The Reactions of Hydrated Electrons with Inorganic Compounds

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The hydrated electron is undoubtedly one of the most fundamental species ever discovered in chemistry and its discovery and investigation should be considered one of the most important achievements in pure chemistry in the present decade. The discovery of e^-_{aq} and the methods of production and investigation of the hydrated electron as well as its physicochemical properties have been recently comprehensively reviewed.[1] The reactions of e^-_{aq} were reviewed over three years ago[2] and the rapid developments in this field made many of the earlier conclusions outdated. As these reactions have far-reaching implications in general chemistry, a revised discussion of the reactions of e^-_{aq} and their mechanisms must be of general interest. This Review covers a limited yet important phase of the chemistry of hydrated electrons, namely, their reactions with inorganic compounds. We shall discuss the available information on the rates of e^-_{aq} reactions and the identity of the products of these reactions. Many of these products are hitherto unknown species, the chemical behaviour of which may engage a great number of inorganic chemists in the coming years. All e^-_{aq} reactions are electron-transfer reactions by definition. The experimental information on e^-_{aq} reactions will be used in the interpretation of these mechanisms, to which we shall devote the second part of this Review.

1 The Reactions of Hydrated Electrons and Their Products

Hundreds of inorganic compounds have been investigated for their reactivities with hydrated electrons in aqueous solutions. The reactivities of these compounds range from diffusion controlled rates down to 16 l. mole^{-1} sec.$^{-1}$ which is the calculated specific rate of reaction (1). In all cases investigated the primary

$$e^-_{aq} + H_2O \rightarrow H + OH^- \qquad (1)$$

product of the electron-transfer reaction (2) acquires an additional electron

$$e^-_{aq} + A^n \rightarrow A^{n-1} \qquad (2)$$

before undergoing any subsequent chemical change. In numerous cases the primary product is thermodynamically unstable and undergoes further reactions such as protonation, dissociation, disproportionation, or charge-transfer.

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[1] D. C. Walker, *Quart. Revs.*, 1967, **21**, 79.

[2] M. Anbar, *Adv. Chem. Ser.*, 1965, **50**, 55.

The reactions of inorganic compounds with hydrated electrons will be described following the elements and their compounds throughout the Periodic Table.

A. Hydrogen and Its Oxides.—Molecular hydrogen is completely inert toward e^-_{aq}. The reaction of hydrogen *atoms* with e^-_{aq}, on the other hand, is a diffusion-controlled reaction, which has been shown to produce hydride ions (3) as the

$$e^-_{aq} + H \rightarrow H^- \qquad (3)$$

primary product.[3] The reaction of e^-_{aq} with H^+_{aq} proceeds at a high rate ($k = 2{\cdot}3\ 10^{10}$ l. mole^{-1} sec.$^{-1}$)[4] which is, however, somewhat lower than the calculated diffusion-controlled limit. It has been suggested that owing to the fact that the electron vacancy in $H_9O_4{}^+$ is rather diffuse, the electron transfer involves an appreciable entropy of activation.[2] This rapid reaction limits the lifetime of e^-_{aq} in the acid range. Even at pH 5 the lifetime of e^-_{aq} is less than 3 μsec., which makes it rather difficult to investigate any other e^-_{aq} reaction much below this pH.

The final products of this reaction (4) are hydrogen atoms which are pro-

$$e^-_{aq} + H^+_{aq} \rightarrow H \qquad (4)$$

duced[3,5] with an H/D isotope effect of 3·7 which can hardly be explained unless an intermediate, *e.g.*, H_3O, is formed as a primary product. The lifetime of H_3O in water is probably shorter than 10^{-8} μsec. as no significant difference has been observed between the rates of reaction of H atoms produced directly by radiolysis and those formed from the reaction of e^-_{aq} with H_3O^+ up to relatively high concentrations of solutes.[5] Reaction (5) can be considered as a special case of

$$e^-_{aq} + H_3O^+ \rightarrow H_3O \rightarrow H + H_2O \qquad (5)$$

reactions of type (6) where HX may be any protonic acid, *e.g.*, HF, $NH^+{}_4$,

$$e^-_{aq} + HX \rightarrow HX^- \rightarrow H + X^- \qquad (6)$$

H_2PO_4, HCO_2H, etc. A Brønsted relation has been shown to exist between the specific rates of certain protonic acids and their dissociation constants.[6] This relation has been suggested to imply that the rate-determining step involves a proton transfer from the acid to the hydrated electron, resulting in the formation of an H atom.[6] It was found, however, that a number of protonic acids which follow the same Brønsted relation produce products other than H atoms from their reactions with e^-_{aq}.[2] Moreover, even when hydrogen atoms are formed, a considerable H/D isotope effect on the H atom formation is observed, which is not reflected in their respective pK's.[5,7] It must be concluded, therefore, that the

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[3] M. Anbar and D. Meyerstein, *Trans. Faraday Soc.*, 1966, **62**, 2121.

[4] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Amer. Chem. Soc.*, 1963, **85**, 1375.

[5] M. Anbar and D. Meyerstein, *J. Phys. Chem.*, 1965, **69**, 698.

[6] J. Rabani, *Adv. Chem. Ser.*, 1965, **50**, 242.

[7] M. Anbar and P. Neta, *Trans. Faraday Soc.*, 1967, **63**, 141.

Brønsted relation reflects the tendency of a protonic acid to accommodate an additional electron and to form HX^- as primary product. This tendency is correlated with the electron vacancy in the same hydrogen atom, which in turn is a prerequisite for its protonic dissociation. Once HX^- has been formed it may lose a hydrogen atom or dissociate in another way, depending on its structure and the strength of its chemical bonds.

The reaction of the hydrated electron with *water* is probably the most important reaction of e^-_{aq}, as it determines its natural lifetime in the pure solvent. Because this reaction is relatively slow, it is possible to observe the hydrated electron and to study its physical and chemical properties. Reaction (7) is over-

$$e^-_{aq} + H_2O \rightarrow H + OH^- \tag{7}$$
$$e^-_{aq} + H^+ \rightarrow H + H_2O \tag{8}$$
$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^- \tag{9}$$
$$OH^- + H \rightarrow e^-_{aq} + H_2O \tag{10}$$

shadowed under most conditions by reactions (8)—(10) as well as by the scavenging of e^-_{aq} by free radicals like H atoms or OH radicals simultaneously produced. Trace impurities in the solvent, such as oxygen, hydrogen peroxide, metal ions, or organic compounds, may also react with e^-_{aq} and shorten its life.

It was necessary therefore to take utmost precautions of reagent purity and to use most refined experimental techniques in order to obtain a reliable value for the unimolecular conversion of e^-_{aq} into H atoms in pure water. In a most careful study a unimolecular specific rate constant of 890 $sec.^{-1}$ was measured from which an apparent bimolecular rate constant $k = 16 \pm 1$ l. $mole^{-1}$ $sec.^{-1}$ can be calculated.[8]

The mechanism of the reaction of e^-_{aq} with H_2O is far from understood. Unlike the majority of e^-_{aq} reactions there is no room for the accommodation of an additional electron in the water molecule at its ground state. The formation of an electronically excited H_2O^- is energetically unfeasible; thus a concerted multimolecular process is much more likely. It seems plausible that this reaction involves a number of water molecules which solvate the OH^- in the transition state, making the reaction thermodynamically feasible.

The reaction of e^-_{aq} with hydrogen peroxide is diffusion-controlled,[4,9] an expected result since fast single-electron reduction reactions of H_2O_2 are well-known processes.

B. The Alkali-metal Ions, Alkaline Earths, and Rare Gases.—The hydrated electron has been shown to have a redox potential of about 2·7 v;[10] therefore it can reduce any species with a *lower* redox potential. All the alkali-metal cations Li^+, Na^+, K^+, Rb^+, and Cs^+ have a higher redox potential than 2·7 v; thus they

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[8] E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, 1966, **70**, 150.
[9] E. J. Hart and E. M. Fielden, 'Pulse Radiolysis', ed. M. Ebert, Academic Press, New York, 1965, p. 253.
[10] J. H. Baxendale, 'Current Topics in Radiation Research', ed. M. Ebert and A. Howard, North Holland, Amsterdam, 1967, vol. 3, no. 1.

cannot be reduced by hydrated electrons to the metal atoms. In fact, there are indications[1] that under certain conditions the reaction of sodium goes spontaneously in the opposite direction (11).

$$Na + H_2O \rightarrow e^-_{aq} + Na^+ \qquad (11)$$

The reactivity of hydrated electrons toward beryllium compounds in aqueous solutions has not been investigated yet. Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions were found to be non-reactive toward hydrated electrons.[11,12] On the other hand, Mg^{II} was shown to be reduced to Mg^{I} by electrons in frozen solutions,[13] most probably because of the diminished stability of Mg^{2+} in the ice lattice compared with that of this ion in aqueous solution. It can be predicted therefore that Mg^{2+} and perhaps also the ions of other alkaline earths may be reduced by solvated electrons in alcoholic solutions.

The rare gases have a highly negative electron affinity and species like He^- or A^- have no chemical stability whatsoever. Therefore the elemental inert gases are not expected to show any reactivity toward hydrated electrons. On the other hand, rare-gas compounds, such as $H_3XeO_6^-$ or XO_3 which are extremely efficient oxidants, are expected to react with e^-_{aq} at diffusion-controlled rates.

C. Compounds of the Elements of Group III and the Lanthanides.—Unlike the alkali metals and alkaline earths, which do not react with hydrated electrons, the tervalent ions of the elements of Group III, with the exception of boron, react with e^-_{aq} at relatively high rates. The very low reactivities of $B_2O_7^{2-}$, $H_2BO_3^-$, and BF_4^- ions[14] are most probably not a consequence of thermodynamic but of kinetic parameters. The reaction (12), for instance, is a highly exoergic process.

$$BF_4^- + e_{aq}^- \rightarrow BF_3^- + F^- \qquad (12)$$

Aluminium salts react with e^-_{aq} in neutral and alkaline solutions, the reactivity ranging from 2×10^9 l. mole^{-1} sec.$^{-1}$ at pH 6·8 to $5{\cdot}5 \times 10^6$ l. mole^{-1} sec.$^{-1}$ at pH 14.[15] The high reactivity in neutral solutions is not surprising since a rough estimate of the free energy of the reaction (13) yields a negative value of

$$AlOH_{aq}^{2+} + e^-_{aq} \rightarrow AlOH_{aq}^+ \qquad (13)$$

over 100 kcal./mole. The decrease in reactivity with pH can be explained by two effects. In the intermediate region polynuclear species prevail, which evidently have an *apparent* lower specific rate when calculated on the basis of the concentration of the monomer. $Al(OH)_4^-$ which prevails in alkaline solution exhibits a very low reactivity toward e^-_{aq}, for reasons which will be discussed in Part 2. The profound effect of ligands on reactivity is demonstrated again in the case of the aluminum–EDTA complex ($k = 3 \times 10^7$ l. mole^{-1} sec.$^{-1}$).[16]

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[11] M. Anbar and D. Meyerstein, *J. Phys. Chem.*, 1964, **68**, 1712.
[12] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 1244.
[13] P. N. Moorthy and J. J. Weiss, *Adv. Chem. Ser.*, 1965, **50**, 180.
[14] M. Anbar and E. J. Hart, *Adv. Chem. Ser.*, 1968, **81**, 79.
[15] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 973.
[16] M. Anbar and D. Meyerstein, to be published.

The aquo- or hydroxy-complexes of the tervalent ions of the other members of Group III are insoluble in neutral or alkaline solutions; thus their reactivity with e^-_{aq} cannot be evaluated. However, the EDTA complexes of gallium and indium have been studied for their rates of reaction with e^-_{aq} and an increase in reactivity in the sequence Al, Ga, In has been observed ($k = 3{\cdot}0$, $7{\cdot}8$, and $41{\cdot}0 \times 10^7$ l. mole^{-1} sec.$^{-1}$, respectively).[16] This increase in rate may be due to the increase in the stability of the bivalent state of these elements.

Tl^{III}_{aq} is unstable in neutral solution; however, Tl^+ is quite stable and has been investigated. Tl_{aq}^+ reacts with e^-_{aq} at a diffusion-controlled rate[17] producing Tl^0 as the primary product. The latter species forms a complex[18] with Tl^+ giving Tl_2^+.

Whereas it is impossible to study the behaviour of gallium and indium aquo-complexes in neutral solutions, this has been possible for other members of Group III, namely yttrium, lanthanum, and the lanthanides. The reactions of these aquo-complexes can be divided into two groups; those that react rapidly with e^-_{aq} ($k > 10^9$ l. mole^{-1} sec.$^{-1}$) including samarium, europium, thulium, and ytterbium on one hand, and those that react more slowly (in the range 10^7—10^9 l. mole^{-1} sec.$^{-1}$).

For the first a correlation has been pointed out[19] between the redox potential of the M^{3+}/M^{2+} couple and the rate of the reaction with e^-_{aq}. If the specific rate constants for these reactions are corrected for the diffusion-controlled rate according to equation (14) a fairly good linear correlation is obtained, indicating that the change in free energy makes a major contribution to the reactivity of these complexes with hydrated electrons.

Table 1

	Eu	Yb	Sm	Tm
E° (M^{3+}/M^{2+}) (v)	0·43	1·15	1·55	>1·5
$10^{10}k_{obs}$ (l. mole^{-1} sec.$^{-1}$)[13]	6·1	4·3	2·5	0·3
$10^{10}k$ (l. mole^{-1} sec.$^{-1}$)	24·6	9·0	3·6	0·3

$$\frac{1}{k} - \frac{1}{k_{obs}} - \frac{1}{k_{diff}} \tag{14}$$

The reduction of Eu^{III} to Eu^{II} by e^-_{aq} has been demonstrated spectrophotometrically by pulse radiolysis.[20] The identification and study of the chemical behaviour of other bivalent cations of the lanthanides produced by e^-_{aq} in aqueous solutions still awaits investigation.

The EDTA complexes of the transition elements of Group IIIA scandium, yttrium, lanthanum, and the lanthanides have been investigated.[16] The rates for these EDTA complexes, excluding the highly reactive lanthanides discussed

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[17] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.*, 1965, *A*, **286**, 320.

[18] B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc.* (*A*), 1966, 612.

[19] J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1964, **68**, 1524.

[20] S. Gordon, ref. 9, p. 285.

above, were correlated with their thermodynamic stability constants. It was found that the reactivity of the members of this family of complexes increases linearly with *increasing* stability of their EDTA complex.[16] As an inverse correlation would be expected if the rate of reaction of e^-_{aq} depended solely on the redox potentials of these complexes, this finding implies that other parameters besides the gross effect of free-energy change determine the rate of the electron transfer.

D. Compounds of the Elements of Group IV.—Relatively little is known about the reactivity of hydrated electrons with compounds of the elements of Group IV, with the exception of the organic compounds. The main reason for this is that relatively few inorganic compounds of this group are stable in a monomeric form in neutral aqueous solutions.

Of the 'inorganic' compounds of carbon investigated for their reactivity with e^-_{aq} one should consider CO, CO_2, CCl_4, $C(NO_2)_4$, CS_2, HCO_3^-, CO_3^{2-}, CN^-, SCN^-, and OCN^-. These compounds range in their reactivity from quite inert species like CN^-, SCN^-, OCN^-, CO_3^{2-}, and HCO_3^- ($k > 10^6$ l. mole^{-1} sec.$^{-1}$)[19] to the extremely reactive CCl_4, CS_2, and $C(NO_2)_4$, which react at diffusion-controlled rates ($k = 3{\cdot}0$, $3{\cdot}1$, and $4{\cdot}6 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$, respectively).[21] Carbon dioxide reacts with e^-_{aq} at a rate which is close to the diffusion-controlled limit, whereas carbon monoxide reacts[22] at an intermediate rate ($k = 1 \times 10^9$ l. mole^{-1} sec.$^{-1}$).

The product of the reaction of CO with e^-_{aq} is probably CO^- which reacts with water to give HCO; HCO then dimerizes to glyoxal.[22] HCO is a strong reducing species and is oxidized by H_2O_2 to formic acid. The chain reaction of CO in alkaline solution to yield formate ions[23] may involve CO^- as chain carrier.

CO_2 is reduced by e^-_{aq} to CO_2^-, which has been shown to combine with various organic radicals to form carboxylates,[23,24] *e.g.*, reaction (15). CO_2^-

$$CO_2^- + CH_2CO_2 \rightarrow CH_2(CO_2^-)_2 \qquad (15)$$

is also an efficient reducing agent which was found to reduce H_2O_2,[25] I_2, Br_2, RBr, NO_3^-, and NO_2^- as well as C_6H_5NO.[26,27]

The only silicon-containing compound investigated for its reaction with e^-_{aq} is SiF_6^{2-}, which is quite inert ($k > 1{\cdot}5 \times 10^6$ l. mole^{-1} sec.$^{-1}$).[14] This is not surprising in view of the thermodynamic instability of Si^{III}.

Whereas none of the germanium compounds have been investigated, both tin(II) and tin(IV) derivatives have been studied for their reaction with e^-_{aq}. The Sn^{II} hydroxy-complex $(SnO_2)^{2-}{}_{aq}$ has been found to react with e^-_{aq} at a diffusion-

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[21] E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 1271.
[22] E. J. Hart, J. K. Thomas, and S. Gordon, *Rqdiation Res. Suppl.*, 1964, **4**, 74.
[23] J. J. Weiss, *Radiation Res. Suppl.*, 1964, **4**, 141.
[24] G. Scholes and M. Simic, *J. Phys. Chem.*, 1964, **68**, 1731.
[25] A. Husain and E. J. Hart, *J. Amer. Chem. Soc.*, 1965, **87**, 1180.
[26] M. Anbar and P. Neta, *J. Chem. Soc.* (*A*), 1967, 841.
[27] K. D. Asmus, G. Beck, A. Henglein, and A. Wigger, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 869.

controlled rate.[14] The fluoro-complexes of Sn^{IV} and Sn^{II}, SnF_6^{2-} and SnF_3^-, react with e^-_{aq} at rates approaching the diffusion-controlled limit ($k = 4{\cdot}1$ and $9{\cdot}3 \times 10^9$ l. mole^{-1} sec.$^{-1}$, respectively).[14]

Lead, the last member of Group IV, has been studied for its reactivity only in the bivalent state. It was found that the aquo-, hydroxy-, and EDTA complexes of Pb^{II} react at diffusion-controlled rates.[14–16] There is an interesting difference between the behaviour of the hydroxy- and EDTA complexes of lead and those of aluminum and zinc.[15] Whereas the hydroxy- and EDTA complexes of Al^{III} and Zn^{II} are *much* less reactive than the corresponding aquo- or aquo-hydroxy-complexes, the hydroxy-complex of lead is just as reactive. Since little change takes place, in all these cases, in the electronic configuration of the central atom on going from the aquo- to the hydroxy- or EDTA complex, the change in reactivity must be, in this case, due to the ligand.

E. Compounds of the Elements of Group V.—The chemistry of nitrogen is characterized by its large number of states of oxidation, most of which include water-soluble compounds. There is no wonder therefore that a large number of different nitrogen compounds have been investigated for their reactivity toward hydrated electrons.

Starting with nitrogen at its lowest state of oxidation N^{-III}, one finds ammonia quite inert toward hydrated electrons. This is to be expected from a molecule with all its low-lying orbitals completely occupied. Liquid ammonia is a medium in which solvated electrons are even more persistent than in water and the lifetime of hydrated electrons in water is not affected even in the presence of molar concentration of ammonia. Ammonium ions do react with hydrated electrons, although slowly ($k = 1{\cdot}5 \times 10^6$ l. mole^{-1} sec.$^{-1}$).[28] The product of this reaction is probably the NH_4 radical[29] which dissociates to $NH_3 + H$ with an H/D isotope effect of $4{\cdot}2 \pm 0{\cdot}1$.[5] Hydrazine and hydroxylamine are relatively inert toward e^-_{aq}.[30]

Elementary nitrogen has a negative electron affinity; thus it will not react with the hydrated electron. On the other hand, N_2O, which represents N^I, is a most useful reagent in radiolytic studies as it 'converts' e^-_{aq} into OH radicals. It reacts (16) with e^-_{aq} rather quickly ($k = 5{\cdot}6 \times 10^9$ l. mole^{-1} sec.$^{-1}$)[9,31] forming nitrogen and OH radicals as final products.

$$N_2O + e^-_{aq} \rightarrow N_2O^- \rightarrow N_2OH \rightarrow N_2 + OH \qquad (16)$$

A significantly slower rate of reaction of e^-_{aq} with N_2O has been observed in acid solution; this has been interpreted to indicate the existence of a less reactive hydrated form of N_2O in acid solution.[32]

Different estimates exist concerning the lifetime of the intermediate

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[28] E. M. Fielden and E. J. Hart, personal communication.

[29] C. E. Melton and H. W. Joy, *J. Chem. Phys.*, 1967, **46**, 4275.

[30] J. H. Baxendale *et al.*, *Nature*, 1964, **201**, 468.

[31] J. P. Kenne, *Radiation Res.*, 1964, **22**, 1.

[32] D. A. Head and D. G. Walker, *Canad. J. Chem.*, 1967, **45**, 2051.

N_2O^- [2,32–36] The lifetime of N_2O^- in the gas phase was estimated to be greater than 10^{-4} sec.[37] In view of this evidence it is likely that the lifetime of N_2O^- is more than 10^{-8} sec., especially in alkaline solutions, and that it may react with solutes when these are present at sufficiently high concentrations.[38,39]

The high reactivity of NO with e^-_{aq} ($k = 3{\cdot}1 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$)[4] is not surprising in view of its electron affinity in the gas phase.

The characteristic compounds of N^{III} in neutral aqueous solutions are nitrite ions. These react with e^-_{aq} at a rate approaching the diffusion-controlled limit ($k = 4{\cdot}6 \times 10^9$).[19] The product of this reaction is probably NO_2^{2-} and it may be most interesting to study the chemistry of the latter species by pulse radiolysis and to compare it with the chemical behaviour of NO dissolved in water.

There is no stable N^{IV} compound in neutral aqueous solution; therefore we shall now consider the behaviour of two N^V compounds, NO_3^- and N_3^-. Whereas the former oxyanion reacts at a diffusion-controlled rate ($k = 8{\cdot}5 \times 10^9$ l. mole^{-1} sec.$^{-1}$), the latter pseudo-halide reacts extremely slowly ($> 1{\cdot}3 \times 10^6$ l. mole^{-1} sec.$^{-1}$). This difference may be considered a rather unexpected result as azide may be formally considered a derivative of amino-nitrate. The difference in reactivity is thus hard to explain in terms of the redox potentials of these anions. It is suggested that the intermediate N_3^{2-} has a much more positive free energy than NO_3^{2-}. N_3^- is a typical electron *donor*; NO_3^-, on the other hand, is a rather poor electron donor and may accept much more readily an additional electron.

There is little information on the chemical behaviour of NO_3^{2-}, the product of the reaction of NO_3^- with e^-_{aq} reaction. Although it has been postulated as intermediate in certain radiolytic reactions,[40] there is no evidence for its being long-lived enough to react with solutes.[26]

Phosphorus oxyanions do not exhibit any spectacular behaviour on reacting with e^-_{aq}. $H_2PO_4^-$ and $H_2PO_3^-$ react at comparable rates ($k = 7{\cdot}7 \times 10^6$, $7{\cdot}2 \times 10^6$ l. mole^{-1} sec.$^{-1}$, respectively).[14] This result indicates that the valency of phosphorus has little effect on the reactivity. As these two ions are protonic acids of comparable strength (p$K = 7{\cdot}2$ and $6{\cdot}6$, respectively), it seems that the electron is incorporated into the orbitals of the hydrogen atom. The H atoms

$$e^-_{aq} + H_2PO_4^- \rightarrow H + HPO_4^{2-} \qquad (17)$$

formed in the overall reaction (17) exhibit[41] an H/D isotope effect of over 6, strongly suggesting the existence of $H_2PO_4^{2-}$ as intermediate. Hypophosphate

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[33] B. Cercek, ref. 9, p. 289.

[34] Y. Raef, ref. 9, p. 145.

[35] E. J. Land, ref. 9, p. 285.

[36] C. S. Munday, J. T. Richards, G. Scholes, and M. Simic, 'The Chemistry of Ionization and Excitation', ed. G. R. A. Johnson and G. Scholes, Taylor and Francis, London, 1967, p. 151.

[37] W. J. Holtstander and G. R. Freeman, *J. Phys. Chem.*, 1967, **71**, 2562.

[38] M. Anbar, R. A. Munoz, and P. Rona, *J. Phys. Chem.*, 1963, **67**, 2708.

[39] G. E. Adams, 'Radiation Research', ed. G. Silini, North Holland, Amsterdam, 1967, p. 195.

[40] M. Daniels and F. F. Wigg, *J. Phys. Chem.*, 1967, **71**, 1024.

[41] C. Lifshitz and G. Stein, *Israel J. Chem.*, 1964, **2**, 337.

ion $H_2PO_2^-$, which is not a protonic acid at all, reacts at a much slower rate ($k > 1 \times 10^5$ l. mole^{-1} sec.$^{-1}$),[14] if it reacts at all.

Arsenic is a more metal-like element than phosphorus and the oxidizing potential of the couple M^V/M^{III} rises rapidly going from phosphorus through arsenic and antimony to bismuth. This trend is reflected in the reactivity of these elements toward e^-_{aq}. Although no As^{IV} compound has been isolated, As^V reacts with e^-_{aq} at an appreciable rate. The oxy-derivative, $HAsO_4^{2-}$, is much less reactive than the hexafluoroarsenate, AsF_6^-, which reacts at a diffusion-controlled rate ($k = 2{\cdot}0 \times 10^8$ and 9×10^9 l. mole^{-1} sec.$^{-1}$, respectively).[15] This difference in rates probably originates from the fact that the ionic character of the As—F bond is about twice as large, making the central atom more electropositive.

The reactivity of oxy-derivative of Sb^V already reaches the diffusion-controlled limit;[15] Bi^V will evidently behave analogously. The measured specific rate for Sb^V_{aq} ($1{\cdot}2 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$) suggests the participation of a singly *positively* charged species. Alternatively one has to assume in this case electron-tunnelling which allows larger reaction cross-sections than the geometrical dimensions of the reactants.

Arsenite ions were found to react significantly more quickly than arsenate ions at the same pH ($k = 2{\cdot}0$ and $5{\cdot}9 \times 10^8$ l. mole^{-1} sec.$^{-1}$, respectively).[14] This difference may originate from the tendency of M^{III} to behave as M^{3+}, a tendency which starts with As^{III} and is most pronounced with Bi^{III}.

Of the transition metals of Group VA only vanadate ions were examined and found to react with e^-_{aq} at a diffusion-controlled rate ($k = 4{\cdot}9 \times 10^9$ l. mole^{-1} sec.$^{-1}$).[14] The rate suggests that the reacting species is singly negatively charged.

F. Compounds of the Elements of Group VI.—Elementary oxygen reacts with e^-_{aq} at a diffusion-controlled rate ($k = 1{\cdot}9 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$).[4,9] It being a biradical with a relatively high electron affinity this high reactivity is expected. O_2^-, which is the primary product, may subsequently undergo disproportionation to give H_2O_2 and O_2.[42] The absorption spectrum of O_2^- formed as a transient from the reaction of O_2 with e^-_{aq} reaction has been investigated.[43,44] Water and H_2O_2 have been discussed in Section (A).

Elementary sulphur is insoluble in monomoric form in water but is expected to be highly reactive toward e^-_{aq} owing to its electron affinity (> 45 kcal./mole).[45]

H_2S is highly reactive toward e^-_{aq} ($k = 1{\cdot}35 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$).[46] This reactivity is evidently considerably higher than expected for H_2S as a protonic acid.[6] The products of the reaction, however, are predominantly H + HS^-, analogous to the behaviour of other protonic acids. The other products formed by the decomposition of H_2S^- are H_2 + S^-, which are produced with a yield

[42] G. E. Adams, ref. 9, p. 57.
[43] S. Gordon, E. J. Hart, and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 1262.
[44] G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, 1964, **68**, 1169.
[45] L. M. Branscomb and S. J. Smith, *J. Chem. Phys.*, 1956, **25**, 598.
[46] G. Meissner and A. Henglein, *Ber. Bunsengesellschaft. Phys. Chem.*, 1965, **69**, 3.

of 35%. There is no information on the reactivity of S^{2-} and HS^- with e^-_{aq} but they are expected to be inert.

Sulphate and sulphite ions are non-reactive ($k < 10^6$ l. mole^{-1} sec.$^{-1}$). There are conflicting results on the reactivity of thiosulphate,[47] and it is possible that the higher rate observed is due to colloidal sulphur usually present in traces in thiosulphate solutions. The only other well established highly reactive sulphur compound is the persulphate ion $S_2O_8^{2-}$ which reacts at a diffusion-controlled rate.

Selenite and selenate ions are much more reactive than their sulphur analogues ($k = 1.2 \times 10^7$ and 1.1×10^9 l. mole^{-1} sec.$^{-1}$)[14] resembling the case of phosphates and arsenates. As expected from this analogy tellurite reacts at an even faster rate (1.1×10^9 l. mole^{-1} sec.$^{-1}$)[14] and tellurates react at diffusion-controlled rates ($k = 1.6 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$) with an unexpectedly large reaction cross-section.[14]

Of Group VIA chromium compounds have been investigated. In this section we shall refer only to Cr^{VI} ions which have been shown to react at diffusion-controlled rates,[47] as expected from such strong oxidizing agents. The formation of a Cr^V transient formed from CrO_4^{2-} has been demonstrated.[48]

G. The Halogens and Their Compounds.—Fluoride ions are completely non-reactive toward e^-_{aq} ($k < 2 \times 10^4$ l. mole^{-1} sec.$^{-1}$).[12] Their inertness is shared by the other halide ions as well.[47] The halide ions have all their low-lying orbitals completely filled in a rare-gas fashion; thus their reactivity with any reducing agent including e^-_{aq} is thermodynamically prohibited.

Hydrofluoric acid reacts with e^-_{aq} at a moderate rate 6×10^7 l. mole^{-1} sec.$^{-1}$)[7] which is expected from it as a weak protonic acid.[6] HF_2^- is slightly less reactive ($k =$ *ca.* 3×10^7 l. mole^{-1} sec.$^{-1}$),[7] again in line with its being a weaker acid than HF. The other halogen hydrides are completely dissociated in aqueous solutions; thus their reactivities, which are probably very high, cannot be measured.

The only elementary halogen which is stable enough in neutral solution and could have been measured is iodine and the tri-iodide ions, both of which react at diffusion-controlled rates;[12] so also does the Br_2^- ion-radical.[49]

Of the oxyanions of chlorine, ClO^-, ClO_3, and ClO_4^- have been investigated. Whereas the reaction of ClO^- is diffusion-controlled ($k = 7{\cdot}2 \times 10^9$ l. mole^{-1} sec.$^{-1}$)[14] both ClO_3^- and ClO_4^- are practically non-reactive. The high reactivity of ClO^- may be due to an oxygen-induced electron vacancy in the chlorine atom. Although the redox potential BrO_3^-/BrO^- is comparable with that of ClO_3^-/ClO^-, bromate reacts with e^-_{aq} at a much faster rate ($k = 2{\cdot}1 \times 10^9$ l. mole^{-1} sec.$^{-1}$),[15] interestingly enough at a rate similar to that of selenate ($1{\cdot}1 \times 10^9$ l. mole^{-1} sec.$^{-1}$).[14] Iodate and periodate ions like tellurate ions react at diffusion-controlled rates.[14,15] The increase in reactivity along the line $ClO_3 \ll$

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[47] M. Anbar and P. Neta, *Inter. J. Appl. Rad. Isotopes*, 1967, **18**, 493.

[48] J. H. Baxendale, ref. 9, p. 15.

[49] M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2092.

$BrO_3 < IO_3^-$ is probably the result of the stabilization of the quadrivalent states of the halogens.

The chemical behaviour of Br^{IV} produced by the reaction of BrO_3^- with e^-_{aq} has been investigated.[50] This species, BrO_3^{2-} or $(BrO_2)_{aq}$, was found to react both as an oxidizing and as a reducing agent. In acid solution BrO_3^{2-} was found to oxidize I^- and Br^- as well as Mn^{2+} ions. In neutral solution BrO_3^{2-} reduces I_2 and Br_2 to I_2^- and Br_2^-, respectively. In the absence of reactive solutes BrO_3^{2-} disproportionates to BrO_3^- and BrO_2^-.

The permanganate ion, representing Group VIIA, reacts with e^-_{aq} at a diffusion-controlled rate.[17,20]

H. The Transition-metal Ions and Their Complexes.—In this section we shall discuss the behaviour of the complex ions of Groups IB, IIB, and VIII, as well as those of Cr^{II}, Cr^{III}, and Mn^{II}. All these ions with the exception of Group IIB have vacant *d* orbitals, which facilitates their reduction by e^-_{aq}. Group IIB element may still be considered as transition metals.[51] These ions may exchange the ligand water molecules for other ligands and these substitutions have been shown to affect their reactivities toward e^-_{aq}. Some of the reduced products of the e^-_{aq} reactions are well-known chemical species, and the existence of others has been demonstrated for the first time through the e^-_{aq} reactions.

The tervalent ions of the first transition series Cr^{III}, Fe^{III}, and Co^{III} react with e^-_{aq} at diffusion-controlled rates. This includes their amino-, ethylenediamino-, EDTA, cyano-, and other complexes.[14–17,52,53]

Most complexes of bivalent ions of the first transition series, Cr^{II}, Mn^{II}, Fe^{II}, Co^{II}, Co^{II}, Ni^{II}, and Cu^{II}, react with e^-_{aq} at fast rates but only certain complexes reach the diffusion-controlled limit. Of the aquo-complexes only Cr^{II}_{aq} and perhaps Cu^{II}_{aq} approach the diffusion-controlled limit, whereas Mn^{II}_{aq} is rather inert.[30] The EDTA complexes show a similar trend,[16] whereas in the case of cyano-complexes one finds $Mn(CN)_6^{4-}$ extremely reactive and $Fe(CN)_6^{4-}$ non-reactive altogether.[54] The behaviour of these complexes as well as those of $d^{10}Zn^{2+}$ are summarized in Table 2.

Table 2 *Rates of reaction of complexes of the first transition-metals series in the bivalent state of oxidation* ($\times$ 10^9 *l. mole*$^{-1}$ *sec.*$^{-1}$)[14,16,47]

	Cr	Mn	Fe	Co	Ni	Cu	Zn
H_2O	42	0·08	0·12	12	22	33	1·5
CN*	4	5	<0·0001	—	4·1	—	0·08
EDTA	—	<0·002	—	0·51	0·1	10·4	<0·002

* Results corrected for salt effect.

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[50] M. Anbar and P. Neta, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1645.

[51] L. E. Orgel, 'An Introduction to Transition Metal Chemistry', 2nd edn., Methuen, London, 1966.

[52] A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 289.

[53] R. G. Pearson, W. L. Waltz, and E. J. Hart, to be published.

[54] M. Anbar, *Chem. Comm.*, 1966, 416.

The kinetic behaviour of the complexes has been correlated with the electron distribution in their *d* orbitals, which are a function of their ligand–metal interactions.[2,54] The effect of the ligand on the electron distribution in the *d* orbitals does not explain all the experimental findings. First, it is found that Zn^{2+}_{aq} is also reduced fairly rapidly although it has no vacancy in the *d* shell. Secondly, it is evident that EDTA, a ligand which has an effect on the electron distribution similar to that of H_2O, has a profound effect on the reactivity of some of its complexes. Moreover, EDTA affects ions when no ligand field effects are expected. Hydroxy-complexes behave in a similar manner, as has been pointed out in connection with the hydroxy-complexes of aluminium and zinc. It has been shown further that the reactivity of both Ni^{II} and Cd^{II} ethylenediamine complexes show the trend $M(H_2O)_6{}^{2+} \sim M(en)_2{}^{2+} \gg M(en)_3{}^{2+}$.[55] It is unlikely that the substitution of the last two H_2O molecules by ethylenediamine has a significant effect on the electron affinity of the complex. The effect of certain ligands on the rate of electron transfer thus implies the participation of additional parameters.

The complexes of the second and third series of transition metals have not been investigated as extensively as those of the first. Of the second series $Ru(NH_3)_6{}^{3+}$, $Rh(NH_3)_6{}^{3+}$, and $Rh(bipy)_3{}^{3+}$ were studied[53] as well as $PdCl_4{}^{2-}$ and $Pd(CN)_4{}^{2-}$.[14] All these complexes were found to react at diffusion-controlled rates. On the other hand, $Ru(CN)_6{}^{4-}$ is extremely non-reactive in analogy to $Fe(CN)_6{}^{4-}$.[14] Several silver salts were also examined including Ag^+_{aq}, $Ag(NH_3)_2{}^+$, $Ag(CN)_2{}^-$, and $Ag(EDTA)^{3-}$, all of which also react at diffusion-controlled rates.[15,16]

The complexes of the third series studied include $Os(NH_3)_6{}^{3+}$ which reacts at a diffusion-controlled rate;[53] $Os(CN)^{4-}$ which is very non-reactive like $Ru(CN)_6{}^{4-}$ and $Fe(CN)_6{}^{4-}$; $IrCl_6{}^{2-}$ and $IrCl_6{}^{3-}$ which react at diffusion-controlled rates;[14] and $Ir(NH_3)_6{}^{3+}$ which was found to be slightly less reactive ($k = 1{\cdot}3 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$).[53] All platinum complexes studied, namely $PtCl_4{}^{2-}$, $PtCl_6{}^{2-}$, and $Pt(CN)_4{}^{2-}$, react at diffusion-controlled rates.[14] $Au(CN)_2{}^-$ and $Hg(CN)_4{}^{2-}$ react at fast but not a diffusion-controlled rates ($k = 3{\cdot}5 \times 10^9$ and $1{\cdot}9 \times 10^9$ l. mole^{-1} sec.$^{-1}$, respectively), whereas the reaction of $Hg(EDTA)^{2-}$ is diffusion-controlled.[14,16]

The primary products of the e^-_{aq} reactions with the bivalent transition-metal ions are evidently the univalent ion formed first at excited states, as will be discussed later. The formation of Mn^+, Co^+, Ni^+, Zn^+, and Cd^+ has been demonstrated through their ultraviolet absorption spectra.[17,31,48,56] Some of these were also observed in frozen solution by e.s.r.[13,57,58] Aq^0_{aq} formed in the reaction of Aq^+ with e^-_{aq} reaction has been detected spectrophotometrically by pulse radiolysis.[59,60]

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[55] D. Meyerstein and W. A. Mulac, to be published.

[56] G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Chem. Soc.*, 1963, 241.

[57] W. Low and J. T. Suss, *Physics Letters*, 1963, 7, 310.

[58] T. Feldman, A. Treinin, and V. Volterra, *J. Chem. Phys.*, 1965, **42**, 3366.

[59] J. H. Baxendale, E. M. Fielden, and J. P. Keene, ref. 9, p. 207.

[60] J. H. Baxendale and P. L. T. Bevan, ref. 36, p. 253.

The chemical behaviour of these unique species has also been studied and, as expected from their calculated redox potentials,[61] they react with various oxidants including permanganate,[62] oxygen,[59,63] N_2O, and H_2O_2[64,65a] and alkyl halide derivatives[26] as well as with nitrite, nitrate, bromate, iodate, and cupric ions.[65b] In the latter study it was shown that the Zn^+, Cd^+, and Ni^+ ions exhibit a salt effect of singly positively charged species. It has been further shown that Zn^+ is more reactive than Cd^+ and that both these univalent reducing agents are much more reactive than Ni^+. As Ni^+ has a d^9 configuration and the additional electron is accommodated in the incomplete *d* shell, the latter result is not surprising.

There is little information available on the fate of these univalent transition-metal ions in the absence of oxidizing additives.[65b] They probably dimerize to form M_2^{2+} intermediates which disproportionate to give $M^{2+} + M^0$; the mechanism of these processes is still open to investigation.

2 The Mechanism of Reactions of Hydrated Electrons with Inorganic Compounds.

Over 250 inorganic compounds have been studied for their reactivity toward e^-_{aq}.[47] The information gathered from this extensive investigation, which included representative compounds of 65 elements and has been summarised in the preceding pages, allows us to predict the reactivity of many additional compounds with reasonable confidence. Further, the e^-_{aq} reactions have given us a simple reagent and a single type of reaction (electron transfer) to be tried on the vast diversity of inorganic compounds. This is an unprecedented chemical achievement. In the following pages we shall try to discuss the mechanisms of these reactions.

A. The Energy of Activation of the Reactions of Hydrated Electrons.— The measurements of the activation energy of e^-_{aq} reactions provided invaluable information which must be discussed before one tries to elucidate the mechanisms of these electron-transfer processes.

The energy of activation of a large number of e^-_{aq} reactions has been measured both by competition kinetics[66,67] and by pulse radiolysis.[17,20,68] The great majority of e^-_{aq} reactions investigated, about 25 different compounds, were found to have an activation energy of $3{\cdot}5 \pm 0{\cdot}5$ kcal./mole. The e^-_{aq} reactions, which have been shown to have such a uniform energy of activation, range in their rates of reaction from the diffusion-controlled limit to 16 l. mole^{-1} sec.$^{-1}$.

Only three compounds were found to deviate significantly from this average,

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[61] J. H. Baxendale and R. S. Dixon, *Z. phys. Chem.*, 1964, **43**, 161.
[62] J. H. Baxendale, J. P. Kenne, and D. A. Scott, ref. 9, p. 107.
[63] J. H. Baxendale, J. P. Kenne, and D. A. Scott, *Chem. Comm.*, 1966, 715.
[64] G. V. Buxton, F. S. Dainton, and G. Thielens, *Chem. Comm.*, 1967, 201.
[65] (*a*) F. S. Dainton, ref. 36, p. 3; (*b*) D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1968, **72**, 784.
[66] M. Anbar and P. Neta, *Chem. Comm.*, 1965, 365.
[67] M. Anbar, Z. B. Alfassi, and H. Bregman-Reisler, *J. Amer. Chem. Soc.*, 1967, **89**, 1263.
[68] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1967, **71**, 3700.

but their different behaviour can readily be explained. Phenyl acetate was found to have an apparent lower ΔE,[66] which is most probably the result of a secondary reaction with the electron adduct of trichloroacetate, which was formed as the competing compound.[69] The higher activation energies observed for Co^{2+} and Mn^{2+} ions[17] are probably due to pre-equilibria with dimeric or polymeric ions formed in the pH range under study. It is expected that metal complexes of ligands which have a lower reactivity than their aquo-analogues will have apparent energies of activation higher than the actual ΔE, owing to the temperature effect of their dissociation constants.

It was reported that the reaction of e^-_{aq} with H_2O ($k = 16$ l. mole^{-1} sec.$^{-1}$) has an activation energy of 6·7 kcal./mole.[70] This value has not been corrected for the temperature effect on the dissociation constant of water. The corrected value is less than 4 kcal./mole, in agreement with other independent results.[71] It has been pointed out[68,72] that reactions whose rates are near the diffusion-controlled limit are expected to have an apparent activation energy of 3—4 kcal./mole, which is the activation energy of diffusion (ΔE_{diff}) of most solutes in water, irrespective of their actual enthalpy of activation (ΔE_{act}). For reaction proceeding at rates slower than 10^8 l. mole^{-1} sec.$^{-1}$ the measured activation energy represents the actual enthalpy barrier of the reaction. There are two possibilities regarding the actual energies of activation (ΔE_{act}) of e^-_{aq} reactions. One is that the fast reactions proceed with $\Delta E_{act} =$ *ca.* 0, like many ion–radical reactions, and that the slower reactions have activation energies of 3—4 kcal./mole. The invariance of the apparent activation energy over the whole range of reactivities would thus be fortuitous. The other possibility is that the majority of e^-_{aq} reactions, fast and slow, have an invariant energy of activation of about 3·5 kcal./mole.

The value of ΔE_{diff} of e^-_{aq} in water is expected to be considerably lower than ΔE_{diff} of conventional solutes in water, as no cavity has to be formed in the former process. In most e^-_{aq} reactions the diffusion coefficient of e^-_{aq} contributes over 80% to the sum of diffusion coefficient. Thus it is likely that the measured ΔE of the diffusion-controlled e^-_{aq} reactions is a measure of ΔE_{act}. One can find supporting evidence for this hypothesis in the fact that reaction

$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+ \qquad (18)$$

(18) which determines the rate of diffusion of H^+ in water, has an activation energy of only 2·4 kcal./mole.[73] As the diffusion of H_3O^+ is the predominant factor in the diffusion in the reaction of H_3O^+ with e^-_{aq}, the observed $\Delta E = 3{\cdot}2$ for the latter reaction[20] cannot be due to ΔE_{diff}. An energy of activation of 2·6 ± 0·2 kcal./mole, which has been reported recently for this reaction,[74] has

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[69] S. R. Logan and P. B. Wilmot, *Chem. Comm.*, 1966, 558.
[70] E. M. Fielden and E. J. Hart, *Trans. Faraday Soc.*, 1967, **63**, 2975.
[71] E. J. Hart, personal communication.
[72] S. R. Logan, *Trans. Faraday Soc.*, 1967, **63**, 1712.
[73] Z. Luz and S. Meiboom, *J. Amer. Chem. Soc.*, 1964, **86**, 4768.
[74] B. Cercek and M. Ebert, *J. Phys. Chem.*, 1968, **72**, 766.

not been corrected for the temperature effect on pKw, a correction which would evidently increase this value.

It has been found that the relative rates of reactions of electrons in ice with different solutes at 77°K are identical, within experimental error, with the relative rates of reaction in the same solutes with e^-_{aq} in water at 300°K.[75] Several of the compounds examined in ice react in H_2O at diffusion-controlled rates (including Cd^{2+}, CrO_4^{2-}, NO_3^-, and NO_2^-) whereas the others react more slowly. The results strongly suggest that all the reactions in ice which take place with 'mobile' electrons have practically no activation energy. ΔF_{act} in ice may be different from that in water but it is still invariant for a large number of reactants of different chemical nature.

It is suggested that most e^-_{aq} reactions in water have the same energy of activation, independent of their rate and the nature of the substrate. It is unlikely that such an invariant energy of activation results from the energy requirements of a transition state involving different substrates of different chemical nature. One has to attribute therefore the observed invariant activation energy as an energy requirement of the *hydrated* electron. If e^-_{aq} required a minimum amount of energy before being ready for transfer into a substrate molecule, one could explain the experimental findings.

B. The Primary Products of Reactions of the Hydrated Electron.—Reactions of e^-_{aq} invariably proceed by the transfer of an electron (19) from its site in the solvent into the acceptor molecule irrespective of the charge of the latter (*n* is a positive or negative integer or zero, and A is an atom or a polyatomic molecule).

$$e^-_{aq} + A^{n+} \rightarrow A^{\,n-1\,+} \tag{19}$$

The electron has to transfer without violating the Franck–Condon restriction, namely, that none of the atoms involved changes position during the instant ($> 10^{-14}$ sec.) of the actual electron transfer. In the case of diffusion-controlled reactions, the acceptor molecule is believed to be in its vibrational and electronic ground states at the instant of electron transfer. It is most probable that after the molecule has accommodated an additional electron, its interatomic distances at the ground state, and in many cases its overall configuration, will differ from those of the acceptor molecule. Thus at the very first instant following electron transfer, a vibrationally and occasionally an electronically excited product has to be formed. A non-excited primary product can be envisaged only when an electron is incorporated into a vacant orbit of an atom, *e.g.*, reaction (20), and

$$e^-_{aq} + I \rightarrow I^- \tag{20}$$

even then a rearrangement of the solvation shell around the solute has to take place immediately ($t_{\frac{1}{2}} < 10^{-9}$ sec.) following the electron transfer.

The de-excitation of the vibrationally excited state may take place within the time of a few vibrations ($< 10^{-12}$ sec.). These excited species have to be con-

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[75] L. Kevan, *J. Amer. Chem. Soc.*, 1967, **89**, 4238.

sidered as intermediates and not as transition states because they evidently persist longer than a single vibration. It should be noted, however, that on the 'chemical' time scale one seldom considers intermediates with lifetimes less than 10^{-12} sec.; thus these excited primary products may be overlooked from the stoicheiometric 'chemical' standpoint One cannot, however, neglect these excited products when considering the detailed mechanism of the electron transfer. These species can be demonstrated only in two cases, when the de-excitation is accompanied by an irreversible cleavage of chemical bonds and when photons are emitted as a result of intramolecular electron transitions.

There is very little experimental evidence for the formation of the excited primary products. The only indicative cases are the formation of $Fe(CN)_6,H_2O^{3-}$ from $Fe(CN)_6^{3-}$[76] and the long-lived excited $Co(dipy)_3^{2+}$.[53,77] No chemoluminescence, which would be emitted on radiative de-excitation, has been demonstrated in inorganic systems. The radiationless de-excitation may be facilitated by the intimate interaction of the product with the highly polar solvent.

C. The Mechanism of Electron Transfer.—The reactivity of hydrated electrons toward inorganic compounds has been shown to be correlated in many cases with the oxidation potentials of the substrates. These oxidation potentials are a measure of the change in free energy on going from the ground state of the reactant to that of the reduced product. There are, however, additional factors which determine the rates of these reactions; these include, *inter alia*, the effect of ligands on the reactivity of complex ions, or the requirement of a finite positive electron affinity of the substrate at its (initial) ground state. In trying to understand the mechanism of e^-_{aq} reactions one has also to consider the low and practically invariant energy of activation, which strongly suggests a similar mechanism for most of these reactions. Such a mechanism should be consistent with each of the experimental findings cited above.

The specific rates of reaction of inorganic compounds with e^-_{aq} range over many orders of magnitude. This is true also of homologous elements like the rare earths as well as of different complexes of the same element at the same state of oxidation. What is the reason for these differences in the rate of reaction?

Three alternatives have been advanced to explain these differences in rate. According to the first, it is the Franck–Condon restriction that requires considerable free energy of activation to organise the electron acceptor to a configuration appropriate for electron transfer.[78,79] The second attributes the free energy of activation to a restricted transport of the electron through the ligands.[15] According to a third mechanism one assumes that electron tunnelling takes place and that the observed slow rates are due to transmission coefficients smaller than unity.[16]

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[76] M. Haissinsky, A. M. Kaulkes, and E. Masri, *J. Chim. phys.*, 1966, **63**, 1129.
[77] W. L. Waltz, Ph.D. Thesis, Northwestern Univ., 1967.
[78] R. A. Marcus, *Adv. Chem. Ser.*, 1965, **50**, 138.
[79] R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 3477.

An attempt has been made[79,80] to draw an analogy between outer-sphere redox reactions, which presumably follow the Marcus theory of electron transfer,[81] and the reactions of the hydrated electron. It was assumed that the rate of electron transfer is limited by the energy necessary to rearrange the acceptor molecule as well as the water molecules of e^-_{aq} to a configuration compatible with the Franck–Condon restriction. This energy requirement is compensated by the gain in free energy of the electron-transfer reaction. At first approximation this theory[79] predicts equation (21) where W, the work necessary to bring the two charged reactants together, makes a negligible contribution to $\Delta F^‡$. The reorganisation energy of both reactants, λ, is of the order of 40—60 kcal./mole[78] and ΔF° is the gain in free energy in the reaction. This amounts to the differences between the standard redox potentials of e^-_{aq} and

$$k = 10^{11}\exp\left(-\ \Delta F‡/\mathbf{R}T\right);\ \ \Delta F‡ = W + \frac{\lambda}{4}\left(1 + \frac{F^\circ - W}{\lambda}\right)^2 \tag{21}$$

the oxidant, minus the free-energy change of about 0·2v due to the loss in translatory degrees of freedom going from the reactants to the product.[79,80]

According to this treatment the rate of reduction of a given inorganic complex by e^-_{aq} is primarily determined by the gain in free energy of the reaction. Although only very rough estimates could be made, this theory requires any e^-_{aq} reaction with a free-energy gain of less than 20 kcal./mole to be immeasurably slow and those with a free-energy gain of over 50 kcal./mole to be diffusion-controlled. If Marcus's assumption is followed, it would be implied that the Cd^{2+}/Cd^+ couple has a redox potential of about 0·5v, Ni^{2+}/Ni^+ about 0·7v, and Zn^{2+}/Zn^+ about 1·0v, whereas *all* the slower reactants and their EDTA complexes have redox potentials in the range of 1·0—2·0v. These predictions are, however, rather unlikely following any physicochemical estimation of these redox potentials.[61,82] A semiquantitative evaluation of the rates of reaction of EDTA complexes showed that the experimental data are in discord with the predictions of the Marcus theory.[16] If a Franck–Condon restriction would reduce the rates of reaction, this effect should be manifested in the activation energy.[83] It has been shown, however, that even the reaction of Mn^{II}–EDTA with e^-_{aq}, which is one of the slowest studied, has an activation energy less than 4 kcal./mole;[68] moreover it seems that the energy of activation of e^-_{aq} reactions does not depend on the nature of the substrate. It is plausible therefore that in the case of Mn^{II}–EDTA as well as of other EDTA complexes, the favourable free energy of the reduction by e^-_{aq} makes the electron transfer feasible, despite the Franck–Condon restriction at the ground state of the substrate.

A second mechanism for electron transfer, which we may name the 'conductance' mechanism, attributes the limitations in the rate of electron transfer to the central atom to a limited conducting capacity of the ligands.[15] This mechanism,

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[80] N. Sutin, 'Exchange Reactions', IAEC Vienna, 1966, 7.

[81] R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; *Trans. Faraday Soc.*, 1960, **29**, 129.

[82] C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry', Oxford, Univ. Press, 1966.

[83] M. E. Sacher and K. J. Laidler, *Trans. Faraday Soc.*, 1963, **59**, 396.

which can be looked at as an analogue of an inner-sphere, or bridged, electron transfer, requires an overlap of the orbitals of the hydrated electron and the ligand as well as those of the ligand and the central metal ion. According to this mechanism an electron is added to the orbitals of the ligand simultaneously with the release of an electron to the metal ion. The ligand, which does not necessarily carry an excessive electron at any time, is still required to have a favourable electronic configuration to allow such an electron transfer to take place.

This mechanism has, however, two major drawbacks. First, it does not imply a correlation between $\Delta F\ddagger$ and ΔF°, which seems to be a major factor in many cases. Moreover, many EDTA complexes react at diffusion-controlled rates, despite their suggested limited electron-conducting capacity, and invariably these are cases of reactions with a high ΔF°. Secondly, it does not explain why a certain ligand, namely H_2O, enhances the rates of electrons compared with cyanide,[15] or hydroxide which is not readily expected from the electronic structure of these ligands. From the available information on the behaviour of outer-sphere redox reactions, there is no evidence for a superior electron-transfer capacity of H_2O. It is still possible that water is outstanding in being capable of bonding an e^-_{aq} and a ligand of a metal ion at the same time and therefore best adapted to act as a bridge in this mechanism. Whether this bridged complex is a transition state or a short-lived intermediate is still an open question.

Before going further with the discussion of the mechanism, one has to answer the question, 'Do all hydrated electron reactions have a transition state?' In any assessment of e^-_{aq} reactions we have to make clear whether we assume that these, like conventional reactions, proceed *via* a transition state or whether they can be considered as intermolecular 'adiabatic' electron-transfer processes analogous to intramolecular 'vertical' electron transitions.

A conventional transition state involves the existence of a state with a higher free energy than both reactants and products, which has a lifetime of the order of a single vibration (10^{-13} sec.). The transition state of an e^-_{aq} reaction, if it existed, is expected to have a lifetime of the order of an electronic transition, namely 10^{-15} sec., and therefore the equilibrium between it and the reactants might involve the electronic states only, as the atoms do not move during the transition. As the suggested transition state should resemble both reactants and product, we cannot envisage the electron in an excited state having the very low and invariant activation energy found for so many e^-_{aq} reactions. A conventional transition state is thus rather unlikely to be involved in e^-_{aq} reactions.

Another approach from the standpoint of the potential-energy profile of the system shows that there is little effect of the potential energy barrier between reactants and products on the rate of electron transfer. The hydrated electron is held in the solvent by an energy of hydration of about 40 kcal./mole and there are additional potential-energy restrictions owing to the repulsive force of the native electrons of the acceptor molecule. The outer sphere of solvent molecules and gegenions is also expected to contribute to the potential barrier. All these should result in a potential-energy barrier much higher than the invariant 3·5 kcal./mole observed. It may be concluded therefore that owing to its small mass the electron manages to tunnel through this energy barrier, without formation of a transition state.

Electron-tunnelling is evidently dependent on the height and width of the potential barrier and also depends on the overall change in potential energy.[83,84] The width of the barrier is a function of the distance of closest approach of the e^-_{aq} to a vacant orbital. A large ΔF° is also accompanied by a decrease in the height of the potential barrier, thus the electron transfer may take place over longer distances. It has been pointed out that in certain e^-_{aq} reactions the cross-sections for reactions with oxidants having very high oxidation potentials ($\Delta F^\circ > 100$ kcal./mole) exceed the geometrical dimensions of the reactants, strongly suggesting electron-tunnelling.[14] The restriction of this pathway by the Franck–Condon principle for e^-_{aq} reactions with a large ΔF° is negligible, owing to the availability of sufficient free energy to allow electron transfer into excited states.

In the quickly reacting EDTA complexes cited in sections 1C and 1H ΔF° is most probably large enough to allow tunnelling with a probability of unity. The electron-tunnelling mechanism may, however, also explain the behaviour of many of the slower reactions. EDTA or (ethylenediamine)$_3$ complexes differ from aquo-complexes by their dimensions much more than by their standard redox potentials. When ΔF° is not very large, it being remembered that the transmission coefficient is an exponential function of the width of the potential barrier,[84] the increase in distance between the hydrated electron and the central atom may result in a substantial diminution of the transmission coefficient.

In its simplest form the tunnelling mechanism should be feasible only when the energy level of the accommodated electron in the acceptor molecule is lower than the energy level of the hydrated electron. In other words, e^-_{aq} would be expected to react only with substrates which have an electron affinity of over 40 kcal./mole before any change in their atomic configuration took place. This would be true of most diffusion-controlled reactions, but might not be applicable to many substrates that have sufficient electron affinity only after reaching the new ground state, including a rearrangement of their solvation shell. We have therefore to modify the description of the electron-transfer mechanism to include these cases.

Let us assume that the substrate in its ground state has a relatively low electron affinity. When such a substrate approaches a hydrated electron to within a critical distance, there will be a certain probability of finding it in the substrate, a probability much smaller than unity and which will drop to zero as soon as the hydrated electron recedes. This probability is synonymous with the tunnelling coefficient discussed above. Now if the substrate molecule rearranges to a configuration which accommodates the additional electron in a lower level, the probability of its escape is diminished. As soon as these rearrangements, including those of the solvation shell, result in stabilisation of the additional electron at an energy level below 40 kcal./mole, the reaction goes to completion. The

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[84] W. L. Reynolds and B. W. Lumry, 'Mechanism of Electron Transfer', The Ronald Press Co., New York, 1966.

overall rate of reaction according to this mechanism will depend on the level of the initial electron trap as well as on the rate of rearrangement to a stable product. If the former parameter is the more important one the reactions will have no activation energy of their own. If the activation energy of intramolecular rearrangement of most molecules is within the range of 3—4 kcal./mole, this mechanism would again be consistent with the experimental results. This mechanism is the only plausible explanation for many of the reactions of e^-_{aq} with aromatic[85] or carbonylic compounds,[86] the rates of which range over many orders of magnitude, but which proceed with a small and practically invariant $\Delta E\ddagger$.[67] Many of these substrates have insufficient electron affinity to compete with the hydration of the electron unless the product rearranges and becomes solvated.

From the standpoint of the absolute rate theory, one may look at the course of a reaction of the latter type as tunnelling followed by a series of transition states, each with a lower potential energy, separated from each other by free-energy barriers which consist predominantly of entropy of activation.

The inclusion of the intramolecular rearrangement *following* the electron-tunnelling in the requirements for completion of certain e^-_{aq} reactions makes electron-tunnelling plausible as the first step in any of the e^-_{aq} reactions hitherto investigated. There is at present no case which requires 'conductance' mechanism and which could not be explained by electron-tunnelling. The efficiency of water as a bridging ligand may be explained by a substantial decrease in the width of the potential barrier, in the reactions of aquo-complexes, which is accompanied by an increase in the transmission coefficient. The 'classical' transition state involving the rearrangement of a molecular configuration before the electron transfer seems to be even less likely, although it cannot be excluded.

The prevalence of electron-tunnelling in e^-_{aq} reactions does not imply that other 'outer sphere' electron-transfer processes in inorganic chemistry proceed by the same mechanism. It is conceivable that while the electron donor reorganises to facilitate electron-transfer at the lowest energy expense, a reorganisation of the electron acceptor also takes place to facilitate the incorporation of an electron into the lowest level possible. The difference between these and e^-_{aq} reactions is that in the latter the electron is much less restricted and localised. None of the conventional reducing agents in homogeneous aqueous solution has an electron bound by as little as 40 kcal./mole.

It should be stated, however, that there is no experimental evidence or theoretical reason that all e^-_{aq} reactions should proceed by the same mechanism. In fact, each of the main three mechanisms discussed, namely the two 'classical' mechanisms and the electron-tunnelling may contribute to the different electron-transfer reactions.

3 Conclusion

The reactions of hydrated electrons have contributed to three different aspects

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[85] M. Anbar and E. J. Hart, *J. Amer. Chem. Soc.*, 1964, **86**, 5633.

[86] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1967, **71**, 3993.

of inorganic chemistry. First, the study of these reactions has given us a new insight into electron-transfer processes and has raised the possibility of the existence of electron-tunnelling in chemical processes. Secondly, in homologous series the rates of e^-_{aq} reactions may be used as a semiquantitative measure of the relative electron affinity of various species in aqueous solution. And lastly, but not least, hydrated-electron reactions provided inorganic chemistry with an extensive series of novel reduced inorganic compounds in aqueous solution. These compounds are presently in their very early stages of study but they will undoubtedly become an important part of modern inorganic chemistry.