31. *The Kinetics of Two Bimolecular Reactions in Solution and in the Vapour Phase.*

By E. A. Moelwyn-Hughes and C. N. Hinshelwood.

The rate of bimolecular reactions in the gaseous state can usually be calculated, at least as regards the order of magnitude, by multiplying the number of collisions between the appropriate kind of molecules by the factor $e^{E/RT}$, where E is the energy of activation found from the Arrhenius equation. This is roughly equivalent to saying that in such reactions activating collisions are not only a necessary but also a sufficient condition for reaction (Hinshelwood, "The Kinetics of Chemical Change," 2nd edtn., Oxford, 1929). An analogous method of calculation can be applied to some reactions in solution (Moelwyn-Hughes, *Chem. Reviews*, in the press), but in other examples (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35; Norrish and Smith, J., 1928, 129) the actual rates are many powers of ten smaller than the calculated values. This has usually been attributed to a very pronounced deactivating influence of the solvent, which has been supposed to deprive the activated molecules of their energy in a ternary collision.

The reactions upon the study of which these conclusions were based had been studied only in solution : but it seemed not unreasonable to assume that the corresponding gas reactions would be found to proceed at about the rate indicated by the theoretical formula, if they could be measured. It was desirable, however, that this should be tested experimentally. Now it has recently been found that two reactions, *viz.*, the decomposition of chlorine monoxide (Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, 1931, **131**, *A*, 177; Hinshelwood and Hughes, J., 1924, **125**, 1841) and the catalytic decomposition of ozone by chlorine (Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, 1931, **134**, *A*, 211; Bodenstein, Padelt, and Schumacher, *Z. physikal. Chem.*, 1929, *B*, **5**, 209), which, although not satisfying a simple bimolecular law, depend essentially on bimolecular processes, take place at very nearly the same rate in carbon tetrachloride solution as in the gaseous state. This suggested that the rate of a reaction in solution in carbon tetrachloride could be regarded as a standard rate, equivalent to the rate in the gaseous state, even when the latter was not accessible to direct measurement.

Accordingly, experiments were made to ascertain whether two representative bimolecular reactions, namely, the combination of triethylamine and ethyl iodide, and the interaction of ethyl alcohol and acetic anhydride, would proceed more closely in agreement with the theoretical formula when carbon tetrachloride was used as solvent, or whether the apparent deactivation effect would persist. Even in carbon tetrachloride, however, and also in hexane (which proved to be an even better " normal " solvent) each reaction was many powers of ten slower than the formula predicted. This suggested that the " deactivating " influence of the solvent was not real, but that the nature of the reactions themselves rather than the intervention of the medium determined their abnormal slowness. Experiments made to determine the rate of the two reactions in the gaseous state confirmed this supposition. A considerable proportion, possibly all, of the measured change occurred on the glass walls of the containing vessel, but even the sum of this catalytic reaction and any gas reaction which might be taking place did not exceed the reaction in solution by a factor of ten. Thus the gas reaction itself must be slower by many powers of ten than the hypothetical change to which the simple formula would apply.

The cause of this is discussed later (p. 239). As far as the question of solvent influence is concerned, however, the explanation is not relevant, since the anomaly is not due, as previously appeared possible, to a deactivating action of the solvent molecules.

The reaction between triethylamine and ethyl iodide is very much subject to solvent influence, but carbon tetrachloride is among the group of solvents, which includes hexane, in which the rate is least. This indicates that the action of other solvents is positively catalytic, the most active solvents in this respect being the alcohols. The rate of interaction of ethyl alcohol and acetic anhydride appears to vary much less from solvent to solvent. In gas reactions which are not chain reactions the influence of foreign gases is usually small or else positively catalytic. To this extent there is a rough parallel with solvent influence.

The Kinetics of the Combination of Triethylamine and Ethyl Iodide in Various Solvents: $(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4NI$.

Menschutkin (*Z. physikal. Chem.*, 1890, **6**, 41) examined the effect of some twenty solvents on the rate of this reaction at 100°, but neither he nor subsequent workers measured the velocity constant for the reaction in carbon tetrachloride solution, or the energy of activation in "inert" solvents.* The experiments described here were performed primarily for the purpose of determining the position of carbon tetrachloride in the catalytic order of solvents. First, however, the constant for benzene solution was measured in order that it might be compared with Menschutkin's value.

The benzene employed melted at 5·47°, and distilled within 0·1°; the triethylamine used was refluxed over potassium hydroxide, and distilled within 0·3°; ethyl iodide was equally pure, and was stored over a little mercury. 5 C.c. of equivalent solutions of the amine and the iodide were mixed and kept in the thermostat in sealed tubes for a measured time, chilled in ice, and poured into 50 c.c. of distilled water, the product being analysed in two ways : (1) by titrating the unchanged amine against 0·1*N*-nitric acid, (2) by estimating the quantity of tetraethylammonium iodide produced, 0·1*N*-silver

---

* The paper by Grimm, Ruf, and Wolff (*ibid.*, 1931, *B*, **13**, 301) appeared after the present investigation had been completed.

nitrate being used in Volhard's method. The two procedures gave concordant results.

In benzene solution at 100·2°, the concentration of each reactant being 0·1 g.-mol. per litre, the bimolecular velocity constant was $3{\cdot}53 \times 10^{-4}$ litre/g.-mol./sec. Menschutkin's value, expressed in the same units, is $3{\cdot}44 \times 10^{-4}$; Grimm, Ruf, and Wolff (*loc. cit.*) give $k = 3{\cdot}98 \times 10^{-4}$.

On dissolving the amine in carbon tetrachloride solution, a white precipitate immediately appeared: this has also been noticed by Norrish and Smith. It was identified as triethylammonium chloride, which must have been produced by traces of moisture in the carbon tetrachloride. Precautions were therefore taken to remove all traces of water. The solvent was twice distilled from phosphorus pentoxide, and the amine was filtered through solid potassium hydroxide into an evacuated vessel; but although the amount of salt produced was diminished considerably, there remained even in the driest solvent sufficient to render it turbid. For the first experiment, where no special precautions beyond the usual drying were taken, graphs showing percentage reaction against time did not pass through the origin, and the bimolecular constants showed a pronounced drift. In the second experiment the same sample of amine solution was used, but after further drying with solid potassium hydroxide, and on mixing the clear filtrate with the solution of ethyl iodide in carbon tetrachloride, a slight cloudiness developed, due to moisture in the iodide solution; the curve of titre against time, however, passed through the origin, and gave bimolecular "constants" rising from $6{\cdot}6 \times 10^{-5}$ to $9{\cdot}3 \times 10^{-5}$ between 25% and 75% completion. For the third experiment, with entirely fresh reactants, and solvent kept as free from contact with the atmosphere as possible, the values for $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ were 185, 570, and 1575 minutes respectively, corresponding to bimolecular constants of $6{\cdot}0 \times 10^{-5}$, $5{\cdot}8 \times 10^{-5}$, and $6{\cdot}3 \times 10^{-5}$ in the above units. Thus the course of reaction in the dry solvent is almost normal, the average value for the bimolecular constant being $6{\cdot}03 \times 10^{-5}$, which is lower by a factor of 5·8 than the value of the constant in benzene.

We are now able to see how carbon tetrachloride is placed in the list of solvents given by Menschutkin. The constants determined by him increased almost 800-fold in passing from hexane to benzyl alcohol. The relative velocity constants in some of the various solvents are: Hexane, heptane, carbon tetrachloride, benzene . . . . . ethyl alcohol, acetone, benzyl alcohol: 1, 1·3, 3·2, 18 . . . . . 211, 352, 769. Carbon tetrachloride thus takes its place in a small group of solvents in which the reaction velocity is lowest. This suggests that the smallest rates are the "normal" rates, and that those solvents in which the reaction is much faster exert a positively catalytic influence. The rate in hexane is even smaller than in carbon tetrachloride: thus hexane appears to approximate even more closely to the ideal inert solvent for this reaction. It was therefore chosen for the purpose of determining the energy of activation of this reaction in a non-catalytic environment.

The reaction in pure hexane is free from complications (see Table I). With different distillates, readily reproducible velocity coefficients were obtained, although occasionally exhibiting a slight tendency to drift. Solvent 2 differed from solvent 1 only in that it was fractionated from phosphorus pentoxide. A summary of the results is given in Table II, and refers to solutions which were 0·5*M* with respect to each reactant.

TABLE I.

Solvent: hexane. Temp.: 100·2°. $[C_2H_5I] = [(C_2H_5)_3N] = 0·5$ g.-mol./litre.

Time (mins.).	Change, %.	$k \times 10^6$ (litre/ g.-mol./sec.).
1584	20	5·23
2820	30	5·04
4500	40	4·91
6666	50	4·97
9360	60	5·31

Average value of $k = 5·09 \times 10^{-6}$

TABLE II.

$[(C_2H_5)_3N] = [C_2H_5I] = 0·5$ g.-mol./l. in different samples of *n*-hexane.

Solvent 1.		Solvent 2.	
Temp.	$k \times 10^6$.	Temp.	$k \times 10^6$.
100·6°	5·09	100·6°	5·31
140·6	35·2	141·1	35·8

The velocity of reaction at 100° and the energy of activation are in fair agreement with the results given by Grimm, Ruf, and Wolff, as

Solvent.	E (cals./g.-mol.).	$k_{100°} \times 10^6$.
Distilled hexane	14,800	4·92
Hexane distilled from P_2O_5	14,400	5·14
Hexane as used by G., R., and W.	16,000	5·00

shown above. Menschutkin's constant is about double this value, but in this solvent he followed the reaction only in its very earliest stages. Taking the best value of k at 100° as $5·02 \times 10^{-6}$, and E as 14,600, we find the equation $k = 2·01 \times 10^3 \times e^{-14,600/RT}$. The rate of chemical change is thus about 10^8 times smaller than would be calculated from the formula *number of molecules reacting* = $Ze^{-E/RT}$, for a gaseous reaction having this critical increment. The calculated value of the term multiplying the exponential is of the order 10^{11}. In the calculation the formula for collisions in a gas is used; but even allowing for any uncertainty so introduced there can be no doubt that a factor of 10^7 or 10^8 is approximately correct, and it becomes a matter of importance to inquire whether the discrepancy is due, as Christiansen and Norrish and Smith suggest, to deactivation by solvent molecules or to some other cause. With this end in view, the kinetics of the gaseous reaction were examined.

The Reaction between Triethylamine and Ethyl Iodide in the Gaseous Phase.

Small, thin-walled, sealed, glass capsules, containing known weights of triethylamine and ethyl iodide varying from 0·05 g. to 0·19 g., were introduced into clean, dry soda-glass tubes of about 20 c.c. capacity. After evacuation, these were sealed off, and the capsules were smashed by shaking the tubes, which were then immersed in the thermostat as before. After cooling, the capillary tips were broken under distilled water, and the dissolved vapours were analysed in the usual way. The bimolecular " constant " was calculated for each sample from a knowledge of the weights of the two reactants initially present, the volume of the reaction vessel, the time of immersion, and the titrations of standard nitric acid and silver nitrate. The results obtained in this way are given in Table III, the initial concentrations being expressed in g.-mols. per litre, and k being in litres/g.-mol./sec. The packed tubes, with the exception of that marked with an asterisk (which contained glass tubing), were partly filled with glass beads so that the ratio surface/volume was about 3 times that in the " empty " tubes. It will be seen that the results are roughly reproducible, that the reaction takes place at least partly on the surface of the glass, and also that the velocity " constant " increases regularly with increase in total concentration. The cause of the latter effect is probably as follows. As the concentration increases the adsorbed film tends to become saturated, and of the " liquid " type : the environment of the reacting molecules thus approximates more and more to a " polar " solvent, in which the reaction velocity is known to be high.

At a concentration of 0·01 g.-mol. per litre for each reactant in the gaseous phase at 140·6°, the velocity constant is $1 \cdot 9 \times 10^{-4}$, so that even in spite of catalysis by the wall of the vessel, the gaseous reaction is only 5·3 times as fast as the reaction in hexane, and is actually slower than the reaction in carbon tetrachloride.

It is therefore clear that, whatever the cause of the slowness of the reaction may be, it is not due to deactivation by solvent molecules, since the observed rates of reaction in the vapour state and in two inert solvents are all of the same order of magnitude. Now, the type of reaction which has been examined ($A + B \longrightarrow AB$) involves the formation of one molecule of resultant from two molecules of reactant, and is of the kind that often requires a triple collision before activation

TABLE III.

Gaseous reaction between triethylamine and ethyl iodide at 140·6°.

Initial conc. × 100.				Initial conc. × 100.			
Amine.	Iodide.	Total.	$k \times 10^4$.	Amine.	Iodide.	Total.	$k \times 10^4$.
2·74	1·70	4·4	3·68	5·27	6·27	11·5	15·0
2·77	1·96	4·7	3·48	6·57	5·31	11·9	11·6
3·02	2·67	5·7	5·58	5·17	8·81	14·0	13·6
3·98	1·98	6·0	5·95	5·56	13·6	19·2	16·4
2·11	4·37	6·5	13·1	7·91	13·6	21·5	18·6
2·83	4·72	7·6	5·44	9·56	12·6	22·2	13·2
4·70	2·90	7·6	6·46	9·50	14·9	24·4	26·0
6·24	4·79	11·0	0·40	11·2	15·4	26·6	26·7
			Packed tubes.				
1·61	5·35	7·0	14·7	10·9	10·8	21·7	37·8
5·90	7·45	13·4	33·7	13·0	18·1	31·1	56·5
9·31	5·98	15·3	18·6 *	15·0	16·7	31·7	47·4
9·25	12·3	21·5	63·1				

becomes effective. Lest the great divergence between the observed rate and those calculated from the simple theory should be due to a special collisional restriction of this kind, it seemed desirable to examine the kinetics of a bimolecular reaction of the type $A + B \longrightarrow C + D$.

The Kinetics of the Reaction between Acetic Anhydride and Ethyl Alcohol in Various Solvents : $(CH_3 \cdot CO)_2O + C_2H_5 \cdot OH \longrightarrow CH_3 \cdot CO_2C_2H_5 + CH_3 \cdot CO_2H$.

The rate of this reaction has also been measured by Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611), and recently by Soper and Williams (J., 1931, 2297), but no values for the heat of activation are available.

Acetic anhydride repeatedly distilled through a long fractionating column boiled within ± 0·5°; 0·0810 g. and 0·1109 g. gave on analysis by titration 0·0802 g. and 0·1109 g. respectively. The solvents were dried and purified as before. Following Menschutkin's method, an experimental sample was allowed to stand for 5—6 hours in 100 c.c. of distilled water, during which the anhydride was completely hydrolysed. The extent to which the reaction has progressed can thus be found by titrating with standard baryta, the initial titre being always double the "infinity" titre. The experimental method was the same as that described previously.

Satisfactory bimolecular velocity constants were obtained in various samples of hexane, all of which had been fractionated from phosphorus pentoxide. The detailed data for one run are given below, and the results are summarised in Table IV, where the in-

Solvent : hexane (2). Temp. : 48·9°. Equivalent concs. of 0·1575*M*.

Time (mins.)	46	110	198	324	524
Change, %	12·5	25·0	37·5	50·0	62·5
$k \times 10^4$	3·29	3·21	3·21	3·27	3·37

Average value of $k = 3{\cdot}27 \times 10^{-4}$ litre/g.-mol./sec.

fluence of both temperature and concentration is recorded. A decrease in concentration causes k to increase, but does not alter the heat of activation, the average value of which is 12,400 calories. The average value of k in the more dilute solutions at 100·2° is $4{\cdot}61 \times 10^{-3}$ (compare Menschutkin's figure of $1{\cdot}26 \times 10^{-3}$ for the rate of reaction between acetic anhydride and *iso*propyl alcohol in *n*-hexane), hence the kinetics of the process is represented by $k = 9{\cdot}16 \times 10^4 \times e^{-12{,}400/RT}$. The "calculated" collision term for this reaction also is of the order of 10^{11}, so that the disparity is almost as great as for the previous reaction.

TABLE IV.

Acetic anhydride and ethyl alcohol in n-*hexane.*

		Initial conc. (g.-mol./l.).		$k \times 10^4$.		
Solvent.	Temp.	Anhydride.	Alcohol.	Obs.	Calc. by Arrhenius equation.	E.
1	48·8°	0·158	0·158	2·92	3·06	12,200
1	60·3	0·158	0·158	6·00	5·89	
1	100·2	0·158	0·158	41·8	42·2	
2	48·9	0·157	0·158	3·27	—	12,700
2	100·2	0·157	0·158	50·3	—	
1	48·9	0·158	0·500	1·62	1·98	12,400
1	60·3	0·158	0·500	3·84	3·60	
1	70·0	0·158	0·500	(10·2)	6·14	
1	100·2	0·158	0·500	26·6	26·6	

The rate of reaction in carbon tetrachloride was also investigated in different dry distillates of the solvent; good bimolecular constants were found, as shown below. The dilution effect has also been

Solvent: carbon tetrachloride. Temp.: 70·6°. Equivalent concs. of 0·1M.

Time (mins.)	47	87	148	255	436
Change, %	25·0	37·5	50·0	62·5	75·0
$k \times 10^3$	1·18	1·15	1·15	1·09	1·15

Average value of $k = 1{\cdot}14 \times 10^{-3}$ litre/g.-mol./sec.

TABLE V.

Acetic anhydride and ethyl alcohol in carbon tetrachloride.

			$k \times 10^4$.		
Solvent.	Temp.	Initial conc. of each reactant.	Obs.	Calc. by Arrhenius equation.	E.
1	49·9°	0·101	2·60	—	13,700
1	100·5	0·101	47·1	—	
2	60·2	0·100	6·28	6·30	13,200
2	70·6	0·100	11·4	11·6	
2	80·9	0·100	20·2	20·3	
2	100·1	0·100	46·6	54·3	
3	100·2	0·201	37·3	—	—
3	100·2	0·104	45·0	—	
3	100·2	0·052	48·0	—	
3	100·2	0·027	51·7	—	

examined somewhat more carefully, as shown in Table V. At 100·2°, the velocity coefficient reaches a limiting value of $5{\cdot}30 \times 10^{-3}$ at a dilution of about 50 litres per g.-mol. Combining this with the average value of the heat of activation, we find the kinetics of the reaction in dilute solution to be given by the relation $k = 4{\cdot}14 \times 10^5 \times e^{-13{,}400/RT}$.

The Reaction between Acetic Anhydride and Ethyl Alcohol in the Gaseous Phase.

Adopting the same procedure as before, the kinetics of the gaseous reactions in glass vessels, with and without packing, were investigated, but by using larger reaction tubes (capacity, 16—230 c.c.) it was possible to work with smaller concentrations. Within the range of concentration examined, the velocity " constant " is not changed to any marked extent (see Table VI), and has an average value of about $1{\cdot}5 \times 10^{-2}$, as compared with about $5{\cdot}0 \times 10^{-2}$ in the packed tubes, for which the ratio surface/volume is about 3 times as great. The reaction rate in carbon tetrachloride at this temperature is $1{\cdot}79 \times 10^{-3}$, so the "gaseous" reaction, in spite of catalysis by the walls of the vessel, is only about 8 times as fast as that in solution.

The esterification reaction, therefore, is closely analogous to the formation of tetraethylammonium iodide, and the divergence between the observed rates and the hypothetical ones cannot be due to the difference in the kinetic type of the two reactions.

TABLE VI.

Gaseous reaction between acetic anhydride and ethyl alcohol at 79·2°.

Initial concs. × 10³.				Initial concs. × 10³.			
Anhydride.	Alcohol.	Total.	$k \times 10^2$.	Anhydride.	Alcohol.	Total.	$k \times 10^2$.
2·32	2·68	5·0	0·21	8·57	42·74	51·3	2·53
5·28	1·85	7·1	1·46	27·19	30·18	57·4	1·56
5·64	5·13	10·8	0·85	39·08	24·77	63·9	1·18
6·10	7·24	13·3	1·24	31·42	38·94	70·4	1·40
4·42	11·61	16·0	1·79	43·43	43·80	87·2	2·52
20·51	16·30	36·8	2·06				
Packed tubes.							
3·57	7·55	11·1	0·86	9·89	14·29	24·3	5·83
6·17	6·49	12·7	1·67	13·13	15·60	28·7	4·57
8·30	14·28	22·6	10·05	18·11	26·01	44·1	7·01

Discussion.

To the question whether the action of the solvent is to be regarded as a deactivating one, the answer yielded by the present investigation is a clear-cut negative.

That the rate of reaction in the two examples examined is very many times smaller than the rate at which the energy of activation (distributed even in two square terms only) could be communicated is a characteristic of the reactions themselves, for which the solvent is not responsible. To attempt to solve the problem why the efficiency of activating collisions should be so small is not part of the real object of this paper, but it may be of interest briefly to speculate about the matter.

In the first place, such behaviour, although relatively uncommon among gas reactions, is not unknown. Only a small proportion of the collisions between sodium atoms and cyanogen molecules leads to reaction although the energy of activation is zero (von Hartel and Polanyi, *Z. physikal. Chem.*, 1930, *B*, **11**, 97). The isomerisation in the gas phase of dimethylmaleic ester takes place about 10^3 as slowly as the molecules could be activated (Kistiakowsky and Nelles, *ibid.*, 1931, Bodenstein Festband, 369).

The small efficiency of the collisions can be explained by assuming that the two molecules react only when in a specially suitable relative orientation, or by assuming that they must be in a suitable internal phase. The former alternative would hardly be likely to account for a discrepancy of many powers of ten. With regard to the second, it seems to have been demonstrated that the phase factor plays a decisive part in determining the rate of unimolecular reactions, which usually involve rather complex molecules. Those involved in the two reactions now under discussion are indeed rather more complex than those taking part in the bimolecular reactions to which the simple theory applies. Thus the phase factor is likely to be more important, but on the other hand, most reactions where there is demonstrably a phase factor have the energy of activation distributed in a number of square terms, so the actual rate of reaction, even allowing for the phase factor, is not less but considerably greater than that given by the simple exponential formula. In the unimolecular reactions the phase factor can be reasonably connected with the necessity for internal redistribution of the activation energy. In the present examples, however, this interpretation can hardly be applied in the same way.

If we were to suppose that the two reactions involved a preliminary stage such as ionisation, *e.g.*,

$$(1)\quad C_2H_5I \rightleftharpoons C_2H_5^+ + I^-;\quad (C_2H_5)_3N + C_2H_5^+ \longrightarrow (C_2H_5)_4N^+;$$
$$(C_2H_5)_4N^+ + I^- \longrightarrow (C_2H_5)_4NI.$$

$$(2)\quad C_2H_5{\cdot}OH \rightleftharpoons C_2H_5{\cdot}O^- + H^+;\quad C_2H_5{\cdot}O^- + (CH_3{\cdot}CO)_2O \longrightarrow$$
$$CH_3{\cdot}CO_2C_2H_5 + CH_3{\cdot}COO^-;\quad CH_3{\cdot}COO^- + H^+ \longrightarrow CH_3{\cdot}CO_2H.$$

then the large proportion of deactivations could be accounted for by assuming the primary process to be reversible. Part of the observed energy of activation would, for example, be that required to ionise the ethyl iodide : in a collision with an activated amine molecule the reaction might be completed. But most of the ions would be lost by recombination before this happened. If the probability of recombination were great enough, the reaction velocity would become extremely slow. In the absence of information about the conditions governing the minute ionisation of substances such as ethyl iodide in inert solvents, of the part played by the solvation of the ions, and of whether minute ionisation could occur in the gas or in the film adsorbed on the glass surface, it is not useful to develop this hypothesis further than to point out that it is of the right form to account for a large deactivation without attributing this to the solvent.

Summary.

The kinetics of the formation of tetraethylammonium iodide and of the esterification of acetic anhydride by ethyl alcohol have been investigated in carbon tetrachloride solution, in hexane solution, and in the gaseous phase. The rate at which the two reactions proceed in the two solvents is about 10^8 times slower than the rate of hypothetical gas reactions with the observed energies of activation. That the discrepancy is not due to deactivation by solvent molecules is demonstrated by the results obtained experimentally for the gaseous reactions, which, in spite of catalysis by the surface of the vessel, proceed at rates which are of the same (low) order of magnitude as those in solution.

The rate of the esterification reaction is less influenced by a change in the solvent than is the formation of tetraethylammonium iodide. The latter reaction is slowest in carbon tetrachloride and in hydrocarbons, and fastest in alcohols : by comparing the rates in various solvents with the rate of the gas reaction, it is concluded that carbon tetrachloride and the hydrocarbons are to be regarded as relatively inert solvents, and alcohols as exerting a positive catalytic influence. It is not correct to regard the "fast" solvents as normal and the "slow" ones as deactivating.

We are indebted to Imperial Chemical Industries, Ltd., for a grant by the aid of which apparatus and materials for this investigation were purchased. One of the authors also wishes to express his indebtedness to the Department of Scientific and Industrial Research for the award of a Senior Research Scholarship.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

[*Received, December* 12*th,* 1931.]