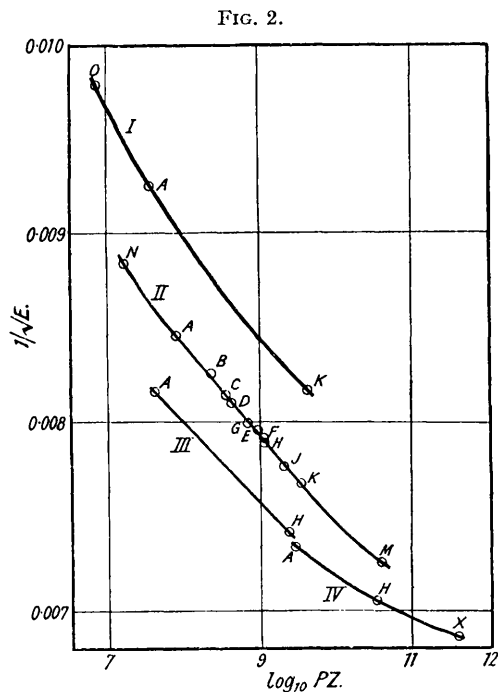
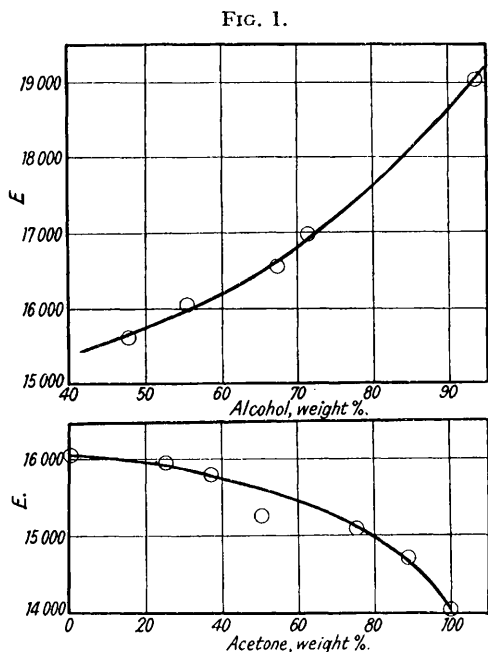


120. The Functional Relation between the Constants of the Arrhenius Equation.

By R. A. FAIRCLOUGH and C. N. HINSHELWOOD.

(1) Introduction.

IN the reaction-velocity equation $k = PZe^{-E/RT}$ the constants PZ and E , instead of being independent, have sometimes been found to exhibit a correlation, PZ increasing with E through a series of reactions (see Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933, p. 167). We have observed and studied some well-defined examples of this effect, where the changes in E and P caused by alteration of the medium show a close functional relation.



I, Alkaline hydrolysis of methyl acetate. II, Alkaline hydrolysis of ethyl benzoate. III, Formation of methylpyridinium iodide. IV, Hydrolysis of ethyl bromide.

In the first section of this paper we shall consider whether these relations can be more than accidental, and then, after a discussion of the experimental results, we shall consider an explanation, based upon general statistical principles (Section 4), which leads us to some general considerations about the function of the medium in chemical reactions, and the nature of the probability factor P .

The correlation of P and E would lose its significance if the data examined related only to reactions selected for study because they proceed at conveniently measurable rates in a given temperature interval. Even if any value of P could occur with any value of E , only those reactions would have been chosen for experiment in which the values of P and E so compensated one another as to give what was considered the convenient rate.

Since our plan has been to study the changes in the velocity of a given reaction caused by systematic variations in the medium, without reference to the convenience of the measurements, there is no question of such automatic selection of data.

There is also doubt about the reality of the correlations when data of unspecified

accuracy are used: $\log PZ$ is calculated by adding $\log k$ to E/RT ; E is less accurately measurable than $\log k$. If E has been overestimated then the value of $\log PZ$ will be correspondingly too large. In the experiments to be described, the possibility of plotting the values of E , as a function, not merely of PZ , but also of the composition of the medium, gives an independent control of their reliability (Fig. 1).

The starting point of the experiments was the observation that the values of E and PZ for the alkaline hydrolysis of ethyl benzoate were both considerably increased when the medium was changed from aqueous acetone to aqueous alcohol (Newling and Hinshelwood, J., 1936, 1357; Ingold and Nathan, J., 1936, 222).

Measurements were then made with a ternary system, the water concentration being kept constant, and the ratio of acetone to alcohol varied. The values of E changed regularly with composition (Fig. 1), and $\log PZ$ increased almost linearly with increasing E . The correlation may also be expressed as a decrease in $\log PZ$ with increase in $1/\sqrt{E}$ (Fig. 2), a form indicated by the theoretical treatment of Section 4.

Experiments were then made with alcohol-water mixtures of various proportions and a dioxan-water mixture. The functional relation of E and PZ persisted throughout.

Three other reactions, the alkaline hydrolysis of methyl acetate and of ethyl bromide, and the formation of methylpyridinium iodide, investigated in a similar range of media, showed analogous relationships (Fig. 2).

(2) Experimental Details and Results.

The solvents used were mixtures of water, acetone, alcohol, and dioxan in various proportions. Acetone was purified by fractionation with a five-foot Dufton column, alcohol by refluxing over freshly burnt lime for five hours and fractionating, and dioxan by repeated crystallisation from the melt. Ordinary distilled water was used, but was freed from carbon dioxide by boiling. Alcohol-water mixtures were prepared, and the percentage of alcohol by weight determined from density measurements. The alcohol-acetone-water mixtures A-F were prepared according to the following scheme: 400 g. of water were made up to one litre with a previously prepared mixture containing a given proportion by weight of acetone in alcohol. Thus the normality of the water was constant throughout this series. The dioxan-water mixture, N, also contained 400 g. of water in one litre of solvent. Some relevant properties of these solvents are given in Table I, ϵ^{20° being the dielectric constant at 20° , and the Jowett correction being $-RT^2 \cdot d \log \eta/dT$ (see p. 541).

TABLE I.

Solvent, and composition. 400 G. of H ₂ O made up to 1 l. by acetone-alcohol containing $w\%$ of acetone by weight.				Solvent, and composition. Alcohol-water mixtures: weight % of alcohol = w , mole-fraction = x .				Jowett correc- tion.	ϵ^{20° .	Jowett correc- tion.
w .	$d_4^{25^\circ}$.	ϵ^{20° .	Jowett correc- tion.	w .	x .	ϵ^{20° .				
A	100.0	0.903	46	—	G	47.9	0.269	51	6520	
B	88.95	0.902	—	4560	H	55.7	0.334	46	6220	
C	75.04	0.901	—	4765	J	67.1	0.444	40	5650	
D	50.50	0.901	—	5030	K	71.3	0.493	38	5400	
E	36.97	0.900	—	5430	M	93.5	0.850	28	3850	
F	25.04	0.898	—	5530	N	Dioxan-water: 400 g. H ₂ O/l.		—	25	—
H	0.0	—	46	6220	O	Water		—	81	—

All the reacting substances were purified by fractionation, and boiled over a narrow range at the correct temperatures. The pyridine had been dried over potassium hydroxide.

All activation energies were determined from measurements at four temperatures. The usual electrically controlled thermostats were used for temperatures other than 0° , where a Dewar vessel containing crushed ice and water was used. Thermometers were compared with N.P.L. standards. Glassware was standardised. All velocity constants were corrected for change of concentration due to thermal expansion of solvent.

Alkaline hydrolysis of ethyl benzoate. This was followed by the usual alkalimetric titration method, cresol-red being used as indicator. With solutions containing acetone, unusual care had to be taken to exclude carbon dioxide.

The concentrations of the mixed reactants were $N/20$. Satisfactory bimolecular constants were found, and the Arrhenius equation was followed.

The dioxan-water solution caused much difficulty: the bimolecular constants fell as the reaction proceeded, as though the solvent were undergoing a progressive change, which, as far as we could tell, was not due to absorption of carbon dioxide. To circumvent the difficulty, initial rates of reaction were taken.

The results are collected in Table II, and the value of $\log PZ$ is plotted against $1/\sqrt{E}$ in Fig. 2.

TABLE II.

*Hydrolysis of ethyl benzoate.**

Solvent A.		Solvent B.		Solvent C.		Solvent D.		Solvent E.		Solvent F.	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.
0.11°	4.05	-0.02°	3.19	0.45°	2.68	0.46°	2.17	0.0°	1.79	0.03°	1.46
15.98	17.2	15.95	15.19	15.98	12.84	15.95	10.78	16.00	9.49	15.97	8.06
25.00	38.6	25.00	32.9	25.00	27.0	25.00	24.02	25.00	21.4	25.00	18.59
39.75	116.5	39.8	101.2	39.70	88.3	39.75	77.6	39.75	73.3	39.8	63.7
Solvent G.		Solvent H.		Solvent J.		Solvent K.		Solvent M.		Solvent N.	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.
0.0	1.78	0.46	1.29	0.35	0.932	0.0	0.731	0.0	0.183	0.0	7.8
16.00	9.20	15.98	6.54	15.98	5.12	16.00	4.14	16.0	1.17	16.0	29.3
25.00	21.05	25.00	15.3	25.00	12.03	25.00	10.02	25.00	3.56	25.0	64.0
39.75	68.4	39.68	55.5	39.7	45.6	39.97	39.6	39.75	15.57	39.7	162

* All constants are in g.-mol./l.-sec. units.

The viscosity data for alcohol-water mixtures given in Table I were taken from the International Critical Tables. Those for the alcohol-acetone-water mixtures were specially determined by Messrs. Vicary and Rowse.

Alkaline hydrolysis of methyl acetate. The method was essentially the same as for ethyl benzoate, but, since the reaction is much faster, the plan described by Newling and Hinshelwood (*loc. cit.*) for dealing with rapid reactions was followed. In solutions containing ethyl alcohol, a gradual direct conversion of the methyl ester into the ethyl ester seems to occur and results in a fall in the rate of hydrolysis. To obtain the true hydrolysis rate in such solutions, the initial rates of reaction were taken from curves. The results are collected in Table III.

Alkaline hydrolysis of ethyl bromide. The results are given in Table IV. In Fig. 2 an earlier result for an alcoholic solution is included (Grant and Hinshelwood, J., 1933, 258).

Formation of methylpyridinium iodide. The method of estimating ionisable halogen could not be used, since the salt is soluble in the solvents used and cannot be separated from the

TABLE III.

Hydrolysis of methyl acetate.

Solvent A.		Solvent K.		Solvent H ₂ O.		Solvent A.		Solvent K.		Solvent H ₂ O.	
Temp.	$k \times 10^2$.	Temp.	$k \times 10^2$.	Temp.	$k \times 10^2$.	Temp.	$k \times 10^2$.	Temp.	$k \times 10^2$.	Temp.	$k \times 10^2$.
0.0°	1.41	0.0°	0.376	0.0°	2.98	25.0°	8.90	25.0°	3.31	25.0°	15.24
16.0	5.21	16.0	1.52	16.0	9.53	39.7	22.2	39.7	12.0	39.7	32.6

TABLE IV.

Hydrolysis of ethyl bromide.

Solvent A.		Solvent H.	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.
25.0°	0.568	25.0°	0.471
39.9	2.66	39.9	2.69
60.1	16.60	60.1	20.2
80.4	80.1	80.4	105.0

TABLE V.

Formation of methylpyridinium iodide.

Solvent A.		Solvent H.	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.
25.0°	1.76	25.00°	0.53
39.9	6.2	39.85	2.11
60.1	27.8	60.0	11.5
80.4	90.8	80.4	59.5

unchanged methyl iodide, which reacts with silver nitrate. Accordingly, the pyridine was determined by titration with acid according to the procedure of Fawcett and Gibson (J., 1934, 396), the indicator consisting of a mixture of equal volumes of aqueous 0.1% methyl-orange and 0.02% methylene-blue. The results are collected in Table V.

(3) *Discussion of Experimental Results.*

Before attempting any general interpretation of these results, we must consider whether the values of E derived from the Arrhenius equation represent the true activation energies,

It should be emphasised at the outset that no inclusion in P of any term variable exponentially with $1/T$ is significant. Such a temperature variation always indicates a process requiring a critical energy. A term of this kind would be measured in determining the temperature coefficient, as part of the exponential containing the activation energy, and since the energy represented by the extra term is necessary for the reaction, it is in reality simply a part of the activation energy, whatever formal designation it may receive. (See, *e.g.*, Hückel, *Z. physikal. Chem.*, 1936, A, **178**, 113, who includes certain energies of orientation in a P -term.)

It has been suggested that observed activation energies should in certain cases be corrected for variation of the viscosity of the medium with temperature (Jowett, *Phil. Mag.*, 1929, **8**, 1059). It is doubtful whether such corrections would be relevant here, but even if applied they would not explain the results, since they would affect the various activation energies in an irregular way, and give rise to a less orderly rather than a simpler picture. For example, in the range of mixtures alcohol-acetone-water the corrections would accentuate the variation of E with composition, while in the alcohol-water series they would diminish it (see Table I). Thus application of the correction in the former case would accentuate the increase of $\log PZ$ through the series.

If the total activation energy contains any considerable contribution from electrostatic potential energies, then the value of P depends upon the dielectric constant and its temperature variation, a matter which becomes very important in reactions between multiply charged ions (Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, A, **157**, 667). The variation in dielectric constant over a large part of the range of solvents we have used is small: and in any case calculation from the formulæ used by Moelwyn-Hughes shows that the changes in P arising even from much greater variations would, for reactions of the type, with which we are concerned, involving nothing more than ion-dipole or dipole-dipole forces, be of a lower order of magnitude than those observed.

The values of E and $\log_{10} PZ$ are collected in Table VI. In Fig. 2 $\log PZ$ is plotted against $1/\sqrt{E}$. This method of plotting is adopted because it is indicated by the theoretical considerations of Section (4). The essential regularity is that $\log PZ$ is proportional to

TABLE VI.

Solvent.	E .	$\log_{10} PZ$.	Solvent.	E .	$\log_{10} PZ$.
Reaction: Ph·CO ₂ Et + NaOH.			Reaction: CH ₃ ·CO ₂ Me + NaOH.		
A	14,010	7·875	A	11,680	7·545
B	14,700	8·335	K	15,000	9·60
C	15,080	8·53	O	10,450	6·87
D	15,250	8·60	Reaction: EtBr + OH ⁻ .		
E	15,800	8·96	A	18,550	9·40
F	15,970	9·02	H	20,150	10·50
G	15,640	8·82	Reaction: C ₅ H ₅ N + CH ₃ I.		
H	16,070	9·03	A	14,700	7·29
J	16,570	9·28	H	18,200	9·05
K	16,980	9·51			
M	19,030	10·55			
N	12,830	7·195			

some simple function of E . If this function were chosen differently, the correlation would be little altered. For example, if we plot E directly, we still obtain an approximately straight line, provided that the logarithmic form of PZ is retained.

Since the correlation of PZ and E is shown by two examples of ester hydrolysis, in which the water molecules probably participate in the reaction, by the hydrolysis of ethyl bromide which is probably a direct attack of the hydroxyl ion on the halide, and by an example of quaternary ammonium salt formation the mechanism of which is different again, explanation in rather general terms not involving the specific properties of individual systems seems to be called for.

(4) Theoretical Considerations.

The following considerations seem to show that a correlation between PZ and E similar to that found is not merely explicable but should even be rather common, as, indeed, scattered indications in the literature had suggested.

We base our theory upon the following picture of a chemical reaction between two molecules. They must come together possessing the activation energy and constitute a preactivated collision complex (Hinshelwood, J., 1935, 1111). The life of this is terminated either by the separation of the constituents, or by deactivation in a collision, or by chemical transformation. The condition for chemical transformation is that existing bonds must be broken and new ones formed. Generally, a bond will only be broken when the atoms it joins are near the extremes of their amplitudes; while new bonds will only be formed when the atoms which they are to unite are at appropriate distances and possess suitable relative velocities. These conditions will in general be fulfilled only in a narrow range of the complicated pattern of motions executed by the system. On the average, therefore, many cycles of the separate vibrations may have to be traversed before the right region of the complete Lissajou figure for the system is reached.

Let the average time which elapses between the formation of the preactivated collision complex and the reversal of this process be θ . In the majority of cases the attainment of the right phase for reaction demands a longer time than this, which we call t , and no reaction occurs. The chance that the preactivated complex survives for this time is, according to well-established statistical principles,

$$W = e^{-t/\theta} \quad \dots \quad (1)$$

t is the time required for the completion of a certain fraction of the complete period of a complex internal motion, which in general will involve a considerable number, n , of cycles of vibration of one of the reacting bonds. If the frequency of the latter is ν , $t = n/\nu$. Thus the probability of reaction is proportional to $e^{-n/\nu\theta}$.

If the structure of the molecules remains constant but the bond strengths are changed by substitution, or by the influence of the medium, ν will vary, and E , the activation energy, will vary also. On the whole, if bond strengths increase, both ν and E will increase together. If we write $\nu = f(E)$, then the rate of reaction becomes

$$k = A \cdot e^{-n/\theta f(E)} \cdot e^{-E/RT}$$

whence $\log k = \log A - n/\theta f(E) - E/RT = \log PZ - E/RT$

whence $\log PZ = \text{constant} - n/\theta f(E) \quad \dots \quad (2)$

When changes in E are small compared with $f(E)$, this approximates to

$$\Delta \log PZ = B \cdot \Delta E, \text{ where } B \text{ is a constant.}$$

The exact relation between ν and E is difficult to determine, and from our point of view is a secondary matter.

To give the expression a definite form, however, we will set the activation energy proportional to the force constant of the link, *i.e.*, to the square of the frequency.

If ν_0 and E_0 are the values for some standard reaction of a series, then for another member $\nu = \nu_0 \sqrt{E/E_0}$. The chance of reaction will now be $e^{-n\sqrt{E_0 E}/\theta\nu_0}$ and the rate of reaction will be

$$A \cdot e^{-E/RT} \cdot e^{-n\sqrt{E_0 E}/\theta\nu_0}$$

We then have

$$\log k = \log A - n\sqrt{E_0 E}/\theta\nu_0 - E/RT = \log PZ - E/RT$$

whence

$$\log PZ = \text{const.} - n\sqrt{E_0 E}/\theta\nu_0 \quad \dots \quad (3)$$

For small changes this reduces as before to

$$\Delta \log PZ = B' \cdot \Delta E$$

The constants n , E_0 , and ν_0 depend primarily on the nature of the reaction, whereas θ will depend principally on the medium.

Since the function of E appears in an exponential, it is not easy to determine empirically what the best function is, the exponential itself being responsible for the characteristic form of the variation. The essential part of the present theory is that we expect the

exponential relation of equation (1). Some alternative theories which we explored did not lead to an exponential relation but predicted that PZ itself rather than its logarithm should increase comparably with E .

(5) *Comparison with Experiment.*

Only when t is appreciably greater than θ in equation (1) should the correlation between PZ and E be observable. When t is much less than θ , equation (1) approximates to $W = 1$, and PZ is no longer dependent upon E . Thus two main types of behaviour are to be expected. The factors making for a large value of θ , and therefore for a constant P , are the formation of a fairly stable collision complex, infrequency of collisions which might deactivate the complex, and poor energy transfer in such potentially deactivating collisions. On the other hand, simplicity of the reacting system tends to diminish t , which has the same result as increasing θ . In this connexion it must be remembered that a reaction in an active solvent, involving as it must do much interference by the solvent molecules, may require the fulfilment of a much more complicated set of conditions than its chemical equation would suggest.

Among reactions which have been investigated, three types of behaviour have been distinguished. In the first, the change of E is accompanied by the sort of change in PZ to be expected from the exponential relation (1).

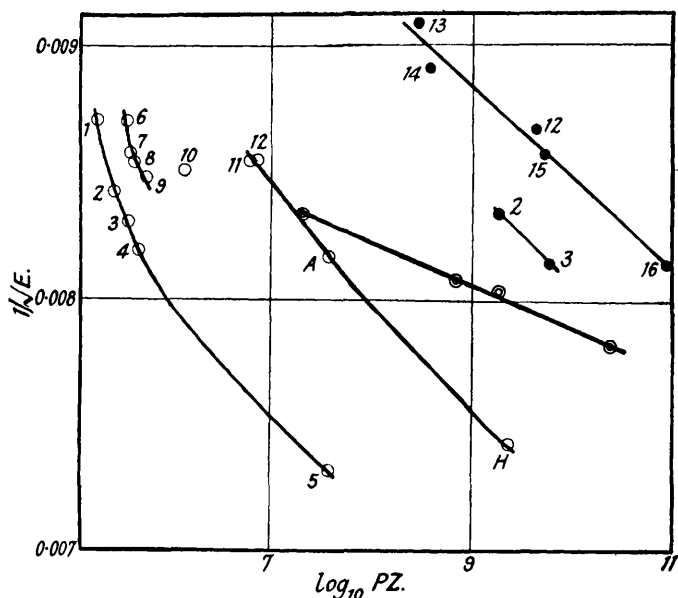
Examples of the following kinds have from time to time been noted: Heterogeneous reactions (see Storch, *J. Amer. Chem. Soc.*, 1935, 57, 1395); unimolecular reactions in different solvents, e.g., decomposition of acetonedicarboxylic acid (Wiig, *J. Physical Chem.*, 1928, 32, 961), and the rearrangement of triazoles (Dimroth, *Annalen*, 1910, 373, 367); unimolecular reactions of series of related compounds such as substituted malonic acids (Bernoulli and Wege, *Helv. Chim. Acta*, 1919, 2, 511); bimolecular reactions such as the formation of allylpyridinium bromide in different solvents (Hawkins, J., 1922, 121, 1170), esterification of acids in different alcohols (Hinshelwood and Legard, J., 1935, 587), formation of sulphonium salts in different solvents (Syrkin and Gladishev, *Acta Physicochim. U.R.S.S.*, 1935, 2, 291); hydrolysis of different arylsulphuric acids in water (Burkhardt, Horrex, and Jenkins, J., 1936, 1649). In the examples quoted, the correlation is fairly well marked (Fig. 4): in others it is detectable though less definite.

A conspicuous part is played by change in medium, as in the examples given in the present paper. In this connexion the results of Gibson, Fawcett, and Perrin (*Proc. Roy. Soc.*, 1935, A, 150, 223) are of much interest. These authors found that in the formation of quaternary ammonium salts large increases in the hydrostatic pressure on the medium could produce increases in the activation energy accompanied by increases in P so great as to increase the reaction rate by a large factor (Fig. 3). From one point of view, increased hydrostatic pressure might be thought of as increasing the number of deactivating impacts and decreasing θ , but the predominating effect at really high pressures will be a different one: the system has become so tightly packed that the components of the collision complex may be actually held together by surrounding solvent molecules in such a way as to increase θ very considerably. For the reverse reaction, which is a unimolecular decomposition, this effect is of no advantage, and pressure produces no increase in rate, but a slight retardation.

In certain well-defined cases (Williams and Hinshelwood, J., 1934, 1079; Ingold and Nathan, J., 1936, 222; Bradfield, *Chem. and Ind.*, 1932, 51, 254) the correlation of P and E does not appear at all, the change in velocity being due almost entirely to change in the activation energy. This would have been most easily understood if P for these cases were near unity, θ being large or t small. But for reactions such as the benzoylation of substituted amines, P is of the order 10^{-7} . This shows that the exponential (1) is by no means the only factor contained in P : there must be correct orientation of the approaching molecules; they must fit together to form the collision complex; they must reach the right internal phase; and finally, a stabilising collision may be necessary in some cases to prevent the reversion of the product. Our attention is drawn to the last of these factors by examples where P varies without corresponding change in E . The study of the form-

ation of methylpyridinium iodide in a series of solvents (Pickles and Hinshelwood, J., 1936, 1353) led to the following results: in a series of substituted benzene derivatives E remains nearly constant, P increasing with the polarity of the solvent. For a series of inert solvents E increases and there is an accompanying increase in P . We have now found that for a series of solvents of about the same polarity as the most polar of those used by Pickles and Hinshelwood there is the usual correlation of P and E . The more complete picture would therefore seem to be as follows: E and $\log PZ$ increase together in a simple manner for solvents of about the same polarity, but the line expressing this correlation shifts towards higher values of P the greater the polarity of the solvent. This view is supported by certain data scattered in the literature (Fig. 3). With regard to the interpretation of this effect, we do not propose to do more at the moment than suggest that it might be due to the necessity for a suitable solvent collision to stabilise the polar

FIG. 3.



Solvents.—1, Chloroform. 2, Benzene. 3, Toluene. 4, Mesitylene. 5, Carbon tetrachloride. 6, Anisole. 7, Dioxan. 8, Bromobenzene. 9, Chlorobenzene. 10, Iodobenzene. 11, Benzonitrile. 12, Nitrobenzene. 13, Acetophenone. 14, *p*-Nitrotoluene. 15, Acetone. 16, Ethyl alcohol.

Open circles: Formation of methylpyridinium iodide (Pickles and Hinshelwood, *loc. cit.*).

Shaded circles: Formation of allylpyridinium iodide (Hawkins, J., 1922, 121, 1170).

Double circles: Formation of ethylpyridinium iodide under high pressures (Gibson, Fawcett, and Perrin, *loc. cit.*).

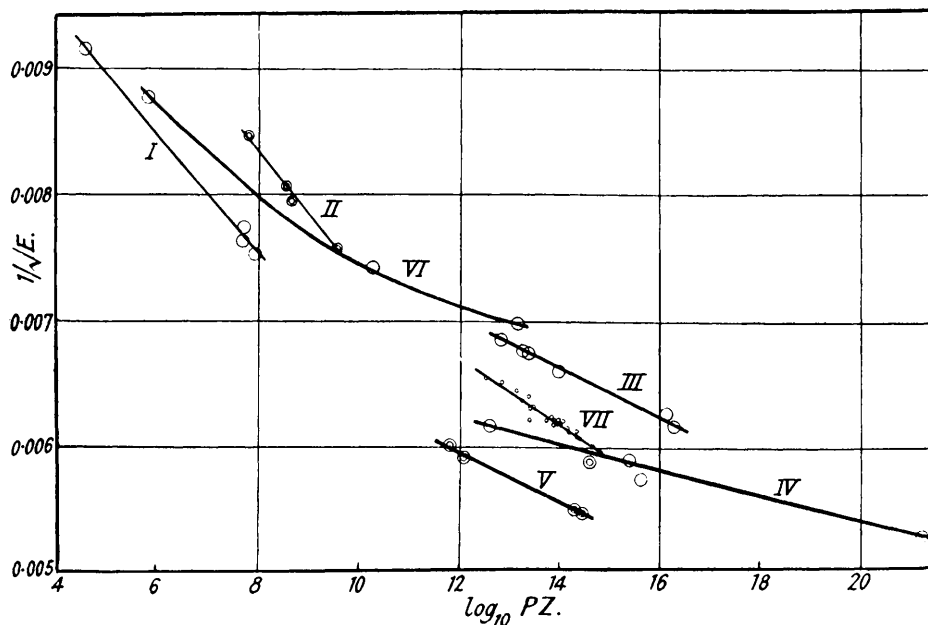
product in the manner indicated in a previous paper (Hinshelwood, *Trans. Faraday Soc.*, 1936, 32, 970). If change in hydrostatic pressure enhances this effect continuously, as well as exerting the influence discussed above, the very considerable rate of increase of P with E found by Gibson, Fawcett, and Perrin becomes more easily understandable.

(6) Collision Rates; Limiting Values of P .

It will be observed that in Figs. 2, 3, and 4 the lines might be extrapolated to obtain the values of PZ when $1/\sqrt{E} = 0$. This gives the value which PZ would possess if the time required for the right phase to be reached were negligible, and gives us Z multiplied by the probability that the other conditions are favourable. Since the curves are not quite linear, the extrapolation is very rough, but the values of PZ so obtained would always be several powers of 10 greater than that corresponding to the gas collision number with $P = 1$, which is of the order 10^{11} . This would suggest one of two things: either that

Z is considerably greater than the value for the gas, or that $P = 1$ loses any significance as a limiting value. That this limit has no absolute significance is already shown by several facts: there is a complete range of P values filling the region between 10^{-8} and 1 (Hinshelwood and Winkler, J., 1936, 371); there are several examples of bimolecular changes with P greater than 1, e.g., the hydrolysis of the arylsulphuric acids (Burkhardt, Horrex, and Jenkins, *loc. cit.*); the line in Fig. 2 for the hydrolysis of ethyl bromide shows no signs of bending over at $P = 1$ ($PZ = 10^{11} - 10^{12}$). The only obvious way of explaining values of P greater than unity is by the introduction of formulæ in which internal degrees of freedom contribute to the activation rate, as in unimolecular reactions. Now, the extrapolated values correspond to a state of affairs where the collision complex is allowed all

FIG. 4.



I. Formation of methyldiethylsulphonium bromide (Syrkin and Gladishev, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 291).

II. Influence of pressure on esterification of acetic anhydride (Williams, Perrin, and Gibson, *Proc. Roy. Soc.*, 1936, *A*, **154**, 684).

III. Decomposition of acetonedicarboxylic acid (Wiig, *J. Physical Chem.*, 1928, **32**, 961).

IV. Isomerisation of methyl 5-hydroxy-1-benzyltriazole-4-carboxylate (Dimroth, *Annalen*, 1910, **373**, 367).

V. Decarboxylation of substituted malonic acids (Bernoulli and Wege, *Helv. Chim. Acta*, 1919, **2**, 511).

VI. Esterification of methyl alcohol by different acids (Hinshelwood and Legard, J., 1935, 587).

VII. Acid hydrolysis of phenylsulphuric acids (Burkhardt, Horrex, and Jenkins, J., 1936, 1649).

V, VI, and VII refer to series in which the nature of the reactants is modified, the others to changes in the medium.

the time it requires to undergo re-arrangement: this differs little from the state of affairs in a unimolecular reaction. The rather rare experimental cases where P is actually greater than unity may involve collision complexes with abnormally long lives, and thus represent a true transition between bimolecular and unimolecular reactions.

Fig. 4 shows that a dependence of P upon E is found for unimolecular reactions also, and here P rises to very high values. In the light of all these considerations the principal factors differentiating one case from another are simply the relative time intervals between activation, deactivation or resolution of the activated system, and the completion of the chemical transformation.

If we do not wish to admit that P can reach values considerably greater than unity in

exceptional cases, then we must suppose that the collision number Z^* itself reaches values considerably greater than the gas-kinetic values. The theory of collision rates in solution is difficult, but the calculations of Leontovitch (*Z. Physik*, 1928, **50**, 58), as well as the experiments of Rabinowitch and Wood (*Trans. Faraday Soc.*, 1936, **32**, 1381) with models, seem to show that the order of magnitude, at least, should be the same as in the gas phase. Both approaches, however, deal with somewhat idealised systems, and it is possible that with real solvents considerable divergences might occur. If, for example, owing to swarm formation, parts of the solvent became impenetrable to solute molecules, the collision rate in the space remaining would be increased. But it is hardly possible to say much that is definite about this at present.

SUMMARY.

For four bimolecular reactions in a range of solvents containing alcohol, acetone, water, and dioxan, a correlation is found between the activation energy and the temperature-independent factor of the Arrhenius equation.

These results, taken in conjunction with data from the literature, lead us to the conclusion that the correlation is unlikely to be accidental, and an explanation is proposed based upon general statistical principles and upon the assumption of a time interval between activation and reaction.

Factors determining the probability of reaction are discussed.

[Received, February 23rd, 1937.]
