

## ON THE KINETICS OF ACID AND BASIC CATALYSIS.

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There are numerous reactions which are catalytically accelerated by acids or bases or both.<sup>1</sup> If  $A \rightarrow B$  is such a reaction, we can express its kinetics in dilute aqueous solutions (*i.e.* solutions poor in electrolytes) with great accuracy by the equation for a series of simultaneous actions, as follows : <sup>2</sup>

$$\frac{d[B]}{dt} = (k_w + k_a[H^+] + k_b[OH'])[A] \quad (1)$$

where the bracketed symbols are concentrations and the  $k$  figures are velocity constants. In this equation (which shows that the reaction is accelerated by hydrogen and hydroxyl ions  $k_w$ ) is the constant of the uncatalysed reaction or "water reaction,"  $k_a$  the constant of the reaction

\* Communicated in summary at the meeting by Professor Lowry.

<sup>1</sup> J. N. Brönsted, *Om Syre- og Basekatalyse*, Kopenhagen, 1926; A. Skrabal, *Z. Elektrochem.*, **33** (1927), 322; F. O. Rice, *The Mechanism of Homogeneous Organic Reactions*, New York, 1928.

<sup>2</sup> R. Wegscheider, *Z. physik. Chem.*, **30** (1899), 593, and **41** (1902), 52.

promoted by  $H^+$  or the "acid reaction," and  $k_b$  is the constant of the "basic reaction" promoted by  $OH^-$ .

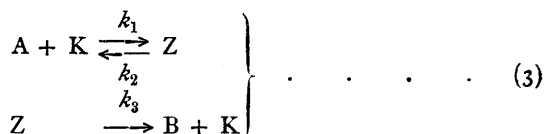
Since  $H^+$  and  $OH^-$  interact with great velocity to form water when their equilibrium is disturbed,  $[H^+]$  and  $[OH^-]$  are not independent of one another but are connected by the equation:—

$$[H^+][OH^-] = w \quad . \quad . \quad . \quad . \quad (2)$$

where  $w$  represents the ion product of the water. The establishment of the fact that a substance  $K$  acts as a catalyst is a matter of classification and provides no explanation of the phenomenon. The explanation or meaning of what happens is first given when the so-called "mechanism" of the reaction is revealed and firmly established; in this respect a catalytic reaction differs in no way from one which is not catalysed, although it may be remarked incidentally that many workers deny the existence of uncatalysed reactions at all.<sup>3</sup>

With the object of understanding the mechanism of the reaction of acid and basic catalysis we will consider the general reaction  $A \rightarrow B$  which, on account of its simplicity, we will take as monomolecular and irreversible. Since we are dealing with homogeneous catalysis, moreover, and suppose that the proportion of catalyst  $K$  is very small, so that it does not substantially influence the medium, and "medium catalysis" is clearly excluded, we are led to explain the phenomenon as "intermediate compound" or "chain" catalysis. We assume also that the catalyst  $K$  forms with the substrate  $A$  (or the product of its reaction) an intermediate compound  $Z$  which reacts either directly or by further formation of intermediates to give  $B$  and set free the catalyst. If  $A \rightarrow B$  is a complex reaction (*i.e.* one which proceeds by stages) the concentrations at any one time of all the intermediate compounds are small, within the range of measurability of the reaction, in comparison with  $A$ ,  $B$  and  $K$ .<sup>4</sup>

We must then divide the reaction  $A \rightarrow B$  at least into the following partial reactions:—



from which the following is deduced for the velocity of the complete reaction

$$\frac{d[B]}{dt} = k[K][A] \quad . \quad . \quad . \quad . \quad (4)$$

Equation 3 contains the idea that every transformation which takes place between two components proceeds also in the opposite direction, a hypothesis which has been suggested by many chemists (H. E. Armstrong,<sup>5</sup> A. Kekulé,<sup>6</sup> H. Wieland,<sup>6</sup> etc.), and to which it is practically impossible to take exception.

From this it follows that the reacting substance  $A$  must have basic properties if the catalyst  $K$  is an acid, and acid properties of the catalyst is a base, for all substances which combine with acids are bases and *vice versa*.

<sup>3</sup> See A. Mittasch, *Ber.*, 59 (1926), 13.

<sup>4</sup> The range during which measurements are possible is in the middle of the reaction; for many reasons measurements cannot be taken at the beginning and end. This middle range corresponds to about 1 to 99 per cent. of the period, but as a rule the reactions are measured over a smaller range.

<sup>5</sup> See J. W. Mellor, *Chemical Statics and Dynamics*, London, 1904, and elsewhere.

<sup>6</sup> *Rec. Trav. Chim.* 41 (1922), 576.

Experience confirms this conclusion. Thus the typical ethers have no acid properties but are most decidedly basic (Oxonium bases); experiment shows that their hydrolysis is only catalysed by acids. The esters on the other hand are both bases and acids, which follows for example from the existence of the compounds  $\text{CH}_3 \cdot \text{COOC}_2\text{H}_5 \cdot \text{HBr}$ <sup>7</sup> and  $\text{C}_6\text{H}_5 \cdot \text{COOC}_2\text{H}_5 \cdot \text{NaOCH}_3$ .<sup>8</sup> This accords with the behaviour of the esters on hydrolysis, since this is accelerated both by acids and by bases.

It follows, further, from what has been said that the intermediate compound Z, since it is formed from an acid or a base must be of the nature of a salt or an ion. Since salt formation or neutralisation proceeds very imperfectly—the intermediate compound Z is always present in only very small concentration—the substrate A can be only a weak base or a weak acid (or pseudo-acid) or an ampholyte. Up to this stage all workers who are concerned with the experimental or theoretical problem are of one opinion. Differences of opinion emerge when we attempt to deduce equation (4) for scheme (3).

According to the relative values of the three velocity constants  $k_1$ ,  $k_2$ ,  $k_3$  two cases can be distinguished.<sup>9</sup>

Case (1).—If the reversible reaction which leads to the formation of Z is sufficiently rapid compared with the further transformation of the intermediate product, the equilibrium  $\text{A} + \text{K} \rightleftharpoons \text{Z}$  is firmly established. When the equilibrium is restored the progress of the reaction in this direction is inhibited and the formation of B can go forward only as the intermediate product is eliminated by the reaction  $\text{Z} \rightarrow \text{B} + \text{K}$ . The latter part of the reaction then determines its velocity and one can write in its time equation the equilibrium values for Z, thus:—

$$\frac{d\text{B}}{dt} = k_3[\text{Z}] = k_3 \frac{k_1}{k_2} [\text{A}][\text{K}] = k_3 \text{G} [\text{A}][\text{K}] \quad (5)$$

where  $\text{G} = k_1/k_2$  represents the equilibrium constant of the reaction  $\text{A} + \text{K} \rightleftharpoons \text{Z}$ .

Combining this with equation (4) it follows that the measured velocity constant  $k$  that:—

$$k = k_3 \frac{k_1}{k_2} = k_3 \text{G} \quad (6)$$

It will be seen that the measured velocity constant  $k$  of the complete reaction is proportional to the kinetic constant  $k_3$  as well as to an equilibrium constant G. We can call such kinetic quantities “complex-kinetic” constants.<sup>10</sup> Arrhenius<sup>11</sup> was the first who, in order to explain the large temperature coefficient of  $k$ , had recourse to velocity constants of the form (6). We will therefore call our unstable intermediate Z an “*Arrhenius intermediate*.”

Equation (6) represents mathematically Euler's hypothesis of acid and basic catalysis, and the Arrhenius intermediate Z is, according to Euler, the reactive ion. I have recently shown<sup>12</sup> that this hypothesis has not yet been proved; in order to prove it one must experimentally ascertain, in addition to  $k$ , both G and  $k_3$  and show that  $k = k_3 \text{G}$ . It is the more

<sup>7</sup> O. Maass and D. McIntosh, *J. Amer. Chem. Soc.*, **34** (1922), 1273.

<sup>8</sup> H. von. Pechmann, *Ber.*, **31** (1898), 501.

<sup>9</sup> See A. Skrabal, *Annalen Physik*, [4], **84** (1927), 624.

<sup>10</sup> A. Skrabal, *Monatsh. Chem.*, **37** (1916), 495. <sup>11</sup> *Z. physik. Chem.*, **4** (1889), 226.

<sup>12</sup> A. Skrabal, *Z. Elektrochem.*, **33** (1927), 322. See also T. M. Lowry, *J. Chem. Soc.*, 1927, 2554.

difficult to bring about this proof inasmuch as both G and  $k_3$  are either only just within or entirely outside the limits of measurement. In order to measure both these values one must moreover use strongly acid or strongly basic solutions and therefore work under quite different conditions of concentration than when ascertaining the value of  $k$ . One must reduce the three values to the same concentration by a procedure of which we have no real knowledge. The more recent papers of the Euler school have not, in fact, appreciably affected this point.

*Case (2).*—The second case is given if the constant  $k_3$  in the reaction  $Z \rightarrow B + K$  is sufficiently large. In that case the formation of Z governs the velocity and the corresponding differential equation reads:—

$$\frac{d[B]}{dt} = k_1[A][K] \quad . \quad . \quad . \quad (7)$$

or if we combine this with equation (4):—

$$k = k_1 \quad . \quad . \quad . \quad (8)$$

This equation also expresses the velocity of formation of the intermediate body Z. We will call the unstable intermediate body with this characteristic behaviour the "*van't Hoff intermediate*," since J. H. van't Hoff has assumed such intermediate products in order to explain many reactions of a lower order than might be expected from their chemical equations.<sup>14</sup>

The van't Hoff intermediate, so far as concerns the part it plays in the stage-by-stage reaction, does not differ in form from the "critical complex" of R. Marcellin<sup>15</sup> and J. N. Brönsted.<sup>16</sup> On the other hand it is considered that compared with the Arrhenius intermediate it is by far more unstable, although intermediate stages between the two intermediates may exist, since by integration of the system (3) the constant  $k$  of equation (4) for an unstable Z assumes the general form:

$$k = \frac{k_1}{k_2 + k_3} k_3 \quad . \quad . \quad . \quad (9)$$

which according to the relative values of  $k_2$  and  $k_3$  becomes either equation (6) or (8).

Erich Müller<sup>17</sup> gave an explanation of acid and basic catalysis which arose from a kinetic consideration of equation (8), *i.e.*, from the assumption of a van't Hoff intermediate Z. Starting from the conception of the electron constituted molecule, he showed that on saponifying an ester with water alone four of the atoms taking place in the reaction must come together in the molecule at the same moment, whereas on the other hand if the saponification were effected by hydroxyl ions or by hydrated hydrogen ion two atoms sufficed. In this case the first stage of the reaction is decisive for its progress, so that the theory of equation (8) serves for Müller's explanation of the phenomena.

The correctness of this theory is still more difficult of kinetic proof than

<sup>14</sup> H. von. Euler and A. Oelander, *Z. Elektrochem.*, **33** (1927), 527; A. Oelander, *Z. physik. Chem.*, **129** (1927), 1; H. von Euler and A. Oelander, *Z. physik. Chem.*, **131** (1928), 107.

<sup>15</sup> See for example J. H. van't Hoff and E. Cohen, *Chemische Dynamik*, Amsterdam and Leipzig, 1896, Seite 104.

<sup>16</sup> *Ann. Physique*, [9], **3** (1915), 120.

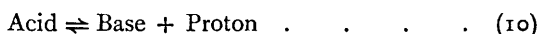
<sup>17</sup> *Z. physik. Chem.*, **102** (1922), 169; **115** (1925), 337.

<sup>18</sup> *Ibid.*, **134** (1928), 190. See also *Z. Elektrochem.*, **31** (1925), 46; **33** (1927), 253 and 561.

that of equation (6), on account of the instability of the van't Hoff intermediate. It can only be proved indirectly, namely by showing that the relation (6) is not correct.

The difficulty, inherent when seeking an explanation of chemical facts by kinetic measurements, lies in the many ways in which the velocity equation can be interpreted, as H. Goldschmidt<sup>18</sup> and especially R. Wegscheider<sup>19</sup> have repeatedly pointed out. Kinetic measurement of the velocity of the reaction  $A \rightarrow B$  furnishes only the constant  $k$  of the total reaction. In order to ascertain the mechanism of the reaction it is necessary to ascertain in equation (9) the constants  $k_1$ ,  $k_2$  and  $k_3$  of the separate intermediate reactions; the possibility of doing this is so much the more improbable as the intermediate products are the more unstable. On the other hand, it is just this great instability which is the reason why the process  $A \rightarrow B$  goes not directly but through intermediate products.<sup>20</sup>

The kinetic studies of T. M. Lowry<sup>21</sup> gave a really clear conception based upon experimental observations; they consisted in the study in non-aqueous media of the reactions to which in aqueous media the time relationship (1) applies. The experiments in these media make it practically essential to modify the old ideas as to acid and base which resulted from the studies in aqueous solution of S. Arrhenius and W. Ostwald. According to the definition given by J. N. Brönsted<sup>22</sup> and T. M. Lowry,<sup>23</sup> acids are bodies which give up a proton and bases are bodies which accept a proton. Between both kinds of bodies the following chemical equilibrium exists—



which can be known as the Acid-Base equilibrium.

In order to avoid confusion with the old narrow views, which can be retained and will be retained, for aqueous solutions, the newly-defined view formulated in equation (10) suggests the new names "*proton-donor*" for acids and "*proton-acceptor*" for bases. Ampholytes are both proton-donor and proton-acceptors, although the later view is really wider.<sup>24</sup>

The phenomenon we have been considering is then proton-donor and proton-acceptor catalysis, and kinetic equation (1) must be generalised and perfected, by introducing a separate figure for each proton-donor and proton-acceptor (J. N. Brönsted,<sup>25</sup> H. M. Dawson<sup>26</sup>). The hydroxyl-ion is a proton-acceptor; the hydrogen-ion itself is not a proton but a proton-donor, *i.e.*, a hydrated (solvated) proton or oxonium-ion in which the hydrogen nucleus has attached itself to a molecule of water and has thus acquired the electron shell of the inert gas helium.<sup>27</sup>

For the study of the medium effect there are several particularly suitable reactions which in water proceed with considerable velocity even when uncatalysed, *i.e.*, in which  $k_w$  of equation (1) is relatively large. Amongst these is the mutarotation of the sugars. For instance the mutarotation of glucose is uninfluenced by acidity throughout the wide range of 6.5 units

<sup>18</sup> *Z. Elektrochem.*, **11** (1905), 5; **14** (1908), 583.

<sup>19</sup> *Z. physik. Chem.*, **36** (1901), 543; *Z. Elektrochem.*, **14** (1908), 133.

<sup>20</sup> See J. N. Brönsted, *loc. cit.*

<sup>21</sup> *J. Chem. Soc.*, **127** (1925), 1371, 1385; **129** (1927), 2539 and 2554. *Structure et Activité chimiques*, Paris, 1926, page 135 *et seq.*

<sup>22</sup> *Rec. trav. chim.*, **42** (1923), 718.

<sup>23</sup> *Chem. and Ind.*, **42** (1923), 43.

<sup>24</sup> See also G. N. Lewis, *Die Valenz und der Bau der Atome und Moleküle*, Braunschweig, 1927, Seite 158.

<sup>25</sup> *Z. physik. Chem.*, **108** (1924), 185; **118** (1925), 299.

<sup>26</sup> *J. Chem. Soc.*, 1926, 2282, 2873; 1927, 2444 and elsewhere.

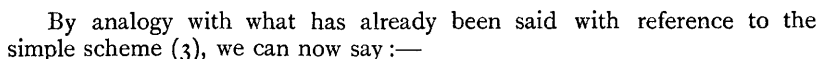
<sup>27</sup> E. Müller, *loc. cit.* Compare also E. Hückel, *Z. Elektrochem.*, **34** (1928), 546.

Lowry and his co-workers have now shown that mutarotation does not take place either in dry pyridine or in dry cresol, but on the other hand that in a mixture of both solvents it proceeds more rapidly even than in water.

Lowry divides solvents into three groups: —

(b) *Solvents which are either acids or bases.* They are of themselves not catalysts but they act in the presence of auxiliary catalysts.

Lowry's theory of the catalysis of the reaction  $A \rightarrow B$ , which supposed two intermediates, can be generalised in the following scheme, which is at the same time an extension of scheme (3):—



If the substrate A is a (weak) acid the catalyst K must be a base, the medium M a (weak) acid or an ampholyte.

If the substrate A is a (weak) base, the catalyst is an acid, the medium a (weak) base or an ampholyte.

If the reaction proceeds in the pure medium M *without* catalyst (*cf.* the term  $k_w$  of equation (I)), the medium M is a base and an acid. Such a reaction necessarily requires an amphoteric medium. If the medium acts in the first part of the reaction as an acid it is in the second part a base, and *vice versa*. The terms acid, base, and ampholyte are used here in the modern sense. If this reaction is to take place, according to scheme (II) proton-acceptor and proton-donor must simultaneously contribute to the effect on the substrate A.

Finally it follows that the intermediate body  $Z_1$  is of the nature of a salt or ion, but the intermediate  $Z_2$  must be an uncharged molecule or a bi-polar molecule (*Zwitterion*).

If, now, we interpret scheme (11) kinetically we can, according to the relative values of the velocity constants (*i.e.* whether the intermediates  $Z_1$  and  $Z_2$  are van't Hoff or Arrhenius intermediate bodies) distinguish the following three limiting cases in all of which the concentration of the medium can be introduced as a constant quantity amongst the velocity constants:—

*Case (i).* The formation of  $Z_1$  decides the velocity:—

$$\frac{d[B]}{dt} = k_1[A][K] \quad (12)$$

Case (ii). The decrease of  $Z_1$  or the formation of  $Z_2$  determines the velocity :—

$$\frac{d[B]}{dt} = k_3[Z_1] = k_3 \frac{k_1}{k_2} [A][K] = k_3 G_1 [A][K] \quad . \quad . \quad (13)$$

Case (iii). The decrease of  $Z_2$  is the deciding factor :—

$$\frac{d[B]}{dt} = k_5[Z_2] = k_5 \frac{k_3[Z_1]}{k_4[K]} = k_5 \frac{k_3 k_1}{k_4 k_2} [A] = k_5 G_2 G_1 [A] \quad . \quad (14)$$

Case (iii) must be rejected because it leads to an equation which is incompatible with the experimental result expressed by equation (4). On the other hand, proposals (i) and (ii) accord to an equal degree with the experimentally ascertained equation (4). The kinetic consequences are thus again ambiguous. We must therefore consider which of the two cases (i) or (ii) is the more probably right.

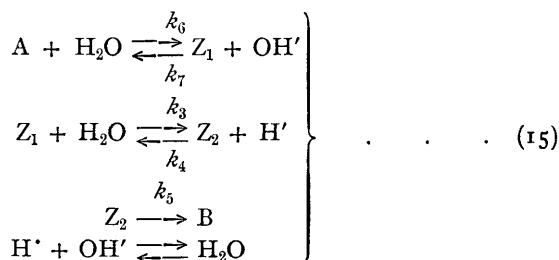
Lowry himself assumes that the first of the stage reactions of scheme (11) is strongly endothermic, the second equally strongly exothermic, and, further, that the two parts of the reaction are coupled by reason of the fact that the necessary energy to promote the first reaction is provided by the energy of the second process. Therefore, it is implied that Lowry favours proposal (12) in which  $Z_1$  is a van't Hoff intermediate. From the purely kinetic standpoint the latter proceeds more readily as the reaction  $Z_1 + M \rightarrow Z_2 + K$  is more rapid in comparison than  $A + K \rightarrow Z_1$ . The relatively large velocity of the first reaction follows in fact with some probability, by reason of the instability of the intermediate body  $Z_1$  and the large surplus of the solvent molecule  $M$  in comparison with the catalyst molecule  $K$ .

We will, however, now discuss the Lowry mechanism for the case when the reaction  $A \rightarrow B$  proceeds along the kinetic lines of a simultaneous reaction.

As a concrete example, let us take the hydrolysis of the ethers  $R_2O$ . The hydrolysis of the typical ethers is only catalysed by acids<sup>28</sup> but very reactive ethers can be hydrolysed by water alone.<sup>29</sup>

According to scheme (11) of the catalysed reaction,  $K$  represents then the hydrogen ion (which for simplicity we will write as  $H'$  not  $OH_3^+$ —a matter of no importance for the moment) and  $M$  is the water molecule. Moreover  $Z_1$  is the oxonium ion  $R_2OH^+$  and  $Z_2$  the undissociated oxonium hydroxide  $R_2OH(OH)$ , i.e. its *Zwitterion*.

For the hydrolysis carried out by water alone and uncatalysed we have :



which according to scheme (11) coexists with the acid hydrolysis. The last reversible reaction of scheme (15) as is known by experience goes so rapidly that the equilibrium is always maintained.

<sup>28</sup> Cf. A. Skrabal and O. Ringer, *Monatsh. Chem.*, **42** (1921), 9; A. Skrabal and A. Schiffrer, *Z. physik. Chem.*, **99** (1921), 290; A. Skrabal and H. Airildi, *Mobath. f. Chem.*, **45** (1924), 13.

<sup>29</sup> A. Skrabal and M. Baltadschiewa, *Monatsh. f. Chem.*, **45** (1924), 39 and 95.



We have then for the uncatalysed reaction again three cases to consider :

Case (i). The formation of  $Z_1$  determines the velocity :

$$\frac{d[B]}{dt} = k_6[A] \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Case (ii). The decrease of  $Z_1$  or the formation of  $Z_2$  is decisive :

$$\frac{d[B]}{dt} = k_3[Z_1] = k_3 \frac{k_6}{k_7} \cdot \frac{[A]}{[OH']} = k_3 \frac{G_3}{w} [A][H'] \quad . \quad . \quad (17)$$

Case (iii). The decrease of  $Z_2$  is the determining factor :

$$\frac{d[B]}{dt} = k_5[Z_2] = k_5 \frac{k_3}{k_4} \frac{[Z_1]}{[H']} = k_5 \frac{k_3}{k_4} \cdot \frac{k_6}{k_7} \cdot \frac{[A]}{[H'][OH']} = k_5 \frac{G_2 G_3}{w} [A] \quad (18)$$

Since in the case of the uncatalysed reaction the equation is :

$$\frac{d[B]}{dt} = k_w[A] \quad . \quad . \quad . \quad . \quad . \quad (19)$$

case (ii) is excluded, but on the other hand cases (i) and (iii) are consistent with equation (19) and are therefore possible.

The velocity equation for the simultaneous reactions is as follows :

$$\frac{d[B]}{dt} = k_w[A] + k_a[H'][A] \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and with this our equations (12), (13), (14), (17), (18) and (19) should coincide. The comparison of these equations as well as of the equations which can be deduced for the three simultaneous reactions (1) gives two possibilities :

*Possibility (a).* The intermediates of Lowry's mechanism are of the van't Hoff type and equations (12) and (16) serve in the case of all simultaneous reactions; the measured velocity is that at which the first of the intermediates ( $Z_1$ ) is formed. This assumption is the simplest, for in this way the interpretation of the time relationship is uniform for all cases of the change  $A \rightarrow B$ .

*Possibility (b).* The intermediate bodies are of the Arrhenius type. If the velocity with which the first intermediate  $Z_1$  reacts be measured in the case of the reaction accelerated by acids or bases, equation (13) is of value. In the case of an uncatalysed reaction, however, the velocity is determined by the transforming of  $Z_2$  according to equation (18). This possibility is not at all definite for it depends upon whether the reaction is catalysed or uncatalysed, but it lies well within the region of possibility. We merely observe that catalysed reactions are more rapid than uncatalysed ones. The more sluggish a process is, the more readily can one detect the equilibria which determine the velocity of the whole. In the case of rapidly catalysed reactions we are concerned only with the first equilibrium (that which leads to  $Z_1$ ), in the case of the more sluggish uncatalysed reaction the equilibrium leading to formation of  $Z_2$  is also involved.

The ambiguity of the time relationship is therefore not done away with, if a secondary effect is attributed to the time relationship (1) for the reaction.

From the purely kinetic standpoint I see on consideration only one criterion, and that is the suitability of assumption (a) according to which the *formation* of the intermediate body is the determining factor as to velocity. For experience shows that the reaction velocity of most of the acid and base catalysed processes can be better represented if one substitutes in equation (1) in addition to H-ion and OH-ion the corresponding terms for the proton-donors and -acceptors. With the exception of the equilibrium



of the typical pseudo-acids the dissociation equilibria of the acids and bases and the hydrolysis equilibria of their salts are established with the greatest rapidity. If then assumption (b) is correct the dissociation equilibrium of the acids and bases are added to the above-mentioned equilibria of the intermediate bodies  $Z_1$  or  $Z_2$ ; we can deduce the effect of the former alone, from the effect of the hydrogen ion concentration equilibrium, by which also the equilibrium concentration of the hydroxyl ions is given.

An example will make this clear. Let us assume a reaction  $A \rightarrow B$  catalysed by acids, which takes place in solution of the weak acid HS and its salts. For greater simplicity let it be assumed that it takes place under the "buffer condition," *i.e.* that the concentration of  $H^+$  is very small in comparison with that of acid and salt. We have then the following equilibrium:

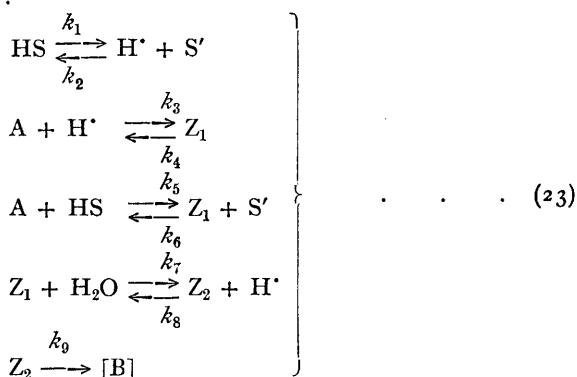


and for  $[H^+]$  the equation

$$[H^+] = \frac{k_1 [HS]}{k_2 [S']} = \delta \frac{[HS]}{[S']} \quad . \quad . \quad . \quad (22)$$

wherein  $\delta$  is the dissociation constant of the acid HS,  $[HS]$  the concentration of the weak acid and  $[S']$  that of its salt.

The stage-by-stage reactions of the catalysis mechanism are according to Lowry, as follows:



If we make assumption (a), whereby  $Z_1$  is a van't Hoff intermediate, we get the kinetic equation of two simultaneous reactions:

$$\frac{d[B]}{dt} = k_3[H^+][A] + k_5[HS][A] \quad . \quad . \quad . \quad (24)$$

wherein  $H^+$  is defined by equation (22).

If on the other hand we make assumption (b), whereby  $Z_1$  is an Arrhenius intermediate, we find only the time equation of a simple reaction (without simultaneous reactions) in which we can define the concentration of  $Z_1$  in the equation of the critical reaction (*i.e.* that one which determines the velocity of the whole) in an arbitrary manner by the equilibria:

$$\begin{aligned} \frac{d[B]}{dt} &= k_7[Z_1] = k_7 \frac{k_3}{k_4} [H][A] = k_7 \frac{k_5}{k_6} \frac{[HS]}{[S']} [A] \\ &= k_7 \frac{k_5}{k_6} \cdot \frac{k_2}{k_1} [H^+][A] = k_7 \frac{k_2 k_5}{k_4 k_1} \frac{[HS]}{[S']} [A] \quad (25) \end{aligned}$$

It is of no great importance that the process  $A \rightarrow B$  can be somewhat more readily written by introducing into the equation all the proton-acceptors and proton-donors; for a better conformity with the time relationship must necessarily go hand in hand with the multiplication of the constants. The fact, however, that reactions, such as the catalysis of nitramide measured by Brönsted, are known which cannot be portrayed by the three terms of equation (1) (and for whose representation it is necessary to introduce, in addition to  $H^+$  and  $OH^-$ , the other proton-acceptors and proton-donors present in the solution) suggests that assumption (a) alone is appropriate. The fact that several reactions can be sufficiently accurately described by means of the three terms of equation (1) proves that in aqueous solution hydroxonium-ion is the most effective proton-donor and hydroxyl-ion the most effective proton-acceptor.

From the form of the velocity equation of the underlying reactions of acid and basic catalysis we must conclude that the first stage of the reaction, the formation of the intermediate body  $Z_1$  of Lowry's scheme is the important one in determining the velocity of catalysed and uncatalysed reactions.

The observations which Lowry has made with regard to the intramolecular character of the changes involved in the molecular transformation  $A \rightarrow B$  lead necessarily to the same conclusion. We are concerned in this case with the individuality and delicacy of the reaction mechanism, which can hardly be given expression in our kinetic reaction scheme.

Lowry's theory is an electrolytic theory of catalysis, according to which the proton-donor attaches itself to one of the points of attack of the changing molecule, immediately thereafter the proton-acceptor attaches itself to the other, and there flows through the molecule from the one to the other point of attachment an electric current in the form of migrating valency electrons. The explanation of the short life or instability of the intermediate compounds is to be found in the rapidity with which these events follow upon one another.

The Lowry theory consists in a re-animation of the conception of A. de la Rive and H. E. Armstrong,<sup>30</sup> according to which, in order to bring about a chemical reaction, it is essential to use a system analogous to a galvanic chain. "Die ganze Materie ist ein elektrisches Phänomen." In these words of H. A. Lorentz it is implied that the transformation of matter, the chemical reaction, is also an electric phenomenon.

### Summary.

An explanation of acid and basic catalysis has been sought in the theories which have been advanced from the standpoint of chemical kinetics.

In all theories it is assumed that acid and basic catalysed reactions proceed through the formation of unstable intermediate bodies.

It has been shown that, from the kinetic point of view, two types of unstable intermediate bodies are postulated: the Arrhenius type which are in chemical equilibrium with the initial materials and the van't Hoff type which is not controlled by this equilibrium. The latter is of greater instability than the former.

It has been shown that Lowry's electrolytic theory of catalysis accords best with experimental facts, and that the intermediate bodies postulated by this theory are of the van't Hoff type.

<sup>30</sup> See J. W. Mellor, *loc. cit.*, page 273 *et seq.*

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