



Outlines of a theory of proton transfer^{☆,☆☆}

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Abstract

Translation of a seminal 1935 paper in the field of reaction rate theory relating the heats of activation to binding energies for a wide range of homogeneous and heterogeneous reactions. Paper republished to mark the 100th birthday of the late professor Juro Horiuti.

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1. Introduction

Our method conforms to the general theory of ionogenic reactions of Ogg and Polanyi [1]. This theory has been applied so far to the reactions of alkali metal vapours with organic halogen compounds [1], as well as to the reactions of alkali metal vapours with the halogens [2] and with the hydrogen halides [3], and further to the reactions of Na₂ molecules with halogen atoms [2]. In addition, applications are available to a group of ion reactions in solutions, more precisely to

the electrolytic dissociation and hydrolysis of organic halogen compounds and to the substitution of organic halogen compounds with halide ions [4]. Further studies concerning the substitution of organic compounds with negative ions have also been performed and will be published in the near future.

It has been established as a characteristic of all these ionogenic reactions that in a series of homologous reactions the heats of activation decrease with increasing heat of reaction. This relationship—which can be understood as an extension of the principle of Berthelot—has proven to be fruitful, particularly in its application to reactions of organic halogen compounds with alkali metal vapours. It leads to the result that the reactivity of a halogen atom in different organic compounds is primarily conditioned by the bond energy of the halogen atom. The heat of activation of the reaction is recognised as a measure of this bond energy. Similar regularities become apparent in the substitution of organic halogen compounds with negative ions.

In what follows, this relationship between the heats of reactions and the reaction rates will be very important. A graphical representation of this relationship will be given here which will prove to be profitable

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^{☆☆} The views to be presented here represent the results of our theory in a simplified form. In view of the large volume of material, more time will be required to finish the detailed development, which apart from an inclusion of all tangible factors should offer more detailed arguments for our ideas, hence it may appear justified to communicate here first of all the results in an abbreviated form.

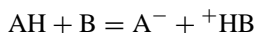
also in its applications to the examples of ionogenic reactions mentioned above.

It is obvious that this relationship can be generalised even further. Its application to reactions which formally can be treated just like the ionogenic reactions is most obvious.¹ One readily sees that such a treatment requires the values of the space coordinates of the transition state to be between the values assumed by the same space coordinates in the initial and final states. We believe that this can probably be regarded as well as a sufficient condition for the antiparallel behaviours of activation energies and heats of reaction.

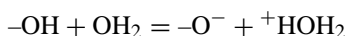
2. Proton transfers: an overview

2.1. Electrolytic dissociation and closely related phenomena

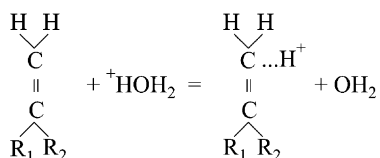
Here we only look at the electrolytic dissociation of acids. The concept of an acid AH is applied in the interpretation of Lowry [6] to all proton donors. That is, we are here looking at the transition of



where the base B (the proton acceptor) is a solvent molecule, for instance



A closely related process is the attack of “anionoid” molecules by H^+ ions, as for instance in the addition of hydrogen halides (HX) to double bonds where primarily the reaction

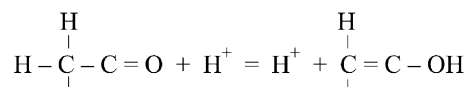


must be assumed to proceed. In organic chemistry, the importance of such processes is wide, though up to now it still can be rigorously defined (the most recent review of this topic can be found in Ingold [7], who designates “anionoid” molecules as “nucleophiles”).

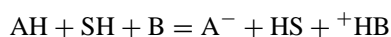
¹ See the treatment of formaldehyde decomposition by Evans and Polanyi [5].

2.2. Prototropy

This is the name used by T.M. Lowry for the migration of a hydrogen atom that is fundamental to a large group of tautomeric rearrangements. In the rearrangement of a ketone to its enol form, for instance, prototropy consists in the addition to an H atom to the $-\text{CO}$ group and simultaneous separation of an H atom, as shown by the reaction equation

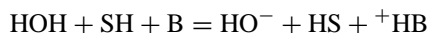


Lowry [6] and Brönsted [8] have pointed out that the added proton is withdrawn from a complex and that the separated proton is added to another complex. The former complex is called an acid (AH), the latter a base (B). Further introducing the designations of SH and HS for the two tautomeric forms of the substrate (S), one finds as a general scheme of prototropy the equation

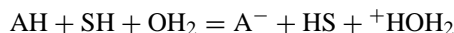


In an amphoteric medium such as water, the catalysis of the rearrangement by bases or acids can be represented by equations in which water alternates in its roles as a base or acid

Base catalysis



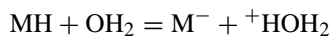
Acid catalysis



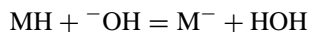
2.3. Electrode processes

Suitable metal surfaces immersed into aqueous or alcoholic solutions transform molecular hydrogen into H^+ ions. This spontaneous ionisation, postulated by Nernst in his theory of the setting up of electrode potentials, could be tracked experimentally with the aid of heavy hydrogen [9]. Following up on a suggestion of Frumkin [10], who relied on his own investigations [11] of the adsorption properties of hydrogen electrodes, we can draw an analogy between this process and electrolytic dissociation. Here the metal M of the

electrode functions as the acid residue, according to the scheme



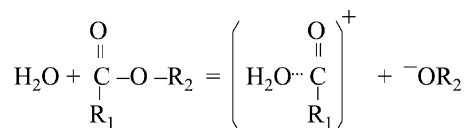
water can also be formed in a direct way



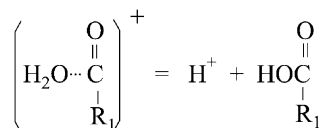
The spontaneous ionisation (and de-ionisation) of hydrogen is a special case of the electrolytic deposition (or anodic dissolution) of hydrogen. Frumkin is of the opinion, which in the following we will argue more closely, that in these processes the effect of the electrode potential is analogous to that of a change in the electrolytic dissociation constant of the acid MH. In this way Frumkin establishes a relation between Tafel's overvoltage equation and the laws of acid–base catalysis. His thinking is based on the concept of Erdey-Gruz and Volmer [12], which we will also adopt in the following section.

2.4. The catalytic hydrolysis of esters

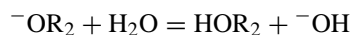
The catalytic hydrolysis of esters is brought into the same context as follows. The uncatalysed hydrolysis is understood as an electrolytic dissociation in the sense of



This primary process is supposed to be followed by the reactions

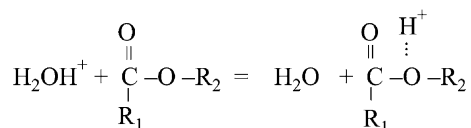


and

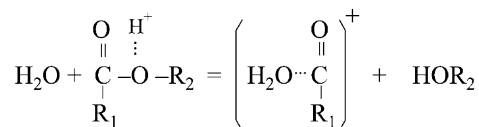


The catalytic effect of the H^+ ion is supposed to consist in facilitating the primary process by addition of a proton to the ester's oxygen bridge. We then have the following reaction phases:

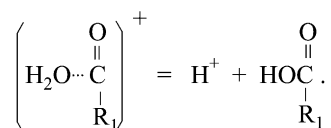
Addition of the proton



catalysed primary process



which then is followed, as before, by



We want to show here how these four closely related groups of phenomena can be visualized in detail. The explanation is supposed to produce the following results:

- (1) Derive the correct order of magnitude of the energy of activation for the processes cited in Sections 2.1–2.3.
- (2) Derive the relation between the electrolytic dissociation constant of acids and bases and their catalytic effect.
- (3) Derive the Tafel equation for hydrogen overvoltage and the series of overvoltages at the metals.
- (4) Explain the order of magnitude of catalytic action of the hydrogen ions.

3. Theoretical treatment of the individual reactions

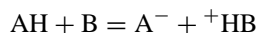
3.1. Electrolytic dissociation of acids—proton transfer to anionoid molecules

Our method is most readily presented in the instance of electrolytic dissociation of acids. We will therefore present a detailed discussion of this reaction, even though a practical application to the electrolytic dissociation rate of acids is not yet possible at this

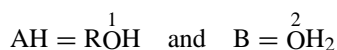
time owing to the lack of experimental data. This is all the more justified as recently, the exchange reaction between the hydrogen atom in acids and the hydrogen atoms in solvents which had first been found by Bonhöffer and Brown [13] for the OH groups of sugar constitutes a tool for measuring the rate of acid dissociation, so that presumably we shall soon gain experimental data to test our theory. In addition, studies of proton transfer to anionoid molecules constitute a wide field of experimental work to which the theory can be applied. This last aspect will not be discussed in detail here, since so far we have not been able to elaborate it sufficiently.

The potential energy scheme for the electrolytic dissociation of an acid AH can be regarded as a special case of the scheme that has been established in earlier work [14] for electrolytic dissociation in general.

This case of



can appropriately be described as the transition of a proton from one centre to another. If for instance



then the two oxygen atoms 1 and 2 are the centres. In Fig. 1 we imagine the two centres held fixed at distance γ apart. The potential energy curve a represents the energy of the H atom in the initial state, i.e. in the

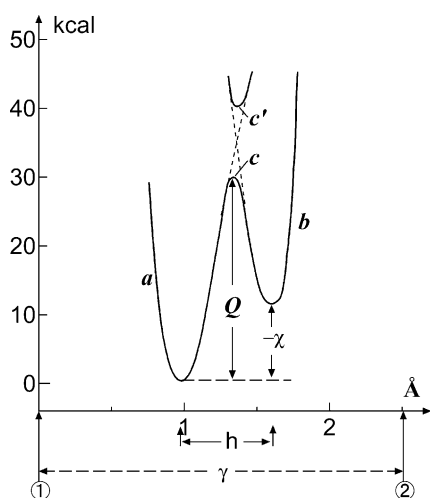


Fig. 1. Energy scheme of a proton transition between two centres 1 and 2.

homoeopolar binding state of $-\text{OH}$. The minimum of this curve indicates the position of rest of the H atom in the initial state. Potential energy curve b represents the energy of the H atom in the final state, that is, in the coordinate bonding of the complex $^+\text{HOH}_2$. The distance between the rest position in the final state and the rest position in the initial state is the total displacement experienced by the proton during electrolytic dissociation. It can be seen from the divisions on the axis of abscissas that the O–H distance in the hydroxyl group has been assumed to be 0.97 \AA , while the $^+\text{H}-\text{OH}_2$ distance is supposed to be 1.4 \AA [14]. The potential energy curves are Morse functions calculated with the following numerical assumptions: potential energies (D) of the bonds, $D_{\text{OH}} = 117$ [15] and $D_{^+\text{HOH}_2} = 270$ [16]; in both cases, a value of $\omega_0 = 3660 \text{ cm}^{-1}$ was assumed for the fundamental frequency, and from this and the values of D the Morse constant a was calculated.

Curves c and c' which arise by the "splitting" at the intersections of curves a and b are drawn arbitrarily.

The reaction proceeds first with a stretching of the $-\text{OH}$ bond, and the energy increasing along curve a up to the branching point of curve c; further withdrawal of the proton brings us onto curve c. As soon as the maximum of this curve is attained, the process continues spontaneously with a liberation of energy along curve b leading to the final state.

The activation energy (Q) is given by the vertical distance between the minimum of curve a and the maximum of curve c, while the vertical distance χ between the minima of curves a and b (to be reckoned with a negative sign) defines the heat of the reaction, that is, the heat of electrolytic dissociation of the acid (η). The quantity $Q - \chi$ must be regarded as the "true heat of activation".

For the sake of simplicity, the zero-point energies have been omitted in Fig. 1; this simplification has been retained throughout the present communication.

An approximation made in this scheme, which is not insignificant, has been to assume that curves a and b have the same shape as that valid for the bonds of $-\text{OH}$ and $^+\text{HOH}_2$ in the free state, that is, outside the solvent and unaffected by mutual proximity. This approximation is unobjectionable for the $-\text{OH}$ bond; however, for the $^+\text{HOH}_2$ bond it is undoubtedly a noticeable omission when we disregard the electrostatic attraction of $-\text{O}^-$ and $^+\text{HOH}_2$.

It is readily seen that the electrostatic attraction that has been neglected acts so as to depress the heat of activation. We can say on the basis of calculations to be published at a later occasion that despite this influence, the overall picture presented in Fig. 1 is generally justified. This approximation will be all the more valid inasmuch as the electrostatic term that was neglected is of no importance or of only a very minor importance in all the processes to be considered below.

It can be seen from Fig. 1 that the heat of activation is primarily a function of the distance γ (or h) when the shape of curves a and b is retained. The quantity dQ/dh depends on the slopes of curves a and b at their intersection; in the case shown in Fig. 1 $dQ/dh \sim 66 \text{ kcal}/\text{\AA}$.

In certain cases, crystallographic studies and interference experiments in liquids will provide some orientation as to the true value of γ . Groups having a tendency to dissociate a hydrogen atom electrolytically (proton donors) and groups adding hydrogen ions (proton acceptors) often are strongly negative. The proton present between these negative centres gives rise to a bonding between them in the form of a so-called “hydrogen bond”. This hydrogen bonding has been recognised as the basis for the associating power of hydroxyl-containing substances. The distance has been determined repeatedly in the instance of OH groups. Time and again a value of 2.5–2.6 Å has been found for the nuclear distance between the two O atoms [17]. Introducing $\gamma = 2.5 \text{ \AA}$ in Fig. 1 we find that $h = 0.1 \text{ \AA}$; that is, the rest positions of the proton in its two possible states practically coincide. We thus obtain the result illustrated in Fig. 2 that the electrolytic dissociation of water as well as that of the alcohols, and probably also that of organic acids in hydroxyl-containing solvents, is a purely electronic process. This strange result will be followed up by us at another occasion.

In situations where the hydrogen ion separates from an atom having a negative character less pronounced than that of oxygen, a larger distance between the centres must be assumed to exist. This may be true in the electrolytic dissociation of hydrocarbons, for instance when acetylene exchanges its hydrogen atoms with the aqueous solvent. This process, so far observed in alkaline solutions only [18], would have to be formulated as

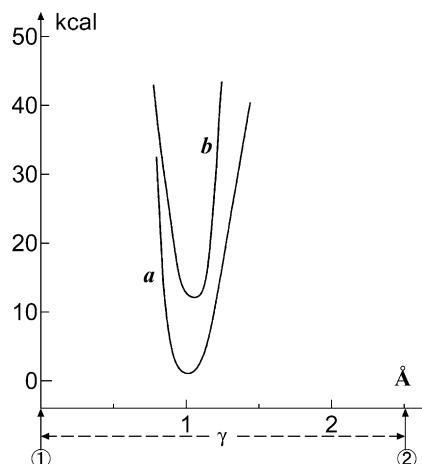
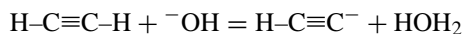
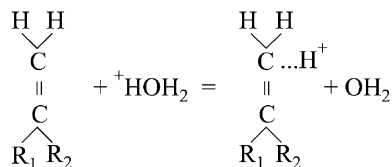


Fig. 2.

The slowness of the process (as well as the fact that it is basically related to tautomerisation, which also is slow) suggests that the same magnitudes of the quantities are applicable as assumed in Fig. 1; that is, a distance h of 0.5–0.6 Å and a resulting heat of activation of about 20 kcal.

Therefore, a value of $h \sim 0.5 \text{ \AA}$ will have to be assumed as well in proton transitions to “anionoid” molecules, for instance in the process mentioned in the preceding section



which must be regarded as the primary process in the addition of hydrogen halides and similar compounds to ethinoid double bonds.

In the case presented in Fig. 1, a value of $\gamma = 3.0 \text{ \AA}$ is associated with $h = 0.63 \text{ \AA}$. This value of the distance between centres is intermediate between $\gamma = 2.5 \text{ \AA}$ present when the centres are “hydrogen-bonded”, and $\gamma = 3.5 \text{ \AA}$ often seen between neighbouring carbon atoms of two molecules [19]. In the former case, the “proton transition” occurs without perceptible displacement of the proton, but in the latter case, a proton transition will not occur at all since the heat of activation is overly large.

We thus conclude that proton transitions occurring with practically measurable rates are tied to the existence of an intermediate value of the distance between the centres, i.e. of $\gamma \sim 3.0 \text{ \AA}$. For a closer consideration, of course, one must also take into account the distances of the rest positions of the protons from the centres, which will differ from one case to the next, as well as the shapes of the potential energy curves and the various factors which for the time being have here been neglected, for instance, the degeneration energy at the point of intersection of the curves, the zero-point energy, and particularly the tunnelling effect.

Thus, for further discussion we shall rely on the case of $\gamma = 3.0 \text{ \AA}$ and $h = 0.6 \text{ \AA}$ presented in Fig. 1.

First we shall examine the way in which the activation energy depends on the heat of electrolytic dissociation. We compare, for instance, a series of $-\text{OH}$ groups with graded heats of dissociation $\eta_1 = -\chi$. Since the solvent (B) is assumed to be constant, then $\eta_1 = -\chi$ will only depend on D_{OH} ; graded values of χ must be reflected in identically graded values of D . Further, if the intended range of variation of χ is chosen not to be excessive, then the shape of the potential energy curve in its lower part which is important here will remain practically unchanged. Thus, for constant h and variable χ we have the situation illustrated in Fig. 3. For every change $-\Delta\chi$ there is a correspond-

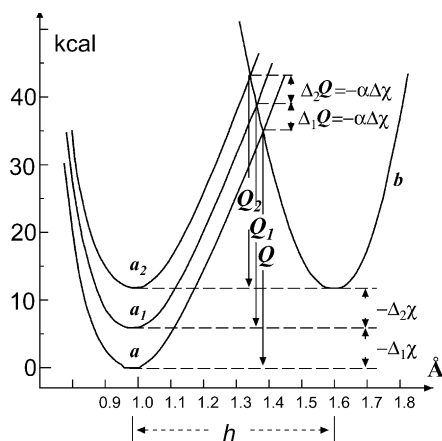


Fig. 3. Relationship between the heat of reaction and the heat of activation: $\Delta Q = -\alpha \Delta\chi$; $\alpha < 1$. Curves a_1 and a_2 have been obtained by shifting curve a vertically. The “degeneration curves” c and c' have been omitted. The distances given on the axis of abscissas are reckoned from centre 1 (Figs. 1 and 2).

ing change ΔQ which is approximately proportional to $-\Delta\chi$ but smaller than $-\Delta\chi$

$$\Delta Q = -\alpha \Delta\chi$$

The proportionality factor $\alpha < 1$ obviously depends on the relative slopes of curves a and b at their point of intersection. One has $\alpha = 0.5$ when these slopes are identical.

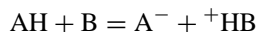
A similar result can be derived analogously for the case where the solvent (that is, the “base”) is varied and χ thus changed. Maintaining h at constant (const) we find that Q again changes by an amount

$$\Delta Q = -\alpha \Delta\chi$$

When the bases are varied, of course, the graded change of $-\chi$ is opposite and equal to the graded change in the heats of electrolytic dissociation of the bases

$$\Delta\eta_2 = \Delta\chi$$

If in the dissociation process



the logarithms of the dissociation constants K_1 and K_2 of the acids or bases are regarded as being proportional to the associated heats of electrolytic dissociation η_1 and η_2

$$\log K_1 = -\frac{\eta_1}{RT} + \text{const}'_1$$

$$\log K_2 = -\frac{\eta_2}{RT} + \text{const}'_2$$

$$\log K_1 = \frac{\chi}{RT} + \text{const}_1 \quad (1)$$

$$\log K_2 = -\frac{\chi}{RT} + \text{const}_2 \quad (2)$$

where for Eq. (1) the acids have to be varied while retaining the solvent, while Eq. (2) applies when the same acid is dissolved in different solvents. For the activation energy Q we then obtain

$$\frac{Q}{RT} = -\alpha \log K_1 + \text{const}_3 \quad (3)$$

$$\frac{Q}{RT} = \alpha \log K_2 + \text{const}_4 \quad (4)$$

$$\frac{Q}{RT} = -\alpha \log K'_2 + \text{const}_{13} \quad (13)$$

while the equations for the rate constant k are obtained by inserting

$$\log k = -\frac{Q}{RT} + \text{const}_{14} \quad (14)$$

After inserting (14), relations (10) and (11) yield the empirical relationships discovered by Brönsted [20] between the catalytically prototropic effect of acids and bases and their dissociation constants. Relations (12) and (13) have not yet been tested.

3.3. Ionisation of hydrogen at electrodes: electrolytic deposition of hydrogen

Because of the analogy explained in the preceding section, between the ionisation of hydrogen that occurs at metal surfaces and the process of electrolytic dissociation, we represent the ionisation process by Fig. 4, which is quite analogous to Fig. 1. It refers to the special case of a nickel surface in contact with water.

Curve a represents the potential energy curve of the adsorbed hydrogen atom, that is, of the Ni–H bond.

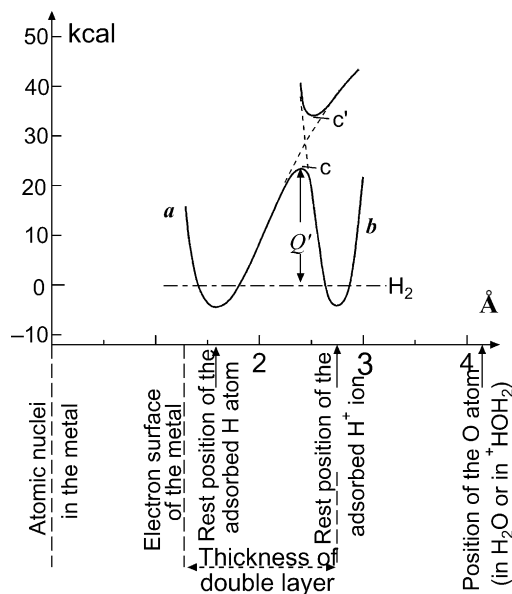


Fig. 4. Energy scheme of the ionisation (and de-ionisation) of hydrogen at a metal surface.

The Morse function used to calculate the curve was based on a distance at rest of 1.56 Å and on a heat of dissociation (D) of the Ni–H bond of 55 kcal, as well as on a Morse constant a of this bond of 1.45 cm^{-1} [21].² For the distance at rest of the proton in the $^+\text{HOH}_2$ bond from the metal's electronic surface, we introduce the thickness of the double layer, which according to electrochemical experience should be close to 1.5 Å [22]. The radius of the Ni atom that is used as the distance of the Ni nuclei from the electronic surface has been taken from lattice dimensions as being 1.25 Å.

Curve b is identical with the curve called b in Fig. 1. The difference in levels between the two low points of curves a and b which in Fig. 1 was labelled χ has here been taken as zero on the basis of approximating considerations to be presented in our detailed communication.

An element in Fig. 4 that is new as compared to Fig. 1 is the straight line labelled “H₂”, which indicates the energy level of gaseous hydrogen. This is the level from which the (gross) energy of activation Q' should be reckoned in the way indicated in the figure. The value thus determined will only be correct, of course, so long as the occupation of the metal surface by H atoms is slight. Experience tells us that this condition is satisfied for hydrogen on platinum at ordinary pressures [23]. It should therefore also be largely appropriate in other cases, and we may at first disregard the complications that might arise from a saturation of the surface layer.

It can be seen that the construction in Fig. 4 yields a value of $Q' \sim 24$ kcal. All omissions that we have admitted in the approximate theory outlined here will only result in an increase of the calculated heat of activation, hence the agreement with values of about 10 kcal that have actually been observed [24] appears to be sufficient.

Among these omissions, mention must be made in particular of the tunnelling effect, which will lead to a lower observed heat of activation. This effect has been pointed out some time ago already when explaining the separation of the hydrogen isotopes by electrolysis [25]. Newer observations made in the research laboratories of Imperial Chemical Industries in Billingham

² We regard the value of $D = 55$ kcal as more likely than $D = 60$ kcal.

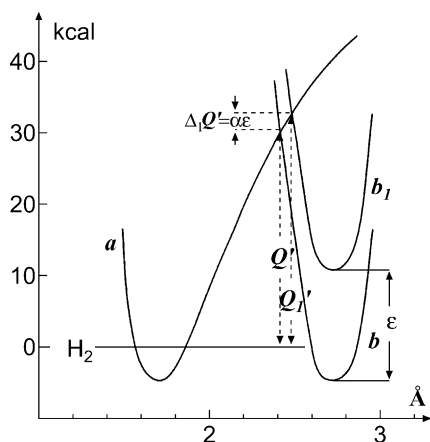


Fig. 5. Relationship between electrode potential and the heats of activation of the processes of ionisation and de-ionisation, $\Delta_1 Q' = \alpha \varepsilon$ and $\Delta_2 Q' = -(1 - \alpha) \varepsilon$ (the “degeneration curves” c and c' have been omitted; the distances given as abscissa values are reckoned from the layer holding the atomic nuclei of the metals).

under the leadership of M.P. Applebey³ have demonstrated that this effect is indeed very powerful. With an electrolyte strongly agitated at the electrodes, separation factors of the order of 100 are found which cannot be explained in any other way than by the tunnelling effect. It should be mentioned at this point that the tunnelling effect will of course have to be taken into account as well in all the proton transfers discussed earlier.

Considerations of the influence exerted on the rate of ionisation by a voltage applied to the electrode lead us to the theory of electrolytic hydrogen deposition. We assume as an approximation that the full polarisation voltage (ε) resides between the metal's electronic surface and the layer of adsorbed hydrogen ions, and that it constitutes a homogeneous field. Departures from this assumption have been pointed out by Frumkin [26].

We then must superimpose a linear potential on the potential energy curves of Fig. 4 as shown in Fig. 5. While we neglect the influence of these fields on the energy of the adsorbed hydrogen atom (that is, we assume that the Ni–H bond does not contain a strong dipole), we find that the field merely produces a ver-

tical shift of curve b by the amount of ε and at the same time a small deformation of this curve attended by a small horizontal shift of its minimum.

The latter two effects will be disregarded in the present, preliminary review. It can be seen from the figure that we then obtain for the ionisation process

$$\Delta_1 Q' = \alpha \varepsilon \quad (15)$$

for deposition of the ions, to the contrary, one readily finds

$$\Delta_2 Q' = -(\varepsilon - \alpha \varepsilon) = -(1 - \alpha) \varepsilon \quad (16)$$

Designating the currents resulting from the two electrode processes as i_1 and i_2 , respectively, we realise that $i_1 - i_2$ must vanish at the rest potential while a current i appears when a voltage is applied

$$i = i_1 - i_2 = \text{const} (e^{-(\alpha \varepsilon)/FRT} - e^{-((1-\alpha)\varepsilon)/FRT}) \quad (17)$$

At higher voltages one of these terms can be neglected, and for the discharge current for instance we find

$$\log i = \frac{(1 - \alpha) \varepsilon}{FRT} + \text{const} \quad (18)$$

This is the Tafel equation, empirically well known. The constant α has been found to be about 0.5 in most cases. We see that this corresponds to the situation in which the two curves a and b have the same slope at their point of intersection.

We want to see now in which way a change in the nature of the metal will influence the ionisation processes discussed above. Following an idea of Frumkin (personal communication) we find that the energies of the H^+ ions adsorbed at the two electrodes are practically the same, as follows. Assume that the two metals, which are in electronic contact, are immersed into the same solution and take into account: (a) that noticeable specific adsorption does not exist for H^+ ions; (b) that it is a matter of just a very slight difference in energy (it corresponds to the Peltier heat) whether an electron is transferred into the solution from one metal or from the other metal. It follows that the de-ionisation of an adsorbed H^+ ion producing

³ We are greatly indebted to Dr. Applebey for his permission to use here these results, as yet unpublished.

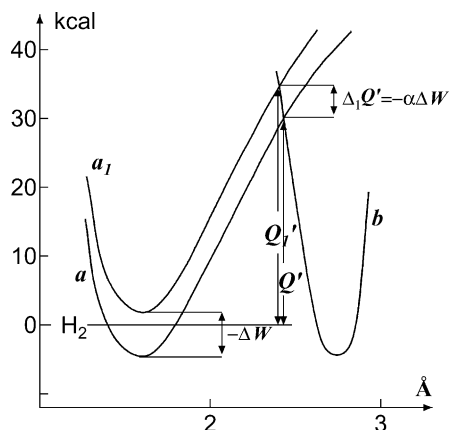


Fig. 6. Relationship between the adsorption potential of the hydrogen atom and the heats of activation of the processes of ionisation and de-ionisation, $\Delta_1 Q' = -\alpha \Delta W$ and $\Delta_2 Q' = -\alpha \Delta W$ (for all other observations see Fig. 5).

a free H atom is associated with the same energy change at the two metal electrodes.⁴

We therefore may characterise the different metals, merely in terms of the different adsorption potentials of the H atom at the different metal surfaces.

We thus regard the adsorption potentials (W) as having graded values among metals, and use a series of curves to introduce this concept into our figure (Fig. 6), again with the simplifying assumption that the shape of the curves remains the same in their lower segments, which here is the only important region, while the level of the minimum will shift by an amount corresponding to the change in adsorption potential. The effect of a change in adsorption potential on the heat of activation of the ionisation process can be described by the relation following from Fig. 6

$$\Delta_1 Q' = -\alpha \Delta W \quad (19)$$

⁴ Referring to different views held in the literature, viz. that in this case the difference in work functions should also be taken into account, Frumkin makes the following remarks: when two metals which are in electronic contact are present in a vacuum, a potential drop exists between two points close to their surfaces (the Volta potential) which is known to be equivalent to the difference in work functions. In an electrolyte solution, this potential drop is compensated by the formation of double layers, and so energetically it will no longer matter from which of the metals the electron comes which neutralises the positive charge of the H^+ ion.

Because of

$$\log k = -\frac{Q'}{RT} + \text{const}_{15} \quad (20)$$

we find for the rate constant of ionisation at the different metals

$$\log k = \frac{\alpha W}{RT} + \text{const}_{16} \quad (21)$$

For the deposition of ions we have

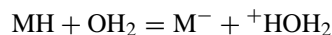
$$\Delta_2 Q' = \Delta_1 Q' = -\alpha \Delta W$$

from which by arguments analogous to those that led from Eq. (16) to Eq. (18) we obtain the overvoltage constant (the logarithm of the current for a given value of polarisation)

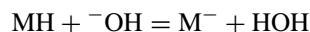
$$\log i = \frac{\alpha W}{RT} + \text{const}_{17} \quad (22)$$

The two Eqs. (21) and (22) correctly reflect the qualitative empirical findings according to which: (a) the spontaneous ionisation of hydrogen only occurs at metals having a high adsorption potential for the H atoms; (b) the overvoltage at different metals will be higher the smaller the adsorption potential of the H atom at a particular metal.⁵

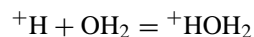
Let us now assume that the solvent is changed but the electrode material is retained. This leads to a change in the difference in levels (designated as χ in Fig. 1 and set equal zero in Fig. 4) between curves a and b, and in parallel to a change in Q , on account of two effects. First, there may be a change in electrode potential by an amount $\Delta\varepsilon$, which will give rise to a change in Q' by an amount $\alpha \Delta\varepsilon$. Secondly, under these conditions there may be a change in the electrode process, for instance from



to



There will then be a change in χ by an amount given by the difference in heats of reaction of the two processes



⁵ A quantitative measure for the adsorption potential is given by the rate of recombination of H atoms [27a]; Bonhöffer found the antiparallel behaviours of the rate of recombination and of overvoltage [27b].

and



and also by an amount given by the difference in the heats of electrolytic dissociation of the different “bases” to which the proton is added; and one has

$$\Delta_1 Q' = \alpha \Delta \chi$$

A correction to the above relations that is important may arise in situations where the change in electrode metal or liquid phase causes a change in double-layer thickness. Assuming, as an approximation, that this change in thickness $\Delta\delta$ produces a change in h of equal magnitude, it follows that

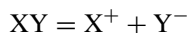
$$-\frac{\Delta_1 Q'}{\Delta\delta} = \alpha f$$

where f is the (negative) slope of curve b at the point of intersection of curves a and b.

The above theory of the processes occurring at the hydrogen electrode adopts the ideas of Erdey-Gruz and Volmer [28] concerning the rate-determining influence of the electric field of the double layer on the ionisation and de-ionisation of hydrogen. Departing from the approach of Gurney [29] we develop these ideas in the direction pointed out by Frumkin [30] in his criticism of Gurney’s theory.

3.4. Catalysis of ester hydrolysis by hydrogen ions

We first introduce in Fig. 7 the scheme of neutral (nuncatalytic) hydrolysis, the primary process of which we visualise as a simple electrolytic dissociation, as outlined in the preceding section. This figure, which is taken from the paper of Ogg and one of us [4], uses the simplified symbolic representation of electrolytic dissociation



Curve a represents the energy in the initial state as a function of increasing X–Y distance; curve b is the energy as a function of distance between the two ions X^+ and Y^- formed primarily; χ the heat of electrolytic dissociation; and Q the heat of activation.

On the other hand, acid hydrolysis must be represented as a “positive ion reaction” in the sense of

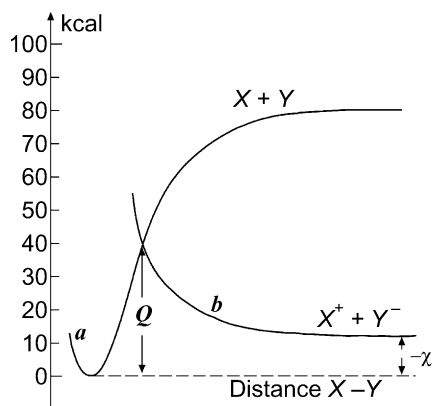
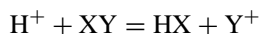


Fig. 7. Energy scheme of an electrolytic dissociation (neutral ester hydrolysis).

The corresponding figure (Fig. 8) is entirely analogous to the scheme of the negative ion reaction $Z^- + XY = ZX + Y^-$ presented in the paper just mentioned [4], and can be understood analogously. The curves a' and b' represent a section through the potential energy curves in the system’s “critical configuration”. They show the potential energy functions in the initial state and final state as plotted against the X–Y distance at fixed H–X distance; where the value of this latter distance is precisely that where the heat of activation has its lowest value.

The fragment of a curve e gives the normal value of energy of the initial state. (The value of the abscissa for the minimum of this curve has been set equal to the value of the abscissa of the minimum of curve

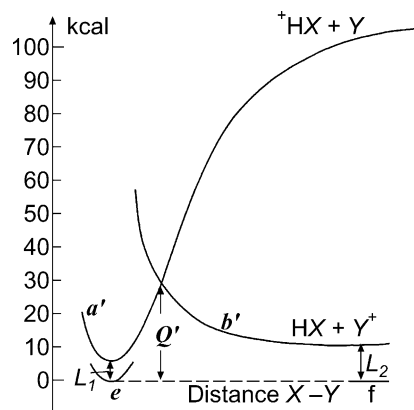
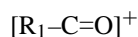


Fig. 8. Energy scheme of an electrolytic dissociation (ester hydrolysis) catalysed by H^+ ions.

a, but this position actually has no physical significance.) The fragment of a curve f gives the energy of the final state; the vertical distance between the minima of curves e and a' represents the work (L_1) that must be expended to bring the H^+ ion to the "critical" distance from the XY molecule; the vertical distance between the horizontal asymptotes of curves b' and f is the energy (L_2) liberated when, after completed reaction and removal of Y^+ to infinity, the newly formed bond returns from the critical configuration to the normal state.

The vertical distance between the minimum of curve e and the horizontal asymptote of f is the heat of the reaction while the energy in the point of intersection reckoned from the energy level of the initial state is the heat of activation Q' shown in the figure.

When this scheme is applied to the hydrolysis of a carboxyl ester, then HO signifies the bond O–C between the bridging oxygen and the carboxyl carbon atom linked to it; HX then is the HO bond of the alcohol that is produced by hydrolysis, and Y^+ is the carbon atom of the carbonium ion



The reason for the catalytic effect of the H^+ ion becomes evident when comparing Figs. 7 and 8.

The energy L_1 , which causes the minimum of curve a' to be higher than the minimum of curve a by an amount L_1 , is the difference between the addition energies S_1 and S_2 of the proton, on one hand to H_2O and on the other hand to



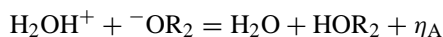
Quantities S_1 and S_2 can be equated approximately to the heats of solvation of H^+ in water and in the (liquid) ester, respectively. Acids when dissolved in a liquid ester will be much less dissociated than in aqueous solution, hence $S_2 < S_1$ and $L_1 \sim S_1 - S_2$ is a positive quantity.

As to the shapes of curves a and a', one can assume that these differ little. The presence of the proton may be assumed as an approximation, to have a purely electrostatic effect that can be neglected in the homoeopolar curve O–C.

Curve b' differs in its nature from curve b. The latter represents the repulsion existing between two ions conditioned by the penetration of a solvent molecule

between the ions, while curve b represents the repulsion between the O atom of a hydroxyl group and a carbonium ion. A closer look at the forces involved will reveal that curve b' should be a little steeper than curve b. However, for the time being we shall neglect this difference and perform a preliminary analysis of the process under the assumption that curves b' and b have the same shape.

For a determination of the level of energy of the asymptote to curve b', we first consider the level of energy of the asymptote to curve f, that is, the heat of reaction of the process. This is smaller than the heat of reaction of simple electrolytic dissociation, the difference being—as can be seen directly—the energy of reaction of the process



that is, the heat of electrolytic dissociation of the alcohol in aqueous solution.

Fixing curve b' now requires merely an estimate of the quantity L_2 . This is the energy liberated when the H atom changes from the "critical distance" $H \cdots O$ retained for curves a and b to the normal distance in the OH group. The shift approximately corresponds to the difference in distances between a proton coordinately added to oxygen and a proton bound with a homoeopolar bond. As to the latter, all that is known is that it amounts to a few tenths of an Ångström. Adopting (arbitrarily) a value of about 0.2 \AA , we find (after subtracting the zero-point energy) that $L_2 \sim 6 \text{ kcal}$.

The relative magnitudes of the quantities that are obtained in this way are represented in Fig. 8, where L_1 has been tentatively taken as 5 kcal. One can see, when comparing Figs. 7 and 8 that the activation energy of the catalytic process, Q' , can be calculated from Q as follows:

$$Q' = Q + \alpha L_1 - (1 - \alpha)(\eta_A - L_2)$$

According to Fig. 8, we find that

$$Q' = Q - 4 \text{ kcal}$$

For H^+ ion concentrations, where the temperature-dependent factor of the catalysed reaction is equal to that of the uncatalysed reaction (that is, for something like $N/1 H^+$), this corresponds to something like a 1000-fold acceleration of the reaction.

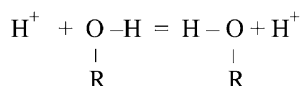
According to this theory, it is the heat of neutralisation η_A of the resulting alcohol that is the effective

quantity in H^+ ion catalysis. Quantities L_1 and L_2 have effects opposing that of η_A . For $\alpha = 0.5$, catalysis comes about when $L_1 + L_2 < \eta_A$.

It follows that only those compounds can be hydrolysed by H^+ ions where a leaving negative group will combine with H^+ ions to an undissociated compound. Experience available to date confirms this conclusion.

Acid ester hydrolysis has here been taken as a catalytic action of the H^+ ions on the electrolytic dissociation of the ester. According to this assumption, the field of the proton has an effect that is analogous to that of the electrode potential on the ionisation of the adsorbed H atom.

It must be expected accordingly that other electrolytic dissociations will also be catalysed by H^+ ions [1]. The rate of electrolytic dissociation of an alcohol should be enhanced in the sense of the positive ion reaction



Such an effect would be demonstrable with the aid of heavy hydrogen, and the above considerations could be more firmly argued if this effect were revealed.

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