, a nearly straight line is obtained, from the slope of which the velocity at the beginning was easily calculated. In the experiments on hydrolysis no such simple relation could be found, and tangents were therefore drawn by hand to the smooth, plotted curves. This method was much less satisfactory than the former, but yields results which are not far from the correct values, and in series VIII the numbers given are identical, because the curves when graphed are indistinguishable in the initial stages.

The function k represents in all cases the diminution of the titre per minute, in c.c., at the commencement (when $t=0$). For comparison, the way in which k changes with the variable is added in each instance.

A. Esterification.

SERIES I.—*Constants: Water, 0.253; Acetic Acid, 1.143.*

Variant. Alcohol.							$k \times 10^{-2}$
(a)	0.873	$t = 1$	34	88	117	158	2.80
		$x = 13.85$	12.97	11.73	11.12	10.41	
(b)	1.098	$t = 2$	36	82	111	152	3.51
		$x = 13.84$	12.70	11.43	10.77	9.96	
(c)	1.713	$t = 2$	33	78	107	147	5.40
		$x = 13.74$	12.27	10.62	9.76	8.78	
(d)	2.043	$t = 3$	30	75	104	144	6.51
		$x = 13.86$	12.32	10.47	9.45	8.35	
(e)	2.728	$t = 2$	35	70	100	139	8.27
		$x = 13.74$	11.51	9.81	8.70	7.52	
(f)	4.566	$t = 2$	29	64	98	133	12.8
		$x = 13.64$	11.20	8.90	7.45	6.29	
		a.	b.	c.	d.	e.	f.
$\frac{k \times 10^{-2}}{\text{alcohol}}$		3.20	3.19	3.15	3.18	3.03	2.80

SERIES II.—*Effect of Alcohol on the Initial Rate of Esterification of Phenylacetic Acid by Alcohol in Ethereal Solution. Constants: Phenylacetic Acid, 2.00; Ether to 50 c.c.*

Alcohol.		$k \times 10^{-2}$.					
(a)	2 c.c.	$t = 4$ $x^* = 13.84$	14 13.16	26 12.22	34 11.70	44 11.10	56 10.48
(b)	4 c.c.	$t = 3$ $x^* = 13.89$	14 12.33	19 11.84	27 11.10	37 10.38	49 9.62
		$k \times 10^{-2}$ alcohol		a. 4.6	b. 4.6		

* These titres include the hydrogen chloride present as catalyst.

SERIES III.—*Effect of Methyl Alcohol on the Initial Rate of Esterification of Acetic Acid in Ethereal Solution. Constants: Acetic Acid, 3.72; Ether to 100 c.c.*

Methyl alcohol.		$k \times 10^{-2}$.				
(a)	10 c.c.	$t = 6$ $x = 30.35$	17 29.06	27 27.50	45 26.30	107 22.30
(b)	5 c.c.	$t = 9$ $x = 30.90$	20 30.30	34 29.30	47 28.60	109 26.15
		$k \times 10^{-2}$ methyl alcohol		a. 1.3	b. 1.1	

SERIES IV.—*Constants: Water, 0.253; Alcohol, 0.873.*

Acetic acid.		$k \times 10^{-2}$.				
(a)	2.738	$t = 32$ $x = 33.74$	86 31.50	115 30.41	197 27.88	271 27.03
(b)	2.223	$t = 29$ $x = 27.31$	58 26.15	111 24.35	194 22.59	267 21.43
(c)	1.840	$t = 26$ $x = 22.86$	55 22.01	110 20.24	192 18.52	266 17.42
(d)	1.473	$t = 21$ $x = 18.54$	52 17.62	105 16.32	190 14.80	264 13.79
(e)	1.124	$t = 17$ $x = 14.19$	51 13.36	104 12.41	188 11.11	263 10.30
(f)	0.721	$t = 15$ $x = 9.29$	49 8.80	100 8.06	184 7.18	261 6.54
		$k \times 10^{-2}$ acetic acid	a. 1.72	b. 2.03	c. 2.12	d. 2.16
					e. 2.21	f. 2.48

SERIES V.—*Constants: Alcohol, 0.873; Acetic Acid, 1.143.*

Water.							$k \times 10^{-2}$.
(a)	0.253	$t = 16$	49	94	143	240	2.60
		$x = 14.38$	13.67	12.70	11.82	10.57	
(b)	0.490	$t = 20$	49	94	144	240	2.00
		$x = 14.45$	13.89	13.21	12.51	11.48	
(c)	0.733	$t = 24$	50	95	144	241	1.38
		$x = 14.57$	14.17	13.67	13.12	12.28	
(d)	0.985	$t = 23$	51	97	146	243	0.87
		$x = 14.71$	14.50	14.10	13.73	13.09	
(e)	1.426	$t = 24$	51	98	244		0.57
		$x = 14.85$	14.63	14.47	13.84		
(f)	2.172	$t = 26$	54	100	246		0.34
		$x = 14.81$	14.77	14.59	14.25		
Water $\times k \times 10^{-2}$		a.	b.	c.	d.	e.	f.
		0.66	0.98	1.01	0.85	0.82	0.74

SERIES VI.—*Effect of Water on the Initial Rate of Esterification of Acetic Acid in Absolute Alcohol. Constants: Acetic Acid, 10 c.c.; Alcohol to 50 c.c.; HCl about N/100.*

Water						
(a)	None	$t = 1.5$	7	12	18	28
		$x = 13.62$	12.97	12.52	12.14	11.51
(b)	0.5 c.c.	$t = 1$	6	12	18	25
		$x = 13.74$	13.33	13.01	12.84	12.52
(c)	1.0 c.c.	$t = 1$	7	13	23	
		$x = 13.76$	13.53	13.32	13.05	

For estimations, 5 c.c. of the solution were added to aqueous sodium acetate, the whole being made up to 25 c.c. with water; portions of 2 c.c. were then titrated, and the mean results are those given.

The depressions here noticed as water is added or formed are greater than could be accounted for on the assumption that water acts by hydrating the acetic acid, unless it be supposed that one molecule of water would render several molecules of carboxylic acid inactive.

SERIES VII.—*Constants: Water, 0.253; Alcohol, 0.873; Acetic Acid 1.143.*

Ethyl acetate.						$k \times 10^{-2}$.
(a)	0.182	$t = 17$	79	134	278	2.53
		$x = 14.60$	13.20	12.26	10.56	
(b)	0.310	$t = 28$	80	136	279	2.40
		$x = 14.22$	13.19	12.26	10.58	
(c)	0.715	$t = 27$	79	135	277	2.29
		$x = 14.23$	13.24	12.40	10.81	
(d)	1.028	$t = 28$	80	136	279	2.13
		$x = 14.30$	13.30	12.48	10.97	

SERIES VII.—*Constants: Water, 0.253; Alcohol, 0.873; Acetic Acid, 1.143 (continued).*

Ethyl acetate.						$k \times 10^{-2}$.
(e)	1.425	$t = 29$	81	137	280	1.98
		$x = 14.32$	13.38	12.59	11.24	
(f)	2.004	$t = 29$	84	140	283	1.82
		$x = 14.40$	13.49	12.79	11.54	
(g)	2.158	$t = 39$	85	141	284	1.75
		$x = 13.96$	13.27	12.59	11.44	

B. Hydrolysis.

SERIES VIII.—*Constant: Ethyl Acetate, 1.666.*

Water.						$k \times 10^{-2}$.
(a)	0.253	$t = 42$	84	134	206	0.72
		$x = 0.27$	0.56	0.83	1.18	
(b)	0.536	$t = 44$	85	136	208	0.79
		$x = 0.35$	0.62	0.95	1.39	
(c)	0.788	$t = 45$	85	136	208	0.79
		$x = 0.33$	0.59	0.92	1.36	
(d)	1.010	$t = 47$	86	137	209	0.79
		$x = 0.35$	0.59	0.88	1.29	
(e)	1.305	$t = 48$	90	140	210	0.79
		$x = 0.34$	0.55	0.77	1.16	
(f)	1.723	$t = 50$	95	140	210	0.79
		$x = 0.29$	0.54	0.74	1.06	
(g)	2.536	$t = 52$	88	143	211	0.64
		$x = 0.26$	0.45	0.65	0.96	

SERIES IX.—*Constants: Ethyl Acetate, 1.666; Water, 0.341.*

Alcohol.						$k \times 10^{-2}$.
(a)	None	$t = 54$	132	220		0.79
		$x = 0.42$	0.96	1.46		
(b)	0.431	$t = 55$	142	231		0.74
		$x = 0.38$	0.90	1.33		
(c)	0.806	$t = 57$	146	233		0.64
		$x = 0.34$	0.83	1.21		
(d)	1.154	$t = 58$	147	234		0.64
		$x = 0.37$	0.83	1.15		
(e)	1.608	$t = 62$	150	236		0.58
		$x = 0.34$	0.74	1.04		
(f)	1.942	$t = 63$	152	237		0.58
		$x = 0.35$	0.73	0.98		
(g)	2.918	$t = 64$	153	238		0.52
		$x = 0.33$	0.63	0.86		

SERIES X.—*Constant : Water, 0.339.*

Ethyl acetate.						$k \times 10^{-2}$.	
(a)	1.066	$t = 53$	89	131	196		
		$x = 0.26$	0.41	0.49 (?)	0.82	0.58	
(b)	1.381	$t = 36$	69	133	177		
		$x = 0.21$	0.41	0.75	0.96	0.73	
(c)	1.833	$t = 49$	83	124	191		
		$x = 0.41$	0.63	0.90	1.37	0.99	
(d)	2.282	$t = 32$	65	135	169		
		$x = 0.31$	0.63	1.22 (?)	1.57	1.18	
(e)	2.806	$t = 44$	80	126	186		
		$x = 0.54$	0.97	1.46	2.00	1.46	
(f)	3.225	$t = 28$	62	140	165		
		$x = 0.41$	0.88	1.73 (?)	2.11	1.64	
(g)	3.576	$t = 41$	76	133	182		
		$x = 0.67$	1.22	1.85 (?)	2.62	1.82	
$\frac{k \times 10^{-2}}{\text{ethyl acetate}}$		<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>
		0.54	0.53	0.54	0.52	0.52	0.51
							0.49

Much of the expense incurred during this work was defrayed from a grant awarded by the Government Grant Committee of the Royal Society, for which the authors desire to express their indebtedness.

GOLDSMITHS' COLLEGE,
NEW CROSS, S.E.