Atoms and Radicals in Aqueous Media.

The Tilden Lecture, Delivered before the Chemical Society at Burlington House on February 15th, 1951, and at the University College, Hull, on March 1st, 1951.

By F. S. Dainton.

The presence in the H_2O molecule of the $(2sa_1)^2$ and $(2xb_1)^2$ non-bonding electrons of the oxygen atom combined with the non-linear arrangement of the two polar O–H linkages has many important consequences in chemistry. One of these consequences, namely, the very high capacity of liquid water to solvate ionic and polar solutes, is probably the greatest single factor determining the special features of the chemistry of atoms and free radicals in aqueous media. In this Lecture my aim will be, not to catalogue all the extensive work in this field, but rather to draw attention to certain recently developed threads of reasoning which are generally applicable, and to the slightly different patterns into which these threads may be woven to account for the observed phenomena. Such a selection of topics has, of course, been to some extent arbitrary and personal, and has certainly led to many important omissions. Some of the material is new, and I am greatly indebted to my colleagues, especially Messrs. Collinson, James, and Smith, for their help and for permission to use their data.

Methods of Detection.

1. *General.*—The majority of the radicals which have been prepared in aqueous systems are of very short life and therefore can only be detected by the stable molecules to which they give rise by chemical reaction. These reactions include all those diverse processes which are characteristic of all odd-electron species. Thus we find hydrogen atoms combining and perhydroxy-radicals undergoing disproportionation :

$$2H \longrightarrow H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Inter-radical reactions of this kind are especially favoured in water because the dissociation energy of the reaction $H_2O \longrightarrow H + OH$ (~120 kcal. in the gas phase) is so large that nearly all reactions which involve the detachment of either a hydrogen atom or a hydroxyl radical from the water are endothermic *e.g.*,[1]

$$\cdot NH_{2(g)} + H_2O_{(g)} \longrightarrow NH_{3(g)} + \cdot OH_{(g)} - 16 \text{ kcal.} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The most important exceptions to this generalisation are the thermoneutral exchange reactions (*e.g.*, $HO + H_2O \longrightarrow H_2O + OH$) discussed later. The rarity of radical–water reactions means that water is in many ways an ideal medium for studying the reactivity of radicals with other solutes. Such radical–molecule reactions are of the kind expected. For example, Weiss [2] has shown that OH radicals abstract H atoms from dissolved benzene (~ 0·01M-solution) with resultant formation of diphenyl and phenol. In addition to such *adiabatic* reactions, many radicals may act as oxidising or reducing agents by virtue of their respective capacities to accept and donate electrons in *single-electron transfer* processes. The driving force of such reactions is discussed in greater detail later, but in passing we may note that a very important part of this driving force is the free energy of hydration of the ion produced. For example, in the reduction of cations such as Fe^{3+} by hydrogen atoms

$$H + Fe^{3+}{}_{aq.} \longrightarrow H^+{}_{aq.} + Fe^{2+}{}_{aq.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the solvation energy of the H^+ ion which is formed is extremely large.[3] Because the amount of product formed in such simple reactions is limited by the stoicheiometry, these reactions can only be used for detection and estimation of small concentrations of radicals, provided a sensitive method of estimating the product is available. Usually, colorimetric methods are employed.[4] Another method of achieving the desired sensitivity is to magnify the effect of individual radicals by employing them as centres for the initiation of chain reactions. The type of chain reaction which is most productive of information concerning the initiating radical is the polymerisation of water-soluble vinyl compounds.

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[1] Based on $D_{NH_2 \ldots H(g)} = 104$ kcal., see Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 267.

[2] Weiss and Stein, *Nature*, 1947, **161**, 650.

[3] Baughan, *J.*, 1940, 1335.

[4] *E.g.*, Miller, *J. Chem. Physics*, 1950, **18**, 79.

2. *The Polymerisation Method.*—Electrophilic substituents in ethylene confer two properties on the molecule : those of enhanced solubility in polar solvents and of increased ease of addition polymerisation by the free-radical mechanism. When radicals (X) are generated in aqueous solutions of a monomer (m_1) such as acrylonitrile, methyl acrylate, or acrylic acid, the following reactions may ensue which result in the formation of an insoluble polymer

Initiation $$X + m_1 \xrightarrow{k_i} m_1^* \qquad (5)$$

Propagation $$m_1 + m_j^* \xrightarrow{k_p} m_{j+1}^* \qquad (6)$$

Mutual termination $$m_j^* + m_k^* \xrightarrow{k_t} P_{j+k} \text{ or } P_j + P_k \qquad (7)$$

Radical termination $$m_j^* + X \xrightarrow{k'_t} P_j \qquad (8)$$

In this scheme m_j^* denotes the growing polymer radical containing j segments of monomer, and P_j denotes " dead " polymer incapable of further growth. Solvent transfer can be omitted from this scheme when water is the solvent, because of the pronounced endothermic character of reactions of this type.

The kinetic chain length of the polymerisation chain, *i.e.*, the number of monomer molecules polymerised per radical X used in initiation, is very large and implies an unusually high ratio, k_p/k_t or k_p/k'_t. This result is very convenient since the kinetic chain length is the " magnification factor " to be used in estimating the concentration of the radicals. Even with very low rates of generation of radicals such as are obtained with low dose rates of ionising radiation, such polymerisations may readily be followed by dilatometric,[5] gravimetric,[6] or turbidimetric [7] methods. The initiation reaction consists of the opening of the double bond of the monomer, thereby fixing the radical X to the polymer in the form of a C–X end-group. An advantage of the polymerisation method is that the nature of such end-groups can readily be determined and the chemical nature of the radical X can therefore be discovered. Chemical methods of end-group analysis can be used, but these are generally less reliable than infra-red spectroscopic analysis of the polymer. Absorption bands present in the polymer produced by X-radical initiation which are either absent from polymers produced from pure monomers or diminish in intensity with increasing chain length of the polymer can be safely ascribed to the end-groups. In this way it has been possible to show that OH radicals are produced by the photo-dissociation of hydrogen peroxide in aqueous solution or when *X*- and γ-rays are absorbed by water.[6b] The great power of the infra-red method is evident when proof is required of the presence of hydrogen atoms derived from the solvent water. When D_2O is the solvent the polymer should contain a terminal C–D link which has a characteristic frequency at ~4·58 μ (2200 cm.$^{-1}$). Fig. 1 shows quite unmistakably that whereas polyacrylonitrile prepared by *X*-irradiation of the pure monomer does not show this absorption band, the polymer formed by irradiation of solutions of acrylonitrile in deuterium oxide does possess this band. The infra-red measurements thus

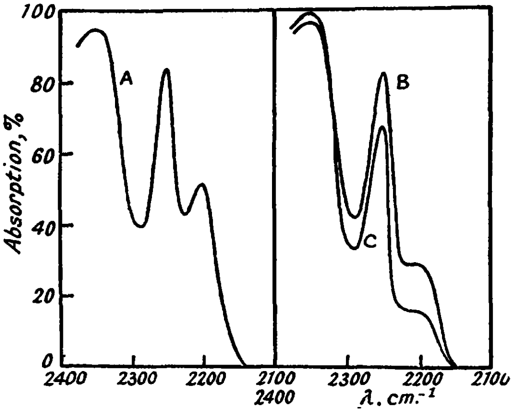

FIG. 1. *The infra-red absorption spectra in the range* 4·16—4·78 μ *of samples of polyacrylonitrile prepared by the action of* 250 kv X-*rays on acrylonitrile :* A *in solution in* D_2O, B *in solution in* H_2O, C *pure monomer. Dose rate,* 680 *r/min. The peak at* ~2200 *cm.*$^{-1}$ *is the* 4·58 μ *band due to* C–D *stretching vibration.*

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[5] Collinson and Dainton, to be published.

[6] (*a*) Dainton, *Nature*, 1947, **160**, 268; (*b*) *J. Phys. Coll. Chem.*, 1948, **52**, 490.

[7] Smith, unpublished data.

provide incontrovertible evidence of the existence of H atoms and OH radicals in water which is absorbing ionising radiation.

One of the features of the polymerisation method is that it may be used to distinguish between a system in which the radicals are uniformly distributed and one in which they are localised. As an example of the type of argument which may be employed we may consider a stationary number (x) of initiating radicals (X) uniformly distributed throughout a reaction volume V, such that the concentration (x/V) is sufficiently low to ensure that the predominant mode of chain termination is by mutual interaction of a pair of growing polymer chains [reaction (7)]. This is substantially, although not exactly, the state of affairs when H atoms or OH radicals are produced photochemically under conditions of low light extinction and low light intensity.[8] The rate of polymerisation is then given by

$$\frac{-\mathrm{d}[\mathrm{m}_1]}{\mathrm{d}t} = \left(\frac{\phi_1 I_{\text{abs.}}}{k_t}\right)^{\frac{1}{2}} k_p[\mathrm{m}_1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which ϕ_1 is the quantum yield of formation of H or OH in the act of light absorption and I_{abs}: is the absorbed light intensity. An alternative situation may also be envisaged in which the same total number of radicals (x) are non-uniformly arranged in the same total volume V. We may imagine them confined to n small, widely separated, elements of volume v, such that $nv \ll V$. The concentration in each volume element ($= x/nv$) may now be so large that radical termination [reaction (8)] predominates over mutual termination, *i.e.*, $k_t[\mathrm{m}_j{}^*]_v{}^2 < k_t[\mathrm{m}_j{}^*]_v(x/nv)$. In this case the overall rate of polymerisation will be given by

$$\frac{-\mathrm{d}[\mathrm{m}_1]}{\mathrm{d}t} = \frac{nv}{V} \cdot \frac{k_i k_p}{k'_t}[\mathrm{m}_1]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

An example of this type of behaviour when the initiation is both by H atoms and by OH radicals will be given in the next section.

In using photosensitisers of high extinction for the initiation of reaction chains, care must be taken to avoid such high rates of generation of initiating centres that radical termination becomes excessive and the polymerisation method misleading. For example, Mr. James has found that, in certain cases in which it was known from the changes undergone by the photosensitiser that hydrogen atoms were being formed, no visible polymerisation occurred. Further analysis of the problem showed that the monomer was either hydrogenated or merely converted into water-soluble short-chain polymers. That this was due to excessive radical termination was strikingly shown by reducing the sensitiser concentration a thousand-fold, whereupon insoluble polymer was freely formed, throughout the reaction vessel.[8]

Certain other precautions must be observed in using polymerisation diagnostically. The most important is to deaerate the solutions thoroughly. Oxygen may act as a powerful chain terminator by direct addition to the growing polymer chain, and is also capable of inhibiting action by destroying certain initiating radicals. For example, hydrogen atoms are removed by the reaction

$$\mathrm{H} + \mathrm{O}_2 \longrightarrow \mathrm{HO}_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and the resulting species can act as a chain terminator,[7] *i.e.*,

$$\mathrm{HO}_2 + \mathrm{m}_j{}^* \longrightarrow \mathrm{P}_j\mathrm{O}_2\mathrm{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The effect of traces of dissolved oxygen is so marked that complete eradication of induction periods due to this cause is only achieved by the most stringent conditions of deaeration. Fortunately, however, the steady rate of the polymerisation reaction is independent of the length of any induction period by which it may have been preceded.

The sensitivity of the polymerisation technique increases with increasing concentration of monomer, and the value of a particular monomer for this purpose is thus enhanced the more soluble it is in water. Acrylonitrile is particularly satisfactory from this point of view, but in one respect, namely, the marked tendency to form complexes with cations, it is somewhat unsuitable. For instance, the bivalent vanadium ion, V^{2+}, gives lavender-coloured solutions, and its electron-transfer spectrum has a long-wave absorption edge at 3500 Å (see Fig. 2). When acrylontrile is added to solutions of vanadous sulphate, VSO_4, the lavender colour is immediately

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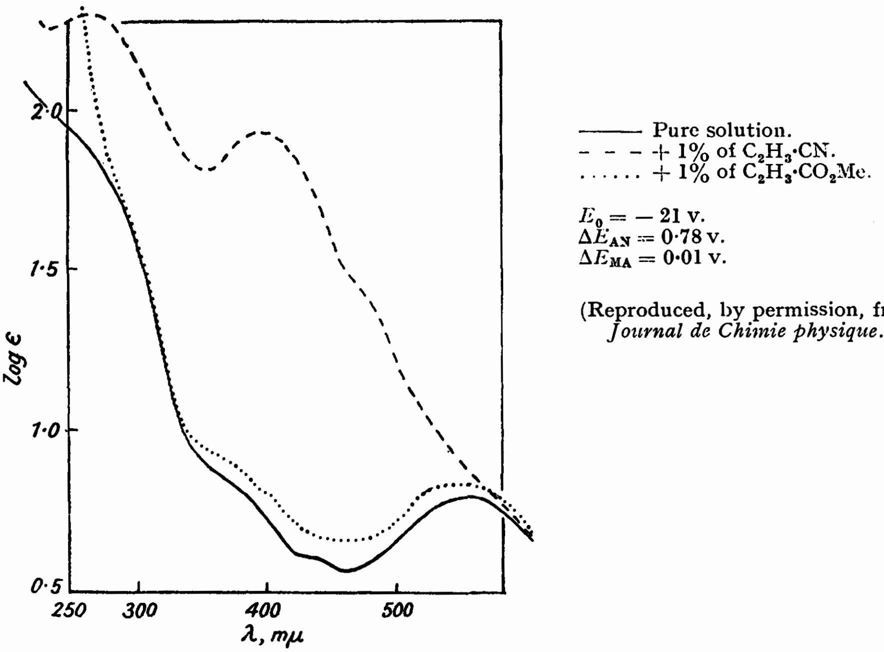
[8] Dainton and James, *J. Chim. physique*, in the press.

replaced by a brown colour similar to that of the vanadocyanide ion $[V(CN)_6]^{4-}$ and an entirely new absorption region between 3500 and 5400 Å is observed (Fig. 2). The spectrum of vanadic sulphate solutions, $V_2(SO_4)_3$, is unaffected by addition of acrylonitrile (Fig. 3). The spectro-

FIG. 2. *The effect of methyl acrylate* (MA) *and acrylonitrile* (AN) *on the absorption spectra of solutions* (0·02M) *of vanadous sulphate* (VSO_4) *in* H_2SO_4 (0·3N).



$E_0 = -21$ v.
$\Delta E_{AN} = 0·78$ v.
$\Delta E_{MA} = 0·01$ v.

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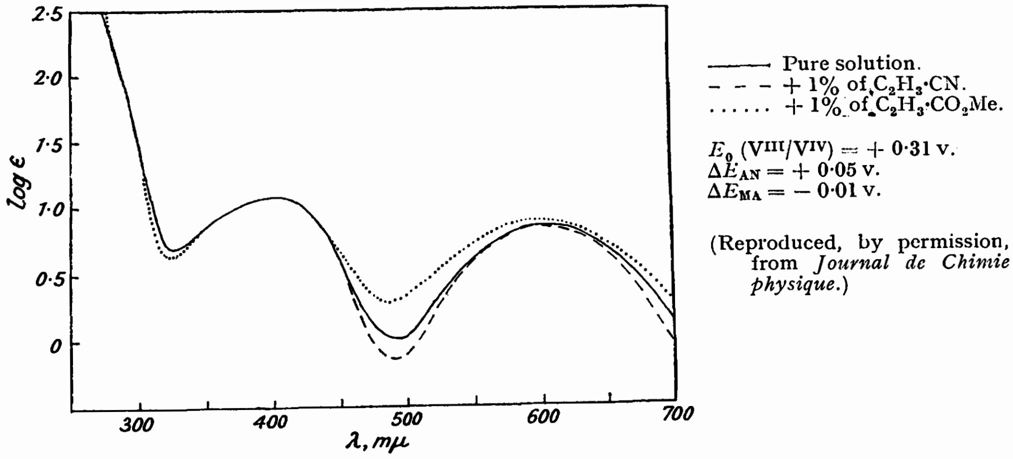
FIG. 3. *The effect of methyl acrylate* (MA) *and acrylonitrile* (AN) *on the absorption spectra of solutions* (0·01M) *of vanadic sulphate* $[V_2(SO_4)_3]$ *in* H_2SO_4 (0·3N).



E_0 (V^{III}/V^{IV}) = + 0·31 v.
$\Delta E_{AN} = + 0·05$ v.
$\Delta E_{MA} = - 0·01$ v.

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scopic evidence thus indicates preferential complexing of the monomer with the V^{2+} ion, and in accordance with this it is found that the V^{2+}/V^{3+} redox potential is shifted 0·781 volt by acrylonitrile. As may be seen from Figs. 2 and 3, no such comparable effect is produced by methyl acrylate. Such complexing has a profound influence on the production of free radicals from such ions, which is discussed in the next section.

Methods of Preparation.

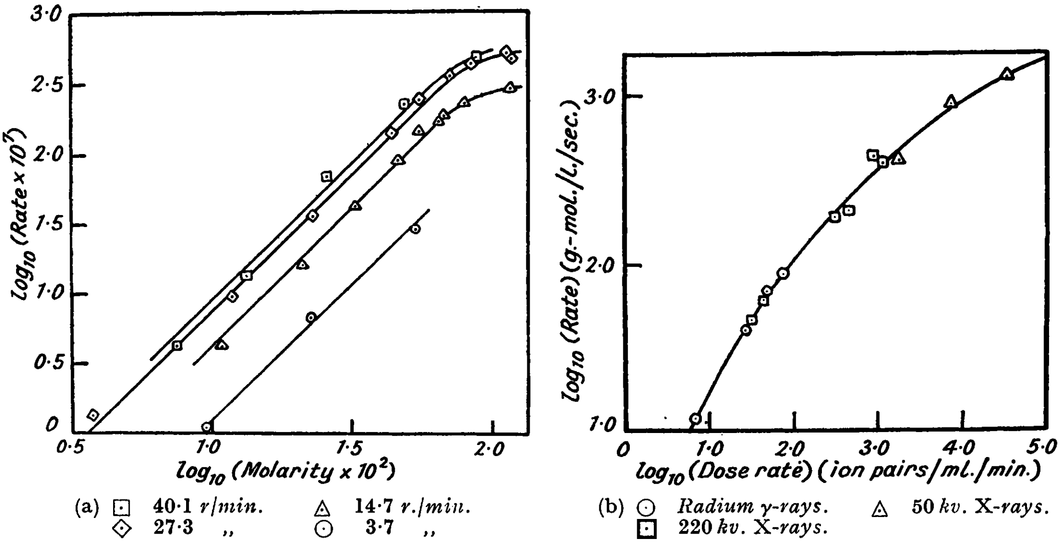
In non-aqueous media free radicals are usually formed by the decomposition of molecules either on surfaces, or homogeneously by heat, light, or other radiation. This is true in aqueous media, where, however, they may also be formed from ions in electron-transfer reactions, in which the solvent plays an important part. It is therefore convenient to discuss the formation under three main headings.

1. *From Molecules.*—The absorption spectrum of dilute solutions of hydrogen peroxide[9] consists of a continuum beginning at ~3800 Å, and absorption of light of any wave-length shorter than this can be shown to cause dissociation into hydroxyl radicals, which may initiate a chain reaction causing the decomposition of the hydrogen peroxide:

$$H_2O_2 \xrightarrow{h\nu} 2OH(^2\pi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In the presence of dissolved vinyl compounds no oxygen is evolved, but polymerisation occurs. The polymer can be shown to contain the terminal OH group,[6b] and the kinetics of the reaction at weak extinction suggest that the radicals are evenly distributed throughout the system. In contrast with photochemical systems the absorption of ionising and nuclear radiations is not only non-selective, but the products of the primary act are thought to be formed initially in the wake of the fast charged particles traversing the medium. In the case of water vapour there are substantial arguments for the view that the fast charged particles ionise some water molecules and dissociate others in inelastic collisions. Similar processes would be expected to take place in liquid water,[10] where the net radiochemical reaction might be represented as

FIG 4. *The polymerisation by* X- *and* γ-*rays of acrylonitrile in aqueous solution:* (a) *order with respect to monomer, full lines correspond to second order;* (b) *dose rate dependence.*



$$H_2O_{(l)} \rightsquigarrow H + OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Confirmation of this view is obtained by irradiation of aqueous solutions of water-soluble vinyl compounds, whereupon the H atoms and OH radicals formed by the action of the radiation on the water initiate polymerisation. It will be recalled that the infra-red evidence proves that both species are effective in this manner. The kinetics of the *X*- and γ-ray-induced polymerisation of acrylonitrile in aqueous solution are illustrated in Figs. 4*a* and *b*, from which it is seen that the rate is proportional to $R^n[m_1]^2$, where R is the dose rate and the exponent varies smoothly from 0·9 at low dose rates to 0·25 at high dose rates and is independent of the wave-length of the radiation used. This result can only be interpreted by assuming that the initiating radicals are not uniformly distributed but are confined to small volume elements randomly distributed throughout

[9] Allmand and Style, *J.*, 1930, 596.

[10] For a detailed discussion see ref. 6(*b*) and Dainton, *Ann. Reports*, 1948, **45**, 5.

the system. In each element the chains undergo radical termination, and the rate in each element is thus $k_ik_p/k'_t[\mathrm{m}_1]^2$. At low dose rates, where individual volume elements are isolated from their neighbours, the overall rate should therefore be equal to $kR[\mathrm{m}_1]^2$ where $kR < k_ik_p/k'_t$, whereas at high dose rates, above a certain minimum value at which almost every element will be overlapping with its neighbours, the rate of formation of radicals will be uniformly high over the whole system and the reaction rate will be equal to $k_ik_p/k'_t[\mathrm{m}_1]^2$. The observed change of the dose rate exponent is taken as evidence of behaviour typical of transition between these two extremes. The fact that a change of wave-length of the incident radiation does not affect the kinetics enables deductions to be made concerning the energy loss of electrons in water which it is inappropriate to discuss here.

Although the photochemical and radiochemical methods of generating radicals in water are associated with different spatial distributions of these species, the system remains single phase in both cases and the radicals are free to diffuse. Recently, Parravano [11] has shown that radicals may be produced in the absorbed phase at metal surfaces. Chemisorbed hydrogen, nitrogen, carbon monoxide, methane, ethylene, and acetylene on different metals, such as nickel, ruthenium, platinum, iron, and osmium were found to initiate the polymerisation of methyl methacrylate in aqueous solution. The efficiency of the initiation is very low, only a small fraction of the adsorbed atoms or radicals initiating reaction chains. The author proposes the initiation mechanism

$$\mathrm{MeX} + \mathrm{m}_1 \longrightarrow \mathrm{Me} + \mathrm{m}_1{}^{\bullet} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where MeX denotes the chemisorbed radical X, and the order of increasing efficiency of different radical–metal complexes MeX in initiating polymerisation has been shown to be the same as the order of increasing exothermicity of the initiation reaction, *i.e.*, $D_{\mathrm{m}_1{}^{\bullet} \rightarrow \mathrm{m}_1 + \mathrm{X}} - D_{\mathrm{Me\text{-}X}}$. Similarly, radicals formed during the catalytic decomposition of hydrazine solutions at a palladium surface or formic acid solution at platinum, palladium, or silver surfaces will also initiate polymerisation. Such studies are clearly of general interest in relation to theories of heterogeneous catalysis and of particular interest in that end-group analysis of the polymer should enable the radicals to be identified.

2. *From Ions.*—The discharge of molecular ions provides an obvious means of production of free radicals, and may be achieved either at electrodes or by an electron-transfer reaction with an ion of opposite sign. Free radicals may also be formed by the breakdown of unstable molecular ions of either sign formed from stable molecules by thermal or photochemical electron-transfer reaction with ions. The most important feature of all these reactions is that a simple means of counting the radicals so produced is available, either by measurement of the discharge current or by analytical determination of the number of ions whose state of oxidation has been altered by one unit.

Several workers have observed that cathodic discharge of hydrions at low current densities brings about the polymerisation of dissolved monomers. Parravano [11] has shown that the efficiency of this initiation reaction is low ($\sim 10^{-6}$) but increases with increasing hydrogen overvoltage at the particular metal cathode concerned. This result is readily accounted for by assuming that the initiation reaction is in competition with the recombination of the adsorbed hydrogen atoms.

Interionic electron-transfer reactions have been described by Professor Evans in a previous Tilden Lecture. If the process is purely one of electron transfer and no bonds are broken, the frequency factors for reactions between ions of like sign are generally low, and between ions of opposite sign are generally high. When the spontaneous electron transfer between ions of opposite charge is very slow because the reaction is endothermic, it is frequently possible to achieve it by photochemical means. Several years ago, Rabinowitch and Stockmayer [12] concluded from an examination of the ultra-violet absorption spectra of various salts and bases of multivalent ions that ion-pair complexes of the type $\mathrm{M}^{x+}(\mathrm{X}^{y-})$ existed in solution with varying degrees of stability, and that the ultra-violet absorption continuum with a high molecular extinction coefficient ($\sim 10^4$) was to be associated with transfer of an electron from the anion to the cation. In the case of the 1 : 1 complexes of ferric ion with univalent anions ($\mathrm{X}^- = \mathrm{OH}^-$ Cl^-, Br^-, N_3^-, SCN^-, etc.) the electron-transfer process could be represented by

$$\mathrm{Fe}^{3+}\mathrm{X}^- \longrightarrow \mathrm{Fe}^{2+} + \mathrm{X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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[11] *J. Amer. Chem. Soc.*, 1950, **72**, 3856, and private communication from Professor H. S. Taylor.

[12] Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.

Evans and Uri [13] have successfully used the polymerisation method to detect the radical X and have proposed the potential-energy diagram shown (Fig. 5) to account for the case of the $Fe^{3+}OH^-$ complex which has a heat of formation of 1·6 kcal. These authors also state that the reaction can be reversed in two ways, a *primary* dark reaction involving the radical and ion formed from the same ion-pair complex, and a *secondary* dark reaction which occurs after separation of the products and does not necessarily involve species formed from the same ion-pair complex. The polymerisation initiation reaction can compete with the secondary reaction only, and when a large excess of monomer is present the secondary reaction is completely suppressed and the true quantum yield of the forward reaction can thus be determined, and is found to be much less than unity. There is still no direct evidence as to the true nature, ionic, $Fe^{3+}X^-$, or covalent, $(FeX)^{2+}$, of such complexes, and the propriety of calling the photochemical process an electron-transfer process has therefore been questioned by Bowen.[14]

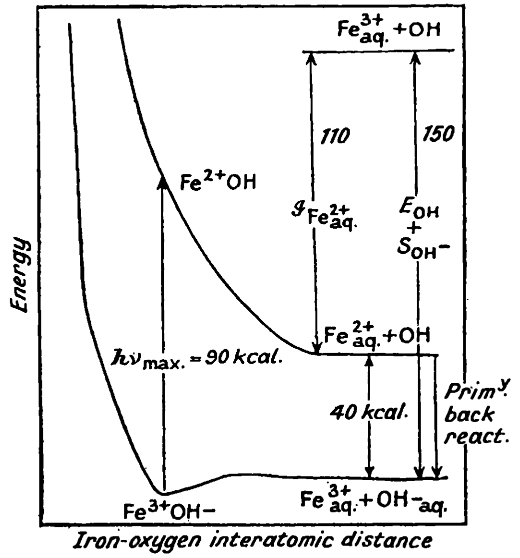


FIG. 5. *The potential-energy curves relevant to the reaction* $Fe^{3+}OH^- \longrightarrow Fe^{2+} + OH$ (taken, by permission, from Evans and Uri, *J. Soc. Dyers Col.*, 1950, 125).

When the radical is produced by rupture of a covalent bond, as for example in the formation of OH radicals by Fenton's reagent [15]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+}OH^- + OH$$

or in the interionic reaction

$$Hg^{2+} + H{\cdot}CO_2^- \longrightarrow H + CO_2 + Hg^+(\tfrac{1}{2}Hg_2^{2+}) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which James has explored by the polymerisation method,[8] the shape of the appropriate potential-energy curve resembles those for the reaction of sodium atoms with alkyl halides.[16] The essential feature of this diagram (see Fig. 6) is that the Morse curve for the dissociation of the formate ion into $H + CO_2^-$ should be intersected by a repulsive curve between the CO_2 radicals and a hydrogen atom. Intersection will only occur if the ionisation potential of the mercurous ($I_{Hg^+_{aq.}}$) is greater than the sum of the electron affinity of the CO_2 molecule (E_{CO_2}) and the solvation energy of the CO_2^- anion ($S_{CO_2^-}$). In view of the fact that the dissociation energy of the reaction $Hg_2^{2+} \longrightarrow 2Hg^+$ is likely to be low, the value of $I_{Hg^+_{aq.}}$ will be not very different from ΔH for the reaction

$$\tfrac{1}{2}Hg^{2+}_{2\,aq.} \longrightarrow Hg^+_{aq.} + e^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which can be shown from Brewer's tables [17] to be ~123 kcal. On the other hand, the other quantities, E_{CO_2} and $S_{CO_2^-}$, are unlikely together to exceed this value. The course of the reaction

[13] Evans and Uri, *Nature*, 1949, **164**, 404; *J. Soc. Dyers Col.*, 1949, **65**, 709.
[14] Bowen, *Quart. Reviews*, 1950, IV, 236. [15] *Trans. Faraday Soc.*, 1946, **42**, 155.
[16] Evans and Polanyi, *ibid.*, 1938, **34**, 11. [17] National Nuclear Energy Series IV—19B, 76 (1950).

is then described by the broken line in the figure, from which it may be seen that a minimum value for the energy of activation is

$$D_{\mathrm{H}\ldots\mathrm{CO}_2} + E_{\mathrm{CO}_2} + S_{\mathrm{CO}_2^-} - I_{\mathrm{Hg}^+_{\mathrm{aq.}}}$$

3. *The Special Rôle of Water.*—Attention has already been directed to the influence of the hydration energy of the various ions on the energy of activation of thermal electron-transfer reactions resulting in radical formation, and in the magnitude of the minimum quantum necessary in photochemical formation of radicals from ion-pair complexes. Water may also be a reactant in such electron transfer, behaving as an electron acceptor. It is instructive to compare the reduction of H_2O_2 and H_2O by reducing ions. The two reactions may be represented by the equations

FIG. 6. *The thermal reaction,* $X^{(z+1)+} + H\cdot COO^- \longrightarrow X^{z+} + CO_2 + H$.

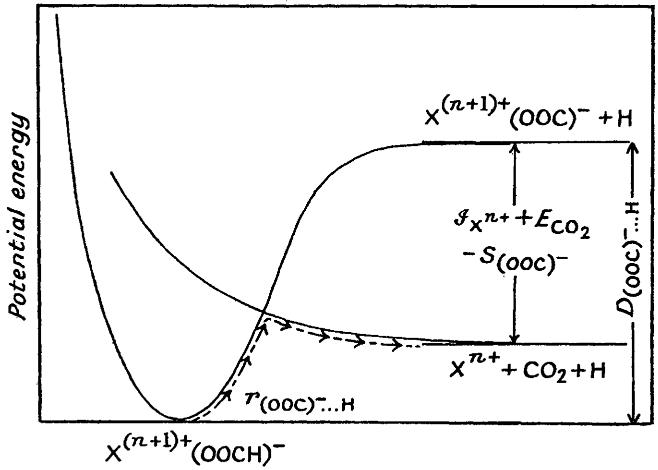
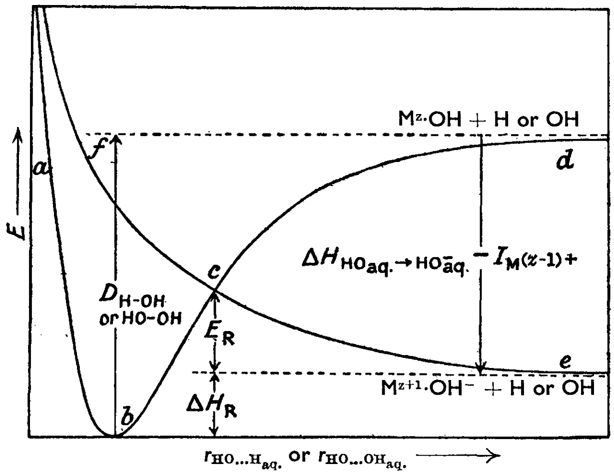


FIG. 7. *The reaction* $M^{z+} . HOX \longrightarrow M^{(z+1)+} . OH^- + X$ (X = OH or H).



$$M^{z+} + H_2O_2 \longrightarrow M^{z+1} . OH^- + OH \quad . \; . \; . \; . \; . \; . \; . \quad (19)$$

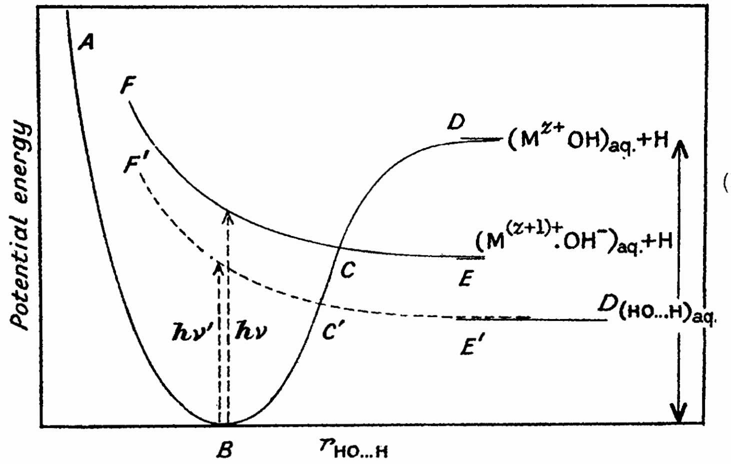
$$M^{z+} + H_2O \longrightarrow M^{z+1} . OH^- + H \quad . \; . \; . \; . \; . \; . \; . \quad (20)$$

and it is clear that the difference in the heats of these two reactions is merely the difference in the dissociation energies $D(H\ldots OH)_{aq.}$ and $D(HO\ldots OH)_{aq.}$. Both H_2O^- and $H_2O_2^-$ are expected on theoretical grounds to be unstable, and experimental support for this view in the former case is provided by electron-swarm experiments in water vapour.[18] The general form of the potential-energy curves relevant to the two cases will therefore be the same although the magnitude of the energies concerned will be different. In Fig. 7 we have used one diagram to summarise the course of both reactions, since this permits points of similarity and difference to be emphasised. The conclusions to be drawn are :

(1) The reaction path of the thermal reaction is *bce*, and the energy of activation is $E_R + \Delta H_R$. For the same reducing ion, the energy of activation will clearly be much greater for the fomation of H atoms from water than for the formation of OH radicals from hydrogen peroxide. This is borne out by the fact that when $M^{z+} = Fe^{2+}$, reaction (20) is imperceptible whereas reaction (19) is quite fast, $E_A + \Delta H_R$ being ~10 kcal.[15]

For the *same* reaction, *i.e.*, either (19) or (20), ΔH_R, and hence the energy of activation also, should decrease with decreasing ionisation potential of the reducing ion. There are no quantitative data yet available for testing this, but qualitative observations concerning the stability of reducing ions in water are in accord with this view. For example, whereas Fe^{2+} ions (ionisation potential ~100 kcal.) are stable in water, Ti^{2+} ions (ionisation potential ~72 kcal.) are not.

FIG. 8. *The photochemical electron-transfer reaction,* $M^{z+} . H_2O \xrightarrow{h\nu} M^{z+1}. OH^- + H$.



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(2) When $E_R + \Delta H_R$ is so large that thermal electron transfer is inconveniently slow, absorption of a light quantum may bring about the reaction. Since this process is almost instantaneous it is most effective when the electron donor and acceptor are already closely bound. Photochemical electron transfer from a cation to a water molecule of its hydration shell, with resultant formation of a hydrogen atom, is therefore to be expected with all ions at a suitable wave-length. The appropriate potential-energy diagrams are given in Fig. 8, and for a series of ions of the same valency and size the curves *ABCD* and *FCE* will be substantially the same, but their relative vertical displacement *DE* will be determined by

$$DE = (E_{OH(g)} + H'_{OH^-} - H_{OH}) - (I_{M^{z+}_{(g)}} + H_{M^{z+}} - H'_{M^{(z+1)+}}) \quad . \quad . \quad . \quad (21)$$

where *I* denotes·ionisation potential, *E* and *H* denote electron affinity and hydration energy, and the superscript is used to denote only that part of the hydration energy which becomes available during the time taken for the configuration to change from *B* to *E*. The second term on the right-hand side is the only one which is dependent on the chemical nature of the reducing ion, and will probably be slightly larger than the true ionisation potential of the ion in the aqueous environment, *i.e.*, $I_{M^{z+}_{aq.}}$, which is equal to ΔH for the reaction

$$M^{z+}_{aq.} \longrightarrow M^{(z+1)+}_{aq.} + e^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

We therefore expect that, in passing from one ion to another in the series of equal valency and size, *DE* and hence $h\nu$ would vary in proportion to changes of $I_{M^{z+}_{aq.}}$ (*i.e.*, $h\nu - h\nu' = I_{M^{z+}_{aq.}} - I_{M'^{z+}_{aq.}}$). Since the entropies of solvation of ions of equal radius and change will be equal,

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[18] Crovath, *Physical Rev.*, 1929, **33**, 605.

changes in $I_{M^{2+}}$ will be equal to changes in the redox potential. Mr. James has investigated the electron-transfer spectra of a large number of ions (V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Ti^{3+}, Mo^{3+}, U^{4+}, Eu^{2+}, Sn^{2+}, I^-, N_3^-, SH^-, SO_3^{2-}, and $H{\cdot}COO^-$) and the appropriate data for the transition elements of the first long period V to Ni are tabulated below. The expected proportionality between redox potential and the minimum quantum necessary to produce electron transfer is shown in Fig. 9.

The relationship between the minimum value of the quantum for the process $M^{2+},H_2O \xrightarrow{h\nu} M^{3+}.OH^- + H$ *and the potential of the couple* M^{2+}/M^{3+}, *for ions of approximately the same size.*

Ion	Atomic number	Radius (Å) M^{2+}	Radius (Å) M^{3+}	Redox potentials [1] (volts)	Long-wave absorption edge of electron-transfer spectrum, λ_0, Å	hc/λ_0 (kcal.)
V^{2+}	23	(0·82)	0·69	−0·21	3500 [2]	81
Cr^{2+}	24	(0·80)	0·62	−0·42	3800 [2]	75
Mn^{2+}	25	0·78	0·66	+1·5	2250 [2]	125
Fe^{2+}	26	0·76	0·64	+0·75	2850 [2]	100
Co^{2+}	27	0·74	0·63	+1·8	2200 [3]	129
Ni^{2+}	28	0·73	—	—	2200 [3]	129

[1] Latimer, "Oxidation Potentials," Prentice Hall, 1938. [2] From measurements by D. G. L. James (Leeds). [3] From M. Kasha, *J. Opt. Soc. Amer.*, 1948, **38**, 929.

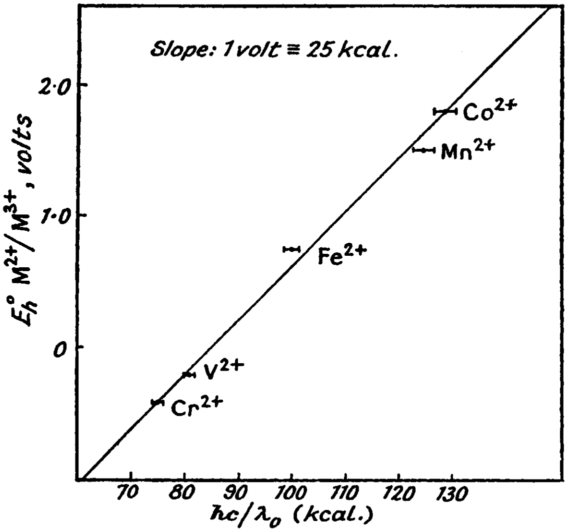

FIG. 9. *The relationship between the electron-transfer spectra and redox potentials of the bivalent ions of the transition elements of the first short period.*

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The effect of formation of a stable complex will be to increase $I_{M^{2+}}$ and cause a shift of the electron-transfer spectrum to shorter wave-lengths. Examination of the spectrum alone may not reveal this effect because additional absorption bands may arise owing to electron excitation within the complex. The wave-length associated with transfer to water and consequent production of hydrogen atoms may be distinguished from the excitation bands by the polymerisation method. An example of this is the addition of acrylonitrile to ferrous sulphate, which produces an extension of the continuous absorption of 800 Å towards *longer* wave-lengths. However, absorption of light in this region is not associated with electron transfer to water since it does not cause polymerisation.

4. *Enzymic Oxidation and Reduction in Aqueous Media.*—The prosthetic group of many enzymes which are catalysts for biological oxidations and reductions, contains a metal element of variable valency, and many authors [19] have from time to time suggested that the intermediates in such reactions might be free radicals. In particular, it is very tempting to regard the hæmoproteins, catalase and peroxidase, which contain ferriprotoporphyrin, as reacting with the hydrogen peroxide which they require to exercise their function, to produce radicals which in the former case lead to a rapid decomposition of peroxide and in the latter case lead to oxidation

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[19] For example, Haber and Willstätter, *Ber.*, 1931, **64**, 2844.

of the substrate. This hypothesis is made the more attractive by the fact that mixtures of ferric ion and hydrogen peroxide initiate the polymerisation of dissolved vinyl compounds. However, it has been found [20] that neither catalase– nor peroxidase–hydrogen peroxide mixtures of a wide range of composition initiate polymerisation. Moreover the function of the enzyme is unaffected by the presence of the monomer. It is therefore unlikely that radicals are intermediates in these reactions.

On the other hand, Parravano [11] has shown that during the dehydrogenation of formaldehyde catalysed by xanthine oxidase, which is an enzyme devoid of any metallic element, dissolved methyl methacrylate may be polymerised, provided that the solution is air-free. Although the initiating species has not been characterised, the simplest mechanism would be that the enzyme acts as a hydrogen atom carrier from the formaldehyde to the monomer.

It is curious that in the only enzymic systems investigated, the application of the polymerisation method has produced results which run counter to expectations based on simple ideas of enzyme action.

5. *Oxygen as a Reduction-activation Co-catalyst.*—With the exception of the heterogeneous, photochemical, and radiochemical methods of decomposition, all the methods described above may be classified as " reduction-activation " methods, *i.e.*, involving the interaction of an oxidising and reducing agent. If oxygen could be made the oxidising partner in such a reduction-activation system, exhaustive deaeration to ensure polymerisation would be unnecessary since the molecular oxygen concentration would be maintained at a very low level by a reaction in which polymerisation-initiating radicals were formed. The reducing partner would be the more effective in this reaction the lower its ionisation free energy, and in accord with this we have found that V^{2+}, Mo^{3+}, and U^{3+} form effective reduction-activation systems with oxygen.[21] This is easily demonstrated in the case of vanadium where the overall reaction may be written

$$V^{2+} + O_2 + H_2O \longrightarrow VO^{2+} + 2OH \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

These reactions undoubtedly proceed in single electron-transfer steps involving H_2O_2 as an intermediate, as may readily be demonstrated when oxygen is bubbled through solutions of UCl_3.

The Properties of Free Radicals in Aqueous Solution.

The usual reactions of free radicals, such as combination, disproportionation, addition to unsaturated compounds, will occur in an aqueous environment, but surprisingly little quantitative information has been obtained about them, and in some cases even the precise nature of the products is still unknown. Thus, there is much discussion as to whether, when two hydroxyl radicals react, H_2O_2 or H_2O and O are the products. The former reaction would be expected to have a low frequency factor and an energy of activation determined by the (unknown) dipole repulsion as the reactants approach, whilst the latter would have a normal frequency factor and an energy of activation of about 7 kcal. The behaviour of dilute solutions of hydrogen peroxide at high light intensities suggests that H_2O_2 is not the product,[22] whereas equally strong evidence to the contrary is provided by the fact that H_2O_2 is always formed by the action of α-rays on deaerated water.[23]

Oxidation and Reduction by Radicals.—The reduction potentials on the hydrogen scale for many hypothetical gaseous atoms or radicals in aqueous solution of normal acidity can readily be calculated. Two important examples are

$$H_g \longrightarrow H^+_{aq.} + e^-, \; E^\circ = 2{\cdot}11 \text{ v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$HO_{aq.}^- \longrightarrow HO_g + e^-, \; E^\circ = -2{\cdot}85 \text{ v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

(U.S. convention with regard to sign, data taken from National Bureau of Standards "Selected Values of Thermodynamic Quantities ") and these potentials are the quantitative expression of the reducing power of H and oxidising power of OH in simple electron-transfer reactions. It is therefore expected that when H atoms are formed in a medium containing solutes of lower oxidation potential, the H atom will be oxidised; and similar arguments would apply to oxidation reactions by OH. For example, we know that

$$Fe^{2+}_{aq.} \longrightarrow Fe^{3+}_{aq.} + e^-; \; E^\circ = -0{\cdot}77 \text{ v}. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

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[20] Dainton and Smith, to be published.

[21] Dainton and James, unpublished data.

[22] Lea, *Trans. Faraday Soc.*, 1949, **45**, 81.

[23] Bonet-Maury and Lefort, *Nature*, 1948, **162**, 381.

and hence in normal acid solution the reactions

$$Fe^{2+}{}_{aq.} + OH_g \longrightarrow Fe^{3+}{}_{aq.} + OH^-{}_{aq.};\ \Delta G^\circ = -48\ \text{kcal.} \quad . \quad . \quad . \quad (27)$$

$$Fe^{3+}{}_{aq.} + H_g \longrightarrow Fe^{2+}{}_{aq.} + H_g{}^+;\ \Delta G^\circ = -50\ \text{kcal.} \quad . \quad . \quad . \quad . \quad (28)$$

will be associated with a decrease of free energy and should take place spontaneously. Reaction (27) is well known. It is the second reaction which is involved in the oxidation of ferrous ions by hydrogen peroxide. It is also the reaction responsible for keeping the quantum yield for the formation of hydroxyl radicals from $Fe^{3+}\cdot OH^-$ complexes at such low values.[13] Likewise, reaction (28) is responsible for maintaining the quantum yield of the formation of H atoms from ferrous ion in water very much less than unity. The potential-energy changes undergone in this reaction may be seen by following the reaction path *ecb* in Fig. 7, from which the relation of ΔH_R and E_R (the energy of activation for this reduction) to the ionisation potential of the ferrous ion may be clearly perceived.

Fig. 7 is also illustrative of a rather surprising possibility, namely, that the hydroxyl radicals might act as a reducing agent, in a reaction which is essentially the reverse of the first stage of the Fenton reaction, *i.e.*,

$$M^{(z+1)+}\,.\,OH^- + HO \longrightarrow M^{z+} + H_2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and for which ΔG° may well be negative when the redox potentials $M^{z+}/M^{(z+1)}$ is large and negative. Reduction by hydroxyl radicals would be favoured by increasing pH, and Haissinsky, Lefort, and Le Bail[24] have suggested that this reaction can actually occur when $M^{(z+1)+} = Ce^{4+}$.

Another possibility in which H atoms play a rather unusual rôle, has been put forward by Weiss,[25] who suggests that in acid media an equilibrium :

$$H + H^+{}_{aq.} \rightleftharpoons H_2{}^+{}_{aq.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

is capable of yielding significant amounts of the hydrated molecular ion $H_2{}^+$ which, as an electron acceptor, would be a powerful oxidising agent. Although theoretical arguments may be advanced against this notion, yet it should be noted that there is one quite strong piece of experimental evidence for it. Douglas and Yost[26] have found that the quantum yield for the photo-oxidation of europous ion by water exceeds unity. The primary act is

$$Eu^{2+} + H_2O \xrightarrow{h\nu} Eu^{3+}OH^- + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and a quantum yield for this process exceeding unity is unlikely. There must therefore be another oxidation step, and the obvious possibility is

$$H + H^+ + Eu^{2+} \longrightarrow Eu^{3+} + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

but whether there is a termolecular process as written, or a bimolecular one between $Eu^{2+} + H_2{}^+$ or $Eu^{2+}\,.\,H + H^+$ cannot be determined.*

It was stated earlier that the net radiochemical act in liquid water was to form an equimolecular mixture of H atoms and OH radicals. The reversible redox potential of such a solution when acid ought to be $-0{\cdot}37$ volt, and it would be expected that, provided the electron-transfer reactions involved are reversible thermodynamically, irradiated water would act as an oxidising agent towards all systems of smaller or positive redox potential and as a reducing agent towards those systems which possess more negative redox potentials. In Fig. 10 we have arranged all the known *X*- or α-ray-induced reactions which occur in water, with the exception of the bleaching of dyes, in order of their redox potentials and have indicated whether oxidation or reduction occurs.[27] Whilst it is obvious there are two fairly well-defined zones of oxidation and reduction and that the assignment to irradiated water of an " equivalent redox potential " (E.R.P.) is justified, the figure shows unmistakably that the observed value ($\sim -0{\cdot}9$ v) is not that expected ($-0{\cdot}37$ v). Several modifications of the simple theory can be suggested which, in some degree at least, would account for the anomalously high oxidative capacity. The first is that the hydroxyl-radical concentration exceeds the hydrogen-atom concentration. This irregularity has always been assumed for other reasons, and is more marked the greater the linear ion density in the

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[24] *J. Chim. physique*, 1950, **48**, 210; *Compt. rend.*, 1950, **230**, 1156.

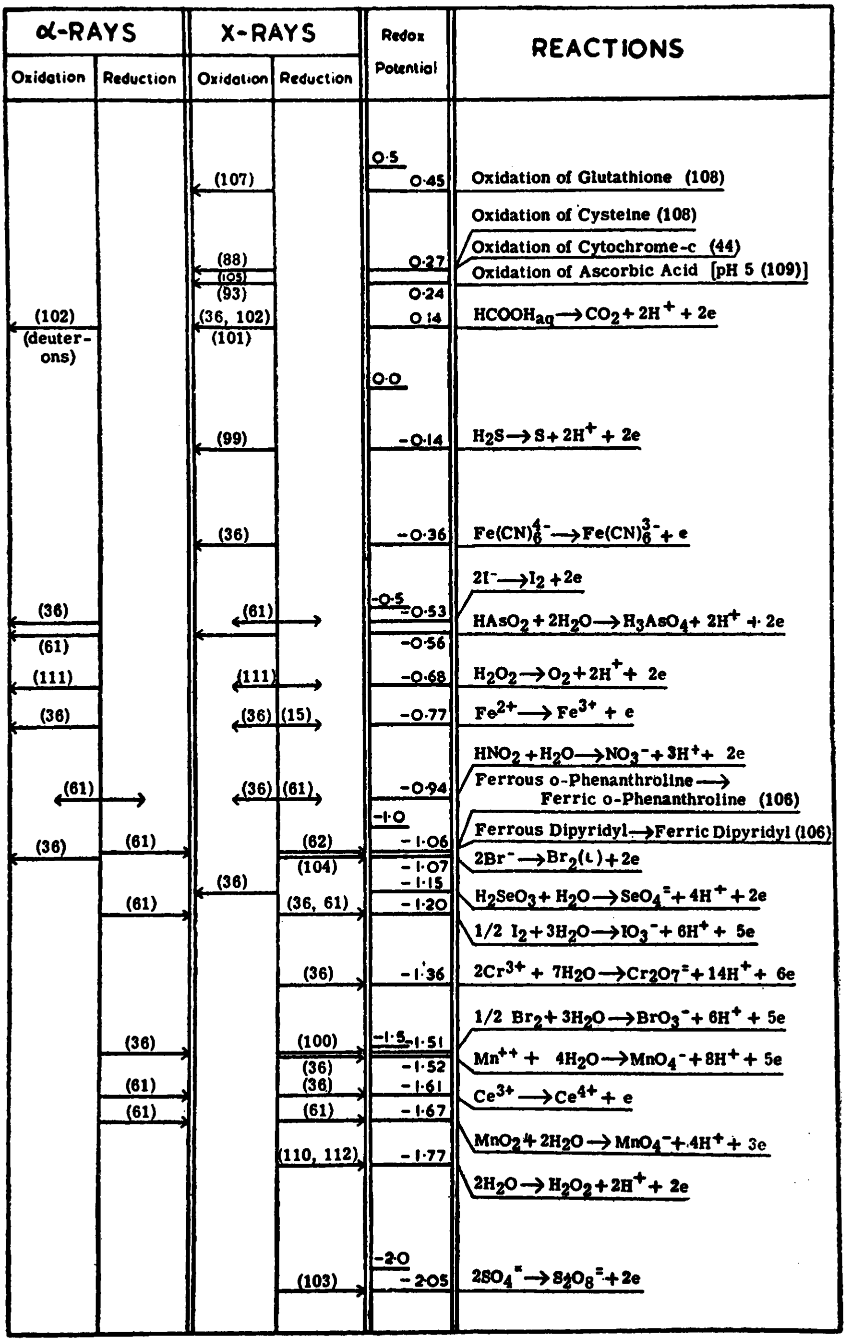
[25] *Nature*, 1950, **165**, 728.

[26] *J. Chem. Physics*, 1949, **17**, 1345.

[27] Collinson and Dainton, *Ann. Rev. Phys. Chem.*, 1951, **2**, 108.

* [*Note added in proof.*] Douglas and Yost (*J. Chem. Physics*, 1950, **18**, 1687) have now stated that the quantum yields given in their paper[26] are too large by a factor of ten. It is therefore no longer necessary to invoke reaction (32) to account for their results.

FIG. 10. *The equivalent reduction potential of irradiated water.*



→ denotes whether oxidation or reduction, ←→ denotes equilibrium attained or equivocal data. For meaning of numbers over the arrows see ref. 28.

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track of the fast charged particle concerned. Calculated values of the ratio [HO]/[H] have, however, never exceeded 10^4, whereas the value required to account for E.R.P. $= -0{\cdot}95$ is $\sim 10^{10}$. The existence of H_2^+ would also tend to reduce the discrepancy, and would also be in accord with the known effect of change of pH, but the magnitude of the effect can only be conjected. Another possibility is that the ion OH^+ is formed in appreciable amounts. The oxidation potential of this species is extremely large, and existing thermodynamic data, which are admittedly incomplete, do not prohibit the possibility that a proportion of OH^+ equal to that found in the mass spectrum of water vapour would account for the whole of the anomaly. Darbyshire and Waters's recent evidence [28] for the existence of the hydrated OH^+ ion in concentrated acidic solutions of hydrogen peroxide affords some support for this suggestion.

For many years after their discovery, the major methods of preparation of free radicals involved the homolytic fission of covalent bonds; and for this reason chemists have been preoccupied with their behaviour in non-polar systems. Ionic solvents, and particularly water, with their known incompatibility with covalent substances therefore came to be regarded as unlikely media for the production of free radicals. The purpose of the present Lecture will have been partly achieved if it creates the impression that odd-electron species may not only be readily formed in water, but may also take part in many varied types of reaction.

[28] *Nature*, 1950, **165**, 401.