CATALYTIC ACTIONS*

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The voluminous literature and the frequent discussions of catalysis have made us aware of both the scientific interest and the technical importance of catalytic processes. The subject of catalysis has so grown that it is no longer self-contained. Even the chemical reactions and processes in living tissues may in one sense be termed catalytic. It would be impossible in the course of a brief discussion even to sketch the various ramifications into which catalytic processes intrude and it therefore seems most suitable to discuss in some detail the various views which have been expressed with respect to the mechanism of the simpler reactions. Even in this limited section of the subject there is ample provocation to discussion, and I assume that it is the function of the opening address at an extended meeting of this kind to provoke and initiate discussion.

CONTACT CATALYSIS

If we direct our attention to even one simple case we will find that we are only at the beginning of a proper understanding of molecular reactions. On examination of the processes of hydrogenation and dehydrogenation of such substances as ethylene or aldehyde and their products we note that over a great range of pressures the process of dehydrogenation is a zero order reaction whilst in hydrogenation there is an optimum ratio to the partial pressures of the reactants. For a number of dehydrogenating reactions the critical energy increment is constant provided that the surface remains unchanged.

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I can refer to the value of $\epsilon = 22{,}000$ cal./gram mol for the dehydrogenation of a series of alcohols for copper, to the values of $\epsilon = 9800$ for nickel, $\epsilon = 15{,}700$ for palladium, $\epsilon = 19{,}000$ for platinised charcoal and $\epsilon = 18{,}500$ for platinum on charcoal in a variety of dehydrogenating processes such as the decomposition of hexahydrobenzene, decahydronaphthalene and piperidine. If we include the decomposition of formic acid we find $\epsilon = 22{,}000$ for platinum black, $\epsilon = 31{,}000$ for silver, $\epsilon = 25{,}000$ for gold and the exceptional value of $\epsilon = 39{,}000$ for palladium.

Whilst a large variety of metals are available for dehydrogenating processes it has been suggested that limits are imposed only by the size of the atomic radius which must lie between 1.23 and 1.39Å.[1] We may note in addition that the hydrides are unstable and are more akin to LiH rather than to HCl. In addition we know that in general the chemical changes produced at the catalyst surface, at not too elevated temperatures, are confined to certain localized areas or patches, but at high temperatures all or a large fraction of the total surface is active. These low-temperature active patches are associated with instability of surface, large energy changes, and long lives of adsorbates. These are the experimental facts and any theoretical treatment of the mechanism must embrace these.

It will be, I think, not disadvantageous to give a brief outline of the views that have been put forward to explain the reactions and to enquire how far these alternative suggestions can be reconciled with all the experimental data that have been established. Faraday's original view involved two assumptions, a multimolecular adsorbed film and a diminution in forces normally preventing chemical action. The existence of multimolecular films, except in gel-like materials (where film-formation can scarcely be said to occur) is now known to be a very rare occurrence and we are confident that reaction, except perhaps in combustive and chain processes takes place at the

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[1] It is interesting to note the following sequence in the data of Remy and Schaefer (*Z. anorg. allgem. Chem.* **136** (1924) for hydrogen-oxygen combination on (a) H_2-treated metals: Os > Pt > Pd > Rh (increasing σ); (b) O_2-treated metals: Ir > Pd > Pt (decreasing σ)

surface of the catalyst. A union of the adsorbate with adsorbent would, by rendering the molecules more complex, effect automatically an increase in the fraction of the collisions causing activation as has recently been shown by Christiansen, Hinshelwood, Fowler and myself. This union, to follow the early conceptions of De le Rive and the more recent views of Sabatier, is identical with that in forming definite chemical compounds. A modification of this view has been expressed in that a number of different types of compounds or hydrides are formed, each one capable of effecting different hydrogenations such as of benzene, a double bond or nitrobenzene. Some of the formulas proposed based upon bulk analyses are of course somewhat extraordinary. I do not think this concept of activation by collisions of the second kind of complex molecules formed by union of adsorbate and adsorbent effected by either adsorbate or substrate molecules can be regarded as adequate; for, *per se* it gives no explanation for the existence of active and inactive areas nor for the variation in the critical energy increments for different substrates.

The simplest hypothesis to adopt, if one does not seek for a formulation of the type of union between adsorbent and adsorbate is to assume adsorption of the molecule and that on suitable portions of the catalyst or at high temperatures the molecule is stretched and as a result of such stretching it undergoes activation. We shall return to this view later. At the limit of such extension dissociation into radicles or atoms is effected. Some investigators take the extreme view that activation only results when this limit is attained. There appears to be but slender evidence for this hypothesis. The much sought after atomic hydrogen in hydrogen palladium has not been discovered, whilst in view of the readiness with which cold metals adsorb hydrogen atoms and their ease of formation at hot surfaces the identification of hydrogen atoms on the plate of a thermionic valve cannot, I think, be regarded as conclusive proof that dissociation has been effected by the cold metal plate. Whilst hydrogen atoms can be identified in a number of surface actions it is difficult to bring evidence to prove that they are not the residuals of a prior chemical action taking place between excited molecules.

Adsorption by electric forces

A number of valuable suggestions have been made to the effect that adsorptive compounds are formed which possess definite electrical structure. It is not difficult to calculate the heat of adsorption for a gas when it consists of dipolar or linear quadripolar molecules, on the assumption that adsorption is effected by attraction into a surface by the mirror image of the molecular electric moment in the substrate material of definite dielectric constant. We may note, however, that this view does not give good values for the relative heats of adsorption on materials of different dielectric constants[2] and that the absolute values are small and constant, thus giving no interpretation for the observed variation in the heat of adsorption with the configuration of the surface.

Again we find expressed in the literature that adsorption is a surface phenomenon caused by the existence of positive and

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[2] For example the heats of adsorption of argon, nitrogen, and methane on mica and uniform carbon in ergs per molecule are

	Mica	Carbon
	ergs. 10^{13}	
A	2.48	0.48
N_2	2.23	1.03
CH_4	3.36	1.11

If the heats of adsorption were due entirely to the loss of potential energy due to the movement of a dipole into an equilibrium position in respect to its mirror image, the ratios of the heats of adsorption on carbon and mica should stand in the ratio

$$\frac{Q_{\text{mica}}}{Q_{\text{carbon}}} = \frac{\dfrac{K_m - 1}{K_m + 1}}{\dfrac{K_c - 1}{K_c + 1}}$$

If K_c is taken as large and K_m given the usual value of 6 we obtain for the ratio $\frac{Q_{\text{mica}}}{Q_{\text{carbon}}} = \frac{5}{7}$. It is clear that K_m should have values lying between 3 and 5 to effect agreement between the experimental values and those calculated on this hypothesis.

negative ions already present in the surface of the adsorbent. In its simplest form it is supposed that one atom in the surface of a metal has lost an electron and on adsorption of a hydrogen molecule a molecular hydrogen ion is formed. This idea may be expressed in the form.

$$M^+ + H_2 \rightarrow MH_2^+ \qquad M' + C_2H_4 \rightarrow MC_2'H_4$$

Several arguments may be advanced in favor of the view that ions are formed on adsorption on the active portions or on non-active areas at high temperatures. We may note the enormous chemical reactivity of charged ions in the gas phase. Thus N^+ and N^+_2 react readily with hydrogen to form ammonia. CO^+ decomposes to form CO_2 and carbon. Many such reactions have been investigated by means of electron and as Lind has shown by α particle collision. Again we may observe in many surface reactions, especially oxidations on hot wires, the copious emission of positive and negative ions which are imagined to be those which have escaped from the adsorptive layer without combination, on the assumption that the ionic form is the normal state in the layer. Finally it has been stated that with palladium electrodes an ethylene hydrogen cell can be constructed and that the free energy of hydrogenation can be measured with tolerable accuracy by this method, the reactions assumed are

$$\left.\begin{array}{r} H_2 \rightleftarrows 2H \rightleftarrows H^+ \\ C_2H_4 \rightleftarrows C_2H_4' \end{array}\right\} C_2H_6$$

The close parallelism between thermionic emission and chemical reaction at surfaces first noted by Thompson and later by Langmuir has frequently been commented upon. There are likewise experiments indicative of the non-uniform character of the thermionic emission from surfaces as well as a lower work function associated with amorphous surfaces or a layer of amorphous material on a crystalline surface. The Schottky electron emission likewise appears to be confined to spots on the surface; these spots of low work function may be the active patches of low temperature catalysis. In spite of these arguments I do not think that the ionic view is tenable in this simple form. This can be shown by studying the reactions of hot wires with oxygen or the halogens to form volatile compounds. Langmuir showed that the oxidation rate of tungsten followed a simple unimolecular law. He assumed the existence of a number of free electrons in the metal, some of which would combine with the oxygen molecules on the surface. If we modify this view so as not to accept the view of the existence of numerous free electrons in a metal we find that the critical energy increment is closely approximated to by the difference between the thermionic work function of the metal and the electron affinity of the reacting gas.[3] It is

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[3] Langmuir showed that the critical energy increment for the surface oxidation of tungsten was 0.6 volts; in our laboratory the value for the analogous process on platinum has been found to be 2.3 volts.

The thermionic work functions for the two metals are

	Platinum		Tungsten
Richardson	5.65v.		
Deininger	5.02	Langmuir	4.25
Wilson	6.0	Smith	4.46
Mean best value	5.5v.	Best value	4.25

If the critical energy increment E of the surface oxidation be the difference between the work function ϕ of the metal and the electron affinity of molecular oxygen Er we obtain

$$E = \phi - Er$$

For Platinum $2.3 = 5.5 - Er$, where $Er = 3.2$ volts,
For Tungsten $0.6 = 4.25 - Er$, where $Er = 3.65$ volts,
For oxygen there is ample evidence for the existence of O_2' and it is probable, according to Mackay, that the normal molecule has an electron affinity of about 3.5 volts, a value in good agreement with the above.

For halogens it appears from Langmuir's work that they are first thermally dissociated and the atoms then attack the metal. The total energies required for the reaction are for dissociation: Cl_2, 5.2v at 1000°C.; Br_2, 2.02; I_2, 1.51. The electron affinities are: 4.1, 3.8, 3.5.
This gives E values on platinum for the reaction, $X_2 \rightarrow X \rightarrow PtX$, of Cl_2, 6.6; Br_2, 3.72; I_2, 3.51; and on tungsten of Cl_2, 5.35; Br_2, 2.47; I_2, 2.26 volts. The E values for halogen atoms are much smaller, viz.:

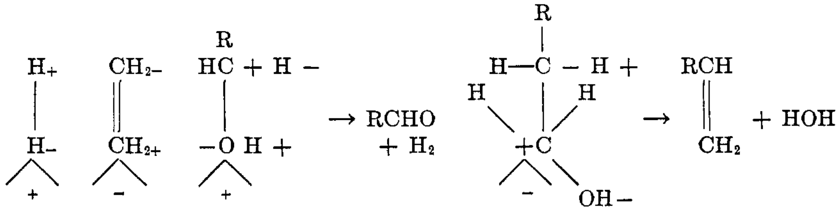
	Cl	Br	I
Pt	1.4	1.7	2.0v
WO	0.15	0.435	0.7v

showing that reaction will take place rapidly even at low temperatures.

It is interesting to note in this connection that Davy in 1807 (Phil. Trans.) showed that negatively charged zinc could not be oxidized and that silver becomes oxidizable on acquiring a positive charge.

clear that all the reacting gas is not present on the surface as ions, but the molecules are only converted to ions after the supply of a certain amount of energy as measured by the critical energy increment. Again, although Thompson many years ago showed that reactions between hydrogen and oxygen on a platinum wire became vigorous at the temperature at which the thermionic emission *in vacuo* became marked, rapid combination can occur at the surface of many metals at very low temperatures. Finally the rate of hydrogen-oxygen combination greatly exceeds the rate of metal oxide formation, an indication that the oxygen need not pass through the oxide form to ensure reaction with hydrogen.

There remains finally one other view which merits some attention, which also involves the existence of or induction of positive and negative charges on the surface of the adsorbate, viz., the polarization of molecules on adsorption and the entry of adsorbate molecules within the double layer on the surface of the adsorbent. These polarized molecules are assumed to be chemically reactive. It is a simple matter to construct the usual kind of picture to indicate the ideas underlying this view, such as:



It seems probable that the readiness with which a gas is adsorbed is dependent on the magnitude of its electric moment, but the mechanism of attraction on metals cannot involve the simple mirror concept. It would appear that in catalytic surfaces the adsorbate must enter the field exerted by the surface[4] and we

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[4] If the free surface energy of a material σ is due to the electrostatic energy of its surface energy of its surface dipoles it has shown that $\sigma = \frac{9V^2}{80\pi r}$ where V is the potential for photo electric emission. For mercury $V = 4.2$ volts, $r = 1.4$ A°, whence $\sigma = 472$ dynes per cm. (observed $\sigma = 465$).

must have the presence of natural or induced dipoles which are characteristic of the metal or other catalyst and which depend on the texture as well as the nature of the material. Some evidence for this view can be obtained from other sources such as in the behavior of metallic beams impinging on cold surfaces originally examined by Wood, Langmuir and Frenkel. The evidence is fairly conclusive that duplets or small aggregates of atoms on a plane surface not only evaporate less freely than single atoms but also exert a marked local field. It may be observed that if Frenkel's concept of a solid metal as a system in which the valency electrons whilst never free are in continuous movement from atom to atom be correct, we obtain a simple mechanism for the formation of dipoles possessing both electrostatic and electromagnetic moments in pairs of atoms resting on the surface.

Thus the surface where adsorption takes place on a catalyst on this view would consist of fluctuating systems of electric moments of various magnitudes which are dependent on the closeness of atom packing and elevation above the mean surface of the catalyst, and the presence of true promoting atoms.

Molecular deformability

On adsorption a distortion of the adsorbed molecule takes place. This may be an actual expansion, but deformation resulting in an increase in the electric moment P may or may not result in an increase in the value of the mechanical moment J, as it does not necessarily follow that on excitation of dipolar molecules with small P values any corresponding movement in the spacing of the atomic centers takes place. From the following data it will be observed that in some cases J decreases as P increases.

	Moments of		
	N_2 10^{-40}	CO 10^{-40}	S_2 10^{-40}
Unexcited (fine structure of band)	3.59	17.83	12.6
Excited	3.33	14.23	13.8
from vapor pressure	2.82 S	3.06 S′	

S is the symmetry number in the expression for the chemical constant

$$i = \lg \cdot \frac{(2\pi m)^{\frac{3}{2}}\, 8\, \pi^2\, J\, R^{\frac{7}{2}}}{5\, h^5}$$

Again, in the case of sodium chloride Reis has noted on the assumption that the condition of equilibrium of the salt molecule both in the gas phase and in the lattice is given by the expression $\frac{d}{dr}\left(\frac{e^2}{r} - \frac{B}{r^9}\right) = 0$ that r is smaller in gaseous NaCl than in the lattice where the deformation is greater.

The conditions of activation on adsorption thus necessitates a dipole of sufficient electrostatic or electromagnetic moment on the surface, the existence of an electrostatic moment in the absorbate,[5] and a readiness for the molecule to undergo deformation. We may note that the deformability of a molecule has been defined by Born in the expression $\alpha = \frac{P}{\epsilon}$ where P is the electric moment of the dipole in an electric field of intensity ϵ. The value of α for a reactant should be the factor on which ease of activation is dependent. The classical method for the calculation of α is from the refractivity $\alpha = \frac{3}{4}\frac{n^2 - 1}{n^2 + 2}\frac{M}{\pi N}$ and the value obtained in this manner can in many cases be compared with those determined from the conditions of crystal

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[5] There is a very considerable difficulty in the case of hydrogen. Generally this gas is treated as a simple dipole and numerous workers such as Reiche, Planck, Ehrenfest, Schrödinger, and Kemble have derived specific heat curves on the basis of various *a priori* probabilities and the exclusion of certain quantum states, and from these curves have obtained an estimate of J, the rotational heat, $\frac{C_r}{R}$, being a function of the temperature. The best value with the observed data is $J = 2.095 \cdot 10^{-41}$ gr.cm² (Reiche); but this does not agree with data, e.g., from pressure, $J = 0.1 \cdot 10^{-40} S$, where S is the symmetry number,– or with the value from the line spectrum, $J = 4.5 \cdot 10^{-41}$. Arbitrary suppression of specially chosen states (Schrödinger) improves matters but the process appears artificial. Dennison's more recent hypothesis of hydrogen existing as a mixture of two gases with different properties although not very intelligible as a physical conception, does in fact give an excellent value for J.

equilibrium, from electrostriction or from the temperature coefficient of the dielectric constant.

We find for example the following values for α in the two oxides of carbon:

		α	P
CO	from structure	1.10 10^{-24}	1.18 10^{-20}
	from refractivity	1.73 10^{-24}	
CO_2	from structure	0.46 10^{-24}	1.42 10^{-19}
	from refractivity	1.43 10^{-24}	

It is clear that carbon dioxide possesses a large electric moment and is thus readily adsorbed but its deformability, and thus its ease of excitation is on the whole somewhat less than carbon monoxide.

The various mathematical problems connected with the question of dielectric constant and temperature such as were originally formulated in the Langevin-Debye expression for susceptibility and temperature seem to be most readily developed by methods of the De Broglie-Schrodinger wave mechanics.

Ultimate disruption of a dipole naturally leads to the formation of ions, not of atoms, and thus the ions observed in surface reactions, especially at high temperatures, may be not only, as Haber suggests, the by-products of a chemical reaction, nor, as Brewer believes them to be, a few which have escaped from the cycle by which the whole surface action operates, but may actually consist of a few molecules which have been ejected by thermal agitation after adsorption on suitable portions of the surface where the gain in potential energy on adsorption is higher than the limiting lower value at which the surface action may progress. It is indeed possible that the character of the surface action changes when the temperature is sufficiently elevated for this ejection of ions to proceed, and we obtain a transition from a surface to a chain reaction, a phenomenon readily noted in the hydrogenation of oxygen or even better of bromine at a platinum surface.

One other point I might allude to in this consideration of electric moments. By examining the modification of an air liquid interface potential by the introduction of a unimolecular film on the surface Guyot and later Frumkin following Guyot's method, as well as Smythe, from determination of the refractive index, came to the conclusion that electric moments could be assigned to a number of so-called polar groups $-OH$, $-COOH$ and the like. Now the very interesting property of residual charge, as well as the energy loss in dielectrics under the influence of an alternating field appears to be associated with substances possessing electric moments or capable of acquiring such when minute displacements take place. This energy is not released immediately but only slowly.

The observations suggest that the act of adsorption proceeds isothermally and the adsorbed molecule is still in possession of the potential energy lost in falling into the surface. Such adsorbed molecules are thus potentially reactive until they loose their potential energy with the evolution of heat, the heat of adsorption. That this thermal evolution occurs but slowly when the surface is sparsely covered is an indication that the means of conversion of the potential energy into kinetic is either by collision with adsorbed neighbors as imagined by Garner or by isochronic induction in its neighbors as indicated from Perrin's work on fluorescence. It may be noted, however, that on adsorption of gases on substrates such as carbon, the substrate undergoes expansion and the energy changes of such should be investigated before definite conclusions can be drawn from heat evolution measurements.

REACTIONS IN SOLUTIONS

One of the most interesting developments in reactions in homogeneous systems has been the regularity with which reactions appear to conform to the ideas of Bjerrum and Brönsted on the mechanism of such actions. You will remember that with the breakdown of the simple formulation of the reaction velocity in solution as a function of the concentrations of the reactants, i.e.

$$\frac{dx}{dt} = K\,(A)\,(B)$$

the activity concept of G. N. Lewis was introduced by McC. Lewis and Scatchard in the form

$$\frac{dx}{dt} = K\, f_A(A)\, f_B(B)$$

where f_A f_B are the activity coefficients of the reactants. Close investigation showed that whilst this formulation appeared to be correct for certain reactions, e.g., the decomposition of hydrogen peroxides by hydrochloric acid it was certainly not generally true. Brönsted and Bjerrum suggested that the mechanism of reaction involved the formation of an "association complex" or "quasi-compound." This complex it was suggested could either revert back to the original reactants with which it was in mass equilibrium or could undergo reaction at a rate proportional to its concentration. We can thus formulate our reaction mechanism in the form

$$\frac{dx}{dt} = K(AB)$$

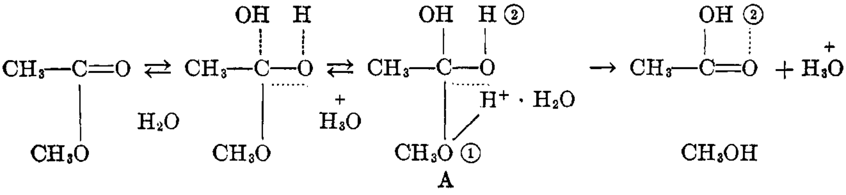
Since by the mass law $\frac{f_A(A)\, f_B(B)}{f_{AB}\, (AB)} = K$ the equilibrium constant, we obtain

$$\frac{dx}{dt} = K\, \frac{f_A(A)\, f_B\, (B)}{K\, f_{AB}}$$

an expression different from that suggested by W. C. McC. Lewis and Scatchard, but closely approximating to it if f_{AB} the activity coefficient of the complex is the activity coefficient of an uncharged complex for as Brönsted has shown experimentally and as the work of Milner, Debye and Hückel has indicated the magnitudes of the activity coefficients are dependent chiefly on the charge on the particular molecular species.

The recent investigations of Dawson can be shown to conform to this concept, but in addition we can draw the inference from his work that in reactions catalysed by oxonium and hydroxyl ions specific catalytic activities can be ascribed to all oxonium ion "donators" and oxonium ion "acceptors" to adopt

Wieland's nomenclature. Thus in the case of catalysis by means of dilute aqueous acetic acid specific catalytic activities may be ascribed to the following, the oxonium ion donators H_2O, CH_3COOH, H_3O^+ and the oxonium ion acceptors OH', CH_3COO'. The original dual theory of Snethlage has by now undergone a very considerable extension. It is not, I think, necessary to postulate in say the hydrolysis of an ester by a dilute acid that an oxonium ion is "donated" at the identical moment that another one is "accepted" but the reactions present interesting features as can be noted from the following sequence.



$$\underset{CH_3O}{CH_3-C=O} \underset{H_2O}{\rightleftarrows} CH_3-\underset{CH_3O}{\overset{OH\quad H}{C-O}} \underset{\overset{+}{H_3O}}{\rightleftarrows} CH_3-\underset{\underset{A}{CH_3O\,\textcircled{1}}}{\overset{OH\quad H\,\textcircled{2}}{C-O}}\; H^+\cdot H_2O \rightarrow CH_3-\underset{CH_3OH}{\overset{OH\,\textcircled{2}}{C=O}} + \overset{+}{H_3O}$$

It will be noted that the reaction involves the addition of one hydrogen ion (1) and the removal of another (2) effected by the passage of an electron from (2) to (1). We must remember that the complex (A) is the critical complex or quasi compound and is consequently capable of reversion to ester and oxonium ion. Whilst we may regard the action of hydrolysis as a species of conduction or even of electrolysis if this is not straining the views of Professor Armstrong unduly, we do not yet know what conditions the forward or reverse change, if hydrolysis occurs at some crisis in the molecular movements or if the supply of the energy of activation affects not the concentration of quasi-compound but its fragility. It is clear, however, that if either of these views be correct the quasi compound (a) must have an objective existence even if present in subanalytical amounts and the two steps in the process, the addition of an oxonium ion at (1) and the loss of one at (2) cannot be simultaneous processes.

Molecular induction

Perrin in the early development of the radiation theory of chemical action suggested that excited molecules would loose their energy of excitation not only by super elastic collisions as proposed by Klein and Rossland but also by isochronic induction. More recently attempts have been made in various directions to calculate the energy available when a molecule enters the field either of another molecule of definite electric moment, or the field of an ion. Such investigations have been carried out notably by Sir J. J. Thomson, Merritt and W. Taylor, with the view of examining the importance of ions and polar molecules on the rates of chemical action. The former has shown that the rate of collision between reactants A and B can be increased very considerably when either reactant is replaced by an ion, e.g., A^+ or by a compound such as bA where bA represents a primary complex between a polar molecule b and the reactant A. All such collisions are, as we know, not effective in promoting chemical action and it is important to enquire whether the critical energy increment of these reactions may be modified as well as the collision frequency by the alteration in field produced by a molecule of definite electric moment or by one ion. It is assumed that when a dipolar molecule B enters the electric field of a polar molecule b or of an ion A^+ it acquires potential energy due to the orientation of its axis to the lines of force, the moment of inertia J as well as the electric moment of B is altered and a quantity of energy ϵ will either be liberated or absorbed in this process. Merritt assumes that this energy contributes to the energy of activation. The following two simple calculations show the relative magnitudes of the energy changes effected in the two cases.

We can, on the assumption of a molecule entering the field at a distance some four molecular radii away, equate the field strength to $\frac{\mu}{(4\sigma)^3}$ or if the molecule be water and $\mu = 1.10^{-18}$ E.S.U. $\sigma = 2.3\text{Å}$, the field strength will be $1.3\ 10^3$ E.S.U., or $3.85\ 10^5$ volts per centimeter. The maximum potential energy of a molecule of moment μ_1 in this field will be $\mu_1 \times 1.3\ 10^3$ E.S.U. For a molecule like hydrogen chloride where $\mu_1 = 3.10^{-18}$ we obtain $= 3.84\ 10^{-15}$ ergs or only some 55 calories per gram molecule. This small value clearly negatives Cathala's view on the catalytic influence of water in the hydrogen chloride combination, but at the same time it shows that intense fields may be produced if the water molecule is more clearly associated with the reactant than at a distance of 4σ as assumed in this calculation. At a distance of one radius ϵ has already risen to 3000 calories per gram molecule.

If the polar water molecule be replaced by an ion we shall obtain round the ion a cluster of molecules as visualised by Langevin, Sir J. J. Thomson, Erikson and Loeb and the average potential energy of a molecule in the first shell at a distance 2.3 Å will be some 12,000 calories per gram molecule.

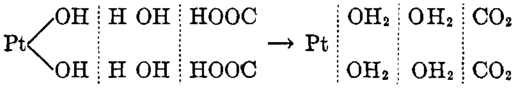
It will be observed that the possible gain in potential energy of a molecule entering the field of an ion is remarkably large and consequently marked catalytic effects might be anticipated for reactions in which ions are involved.

Oxidative processes

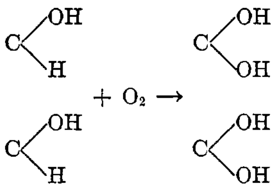
Attention is again being devoted to the mechanism of slow and rapid combustion and in view of the technical importance of explosive reactions on the one hand and of autoxidation and slow combustion on the other this renewed vigour exhibited in this field during recent years is very welcome.

It appears certain that a number of oxidations in solution are brought about on surfaces, we may mention the oxidation of oxalic and other acids on charcoal, and of benzaldehyde and turpentine on glass, pumice and similar surfaces. By the method of selective poisoning it can be shown that but a small portion of the total surface of say powdered glass is catalytically active. Many substances exert what Moureau terms an antioxygenic action by selective adsorption on these surfaces; this is true for iodine, diphenylamine and even organic acids. These oxidation reactions involve in many cases the formation of a definite and relatively stable peroxide which in the case of aldehyde peroxide undergoes reaction in the homogeneous liquid phase to the acid. It is, I think, almost certain that prior to the formation of the stable peroxide there exists another and more reactive form of peroxide which is capable of propagating chains in the sense suggested by Christiansen and Kramers. On surfaces at any rate it is very probable that typical interface reactions take place the combustion of one molecule of aldehyde on a glass surface results in the "clean up" of many molecules on the surface, by a spreading of the combustive process. On charcoals at least five different types of surface can be identified. There exists a small area which is autoxidizable and recently Ward has shown that these autoxidizable areas are identified as the areas in which Blench and Garner noted large values for the heats of adsorption of oxygen. In addition there exists catalytically active areas on which various oxidative processes as shown by Warburg and Miss Wright can take place. It is an interesting fact that the rates of oxidation on this surface for various substances at their respective optimum concentrations run parallel to the ease with which they reduce the oxygen overpotential at a platinum anode. Finally there exist two promoted areas, one associated with a complex containing both carbon and iron and another extremely active area associated with a complex containing iron, carbon, and nitrogen. These curious reactions call attention to a possible connection with the suggestions of Professor Armstrong concerning the nature of reactions as a species of electrolysis, these may be depicted formally by the following equations:

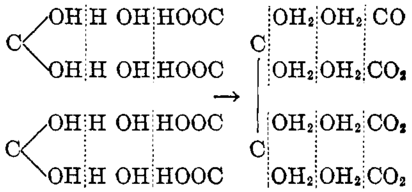
(1)



(2a)



(2b)



It must not be forgotten, however, that the existence of a carbon "perhydrol" similar to that postulated for platinum rests on somewhat slender experimental basis.

In explosive oxidations affairs are certainly more complex. We may observe in rapid oxidations such as of phosphorus vapor or of benzaldehyde vapor at high temperatures, the emission of radiation. These reactions are undoubtedly chain reactions and since in several cases emission of radiation can actually be observed it is probable that "quantum" chain reactions do occur. Further work is still required I think to demonstrate the existence of the chains formed by collision of the second kind between excited products and reactants as postulated by Christiansen and Kramers. Whilst it has been suggested especially by Egerton that peroxides play an important part in explosive reactions the view that these are formed after primary dissociation of a saturated hydrocarbon into an unsaturated one and hydrogen has taken place does not rest upon such a firm foundation and it is equally probable that peroxide formation can occur on reaction between excited molecules of the saturated hydrocarbon and oxygen. Egerton considers that the conditions determining peroxidation of oxidizable substances likewise determine the conditions for detonation. This view is at variance with that suggested from examination of the spectrum emitted during explosions of gaseous mixtures. Whilst it has long been suggested that a zone of electrons or radiation travels in front of the explosive wave and acts as an exciting agent for the inherent gas yet Garner concludes that the ionization produced during gaseous reactions is no greater than that which would normally occur due to thermal ionization at elevated temperature on the explosion. Affairs appear to be otherwise with respect to the quantity and nature of the infra red radiation emitted. In dry gas mixtures, e.g., carbon monoxide the emisson of such radiation is far greater than in wet mixtures or in mixtures which form water on combustion. The fine structure of the band spectrum indicates that excited water molecules containing both rotational and vibrational energy are the sources of the radiation. Garner regards water as an energothermic catalyst in that it absorbs radiation otherwise emitted and facilitates the distribution of energy in the system. We might represent the sequence of events somewhat as follows:

$$\text{First stage}\quad CnH_{2n+2} \rightarrow CO + H_2 + \text{other products}$$

$$\text{Second stage}\ \begin{cases} CO + O_2 \rightarrow CO_2 \\ H_2 + O_2 \rightarrow H_2O \end{cases}$$

Antiknock compounds are assumed to slow down the rate of water formation and thus permit of an increased dissipation of energy in the form of radiation.

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