GENERAL DISCUSSION.*

Dr. R. P. Bell (*Oxford*) in introducing his paper said : The so-called "tunnel effect" has been treated in Wigner's paper and mentioned by other speakers, and I should like to add a few remarks on this subject. In the first place, it is misleading to speak of this effect as though it were an additional or optional mechanism by which the reaction can take place. The usual methods of treating reaction velocity apply the laws of classical mechanics to the motion of the nuclei in the direction corresponding to reaction, while this motion is in reality governed by quantal laws.   It is the error involved in applying classical mechanics (which may be very large for light nuclei) which is loosely referred to as the " tunnel effect."

Two methods have been used for attempting to derive the correct quantal expressions for the motion of the nuclei.   The first of these [1] is general, and can in principle be applied to the potential surfaces in several dimensions which occur in actual reactions.   Unfortunately it is only possible to treat the case when the motion is nearly classical, the final result being expressed in powers of $\left(\dfrac{h\nu^*}{kT}\right)$, where $i\nu^*$ is the imaginary frequency characterising the curvature of the potential surface in the direction of motion.   Wigner [1] shows that if $\dfrac{h\nu^*}{kT} \ll 1$ the true velocity is obtained by multiplying the classical expression by $\left\{1 + \dfrac{1}{24}\left(\dfrac{h\nu^*}{kT}\right)^2\right\}$, which is the factor generally used in calculations by the transition state method. However, when this is applied to the reaction $H + H_2$, it is found [2] that the value of $\dfrac{h\nu^*}{kT}$ is about 5, and the departure from classical behaviour is thus far too large for this method to be of any value.   It is likely to fail

---

* On the four preceding papers.

[1] E. Wigner, *Z. physik. Chem.*, B, 1932, **19**, 203.
[2] L. Farkas and E. Wigner, *Trans. Faraday Soc.*, 1936, **32**, 708.

still more badly for proton transfer reactions, in which the transition from non-ionic to ionic binding will give rise to barriers with much larger [3] values of ν^*.

If the correction to the classical value is not small, there are great difficulties in applying a strict treatment to an energy surface in several dimensions. We can, however, obtain an idea of the correct order of magnitude by treating the corresponding one-dimensional barrier, and the results of such calculations have been already dealt with in Wigner's paper and in my own. The estimates which I have made here and elsewhere [4] of departures from classical behaviour are likely to be conservative when applied to proton transfers, since they are based upon much flatter barriers than those which probably occur in ionogenic reactions. (The type of barrier treated in equations 5-7 of Wigner's paper is probably more suitable.) In spite of our ignorance as to the exact dimensions or shape of the energy surfaces involved, it seems difficult to avoid the conclusion that the " tunnel effect " is of considerable importance for proton transfer reactions at ordinary temperatures.

Dr. E. A. Moelwyn-Hughes (*Cambridge*) said : I wish to comment on the following statement made by Wynne-Jones : " A procedure which is particularly unjustified is to correct the observed activation energy for the supposed energy of some intermediate step ; this is contrary to all thermodynamic requirements and is equivalent to replacing a free energy with a total energy." If this conclusion is correct, physical chemistry becomes bereft of all knowledge of thermal reactions wherein free atoms take part in the rate-determining steps [5] for, in all these, pre-equilibria are postulated, and the observed energy of activation is drastically corrected for the intermediate steps. The Arrhenius energy of activation for the *ortho-para*-hydrogen reaction is about 60,000 calories ; the correction for the " supposed intermediate step " is about 50,000 ; and the true energy of activation for the measurable reaction is about 10,000 calories.[6]

Prof. V. K. La Mer (*Columbia, N.Y.*) said : Bell has emphasised very clearly in his equations (5) and (6) the sort of error which an indiscriminate application of the Arrhenius equation is likely to lead. Since quasi-thermodynamic analysis points inescapably to the conclusion that abnormal values [7] of the frequency factor A are to be explained by a temperature dependence of E and consequently of A in $k = A e^{-E/RT}$ in a range of temperature below that at present available, it is highly important that kinetic investigations at low temperatures be undertaken for experimental confirmation.

When the solvent effect arises from salt addition to water and the concentration is low enough for the Debye-Hückel limiting law to be obeyed, the dependence of A, E and $\log k$ assumes a remarkably simple form namely :

$$\log k = \log k_0 + 1 \cdot 0 \, Z_A Z_B$$
$$A = A_0 + 1 \cdot 5 \, Z_A Z_B$$
$$E/RT = E_0/RT + 0 \cdot 5 \, Z_A Z_B.$$

The entropy of activation operates to increase the rate of reaction three times as rapidly for variations in ionic strength as the increase in energy of activations depresses it. The classical view that catalytic effects are exercised primarily through the energy of activation is quite erroneous.

[3] *Cf.* Polanyi, this discussion.

[4] *Proc. Roy. Soc.*, 1935, **148**, 421 ; 1936, 154, 414.

[5] For a list, see Annual Reports on the Progress of Chemistry, 1936.

[6] For details, Farkas, *Light and Heavy Hydrogen*, Cambridge University Press, 1935.

[7] La Mer, *J. Chem. Physics*, 1933, **1**, 289.

[8] La Mer and Kamner, *J.A.C.S.*, 1935, **57,** 2662.

When a high valence ion like La^{+++} ion is added in minute amounts (0·001 M) to catalyse the reaction :

$$BrCH_2COO^- + S_2O_3^- \rightarrow S_2O_3CH_2COO^- + Br^-$$
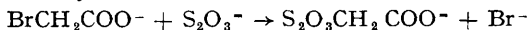
the ten-fold increase in rate arises primarily from a marked increase in the entropy of activation which overwhelms the not inconsiderable increase in energy of activation from 16,000 to 18,000 cals.

Dr. J. E. Wynfield Rhodes (*Blackburn*) said : The low concentration of the *enol form* in acetone may be due to the high tendency of the enol form to self-association. The partial vapour pressures of acetone in a wide variety of solvents have been measured and support the hypothesis that pure acetone is self-associated and that the complexes are partly broken up by active solvents. In the case of certain alcohol-acetone mixtures there are indications of acetal formation, but the reaction is slow and probably far from complete.

Prof. Ph. Gross (*Istanbul*) said : I agree with Wynne-Jones that at the moment one cannot draw any definite conclusions regarding cane sugar inversion, but I think that this is mainly caused by the fact that we used sulphuric acid at a rather high concentration as a catalytic acid and that our experiments carried out on a micro scale are not as exact as they could be. I do not think, however, that any serious difficulty arises from the question of the true activation energies. We have already stated in our paper [9] that in the case of sugar inversion the introduction of a linear term, which is the most plausible in this case, does not decrease the deviations to a satisfactory extent. But I must admit that the correction term is not necessarily a simple linear one and that small deviations between the purely thermodynamic and the kinetic Q-curve are to be expected. And as a matter of fact there seems to me to be a small difference of this kind in the summarising curve given by Orr and Butler.[10]

If one tries to recalculate the Q-curve from the data of Reitz a fairly good agreement occurs, in contradiction to the statement of Reitz. This seems to me to mean that the consecutive reaction has no very great influence, even in this case, where a square correction term would be more plausible. Therefore, I think, definite conclusions could be obtained also in the case of cane sugar inversion, if new and more exact measurements were made.

But in my opinion another point is of greater importance. As there is now no doubt that at least in some cases pre-equilibrium is established, one should try to find the concentration of the pre-equilibrium complex. So long as the reacting complex concentration can be regarded as infinitely small in comparison with the solvated hydrogen ion concentration, there is, as already stated by Wynne-Jones, no difference in the apparent order of reaction, whether pre-equilibrium exists or not. If, however, the complex concentration cannot be neglected, which will be the case in a medium which is a weaker base than water, a dependence on the initial concentration of the substrate will occur. Experiments, for example on the decomposition of diazo acetic ester in some of the alcohols, should give at least the order of magnitude of the equilibrium concentration of this complex. It would then be possible to calculate the concentration in water from the known[11] equilibrium : (Alcohol H$^\bullet$) + H$_2$O = H$_3$O$^\bullet$ + Alcohol, *i.e.*, from the distribution coefficient of proton between alcohol and water molecules. Admittedly this also is not quite correct, because the influence of the medium cannot be taken in account, but it would give a first approximation. Fräulein Krauss, who has worked with me in Wien will, I hope, be able to make such measurements there in the near future.

Finally I would like to point out the difference between La Mer's

[9] *Trans. Faraday Soc.*, 1936, **32,** 877, 879 and 833.

[10] *Journ. Chem. Soc.*, 1937, 330.

[11] Gross, Jamöck and Patat, *Sitzber. Akad. Wiss. Wien.*, II *b*, 1933, **142,** 327, or *Monatsh. Chemie*, 1933, **63,** 117.

treatment, and our own, of the relation between H- and D-activity in mixtures of light and heavy water. La Mer simply assumed that the sum of the D- and H-activities is constant, if the total acidity is kept constant. Whereas the comparison with the analysis of the whole question which we undertook independently at about the same time, shows that this assumption is mistaken. Our treatment is summarised very clearly by Wynne-Jones, to whom I owe the following very illustrative manner of demonstrating this result. If one plots the D- and H-activities and the sum of both at constant acidity against the water composition, the diagram is very similar to that of the different vapour pressures (partial pressures and total pressure) of *a non-ideal* solution. The sum of the H- and D-activities is by definition the same at both ends and equal to the analytic acidity, but there is a maximum (of about 15 per cent.) somewhere between (at a mole fraction of about 0·6).

Dr. R. P. Bell (*Oxford*) said : In the paper by Wynne-Jones there are some comments on the probable accuracy of the results obtained by Baughan and Bell for the catalysed decomposition of nitramide. The " probable error " of about 200 calories in the activation energies specified by the authors was calculated by standard statistical methods, and is defined in such a way that the chance of an error greater than $\pm$ 200 calories is equal to the chance of an error less than $\pm$ 200 calories. Wynne-Jones states that " with the accuracy normally obtainable, activation energies are not known to better than about 500 calories." The chance of an error of more than $\pm$ 500 calories in our activation energies is about 10 per cent., and it is obviously a matter of taste as to whether the value of E is said to be " known " to any higher degree of accuracy. The values of E found for different catalysts vary by more than 5000 calories, which is clearly a significant variation. It should, however, be emphasised that the estimates of probable error in E depend upon the assumption that the simple Arrhenius equation is obeyed. Our experimental data exhibit no significant deviations from this equation, and in the absence of such experimental deviations there is no alternative method of analysing the data.

As regards the accuracy with which the Brønsted equation is obeyed at different temperatures, the root mean square of the deviations between the observed and calculated velocity constants is about 5 per cent., *i.e.*, about the same as the probable experimental error. The dissociation constants of five of the acids used (acetic, benzoic, formic, salicylic and *o*-nitrobenzoic) are almost certainly known with this degree of accuracy, and there is thus good support for the validity of the equation within these limits. The question of the temperature variation of the exponent α is a more difficult one, and I agree with Wynne-Jones that the existence of such a variation is not definitely established by the data on the nitramide decomposition.

It is interesting to note that the data of Wynne-Jones, Smith and La Mer for the water-catalysed mutarotation of glucose indicate deviations from the Arrhenius equation. It seems doubtful, however, whether this example lends support to the general grounds for anticipating such deviations. In a reaction involving water molecules the anomalous temperature variation in the properties of water may introduce factors which are not present in reactions between solute molecules. The change in E is in any case in the wrong direction to be accounted for by quantum-mechanical effects, as suggested by Smith.[12]

Dr. J. A. V. Butler (*Edinburgh*) (*communicated*) said : The greater rate of hydrolytic reactions in D_2O than in H_2O is usually ascribed to the greater stability of the D^+ than the H^+ complex. It is rather difficult to understand why this should be so, since the bond between H^+ or D^+ and the substrate is very weak, and it would appear that the relative stability

[12] G. F. Smith and M. C. Smith, *J. Chem. Soc.*, 1937, 1413.

of D and H compounds increases with the bond strength. Can Bonhoeffer suggest any reason for this ?

Gross has referred to the deviation of the rates of the cane sugar hydrolysis in H_2O—D_2O mixtures from the thermodynamic curve. Nelson has made similar measurements with methyl formate and acetate, and has obtained curves very close to that of cane sugar. We think, however, that the divergence from the thermodynamic relation is not greater than the experimental error. Wynne-Jones refers to Reitz's experiments on the bromination of acetone as upsetting the validity of the method of distinguishing general and specific hydrogen ion catalysis by comparing the rates in D_2O and H_2O. Reitz's experiments show that when the catalyst is the hydrogen ion the rate is determined by the equilibrium concentration of the complex ; while the experiments of Dawson and others show that weak acids like acetic acid have specific effects, and therefore the rate is not then determined by equilibrium conditions. This situation is easily understood if, in the equation $k = k_1 k_3/(k_2 + k_3)$ $k_2 > k_3$ for hydrogen ion catalysis and $k_2 < k_3$ for catalysis by weak acids. There is nothing inherently improbable in this. In every case which has been investigated the thermodynamic relation holds when the reaction goes faster in heavy water than in light water, so that it appears that k_D/k_H can still be used as an index of the nature of the reaction, if it is recognised that the same reaction may show either type of behaviour with different catalysts.

Dr. E. A. Guggenheim (*London*) said : I am in agreement with every word of Mr. Bell's paper—except one. In the first line of the second paragraph of the section on " The Brønsted relation " the word " now " suggests that there has been significant recent progress. In my opinion the qualitative significance of the " Brønsted relation " was clearly realised in the original paper of Brønsted and Pedersen in 1924. Subsequent discussion has added little or nothing of value. As a quantitative relation it is still empirical and the claims to " derive " it involve assumptions, explicit or implicit, virtually equivalent to the relation itself. This point is elaborated in the contribution by Weiss and myself.

Prof. V. K. La Mer (*Columbia, N.Y.*) said : The investigations on the solvent decomposition of Nitramid have appeared in September, 1937, issue of *The Transactions* (p. 1260). Hochberg has since proved that deutero nitramid decomposes at precisely the same rate in H_2O as does proto-nitramid. Hence both protons are exchanged, and the lowered rate in D_2O is to be attributed to a decreased basicity of the solvent acceptor as well as to a slower rate of acidic dissociation of the substitute. Liotta finds that

		$k_{25°}/k_{15°}$.	
		H_2O (B. and B.).	D_2O (L. and L.).
A$\bar{c}$	.	3·05	3·50
B$\bar{z}$	.	2·9	3·17
Sal$\bar{I}$	.	3·18	3·36
H_2O	.	3·3	2·9

$$\frac{k_{A\bar{c}(H_2O)}}{k_{A\bar{c}(D_2O)}} = 2 \cdot 0 \; ; \; \frac{k_{B\bar{z}(H_2O)}}{k_{B\bar{z}(D_2O)}} = 1 \cdot 9 \; ; \; \frac{k_{Sal(H_2O)}}{k_{Sal(D_2O)}} = 1 \cdot 8$$

Where A$\bar{c}$ = acetate, B$\bar{z}$ = benzoate and Sal$\bar{I}$ = salicylate ions.

Here we have a pure basic catalysis. As the basic strength decreases the relative rate decreases. A comparison of Baughan and Bell's (B. and B.) temperature coefficients with Liotta's data in D_2O show an 8 to 10 per cent. increase in energy of activation for anion catalysis whereas the reverse is true of the more complex solvent catalysis.

Dr. R. P. Bell (*Oxford*) said : La Mer has presented to the meeting some interesting data on the effect of substituting deuterium for hydrogen in the nitramide decomposition. It is particularly interesting to note that in the anion-catalysed reaction the change in reaction velocity is much smaller than would be anticipated from the change in measured activation energy : *i.e.*, there is simultaneously a considerable change in

the entropy of activation or P-factor. It is very difficult to see how such a change could be produced merely by the substitution of one isotope for another, and I should like to suggest tentatively that non-classical proton (or deuteron) transfer may be important in this case : this would affect P in the observed direction.

Prof. V. K. La Mer (*Columbia, N.Y.*) called attention to the marked sag curves of log k when plotted against the deuterium content of the solvent. In the case of mutarotation of glucose, this sag arises from the unequal distribution of deuterium in the substrate and disappears when log k is plotted against the mol fraction of heavy glucose.[13]

In the case of hydrogen-ion-catalysed reactions the non-linear character is even more pronounced and arises from the exceedingly large exchange constant [14] for the reaction $2D^+ + H_2O = D_2O + 2H^+$; $K = 15.3$.

In this connection we wish to acknowledge the simultaneous and independent contributions of Gross and collaborators.[15] At the present time the experimental data are hardly of sufficient accuracy to warrant analysis by Gross' more elaborate and theoretically more correct treatment. Our treatment must be considered as a first approximation justifiable on practical grounds in the present state of knowledge.

Mr. W. F. K. Wynne-Jones (*Reading*) : I agree largely with Bell's remarks and, as he suggests, some of our differences may be a matter of taste. The object of my comments on the paper by Baughan and Bell was to point out that the existing data do not allow of an unequivocal answer to important questions regarding acid and base-catalysed reactions, and that it is important to use self-consistent methods of testing relationships between kinetic and equilibrium data. The marked curvature of the log $k - 1/T$ plot for the mutarotation of glucose may of course be peculiar to a reaction involving water, but it is noteworthy that the curvature was not observed until recent investigations made with high accuracy (of the order of $\frac{1}{2}$ per cent.) over a wide temperature range. Incidentally one may recall that the classical work of Bodenstein showed that for the decomposition of HI there is definite curvature of the plot of log k against $1/T$; evidently deviations from the Arrhenius equation are nearly as old as the equation itself.

Moelwyn-Hughes has misunderstood my criticism of the procedure adopted by Sherman and himself. The introduction of intermediate equilibria is formally quite correct, provided the *entire* equilibrium constant is used as in the example quoted by Moelwyn-Hughes : the procedure which I criticised is the introduction of the heat of reaction alone. La Mer has given an interesting example in the inactivation of pepsin of the necessity for careful examination of the kinetics of reactions, but it is not correct on any theory to regard the unimolecular change of an uncharged molecule as equivalent to the unimolecular change of an ion produced from this molecule. It is only when mechanisms are kinetically indistinguishable that intermediate equilibria may be disregarded.

In reply to Polanyi's question if the Brønsted equation can hold at different temperatures when the variations in the dissociation constants of acids are not determined by changes in the heats of dissociation, there seems to be no doubt that the Brønsted equation holds, at least over small temperature ranges, while the data of Harned show clearly that there is no relation between acid strengths and heats of ionisation. One would therefore expect parallel variations of the energies and entropies of activation and dissociation and, in certain cases, the rather inadequate data support this.

Prof. K. F. Bonhoeffer (*Leipzig*), in reply, said : With regard to Butler's question, I hardly think that there is a relation between the ratio

[13] Hamill and La Mer, *J. Chem. Physics*, 1936, **4,** 395.
[14] *Ibid.*, 294 ; Korman and La Mer, *J. Am. Chem. Soc.*, 1936, **58,** 1396 ; La Mer, *Chem. Rev.*, 1936, **19,** 363.
[15] *Trans. Faraday Soc.*, 1936, **6,** 879 and 883.

of dissociation constants of an acid in ordinary and heavy water K_{D_2O}/K_{H_2O} and the absolute strength of that acid. The theory of Halpern which postulated an increase of K_{D_2O}/K_{H_2O} with increasing acid strength does not in fact, hold, as is shown by the newer measurements of Schwarzenbach. The main reason, why the ratio K_{D_2O}/K_{H_2O} is mostly much less than one, is the lower basicity of D_2O compared with H_2O, an effect which is independent of acid strength.

In reply to Guggenheim I think that the proton affinity of the substrate in comparison with the proton affinity of the medium gives us an idea whether the addition or the removal of a proton to or from the substrate is the first step to be considered. In cases with substrates of high proton affinity one has naturally to assume the proton addition as being the first step.