QUARTERLY REVIEWS

ISOTOPIC EXCHANGE BETWEEN DIFFERENT OXIDATION STATES IN AQUEOUS SOLUTION

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Introduction

Although tracers have been used for nearly forty years in the study of isotopic exchange reactions, it is only relatively recently that attempts have been made to elucidate the detailed kinetics of even the simplest systems. An analysis of more than one hundred publications, covering a similar number of systems in aqueous solution, reveals that only seven systems have been studied in detail; only fifteen have been the subject of reasonably detailed rate measurements. This statement excludes reactions involving the hydrogen nuclides, which present unique features and possess an extensive literature of their own. It also excludes the numerous investigations involving organic molecules, which have thrown much light on the structure and reactivity of organic species. The interchange of water molecules between hydrated ions and the solvent, which has been studied in some detail by Taube and his co-workers, is mentioned in this Review only where it provides information relative to the main theme. The latter is concerned with homogeneous exchange between different valency states, which possesses much in common with the study of oxidation–reduction reactions; some of the examples chosen, *e.g.*, those for strong complexes (p. 240), do not conform strictly to this definition, but are of interest in the development of the subject as a whole.

The growing importance of this field is reflected in the fact that three symposia have recently been devoted entirely to it and to the related subject of electron-transfer reactions—at Brookhaven (1948), Paris (1951), and Notre Dame (1952). It has also been the subject of several recent reviews.[1]

Before proceeding to describe in some detail the methods and results of these studies, a brief indication will be given of some of the many fields in which they have been of use.

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[1] (*a*) Haissinsky and Daudel, *Bull. Soc. chim.*, 1947, **14**, 552; (*b*) Haissinsky, *J. Chim. phys.*, 1950, **47**, 979; (*c*) Edwards, *Ann. Review Nuclear Sci.*, 1952, **1**, 302; (*d*) Myers and Prestwood, " Radioactivity Applied to Chemistry ", ed. Wahl and Bonner, Wiley, New York, 1951, Chap. I; (*e*) Betts, Collinson, Dainton, and Ivin, *Ann. Reports*, 1952, **49**, 42.

Behaviour of ions in solution. The earliest work [2] showed that the lead ions formed by dissolving lead chloride and lead acetate in aqueous solution were chemically indistinguishable, the activity present initially in the one species being distributed equally between both on subsequent separation. The extension of this work to the di- and tetra-acetates of lead in acetic acid solution [3] was considered to prove the existence of a very rapid exchange of electrons between plumbous and plumbic ions in solution. More recent work [4] has, however, shown this exchange to be slow, and suggests that the exchange originally observed occurred not homogeneously, but on separation of the two species.

Nature and strength of bonds. Much of the earlier qualitative work was designed to obtain information of this type, on the assumption that an ionic bond will interchange groups or atoms more readily than a covalent bond, and that for a series of bonds of similar type the weaker bond will interchange more readily. Considerable success has been attained in interpreting substitution reactions in organic systems, and much information obtained about the mechanism of the reactions, but in considering the problem as a whole several modifying influences may be detected. For example, the ferrous–dipyridyl complex, in which the Fe–N bonds are shown by magnetic evidence to be covalent, undergoes exchange at a measurable rate with ferrous ion,[5] while the porphyrin complexes of ferric ion, which are similarly shown to have ionic Fe–N bonds, do not.[5, 6] The former fact is attributed to the small but finite dissociation of the dipyridyl complex, permitting exchange *via* the very small concentration of ferrous ion so formed; in the porphyrin complex, the ferric ion is so bound within a single ligand molecule that a very stable structure results, and exchange *via* dissociation is not possible. Here the influence of structure predominates over considerations of bond type. A good example of this type of investigation is provided by West's results [7] on the exchange between cobaltous ion and a series of cobalt(II) complexes. The question of bond type has also been discussed by Haissinsky and Daudel,[1a] who point out that the bond type may be altered owing to solvent effects, particularly in polar solvents such as water.

Extent of exchange. In choosing suitable materials incorporating tracer elements for biological studies, it is important that exchange with the bulk of the non-radioactive nuclides in the parent system should be as small as possible, in order to minimise dilution effects and economise in the amount of radioactive material to be used. Likewise, in the preparation of carrier-free species by the Szilard–Chalmers method, exchange should be as small as possible. Auxiliary studies of exchange reactions are of value in both these fields.

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[2] Hevesy and Rona, *Z. physikal. Chem.*, 1915, **89**, 303.
[3] Hevesy and Zechmeister, *Ber.*, 1920, **53**, 410.
[4] Evans, Huston, and Norris, *J. Amer. Chem. Soc.*, 1952, **74**, 4985.
[5] Ruben, Kamen, Allen, and Nahinsky, *ibid.*, 1942, **64**, 2297.
[6] Haenny and Wikler, *Helv. Chim. Acta*, 1949, **32**, 2444.
[7] West, *J.*, 1952, 3115.

Chemical kinetics. Exchange reactions may be studied either for their own interest, or to gain information regarding individual steps in complex reactions. Thus, Wilson and Dickinson [8] showed that arsenate and arsenite did not undergo exchange in acid solution except in the presence of iodine, and it is also known that only in the presence of the iodine–iodide couple is a reversible oxidation potential established,[9] showing that the electron transfer proceeds only *via* the two reversible couples. In addition, it was shown that values of the equilibrium constant obtained by studying the exchange reaction at chemical equilibrium were in good agreement with those derived from the ratio of velocity constants for the forward and the reverse reactions, measured far from equilibrium.[10] Much work has been done recently with simple systems in which the net reaction is a simple electron-transfer between two species, *e.g.*, the exchange between ferrous and ferric ions. Since the initial and the final state are chemically identical, ΔH is zero ; the free energy change is, however, negative, since the even distribution of activity between the two states is accompanied by a positive entropy change. It is sometimes stated erroneously that exchange reactions of this type may be rapid despite the fact that there is no free-energy change ; ΔG must, however, be negative, although it may be small. The study of such simple systems has revealed many interesting features, some of which will be elaborated below.

Methods and Techniques

The method of investigating exchange between two species is, in principle, quite simple. One of the species is mixed with a suitable tracer nuclide, chosen from the viewpoint of ease of preparation and suitability of nuclear properties, such as type and energy of radiation and half-life. The two species are mixed under the required conditions at zero time, and aliquot portions are taken at suitable intervals ; the two species are then separated, and the fractions analysed and their activities counted under standard and strictly reproducible conditions. The decay of activity in the initially active fraction, or the growth in the other fraction, or sometimes both, are used as measures of the exchange ; all activities are corrected for decay during the time which has elapsed. The operations are thus those normally encountered in inorganic, analytical, and radiochemical investigations ; in particular, scrupulous care must be taken to avoid undue chemical or radiochemical contamination, and frequent checks of balance of mass and of activity are necessary if accurate results are to be obtained. Each system is treated on its own merits, and the reader is referred to the original literature for details of the lengthy procedures adopted by various workers. Standard counting techniques are employed, as described in textbooks of radiochemistry.

The procedure adopted for separation of the two species should be rapid, especially where a short half-time is concerned, and should give complete

[8] Wilson and Dickinson, *J. Amer. Chem. Soc.*, 1937, **59,** 1358.

[9] Loimaranta, *Z. Elektrochem.*, 1907, **13,** 33.

[10] Liebhafsky, *J. Phys. Chem.*, 1931, **35,** 1648.

separation. Both chemical and physical methods have been employed, and each has its own advantages and disadvantages. Chemical methods are usually complete, if suitably chosen, and may be made fairly rapid under suitable conditions; precipitation is an obvious example, while solvent extraction and ion exchange have also been employed. Chemical methods suffer from the disadvantage that they may induce exchange between the two species either on addition of the reagent or in the interval between precipitation and separation: the homogeneous exchange being followed is then complicated either by a heterogeneous exchange involving the precipitated species, or by a second homogeneous exchange involving an intermediate species which has a transient existence before actual physical separation. The possibility of heterogeneous exchange can easily be tested in a subsidiary experiment, but no such simple means exists for checking induced homogeneous exchange; it is generally agreed, however, that if similar results are obtained by several different chemical techniques, then the possibility of separation-induced exchange is small. Haissinsky [11] has pointed out that in general a greater degree of induced exchange would be expected when the species of higher valency is precipitated, since there is a greater number of possible intermediate states before precipitation; this is in agreement with the results on the thallous–thallic system (see p. 231). If the degree of separation-induced exchange is small, the kinetics of the homogeneous exchange may still be studied, but if large it may obscure the results entirely; many cases of rapid exchange reported in the early literature are suspect for this reason, and reports of complete exchange during the time of mixing and separation should be treated with caution. The only thorough study of separation-induced exchange is that by Prestwood and Wahl [12] on the thallous–thallic system, in which separation was effected by four different precipitation techniques, *viz.*, thallium(III) as $Tl(OH)_3$, and thallium(I) as TlBr, Tl_2CrO_4, and Tl_2PtCl_6. The amount of induced exchange decreased in the order $OH^- > Br^-, PtCl_6^{2-} > CrO_4^{2-}$, falling from $\sim 50\%$ to $\sim 5\%$; the latter figure is confirmed by other workers,[13] also using a chromate separation. The observed induced exchange was found to be partly homogeneous and partly heterogeneous, and to vary in magnitude with experimental conditions.

Solvent-extraction separation has been employed [14] in the system cerium(III)–cerium(IV), and also in the exchange between manganate and permanganate; [15] for the latter, the results agreed with earlier work [16] in which separation was effected by precipitation of barium permanganate, and suggest that the observed complete exchange is homogeneous. In the iodine–iodate system, iodine is extracted into carbon tetrachloride,[17, 18] and

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[11] Haissinsky, *J. Chim. phys.*, 1951, **48**, C11.

[12] Prestwood and Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137.

[13] Harbottle and Dodson, *ibid.*, 1951, **73**, 2442.

[14] Gryder and Dodson, *ibid.*, p. 2890.

[15] Hornig, Zimmerman, and Libby, *ibid.*, 1950, **72**, 3808; Bonner and Potratz, *ibid.*, 1951, **73**, 1845.

[16] Libby, *ibid.*, 1940, **62**, 1930.

[17] Myers and Kennedy, *ibid.*, 1950, **72**, 897.

[18] Connick and Hugus, BNL-C-8, 164 (Brookhaven National Laboratory report).

the method has also been used to separate uranium(IV) from uranium(VI) in sulphuric acid.[19]

Ion-exchange methods have not been studied extensively, but appear very promising. The rapid exchange between ferrocyanide and ferricyanide has been confirmed by separation on a column of Amberlite resin IR–4 in carbonate form, which retains ferricyanide.[20] Alumina columns have also been used for the separation of cobaltous and cobaltic ions.[21]

Although physical methods of separation, such as diffusion or migration of ions in an applied field, appear at first sight to be preferable to chemical methods, they suffer from certain disadvantages. The time for complete separation is long, and usually one must be satisfied with an enrichment only ; even this is too slow to be of use for rapid exchange reactions. The exchange may be subject to heterogeneous catalysis in either case, and the diffusion method in particular seems subject to uncontrollable variations that may lead to discordant results. Diffusion separation has been employed in the ferrous–ferric system,[22] the cerous–ceric system,[23] and also [20] in the system $Fe(CN)_6{}^{4-}$–$Fe(CN)_6{}^{3-}$; migration techniques have been also employed in the last two systems.[20, 22b] Results obtained on the ferrous–ferric system by diffusion separation [22] give half-times ranging from less than 2 hours to 166 days, while the results are further complicated by disagreement regarding the relative mobilities of the two ions. A careful study of this system by the diffusion method [24] has since shown that the exchange is in fact rapid, and that ferrous ion diffuses more quickly than ferric ion, as would be expected. The exchange results are in agreement with those obtained by Silverman and Dodson who employed chemical separation.[25]

To summarise, it might be said that physical methods of separation may provide useful confirmatory evidence, but that in general chemical methods are to be preferred, particularly if more than one method is available, or if the induced exchange can be measured and suitable corrections made. Reference should be made also to a paper discussing the factors which limit the accuracy attainable in exchange experiments, and showing how these may be minimised by suitable planning of the experiments.[26]

Kinetics of exchange reactions

For a system in which the reactants are uniformly distributed throughout a single phase and are at chemical equilibrium, and in which the exchanging atoms are chemically equivalent in both species, it can be shown [27, 28] that

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[19] Betts, *Canad. J. Res.*, 1948, **26**, *B*, 702.

[20] Cobble and Adamson, *J. Amer. Chem. Soc.*, 1950, **72**, 2276.

[21] Hoshowsky, Holmes, and McCallum, *Canad. J. Res.*, 1949, **27**, *B*, 258.

[22] (*a*) Van Alten and Rice, *J. Amer. Chem. Soc.*, 1948, **70**, 883 ; (*b*) Linnenbom and Wahl, *ibid.*, 1949, **71**, 2589 ; (*c*) Kierstead, *J. Chem. Phys.*, 1950, **18**, 756.

[23] Gryder and Dodson, *J. Amer. Chem. Soc.*, 1949, **71**, 1894.

[24] Betts, Gilmour, and Leigh, *ibid.*, 1950, **72**, 4978.

[25] Silverman and Dodson, *J. Phys. Chem.*, 1952, **56**, 846.

[26] Davidson and Sullivan, *J. Amer. Chem. Soc.*, 1949, **71**, 739.

[27] McKay, *Nature*, 1938, **142**, 997.

[28] Duffield and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 557.

the transfer of activity from one species to the other will follow a first-order rate law, whatever the form of the exchange law itself; this follows from the fact that the overall concentrations of the reactants remain constant throughout the exchange. A full derivation of the rate law is given elsewhere,[1d, 29] and it will suffice here to detail only the results. If we consider the exchange of an atom X between two species AX and BX, *i.e.*, $AX + BX^* \rightleftharpoons AX^* + BX$, where the starred atom represents the active species, then it can be shown that the following relation holds for a homogeneous exchange reaction:

$$\ln (1 - F) = -Rt.\frac{[A] + [B]}{[A][B]} \quad . \quad . \quad . \quad (1)$$

where [A] and [B] represent the total concentration of X (both active and inactive) in AX and BX respectively at time t, R is the rate of exchange of X, and F is the fractional exchange at time t; if AX is the initially inactive species, then F is equal to the ratio of the specific activities of AX at time t and at radioactive equilibrium, as obtained by counting the separated fraction. This expression holds whatever the form of R; for a simple exchange reaction the rate of exchange may thus be calculated from the slope of the linear plot of $\ln (1 - F)$ against time, or alternatively from the half-time of exchange ($t_{\frac{1}{2}}$), since substitution of $F = 0{\cdot}5$ when $t = t_{\frac{1}{2}}$ leads to the expression

$$R = \frac{[A][B]}{[A] + [B]}.\frac{0{\cdot}693}{t_{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (2)$$

R represents the *total* number of exchanges, both active and inactive, occurring in unit time;[30] it is dependent upon the concentrations employed, and is constant throughout a run and independent of the specific activity. If the specific rate constant for exchange is k, then we may write $R = k\text{f}[A]\text{f}'[B]\text{f}''[H^+] \ldots$, and the dependence upon the parameters shown may be investigated by following the change in R when one of them is varied, the others remaining constant. For an exchange reaction which is bimolecular with respect to the two species, the second-order rate constant may be obtained directly under constant conditions of acidity, temperature, inert salt concentration, etc., since

$$k = \frac{R}{[A][B]} = \frac{1}{[A] + [B]}.\frac{0{\cdot}693}{t_{\frac{1}{2}}} \quad . \quad . \quad . \quad (3)$$

The simplest form of the exchange equation has been given here; Norris[30] has given several different forms, each of which is best suited to a particular set of conditions; these yield identical results, but in most cases the form given here will suffice. Although it has been derived for an exchange involving only one atom or group in a molecule, it holds equally well for exchange involving one of several chemically identical groups, provided that the concentrations are expressed in terms of g.-atoms or g.-equivalents relative to the groups concerned, *e.g.*, it will hold for the

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[29] Friedlander and Kennedy, " Introduction to Radiochemistry ", Wiley, New York, 1949.

exchange between AX and BX_n if all the X atoms in the latter undergo exchange at equal rates with those in AX. If, however, this condition of equivalence is not satisfied, the semi-logarithmic exchange curve will be complex and non-linear, and will resemble the decay curve for a mixture of radioactive species. In certain limiting cases such a curve may be resolved into its components, and individual exchange rates obtained.[1d] Many other factors may lead to a non-linear exchange law, but these are usually capable of experimental investigation.[30, 31] The exchange may be catalysed either by labile impurities in the system or heterogeneously at a surface, or it may be accelerated by the radiation ; the level of activity employed is usually sufficiently small for the last-named to be very improbable, and the possibility is easily checked. Complex exchange rates will be obtained if exchange proceeds by more than one mechanism when the individual rates are different but of comparable magnitude. This could be resolved by working over a wide range of conditions. A more serious possibility arises if the chemical equilibrium responsible for exchange is not rapidly established, particularly when the concentrations of the intermediates concerned are not small compared with the concentrations of the reactants ; we may then have secular variations in concentration which may lead in turn to a slowly varying exchange rate. This appears to be the case in the exchange between bromine and bromate ion.[31, 32]

Another cause of complex exchange relationships is the " isotope effect " observed when using nuclides of low atomic number. The foregoing treatment assumes that the alteration in natural mass abundance of the species employed is without effect either upon the rates of the reactions concerned or upon the position of chemical equilibrium attained. As is well known, the effect upon rates and equilibria is quite large for the isotopes of hydrogen, and even for carbon the differences are appreciable, although for the higher elements they are unimportant. In cases where exchange studies are being made with ^{14}C a modified exchange expression has been derived by Harris.[33]

In a system where separation induces some exchange, extrapolation of the exchange curve leads back, not to $(1 - F) = 1$ at zero time, but to a value representative of the induced exchange. Prestwood and Wahl [12] have shown that, so long as the effects are reproducible and consistent techniques are used throughout, these effects may be eliminated. If F represents the fractional exchange at time t before separation, $\overline{F}$ that after separation at time t, and $\overline{F}_0$ the zero-time exchange after separation, and if S_0, S_t, and S_∞ are the specific activities of the separated fraction at zero time, time t, and at equilibrium respectively, we can derive the following expression :

$$F = (S_t - S_0)/(S_\infty - S_0) = (\overline{F} - \overline{F}_0)/(1 - \overline{F}_0) \quad . \quad . \quad (4)$$

The quantities measured in an experiment are $\overline{F}$ and $\overline{F}_0$, the latter being obtained from a separation immediately after mixing ; if values of F are

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[30] Norris, *J. Phys. Chem.*, 1950, **54**, 777.

[31] Betts and Mackenzie, *Canad. J. Chem.*, 1951, **29**, 655.

[32] *Idem, ibid.*, p. 666.

[33] Harris, *Trans. Faraday Soc.*, 1951, **47**, 716.

calculated in this way, the points all lie on the same exchange curve passing through $(1 - F) = 1$ at $t = 0$, whatever the method of separation. Uncorrected points give $F = \bar{F}_0$ at $t = 0$. Alternatively, if we plot $\ln(1 - \bar{F})$ against t, values of R and $t_{\frac{1}{2}}$ may still be derived directly as for a separation procedure which does not induce exchange, since by substituting for F from equation (4) into equation (1) we obtain the expression

$$\ln(1 - \bar{F}) = -Rt.\frac{[A] + [B]}{[A][B]} + \ln(1 - \bar{F}_0) \qquad . \qquad . \qquad (5)$$

The slopes of the corrected and the uncorrected curve are thus the same; in practice, uncorrected curves are usually employed, and the extent of induced exchange calculated from the intercept on the vertical axis.

Reactions involving simple ions in solution

In this and the following section a survey is given of certain individual systems; the division is to some extent arbitrary, the present section dealing with simple hydrated ions, oxy-ions, and the relatively weak complexes which the former may form with anions such as hydroxyl, chloride, etc. While the particular mechanisms concerned will be presented in these two sections, more general matters concerning the mechanism of exchange will be deferred to the final section.

One-electron Transfer Reactions Involving Cations.—*Iron.* A thorough study of this system by Silverman and Dodson,[25] using a chemical method of separation which induced about 35% zero-time exchange, has yielded valuable kinetic data. The rate was found to be of the first order with respect to each of the species, and to increase with decreasing acidity, all experiments being carried out at constant ionic strength (μ) in perchloric acid–sodium perchlorate solutions. Appreciable catalysis by chloride ion was also found, confirming the results of earlier work in which immeasurably rapid exchange was found in 6N-hydrochloric acid at room temperature.[34] The observed rate constant increased with ionic strength, but was unaffected by variations in perchlorate-ion concentration at constant acidity and constant ionic strength, this being achieved by substituting lanthanum perchlorate for sodium perchlorate.

If the second-order rate constant, $k = R/[\mathrm{Fe^{II}}][\mathrm{Fe^{III}}]$, is plotted against $1/[\mathrm{H^+}]$ for solutions containing only perchlorate ion, a straight line is obtained, leading to the relation

$$k = A + B/[\mathrm{H^+}] \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

Since an appreciable fraction of ferric ion is hydrolysed under the conditions employed, it is assumed that the two terms represent exchange proceeding simultaneously by two independent paths, (*a*) between $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$, and (*b*) between $\mathrm{Fe^{2+}}$ and $\mathrm{FeOH^{2+}}$. This would lead to the following rate law:

$$R = k_1[\mathrm{Fe^{2+}}][\mathrm{Fe^{3+}}] + k_2[\mathrm{Fe^{2+}}][\mathrm{FeOH^{2+}}] \qquad . \qquad . \qquad . \qquad (7)$$

i.e.,

$$k = \frac{R}{[\mathrm{Fe^{II}}][\mathrm{Fe^{III}}]} = \frac{k_1[\mathrm{H^+}]}{[\mathrm{H^+}] + K_h} + \frac{k_2K_h}{[\mathrm{H^+}] + K_h} \qquad . \qquad . \qquad (8)$$

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[34] Ruben, Seaborg, and Kennedy, *J. Appl. Phys.*, 1941, **12**, 308.

Here K_h is the first hydrolysis constant of ferric ion, and $[\mathrm{Fe^{II}}]$ and $[\mathrm{Fe^{III}}]$ represent the total (analytical) concentrations of the two species. Since $K_h \ll [\mathrm{H^+}]$ under the conditions employed,[35] this expression reduces to one identical with (6), *viz.*, $k = k_1 + k_2K_h/[\mathrm{H^+}]$. Values of k_1 and of k_2K_h were estimated from plots of k and $1/[\mathrm{H^+}]$ at four temperatures from 0° to 21·6°, and, by using known values[35] of K_h, k_2 was calculated. At 21·6°, $R_1 = 3{\cdot}3$ l. mole^{-1} sec.$^{-1}$, $k_2 = 2700$ l. mole^{-1} sec.$^{-1}$, so that exchange involving the hydrolysed ferric species is almost a thousand times as fast as that for hydrated ferric ion.

Catalysis by chloride ion suggests the participation of chloride complexes of ferric ion, and it may be shown that both $\mathrm{FeCl^{2+}}$ and $\mathrm{FeCl_2^+}$ are present to an appreciable extent under the conditions employed.[35b] The overall rate law then assumes the form

$$R = k_1[\mathrm{Fe^{2+}}][\mathrm{Fe^{3+}}] + k_2[\mathrm{Fe^{2+}}][\mathrm{FeOH^{2+}}] + k'[\mathrm{Fe^{2+}}][\mathrm{FeCl^{2+}}] + k''[\mathrm{Fe^{2+}}][\mathrm{FeCl_2^+}]$$

Although the treatment is more complex than in the absence of chloride, this expression was found to give good agreement with the results on chloride-ion dependence except at low concentrations of chloride ion, where the expression is very sensitive to experimental inaccuracies. Values of k' and k'' were obtained from experimental plots, with the aid of previously determined values of the respective chloride complexing constants K' and K'' for formation of $\mathrm{FeCl^{2+}}$ and $\mathrm{FeCl_2^+}$ respectively. At 20° and $\mu = 0{\cdot}55$, $k' = 29$ l. mole^{-1} sec.$^{-1}$ and $k'' \simeq 51$ l. mole^{-1} sec.$^{-1}$; it will be noted that chloride catalysis is much less efficient than is hydroxyl-ion catalysis. From an analysis of rate data over a range of temperature, heats and entropies of activation have been obtained for the separate steps involving ferrous ion and each of the four ferric species; the heats of activation are all slightly less than 10 kcal. mole^{-1}, and the values of $\Delta S^{\ddagger}$ lie between -18 and -25 cal. deg.$^{-1}$ mole^{-1}. The values for the complex $\mathrm{FeCl_2^+}$ are much less certain than for the other species, since an assumed value has had to be used for the temperature dependence of K''.

Weiss has suggested[36] that this exchange might also be catalysed by dissolved oxygen, *via* the equilibrium $\mathrm{Fe^{2+} + O_2 \rightleftharpoons Fe^{3+} + O_2^-}$, which involves two reactions derived from work on the oxidation of ferrous solutions. It has been shown, however, that equilibration of the solution with oxygen, nitrogen, or argon is without effect on the exchange, so that oxygen cannot participate.[37]

Cerium. Cerous and ceric ions undergo exchange with a half-time of several minutes in sulphuric, nitric, or perchloric acid; [22b, 23] a complete kinetic study in the last two solutions has revealed some interesting features.[14] Experiments at a constant ionic strength of $\mu = 6{\cdot}18$ and at acidities from 1–6N showed the kinetics to be appreciably different in the

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[35] (*a*) Bray and Hershey, *J. Amer. Chem. Soc.*, 1934, **56,** 1889; (*b*) Rabinowitch and Stockmayer, *ibid.*, 1942, **64,** 335.

[36] Weiss, *J. Chem. Phys.*, 1951, **19,** 1066.

[37] Dodson, Eimer, and Medalia, *ibid.*, 1952, **20,** 744.

two cases. In nitric acid solutions, the rate was of the first order in cerous ion and of somewhat less than first order in ceric ion, the divergence being considered significant. The rate constant was found to vary inversely with the square of the hydrogen-ion concentration, and to be given by the expression:

$$k\ (\text{l. mole}^{-1}\ \text{min.}^{-1}) = 2{\cdot}09 \times 10^{6} \exp(-7700/\boldsymbol{RT}) + \frac{2{\cdot}61 \times 10^{20}}{[\mathrm{H}^{+}]^{2}} \exp(-24000/\boldsymbol{RT})$$

The first term presumably refers to exchange between species whose concentrations are independent of acidity, while the second would involve two stages of hydrolysis, *viz.*, either two singly hydrolysed species or one doubly hydrolysed and one unhydrolysed species. Redox potentials [38] and migration data [14] suggest that ceric ion will be present to some extent as a complex in nitric acid solution, and will probably be present as more than one species over the acidity range studied. Cerous ion is usually assumed to be uncomplexed, but this is uncertain, and the overall picture is very complicated.

In perchloric acid solutions the acid-dependence is not as clearly defined, and further work is obviously required. At moderate acidities the rate appears to be proportional to $1/[\mathrm{H}^{+}]$, but at high acidities the mechanism appears to alter. The species present in perchloric acid solutions are probably very different from those in other mineral acids; at high acidity, cerium(IV) is probably virtually uncomplexed, while considerable hydrolysis occurs in dilute perchloric acid solutions [39] with the formation of CeOH^{3+} and also of polymeric species of the type $[\mathrm{Ce{-}O{-}Ce}]^{6+}$. Such polymers appear not to be formed in solutions in which ceric ion is complexed.[40] It is not therefore surprising that perchloric and nitric acid solutions should show different orders of dependence on acidity, but more data are required on the species present in these solutions before the position can be resolved. The exchange in perchloric acid solutions was found to be of the first order in cerous ion and of fractional order in ceric ion; in 6·18N-perchloric acid the observed rate law is as follows:

$$R\ (\text{mole l.}^{-1}\ \text{min.}^{-1}) = [\mathrm{Ce^{III}}]\left\{1{\cdot}60 \times 10^{13} \exp(-19{,}400/\boldsymbol{RT}) + 1{\cdot}11 \times 10^{13}[\mathrm{Ce^{IV}}] \exp(-16{,}800/\boldsymbol{RT})\right\}$$

The intermediate order with respect to ceric ion is explained on the assumption of a dual exchange mechanism involving cerous ion in both ground and excited states; evidence is quoted from spectroscopic data and by analogy with fluorescence data for the uranyl ion to show that this is feasible, and that the observed exchange could be accounted for by the existence of only $10^{-3}\%$ of the cerous ion in the excited state at room tempera-

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[38] Latimer, "Oxidation Potentials", Prentice-Hall, New York.

[39] (*a*) Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 818; (*b*) King and Pandow, *J. Amer. Chem. Soc.*, 1952, **74**, 1966.

[40] Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 828.

ture. The transition is a forbidden one, and must take place by collision with solvent molecules ; the mechanism suggested is as follows, where S represents a solvent molecule and Ce^{III*} the excited state.

$$Ce^{IV} + Ce^{III} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \text{Exchange}$$

$$Ce^{III} + S \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Ce^{III*} + S$$

$$Ce^{IV} + Ce^{III*} \underset{k_4}{\overset{k_4}{\rightleftharpoons}} \text{Exchange}$$

If we assume that $k_4[Ce^{IV}] \gg k_3[S]$, the observed rate law follows, since

$$R = k_1[Ce^{III}][Ce^{IV}] + k_4[Ce^{III*}][Ce^{IV}]$$

$$= k_1[Ce^{III}][Ce^{IV}] + k_4[Ce^{IV}]. \frac{k_2[Ce^{III}][S]}{k_4[Ce^{IV}] + k_3[S]}$$

$$= k_1[Ce^{III}]\left\{[Ce^{IV}] + k_2[S]/k_1\right\} = k_1[Ce^{III}]\left\{[Ce^{IV}] + k_2'\right\}.$$

Since the degree of splitting of the levels, and also the rate of excitation, will depend on local conditions such as complex formation, electron density, and so on, we might expect a difference between perchloric and nitric acid solutions. The authors consider that the small deviation from first-order dependence in nitric acid solutions is due to a similar cause, and that experiments at lower ceric-ion concentrations should show this more clearly. Since the acid-dependence in perchloric acid solution was studied under conditions where the reaction was predominantly of zero order in ceric ion, the results suggest that slight single-stage hydrolysis of cerous ion is involved.

By analogy with the chloride-ion catalysis of the ferrous–ferric exchange, we might expect a similar catalysis in the present system, and this has been found.[41] The chloride catalysis is small, but fluoride ion is a very powerful catalyst, *e.g.*, for 0·002M-solutions in 6N-nitric acid, the half-time at − 14·5° is reduced from 220 to 26 minutes on making the solution $1{\cdot}26 \times 10^{-4}$M in potassium fluoride, corresponding to ~ 10^{-6}M-fluoride ion. The catalysis is of the first order in fluoride ion over a seven-fold concentration range.

Europium and vanadium. The exchange between europous and europic ions cannot be studied in perchloric acid because of the rapid oxidation of the former ; above 0·1N-chloride ion concentration the oxidation is slow, and the chloride-catalysed exchange was studied under these conditions.[42] The reaction is of the first order in both species, and also in chloride ion ; extrapolation of the data to zero chloride-ion concentration suggests that exchange between the uncomplexed species is negligibly small. The result of varying the acidity suggests that there is no effect due to hydrolysis as in the case of iron, cerium, and thallium, but that the small change in rate observed is probably due to activity variations associated with the replacement of H^+ by Na^+ when maintaining constant ionic strength. The rate law may be written $R = k[Eu^{II}][Eu^{III}][Cl^-]$, where

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[41] Hornig and Libby, *J. Phys. Chem.*, 1952, **56**, 869.

[42] Meier and Garner, *J. Amer. Chem. Soc.*, 1951, **73**, 1894.

$k = 6{\cdot}5 \times 10^{11} \exp(-20{,}800/\boldsymbol{RT})$ l. mole^{-1} sec.$^{-1}$ at $\mu = 2{\cdot}0$. The results suggest that exchange probably occurs between the ions Eu^{2+} and $EuCl^{2+}$, the latter being present at quite low concentrations. They do not enable us to decide whether the rate-determining step is a simple electron-transfer between these two species (followed by $EuCl^+ \rightarrow Eu^{2+} + Cl^-$), or whether an electron and a chloride ion are transferred simultaneously.[42a]

Three oxidation couples of vanadium have been investigated, namely, V^{II}–V^{III}, V^{III}–V^{IV}, and V^{IV}–V^{V}. The first and third of these undergo complete exchange within the time of separation ; [43, 44] in the third, three different methods of separation were used, so that the exchange is probably homogeneous, the experiments being carried out in both perchloric and hydrochloric acid. This case is interesting because it is known that vanadyl and pervanadyl ions attain electrochemical equilibrium only slowly in hydrochloric acid solution,[45] whereas rapid exchange is usually (although not always) accompanied by rapid reversibility of the system at an inert electrode.[46] Exchange between vanadic and vanadyl ions was studied in perchloric acid solutions at $\mu = 2{\cdot}5$, by using an ion-exchange method of separation.[47] The rate law is of the form $R = k[V^{III}][V^{IV}]/[H^+]$, with negligible contribution from unhydrolysed species over the range 0·5—2·0N-acid ; k is given by the expression $k = 4{\cdot}5 \times 10^{12} \exp(-20{,}700/\boldsymbol{RT})$ sec.$^{-1}$. Under the conditions employed, vanadium(IV) will be present largely as VO^{2+} or $V(OH)_2{}^{2+}$, and the pH-dependence is considered to arise from the equilibrium $V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+$ ($K_h \sim 2 \times 10^{-3}$ mole l.$^{-1}$). The specific rate constant for exchange between the species VOH^{2+} and VO^{2+} [or $V(OH)_2{}^{2+}$] will then be given by $k = k'K_h$, whence $k' = 1 \times 10^8 \exp(-10{,}700/\boldsymbol{RT})$ l. mole^{-1} sec.$^{-1}$. The exact mechanism is unknown, but it is suggested that exchange may occur through an intermediate complex containing vanadium ions in both valency states, linked together by oxygen bridges ; the mechanism might involve transfer either of hydroxyl groups or of protons.

Mercury. Mercurous and mercuric ions undergo complete exchange within the time of separation in both nitric and perchloric acid,[34, 48—50] and the different methods employed suggest that the exchange is homogeneous and that the bond in the ion $Hg_2{}^{2+}$ is easily broken. The rate may, however, be reduced to a measurable value by adding cyanide ion,[50] showing a slow exchange involving cyanide complexes, and the kinetics have been studied under these conditions. The rate is approximately of the first order in each species, and is reduced two-fold by increasing the

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[42a] See Taube, Myers, and Rich, *J. Amer. Chem. Soc.*, 1953, **75**, 4118, for some observations on this problem.

[43] King and Garner, *ibid.*, 1952, **74**, 3709.

[44] Tewes, Ramsey, and Garner, *ibid.*, 1950, **72**, 2422.

[45] Coryell and Yost, *ibid.*, 1933, **55**, 1909.

[46] Haissinsky, *J. Chim. phys.*, 1948, **45**, 224.

[47] Furman and Garner, *J. Amer. Chem. Soc.*, 1952, **74**, 2333.

[48] Haissinsky and Cottin, *J. Chim. phys.*, 1949, **46**, 476.

[49] King, *J. Amer. Chem. Soc.*, 1949, **71**, 3553.

[50] Wolfgang and Dodson, *J. Phys. Chem.*, 1952, **56**, 872.

ratio $[CN^-]/[Hg^{II}]$ from 0·5 to 1·8 ; further increase in this ratio is precluded by the rapid dismutation of Hg_2^{2+} under these conditions. The exchange was insensitive to oxygen, sunlight, or heterogeneous catalysis, and no appreciable effect of acidity was noted over the pH range 0·85—2·7 at $\mu = 0{\cdot}125$, or of ionic strength 0·125—2·0 at pH = 2·5. The overall activation energy from 0° to 30° was 14 kcal. mole^{-1}.

The authors have calculated a rate constant for the dismutation reaction $Hg_{2\,aq.}^{2+} \longrightarrow Hg_{aq.}^{2+} + Hg_{aq}$, based on thermochemical data, and show that exchange between mercurous and mercuric ion, if it proceeds by this mechanism, will be immeasurably fast ($t_{\frac{1}{2}} \leqslant 10^{-3}$ sec.). The exchange in the presence of cyanide ion must therefore, they consider, involve a different rate-determining step ; on the basis of the observed kinetics, and particularly the lack of dependence on pH or ionic strength, they suggest this to be exchange between Hg_2^{2+} and an uncharged cyanide complex of mercury(II), which they tentatively suggest is $Hg(CN)ClO_4$; there are insufficient data to suggest whether higher cyanide complexes react at different rates. King [51] has suggested two possible alternatives to this mechanism, one involving transfer of a mercury atom between Hg^{2+} and Hg_2^{2+}, and the other electron transfer between Hg^{2+} and Hg^+ (in equilibrium with Hg_2^{2+}) ; if the direct exchange proceeds by either of these steps, complex-formation with cyanide would presumably diminish the rate. There is disagreement regarding the actual role of cyanide ion in the exchange, as well as the relative possibilities of dismutation or dissociation of mercurous ion as a rate-determining step.[51] It would seem that further supporting evidence on the chemistry of solutions of this system is required.

Two-electron Transfer Reactions.—*Thallium.* Exchange involving transfer of two electrons is usually much slower than for one, the half-time for exchange between thallous and thallic ions varying according to conditions from several hours to several weeks in both nitric and perchloric acid solution.[52] Thorough kinetic studies have been made by two groups of workers,[12, 13] with results that are in excellent agreement, although the interpretation differs appreciably. Prestwood and Wahl,[12] working in 0·8—3·5N-perchloric acid solutions at $\mu = 3{\cdot}68$, found first-order dependence on both species, the rate increasing on decreasing the acidity and being catalysed by nitrate ion ; a linear dependence was found over the range 0·1—1N-sodium nitrate. The exchange is also catalysed by platinum black ; this was considered to be due to increased ease of electron transfer and not to surface catalysis, since silica gel is without effect. Harbottle and Dodson,[13] working in 0·3—6N-perchloric acid at $\mu = 6{\cdot}0$, also found first-order dependence on thallous and thallic ion, and an increased rate on decreasing the acidity. Dodson [53] has since extended this work to cover the range 0·5—6N-acid and $\mu = 0{\cdot}5$—$6{\cdot}0$, so that a comparison between the two sets of results is possible, and the agreement is excellent.

[51] See discussion following ref. 50.

[52] Prestwood and Wahl, *J. Amer. Chem. Soc.*, 1948, **70**, 881.

[53] Dodson, *ibid.*, 1953, **75**, 1795.

The inverse dependence upon acidity suggests that a path involving a hydrolysed species is concerned; if we consider the general case of exchange between thallous ion and the two species Tl^{3+} and $TlOH^{2+}$, then the overall rate law will be given by $R = k_1[Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH^{2+}]$, and the observed rate constant will be given by the expression

$$k = \frac{k_1[H^+]}{[H^+] + K_h} + \frac{k_2K_h}{[H^+] + K_h} \quad . \quad . \quad . \quad . \quad (9)$$

where K_h is the first hydrolysis constant of thallic ion. If we assume that hydrolysis is small, *i.e.*, $K_h \ll [H^+]$, this becomes

$$k = k_1 + k_2K_h/[H^+] \quad . \quad . \quad . \quad . \quad (10)$$

This assumption was made by Prestwood and Wahl, together with the assumption that both thallic species exchange at comparable rates; when their results were plotted in this form a straight line was obtained, from which values of k_1 and k_2K_h were obtained. Their plot is somewhat curved at both ends of the acidity scale, which, in the absence of further points, they considered to be due to experimental inaccuracies. Harbottle and Dodson found, however, that over the greater range of acidity studied by them the plot is a smooth curve. They suggest that the hydrolysis of thallic ion is not small and that thallic ion exchanges negligibly compared with the species $TlOH^{2+}$, *i.e.*, $k_1 \ll k_2$. Under these conditions, the expression (9) reduces to

$$k = \frac{k_1[H^+] + k_2K_h}{[H^+] + K_h} \simeq \frac{k_2K_h}{[H^+] + K_h} \quad . \quad . \quad . \quad . \quad (11)$$

Their results give a good linear relation between $1/k$ and $[H^+]$, which appears to support their hypothesis; the values of k_2 and K_h, together with the heats and entropies concerned, were calculated in this way from measurements at 25—42°. At 25°, $k_2 = 0{\cdot}094$ l. mole^{-1} hr.$^{-1}$, with activation energy $\simeq$ 16 kcal. mole^{-1} and $\Delta S^{\ddagger} = -32$ cal. deg.$^{-1}$ mole^{-1}. In view of the wider range of acidity covered by this work, and of the good agreement provided by the more recent work of Dodson, it seems likely that the latter explanation is the correct one. Confirmation would be provided if an independent value for K_h were known, but the only available figure refers to widely different conditions,[54] and in the absence of accurate activity data no extrapolation can be made to compare with the value of 3·2 deduced from the kinetic data at 25° and $\mu = 6{\cdot}0$. The data obtained by Dodson at lower ionic strength suggest that hydrolysis of Tl^{3+} is almost complete, and that further hydrolysis may occur at $\mu < 2$ to give a species which exchanges less readily than $TlOH^{2+}$; such an effect would be inexplicable if Prestwood and Wahl's mechanism were correct.

The actual exchange mechanism, as in the case of the exchange between europium(II) and europium(III), may involve either transfer of two electrons

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[54] Benoit, *Bull. Soc. chim.*, 1949, **5—6,** 518.

followed by removal of the complexing group, or simultaneous transfer of electrons and the complexing group :

$$\left.\begin{array}{rcl} \mathrm{Tl^{*}OH^{2+} + Tl^{+}} & \longrightarrow & \mathrm{Tl^{3+} + Tl^{*}OH}\ \text{(rate-determining)} \\ \mathrm{Tl^{*}OH + H^{+}} & \longrightarrow & \mathrm{Tl^{*+} + H_2O}\ \text{(rapid)} \end{array}\right\}$$

or

$$\mathrm{Tl^{*}OH^{2+} + Tl^{+}} \longrightarrow \mathrm{Tl^{*+} + TlOH^{2+}}\ \text{(rate-determining)}$$

Catalysis by nitrate ion is presumably due to a species such as $TlNO_3{}^{2+}$ exchanging more rapidly than does Tl^{3+}. Harbottle and Dodson found that traces of chloride ion reduce the rate appreciably, while at higher concentrations it is increased several million times between 0 and 1·5N-hydrochloric acid without affecting the overall kinetics ; analogous results are obtained in the reduction of ferric ion by stannous ion in perchloric acid solutions. The effects are ascribed to the differing reactivities of various chloride complexes of thallium ; the reduced rate is attributed to reaction between thallous ion and thallium(III) chloro-complexes, while the greatly increased rate probably results from exchange between anionic complexes of both valency states, *e.g.*, $TlCl_4{}^-$ and either $TlCl_3{}^{2-}$ or $TlCl_4{}^{3-}$. These pairs would present a greater equivalence of structure than would, for example, $TlCl_4{}^-$ and Tl^+, and this might in itself favour exchange.

Dodson has shown [53] that the decrease in rate with increasing ionic strength is compatible with the expected changes in activity coefficients, using activity data for ions of like charge. It will have been noted that in all the work so far reviewed, it has been assumed that the substitution of sodium ion for hydrogen ion in varying the acidity at constant ionic strength is without effect upon the activity coefficients of the species in solution ; the activity coefficient product is assumed to remain constant throughout, and molar or equivalent concentrations are used without correction. Although this assumption cannot be strictly true, the success in explaining the kinetics of these systems appears to indicate that the error involved is small compared with the magnitude of the effects observed.

Antimony and tin. Exchange reactions involving antimony and tin involve close resemblances in their interpretation, and for this reason they have been grouped together. A complex rate law was found for the exchange between Sb^{III} and Sb^{V} in hydrochloric acid solution (6N and 12N) ; [55] the total chloride concentration was kept constant, and individual concentrations were calculated on the assumption that the predominant species present are $SbCl_4{}^-$ and $SbCl_6{}^-$. The following empirical rate relation was derived over the range of conditions 4·7—6·1N-HCl, 5·4—6·1N-Cl^-, 0·0008—0·040N-Sb^{III} and -Sb^{V}, 0—0·8N-Na^+, at 25° :

$$R\ (\text{mole l.}^{-1}\ \text{hr.}^{-1}) = (8{\cdot}8 \pm 0{\cdot}9) \times 10^{11}.[\mathrm{Sb^{III}}]^{0{\cdot}6}[\mathrm{Sb^{V}}]^{1{\cdot}1}[\mathrm{H^+}]^{4}[\mathrm{Cl^-}]^{9}$$

No fundamental significance is attached to the exponents, and those relating to hydrogen ion and chloride ion are subject to any errors arising from changes in activity coefficients ; those for the antimony ions, on the other hand, are probably less subject to error, since the rates used in deriving them were corrected empirically for such changes. The authors suggest that the

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[55] Bonner, *J. Amer. Chem. Soc.*, 1949, **71**, 3909.

true values should be 0·5 and 1·0, although in view of the obvious complexity of the system we should not exclude the possibility of a fractional order other than 0·5. Exchange between $SbCl_6^-$ and $SbCl_6^{3-}$, *via* an intermediate of the type $Sb_2Cl_{12}^{4-}$, would be of the first order in each species, and it is suggested that the fractional order observed results from an equilibrium between $SbCl_6^{3-}$ and one or more polymerised species. Two lines of evidence are quoted to support the hypothesis of an intermediate complex such as $Sb_2Cl_{12}^{4-}$. Magnetic evidence on salts of the type $M_2^ISbCl_6$ suggests that the antimony ions are not equivalent and quadrivalent, but that the anionic structure consists of pairs of $SbCl_6^{3-}$ and $SbCl_6^-$ ions in resonance with each other. Furthermore, mixed solutions of antimony(III) and antimony(V) in hydrochloric acid exhibit optical interaction absorption, *i.e.*, the optical density of the mixed solutions is greater than the sum of their separate optical densities.[56] The increase is proportional to the first power of each species, and increases with increasing hydrochloric acid concentration ; it is attributed to electron transfer between the two valency states within an interaction complex.

Solutions of stannous and stannic ions in hydrochloric acid also exhibit this phenomenon, although not in the visible region as do antimony solutions. Exchange takes place [57] at a measurable rate in 9N-hydrochloric acid, the observed [58] rate expression being

$$R = 4{\cdot}5 \times 10^7[Sn^{II}][Sn^{IV}].\exp\,(-\,10{,}800/\boldsymbol{R}T)\ \text{mole l.}^{-1}\ \text{min.}^{-1}$$

between 0° and 25° ; the first-power dependence on both species suggests that no equilibrium involving the anionic form of tin (II) is concerned. If the interaction complex is responsible for part at least of the exchange, we should expect an increased rate of exchange on irradiation with light of appropriate wave-length ; this was found to be so.

One difficulty which arises if we adopt the above mechanism is that for both antimony and tin the exchange rate is much slower than would be expected if electron transfer within the complex were the rate-determining step. It is unlikely that the interaction complex differs from the one responsible for exchange ; a more likely explanation [57] is that the complex is present only in low concentration, and that the rate-determining step is an equilibrium between two different complexes of the same valency state, *e.g.*, in the case of tin, the authors postulate a rapid exchange between $SnCl_6^{2-}$ and $SnCl_6^{4-}$ followed by slow exchange between $SnCl_6^{4-}$ and the predominant stannous species, which they write $SnCl_4(H_2O)_2^{2-}$. Although this may not be correct in detail, the general outline appears reasonable.

Uranium. Uranyl and uranous ions exchange at measurable rate in hydrochloric,[59] sulphuric,[19] and perchloric acid solutions ;[60] kinetic studies have been made in the first two cases.

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[56] Whitney and Davidson, *J. Amer. Chem. Soc.*, 1947, **69**, 2076.

[57] Whitney, Brown, McConnell, and Davidson, BNL-C-8, 196 (1948).

[58] Brown, Craig, and Davidson, Abs. 117th Amer. Chem. Soc. Meeting, Detroit, 1950.

[59] Rona, *J. Amer. Chem. Soc.*, 1950, **72**, 4339.

[60] King, MDDC-813 (1947), U.S. Atomic Energy Commission Declassified Report.

In hydrochloric acid solutions in the presence of nitrogen [to prevent oxidation of uranium(IV)] the results gave the expression

$$R = k[\mathrm{U^{IV}}]^2[\mathrm{U^{VI}}][\mathrm{H^+}]^{-\frac{1}{3}},$$

with an overall activation energy of 33·4 ± 0·8 kcal. mole^{-1} from 25° to 43·5° ; the range of acidity was limited to pH 0·85—1·6 by considerations of hydrolysis and of exchange rate. Constant ionic strength was maintained with sodium perchlorate and with sodium chloride, and no evidence was found either of chloride-ion catalysis or of a neutral-salt effect. The species present under the conditions obtaining [61] are UO_2^{2+} and U^{4+} in rapid reversible equilibrium with UOH^{3+} ; the very low rate at high acidity suggests that exchange involving U^{4+} is extremely slow. The observed rate law can be explained on the assumption of a two-stage exchange step : first, the formation of a complex between UO_2^{2+} and UOH^{3+}, containing oxygen bridges (cf. the bridged polymeric species formed on hydrolysis of uranyl salts [62]), followed by exchange between this complex and a second UOH^{3+} ion. Denoting the first complex by Y^{3+}, and the transition-state complex by Z^{6+}, the complete mechanism is as follows :

$$\begin{aligned} U^{4+} + H_2O &\overset{K_h}{\rightleftharpoons} UOH^{3+} + H^+ \\ UOH^{3+} + UO_2^{2+} + 2H_2O &\overset{K_1}{\rightleftharpoons} Y^{3+} + 2H^+ \\ Y^{3+} + UOH^{3+} &\overset{k}{\rightleftharpoons} Z^{6+} \quad \text{Exchange, rate-determining} \end{aligned}$$

Since $[\mathrm{U^{IV}}] = [U^{4+}] + [UOH^{3+}]$, this leads to the following rate-expression :

$$\begin{aligned} R &= k[Y^{3+}][UOH^{3+}] = kK_1[UOH^{3+}]^2[UO_2^{2+}]/[H^+]^2 \\ &= kK_1 \frac{[\mathrm{U^{IV}}]^2[\mathrm{U^{VI}}]}{[H^+]^2([H^+]/K_h + 1)^2} \end{aligned}$$

This expression agrees quite well with that observed (above), since the data of Kraus and Nelson [61] on K_h yield a dependence upon $[H^+]^{-3{\cdot}26}$ under the conditions employed.

In sulphuric acid solutions (0·886M and 2·79M in H^+, 1·91M total sulphate) the rate of exchange was found to be increased twenty-fold on illumination with light from a tungsten lamp, the rate law for the photosensitised exchange being $R = k[\mathrm{U^{IV}}]^{0{\cdot}5}[\mathrm{U^{VI}}]^{0{\cdot}5}[H^+]^{-0{\cdot}32}$. The dark rate was of the same order as that observed for hydrochloric acid solutions, but since no detailed measurements were made the two systems cannot be compared ; it is obvious that on illumination a much more rapid mechanism is made available, which appears to resemble the dark mechanism only in acid-dependence. It is suggested that the photosensitized exchange may occur through the intermediate valency state uranium(V), which occurs in the form UO_2^+ as an intermediate in the polarographic reduction of uranyl ion.[63] This exists in rapid reversible equilibrium with uranium(VI), and also in equilibrium with

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[61] Kraus and Nelson, ORNL-496 (1950), Oak Ridge National Laboratory Report.

[62] Sutton, *J.*, 1949, S 275.

[63] (*a*) Heal, *Trans. Faraday Soc.*, 1949, **45**, 11 ; (*b*) Kolthoff and Harris, *J. Amer. Chem. Soc.*, 1945, **67**, 1484 ; 1946, **68**, 1175 ; 1947, **69**, 446.

uranium(VI) and -(IV) when both are present in acid solution. It is estimated that on mixing 0·03M-solutions of these species the solution is $\sim 10^{-6}$M in uranium(V). The equilibrium concentration of uranium(V) is greatly increased on illumination in sulphuric acid, but not in hydrochloric acid solutions, and it appears that uranium(V) may be concerned in the exchange in the former case ; no photosensitisation was found by Rona [59] in hydrochloric acid solutions. The detailed mechanism is not clear, and furthe work is necessary ; in particular, the dark rate observed in sulphuric acid solutions is far greater than that which would be given by disproportionation of uranium(V), so that the mechanism is probably rather complex and may in part resemble that suggested for hydrochloric acid solutions. Crude experiments with weak monochromatic light sources showed that absorptio within the uranium(IV) band was without effect upon the dark rate, onl absorption within the uranium(VI) band increasing it.

Exchange between Halogens and Halide Ions.—Since complete exchang occurs within the time of mixing and separation,[64—67] no kinetic studies ca be carried out and interest attaches itself to the mechanism of the exchange In the case of iodine rapid exchange also occurs between iodine and the mixe polyiodide species prepared by shaking an excess of iodine with an iodid solution for several months,[68] and it is natural to assume that the iodine iodide exchange at least occurs *via* the intermediate formation of the ion I_3

Two possible modes of exchange may be considered :

$$X^- + X_2^* \rightleftharpoons X_3^{*-} \rightleftharpoons X^{*-} + X_2 \quad . \quad (1$$

and either $$X_2 + H_2O \rightleftharpoons H^+ + X^- + HOX \quad . \quad . \quad (13$$

or, in alkaline solution, $$X_2 + OH^- \rightleftharpoons X^- + HOX \quad . \quad . \quad . \quad (13$$

Long and Olson [64] attempted to measure the rate of the chlorine–chlori exchange by competition with the chlorination of acetanilide, which extremely rapid ; on adding radioactive chloride ion they found exchan to be at least 99% complete before chlorination took place, so that t exchange rate must be at least one hundred times the rate of chlorinatio Halford has used this result, together with data on the chlorination reactio to estimate a lower limit of $k = 10^6$ l. mole^{-1} min.$^{-1}$ for the exchange. He has also calculated lower limits for the exchange rate based on equi brium data for the above mechanisms, and upper limits based on absolu rate theory with the aid of known thermochemical data. After allowan for possible errors in the calculations, only the association mechanism (1 leads to a range within which the probable experimental value can accommodated.

Exchange involving Oxy-anions.—*Manganese.* The rapid exchange tween manganate and permanganate ion in alkaline solution [15, 16, 70]

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[64] Long and Olson. *J. Amer. Chem. Soc.*, 1936, **58,** 2214.
[65] Grosse and Agruss, *ibid.*, 1935, **57,** 591.
[66] Dodson and Fowler, *ibid.*, 1939, **61,** 1215.
[67] Hull, Schiflett, and Lind, *ibid.*, 1936, **58,** 535.
[68] Peschanski, *Compt. rend.*, 1950, **230,** 85.
[69] Halford, *J. Amer. Chem. Soc.*, 1940, **62,** 3233.
[70] Adamson, *J. Phys. Chem.*, 1951, **55,** 193.

probably homogeneous, since it is obtained with widely different means of separation. Since permanganate ion does not exchange its oxygen with solvent water [71] it is probable that the reaction involves electron transfer, probably of 3*d* electrons, since exchange of manganese is unlikely if the oxygen atoms are not labile. Duke [72] has suggested the following possible alternative mechanism :

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^{2-} + OH + H^+$$

but this appears to be unlikely on energetic grounds.[11]

Adamson [70] has reported exchange experiments on various manganese couples in a careful study of the reaction between the ions Mn^{2+} and MnO_4^-. This reaction is subject to autocatalysis by the manganese dioxide produced, but by careful choice of conditions production of the latter can be delayed considerably ; in this way it was possible to measure the exchange between Mn^{2+} and MnO_4^- in 3M-perchloric acid. A half-time of 20 hours was found in 10^{-3}M-solutions, considerably reduced by a platinised surface ; on the appearance or addition of manganese dioxide exchange ceased. Addition of fluoride ion reduced the exchange rate, and also delayed the appearance of manganese dioxide. The rate law during the period prior to precipitation of manganese dioxide, when the system is assumed to be at chemical equilibrium, was of the form $R = k[H^+]^{1\cdot0-1\cdot6}[Mn^{2+}]^{1\cdot0-1\cdot6}[MnO_4^-]^{0\cdot0-0\cdot6}$, the range of the exponents indicating experimental uncertainty. Exchange between Mn^{2+} and Mn^{3+} in perchloric acid solutions was rapid but not instantaneous. The results are discussed in terms of exchange between manganese oxy-ions in the ter- and the quadri-valent state, the rate-determining step being written $MnO^+ + MnO^{2+} \longrightarrow$ exchange. These two species are assumed to be in rapid and reversible equilibrium with the original species present in solution, and by making certain assumptions regarding the magnitudes of the equilibrium constants a rate law may be derived which is similar to the experimental one. The ion MnO^{2+} is considered to be normally present under conditions of considerable supersaturation, and thus to be removed from solution on addition of manganese dioxide ; since manganese(III) and manganese(IV) are related in concentration by the disproportionation reaction $Mn^{II} + Mn^{IV} \rightleftharpoons 2Mn^{III}$, removal of MnO^{2+} also leads to a decrease in concentration of manganese(III), the exchange rate thus being considerably reduced.

Iodine–iodate. Hull, Schiflett, and Lind,[67] reporting the slow exchange between iodine and iodate in acid solution, suggested that it must proceed by an oxidation–reduction mechanism proceeding at a measurable rate. The kinetics have since been extensively studied and the mechanism elucidated ; [17, 18, 73] observed half-times vary according to the conditions from three hours to more than three years. Care has been taken to introduce known activity-coefficient data into the rate expressions, without which no progress could have been made beyond obtaining an empirical rate law ; since iodic acid (HIO_3) is a weak acid, the concentration of iodate ion in

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[71] Hall and Alexander, *J. Phys. Chem.*, 1951, **55**, 3455 ; Mills, *ibid.*, p. 2833.
[72] Duke, *ibid.*, 1948, **70**, 3975.
[73] Zaborenko, Neuman, and Samsonova, *Doklady Akad. Nauk S.S.S.R.*, 1949, **44**, 541.

solutions containing iodic acid depends on the neutral salt concentration. Consequently, the observed iodate-ion dependence is controlled by whether or not a neutral salt of another acid is present.

In solutions containing only iodine and iodic acid, the observed rate law is:

$$R \text{ (mole l.}^{-1}\text{ h.}^{-1}) = 7{\cdot}40 \pm 0{\cdot}25\gamma^{3\cdot6}_{\pm(\mathrm{HIO_3})}\cdot[\mathrm{I_2}]^{0\cdot6}[\mathrm{H^+}]^{1\cdot8}[\mathrm{IO_3^-}]^{1\cdot8} \text{ at } 25^\circ \text{ c.}$$

in which correction has been made for the activity of iodic acid; $\gamma_{\pm(\mathrm{HIO_3})}$ is the mean activity coefficient of the iodic acid ($= \sqrt{\gamma_{\mathrm{H^+}}\gamma_{\mathrm{IO_3^-}}}$ where γ is the activity coefficient of the ion, etc.). Connick and Hugus,[18] working in presence of lithium perchlorate as neutral salt, found a 0·8-power dependence on iodate concentration, and this is confirmed to some extent by Myers and Kennedy [17] who found that in the presence of other negative ions $\mathrm{X^-}$ ($\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, or $\mathrm{SO_4^{2-}}$) the above rate law becomes

$$R' = R + k'\gamma^{1\cdot6}_{\pm(\mathrm{HIO_3})}\cdot\gamma^{2}_{\pm(\mathrm{HX})}\cdot[\mathrm{I_2}]^{0\cdot6}[\mathrm{IO_3^-}]^{0\cdot8}[\mathrm{H^+}]^{1\cdot8}[\mathrm{X^-}]$$

where $k/k' \simeq 10$—100. The exchange is considered to proceed *via* the equilibrium:

$$5\mathrm{I^-} + \mathrm{IO_3^-} + 6\mathrm{H^+} \rightleftharpoons 3\mathrm{I_2} + 3\mathrm{H_2O}\,; \quad K \approx 10^{47}$$

Under the conditions of the exchange experiments the equilibrium concentration of iodide ion is calculated to be about 10^{-9}M. If we substitute from the equilibrium expression into the observed rate law, the latter is converted into the following sixth-order expression involving integral powers of all reactants:

$$R = \{\gamma^2_{\pm(\mathrm{HI})}\cdot\gamma^2_{\pm(\mathrm{HIO_3})}/\gamma_c\}\cdot[\mathrm{IO_3^-}][\mathrm{I^-}][\mathrm{H^+}]^3\cdot\{k_1\gamma^2_{\pm(\mathrm{HIO_3})}\cdot[\mathrm{IO_3^-}] + k'_1\gamma^2_{\pm(\mathrm{HX})}\cdot[\mathrm{X^-}]\}$$

$$\left.\begin{array}{ll}\text{where} & k_1 = (5{\cdot}7 \pm 1{\cdot}3) \times 10^6 \text{ l.}^5 \text{ mole}^{-5} \text{ sec.}^{-1} \\ \text{and} & k_1' = 1{\cdot}1 \times 10^5 \text{ l.}^5 \text{ mole}^{-5} \text{ sec.}^{-1}\end{array}\right\}\text{at } 25^\circ$$

and γ_c is the activity coefficient of the transition-state complex. Earlier workers [74] have obtained fourth- and fifth-order relations for the reaction between iodide and iodate ions; it is concluded that these probably resulted from neglect of corrections for the incomplete dissociation of iodic acid and failure to work at constant ionic strength.

The mechanism proposed by Myers and Kennedy is based upon exchange of two electrons between the ions $\mathrm{IO_2^+}$ and $\mathrm{I^-}$ within a transition complex which also contains the ions $\mathrm{H^+}$ and $\mathrm{X^-}$; in the absence of neutral salt other than iodate, a second iodate ion is involved, but it is considered that this is not involved in exchange with $\mathrm{IO_2^+}$ within the complex. The complete mechanism is then as follows:

$$\begin{array}{rcl}
\mathrm{IO_3^-} + 2\mathrm{H^+} + \mathrm{X^-} & \rightleftharpoons & \left.\begin{array}{l}\mathrm{IO_2^+X^-} + \mathrm{H_2O} \\ \mathrm{H^+I^-}\end{array}\right\}\text{Rapid, reversible equilibria} \\
\mathrm{I^-} + \mathrm{H^+} & \rightleftharpoons & \\
\mathrm{IO_2^+X^-} + \mathrm{H^+I^-} & \rightleftharpoons & (\mathrm{IO_2^+},\ \mathrm{X^-},\ \mathrm{H^+},\ \mathrm{I^-}) \\
 & \rightarrow & \mathrm{IO_2^-} + \mathrm{I^+} + \mathrm{H^+} + \mathrm{X^-}, \text{ Rate-determining} \\
\mathrm{IO_2^-} + 4\mathrm{H^+} + 3\mathrm{I^-} & \rightarrow & \left.\begin{array}{l}2\mathrm{I_2} + 2\mathrm{H_2O} \\ \mathrm{I_2}\end{array}\right\}\text{Rapid} \\
\mathrm{I^+} + \mathrm{I^-} & \rightarrow &
\end{array}$$

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[74] (*a*) Abel and Hilferding, *Z. physikal. Chem.*, 1928, **136**, 186; (*b*) Abel and Stadler, *ibid.*, 1926, **122**, 49.

The exchange between iodine and periodate ion is slow compared with that for the I_2–IO_3^- couple, and it is suggested that the mechanism is related to that of the chemical reaction between iodide and periodate ions, since the two systems show a similar dependence on temperature and acidity.[75] Exchange between iodate and periodate ions is very slow, but is catalysed by molecular iodine ; since other general redox catalysts (*e.g.*, Ce^{III}, $KReO_4$) are ineffective, a specific chemical mechanism is indicated.

Sulphite–thiosulphate. Slow but measurable exchange takes place between the ions SO_3^{2-} (or HSO_3^-) and $S_2O_3^{2-}$ over a wide range of acidity,[76a] corresponding to transfer of a sulphur atom. No exchange occurs [76, 77] between the two sulphur atoms in $S_2O_3^2$, even on boiling in aqueous solution. The kinetics of the former reaction have been studied [76a] over the pH range 5—14 and at ionic strengths of 1 and 2 ; at low concentrations sodium chloride or sulphate was used to maintain constant ionic strength. Variation of pH had little effect, while doubling the ionic strength approximately doubled the rate, as also did doubling the sodium-ion concentration ; this suggests that ion-pair complexes such as $NaS_2O_3^-$ might be involved in the exchange. The reaction was of the first order in sulphite and thiosulphate concentrations over the whole pH range for solutions containing either sodium sulphate or no neutral salt, but in sodium chloride solutions a puzzling deviation was noted, the power of the thiosulphate dependence being 0·8 at pH 5 and 0·6 at pH 12·7, although normal at other values. It might be expected that, if the ion $NaS_2O_3^-$ were concerned in the exchange, variation in thiosulphate concentration at constant ionic strength would reduce the sodium-ion concentration ; however, the quantitative lowering appears to be much too small to account for the observed decrease in rate. In addition, this would not explain why first-order dependence is found on either side of pH 5 and 12·7, and the cause of the observed deviations remains obscure. First-order dependence on both species being assumed, the results over the temperature range 60—96° give a value for the rate constant of $k = 2{\cdot}3 \times 10^6 \exp(-14{,}500/\boldsymbol{RT})$ l. mole^{-1} sec.$^{-1}$. Several possible explanations are suggested to explain the low value of the temperature-independent factor, which is some 10^5 times smaller than that frequently shown by bimolecular reactions. Among these is the possibility of the exchange involving specific ion-pair complexes such as $NaS_2O_3^-$ (and possibly also $NaSO_3^-$), and the physical chemistry of sulphite and thiosulphate solutions is quoted in support of this hypothesis ; in conjunction with the effects noted when the ionic strength is altered, and when the neutral salt is changed from a uni-univalent electrolyte to a bi-univalent electrolyte, this possibility appears to be very real indeed, although further work is required. The absence of any pH effect indicates that any of the species present over the pH range 5—14 can undergo exchange with equal ease ; sodium-ion complexes being neglected, the species will be predominantly $S_2O_3^{2-}$ and either HSO_3^- or SO_3^{2-}. The first-order dependence

[75] Cottin and Haissinsky, *Compt. rend.*, 1947, **224,** 636.

[76] (*a*) Ames and Willard, *J. Amer. Chem. Soc.*, 1951, **73,** 164 ; (*b*) Voge, *ibid.*, 1939, **61,** 1032.

[77] Andersen, *Z. physikal. Chem.*, 1936, *B*, **32,** 237.

on both species eliminates the possibility of exchange proceeding *via* dissociation of $S_2O_3^{2-}$ into SO_3^{2-} and S, since the rate would then be independent of sulphite concentration ; the authors favour a mechanism whereby a sulphur atom is transferred within a transition complex of the form $(O_3S{\cdot}S{\cdot}SO_3)^{4-}$.

Slow exchange is also observed between sulphide and thiosulphate ions on several hours' boiling ; [76, 78] the activation energy is similar to that for the exchange between sulphite and thiosulphate, but the temperature-independent factor is much smaller. This is attributed to the greater complexity of the reaction. The mechanism is unknown, but it is suggested that it may involve reversible dissociation of $S_2O_3^{2-}$ followed by exchange between sulphur and sulphide ion ; the latter exchange, which proceeds *via* reversible equilibria involving polysulphide ions, is well-known.[76b, 79]

Exchange Reactions involving Strong Complexes

Little is known concerning the detailed kinetics and mechanism of exchange reactions of this type, although considerable effort has been devoted to obtaining results which may be correlated with the type and strength of bonds involved. Three types of system may be distinguished : first, exchange between a complex and a ligand species ; secondly, exchange of a central ion with an uncomplexed species ; and, thirdly, interchange between two complexes in which the central ion has different valencies. Of these, the first type is much more common than the second, since it is easier to exchange one ligand, involving a single dissociation, than to dissociate the complex completely and so enable the central ion to undergo exchange. It should be noted that exchange of the third type, which may involve only electron transfer, leads to an *apparent* exchange of the central ion. In view of the wide range of data available, selected systems have been chosen to emphasise particular points.

Complex Tervalent Metal Oxalates.—The ions $M^{III}(C_2O_4)_3^{3-}$, where M = Al, Fe, Cr, or Co, fall into two distinct classes. Magnetic measurements indicate strong covalent bonding between metal and ligand in the chromium and cobalt complexes, which may be resolved into optical isomers of appreciable stability in aqueous solution. Resolution of the aluminium and ferric complexes is extremely difficult, if not impossible ; [80] the bonding in $Fe(C_2O_4)_3^{3-}$ is ionic, while that in $Al(C_2O_4)_3^{3-}$ would also be expected to be ionic, since the Al^{3+} ion possesses a rare-gas structure, and hybridisation to form covalent d^2sp^3 bonds would not be expected. Exchange experiments provide a complete parallel to these properties ; when ^{11}C is used as tracer, the ferric and aluminium complexes readily undergo exchange with added oxalate ion, whereas the others do not.[81] This would also imply an intramolecular mechanism for the racemisation of $Co(C_2O_4)_3^{3-}$ and $Cr(C_2O_4)_3^{3-}$ ions, and not one based on dissociation. The extent of dissocia-

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[78] Voge and Libby, *J. Amer. Chem. Soc.*, 1937, **59**, 2474.

[79] Haissinsky and Peschanski, *J. Chim. phys.*, 1950, **47**, 191.

[80] Johnson, *Trans. Faraday Soc.*, 1932, **28**, 845.

[81] Long, *J. Amer. Chem. Soc*, 1939, **61**, 570 ; 1941, **63**, 1353.

tion in the ion $Fe(C_2O_4)_3^{3-}$ must be considerable, since it also undergoes exchange with ferric ion itself.[82]

A similar dependence upon bond type has been found in certain complexes of nickel,[83] by using data from *X*-ray and magnetic measurements to determine the bonding. In general, complexes containing predominantly ionic or weak covalent (sp^3) bonds undergo exchange readily, while those with strong covalent bonds (sp^2d) do not; in some cases, however, the position is complicated by the effect of the solvent upon the bond properties as deduced for the solid.

Complex Cyanides.—Rapid exchange has been observed between ferrocyanide and ferricyanide [6, 20, 82, 84] and between molybdocyanide and molybdicyanide; [85] since neither of the complex iron cyanides undergoes exchange with either ferrous ion or ferric ion,[6, 82, 84] and since none of these four complex cyanides undergoes exchange rapidly with cyanide ion, exchange is presumably a direct electron-transfer reaction. It has been suggested [20] that the high net electron density at the periphery of the cyanide complexes will favour electron transfer (cf. Pauling [86]), but it should be noted that this may favour the donation of an electron by one species while hindering its acceptance by the other.

The exchange between a series of complex cyanides of heavy metals and cyanide ion has been studied by Adamson and his co-workers,[87] and the nickel cyanides have also been investigated by Long.[88] Di- and tetra-cyanides [$Hg(CN)_2$, $Hg(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, $Pd(CN)_4^{2-}$] undergo instantaneous exchange at room temperature; hexacyanides (of Fe^{II}, Fe^{III}, Co^{III}, and Cr^{III}) and $Mo(CN)_8^{4-}$ exchange very slowly, although $Mn(CN)_6^{3-}$ undergoes rapid exchange in neutral or alkaline solution. The mechanism of exchange involving the ferrous and ferric complexes is undoubtedly complex, and both ferrocyanide and molybdocyanide exchange reactions are photocatalysed. Since the $Mn(CN)_6^{3-}$ ion is decomposed in aqueous solution with the formation of free cyanide ion, its rapid exchange probably occurs *via* dissociation; this would explain the unique position of this ion among the hexacyanide complexes. Since the observed rates for the whole series do not parallel the dissociation constants, it is considered that exchange probably takes place by association, and not by dissociation. Such a mechanism would favour exchange in the di- and tetra-cyanides, which are planar in structure, since an intermediate five-co-ordinated structure could be formed by increasing the co-ordination number of the central ion. The octahedral six-covalent structures, on the other hand, cannot readily expand their co-ordination sphere to accommodate a seventh group, and exchange would be slow. The entering group might in some cases be other than the cyanide ion, if subsequent rearrangements could lead to the final product; in

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[82] Haenny and Rochat, *Helv. Chim. Acta*, 1949, **32**, 2441.

[83] Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344.

[84] Thompson, *ibid.*, p. 1045.

[85] Wolfgang, *ibid.*, 1952, **74**, 6144.

[86] Pauling, *J. Chim. phys.*, 1948, **45**, 142.

[87] Adamson, Welker, and Volpe, *J. Amer. Chem. Soc.*, 1950, **72**, 4030.

[88] Long, AECU-848, U.S. Atomic Energy Commission Unclassified Report.

the case of the chromium(III) and iron(III) complexes, the observed pH dependence could be explained if the entering group were the ion H_3O^+. Similar views have been expressed as a result of work on the exchange of PtX_4^{2-} complexes with the ion X^-, where X = CN, I, Br, or Cl.[89]

Complex Cobalt Ions.—Hydrated cobaltous and cobaltic ions undergo exchange rapidly in acid solution,[21, 90] the calculated second-order rate constant being 46 l. mole^{-1} min.$^{-1}$ in 1·0M-perchloric acid at 0°. On the other hand, Flagg [91] found no exchange between cobaltous ion and a series of cobaltic complexes, which included cyanide and amine derivatives. He concluded that if exchange proceeded by dissociation of the cobaltic complex, then the destruction of cobaltic ion by water must be faster than exchange ; this, however, would lead to a much more rapid destruction of the complex than is actually observed, and a more reasonable explanation is that dissociation is very slight. Hoshowsky and his co-workers [21] found exchange between hexamminocobaltic ion and either cobaltous or cobaltic ion to be very slow, while slow but measurable exchange was reported between the ions $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$; exchange between the ions Co^{3+} and $Co(en_3)^{3+}$ is also very slow.[94] These results suggest that exchange between the two complexes proceeds by electron transfer and not by dissociation (cf. the exchange between ferro- and ferri-cyanide ions). Attention has been drawn to the striking difference between the aquo- and ammine-complexes of cobalt.[92] Although magnetic measurements show that in perchloric acid solution both $Co^{3+}_{aq.}$ and $Co(NH_3)_6^{3+}$ are diamagnetic, the former appears to be an exception to the rule that penetration complexes are relatively non-labile ; thus, not only does $Co^{3+}_{aq.}$ exchange rapidly with $Co^{2+}_{aq.}$ (unlike the ammine-complexes), but it also exchanges water of hydration rapidly with the solvent. It is suggested that a small fraction of $Co^{3+}_{aq.}$ ions is present in a higher, paramagnetic state, a few kilocalories above the normal diamagnetic ground state, and that these are responsible for exchange. The fact that water is intermediate in polarisability between fluoride ion and ammonia, which give rise to complex ions whose ground states are paramagnetic and diamagnetic respectively, is adduced as evidence in support of this hypothesis.

Lewis, Coryell, and Irvine [93] have investigated the ammine and ethylenediamine complexes, and have drawn an interesting parallel between exchange rates and free-energy changes in the systems where the two valency states are co-ordinated with different ligands. Slow exchange was found between the ions $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ ($t_{\frac{1}{2}} > 80$ days at 0·089M-reactants in 5·7M-aqueous ammonia solution with pH 10·7) ; the rates are based upon the minimum slope of the exchange curve, since the exchange is catalysed by oxygen, the rate still falling after thirty hours.[94] The ions $Co(en_3)^{2+}$ and

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[89] Grinberg and Nikol'skaya, *Zhur. Priklad. Khim.*, 1951, **24**, 893.
[90] Bonner and Hunt, *J. Amer. Chem. Soc.*, 1952, **74**, 1866.
[91] Flagg, *ibid.*, 1941, **63**, 557.
[92] Friedman, Hunt, Plane, and Taube, *ibid.*, 1951, **73**, 4028.
[93] Lewis, Coryell, and Irvine, *J.*, 1949, S 386.
[94] Lewis and Coryell, BNL-C-8, 131 (1948).

$Co(en_3)^{3+}$ exchanged more rapidly, with $t_{\frac{1}{2}} = 2$—50 hours, and it proved possible to study the kinetics of this system. Oxygen catalysis was again observed with high initial rates even under nitrogen which were believed to be due to transitory oxygen catalysis. Since the latter is much greater than would correspond to oxidation of the cobaltous complex, the effect is ascribed to alternate formation and destruction of an oxygen-containing cobaltous complex which undergoes exchange more rapidly than does $Co(en_3)^{2+}$, each oxygen molecule being used several times before it is finally removed. It is supposed that the presence of oxygen in the complex enables the lone electron of the cobaltous ion to be extended further in space, thus increasing the overlap with the orbitals of the cobaltic complex and so facilitating transfer. This principle has also been suggested in certain other cases (see below ; also the case of tin). The reaction was found to be of the first order with respect to both species, provided that the rates were corrected for the variation in activity coefficient resulting from the association of chloride ions with $Co(en_3)^{3+}$ ions when the concentration of the latter was varied at constant ionic strength. No specific anion effects were noted when chloride was replaced by chlorate, and since alterations in concentration of free base had no effect, a dissociation-controlled mechanism is unlikely. The striking difference in exchange rates between the ammonia and ethylenediamine complexes is presumably due to difference in activation energy, since the entropy change will probably not alter appreciably. The respective electrode potentials indicate rather more covalent bonding in $Co(en_3)^{2+}$ than in $Co(NH_3)_6{}^{2+}$; this would lead to greater hybridisation of the lone electron in the former, *i.e.*, to a wider orbit and greater probability of exchange.

Exchange between the ions $Co(en_3)^{2+}$ and $Co(NH_3)_6{}^{3+}$ is rapid, with a half-time of a few minutes ; the free-energy change in this reaction ($\Delta G = 7{\cdot}3$ kcal.) is twice that corresponding to the difference in rates between this reaction and the exchange between the two ethylenediamine complexes. The reverse exchange between $Co(en_3)^{3+}$ and $Co(NH_3)_6{}^{2+}$ is very slow ($t_{\frac{1}{2}} > 500$ days), as would be expected ; the results of this exchange cannot be analysed further, since they include contributions from the slow reaction $Co(en_3)^{2+} + 6NH_3 \longrightarrow Co(NH_3)_6{}^{2+} + 3en$, the rate of which is unknown.

Miscellaneous Complexes.—Rapid exchange has been observed between the 5 : 6-dimethyl-1 : 10-phenanthroline complexes of ferrous and ferric ion ;[95] exchange occurs presumably by electron transfer since dissociation is very slight. The dipyridyl complexes of osmium(II) and osmium(III) also undergo rapid exchange.[96] This exchange has been followed without the use of tracers, and is free from problems of separation and induced exchange. The osmium complexes may be resolved into optical isomers, and the exchange studied by following the change in optical activity after mixing solutions of the (+)-form of one species and the (−)-form of the other. With both ions present at 5×10^{-4}M-concentration, exchange was complete in 95 seconds at 5°.

[95] Eimer and Medalia, BNL-1022 (1952).

[96] Dwyer and Gyarfas, *Nature*, 1950, **166**, 1181.

Interesting results have been obtained with the complexes formed by iron, nickel, and cobalt with ethylenediaminetetra-acetic acid (H_4Y).[97] The complexes are of two types, $M^{II}Y^{2-}$ (for Co^{2+}, Fe^{2+}, Ni^{2+}) and $M^{III}Y^{-}$ (for Co^{3+} and Fe^{3+}). Cobaltous ion undergoes exchange rapidly with the cobaltous complex in acid solution, but not with the cobaltic complex. For the nickel ion exchange is rapid with NiY^{2-} in acid solution, the rate decreasing considerably as the pH is increased, and then increasing again in alkaline solution; this is attributed to the effects of hydrogen ion and of excess of ammonium ion on the dissociation equilibrium of the complex. Ferrous and ferric ions undergo exchange with the respective complexes, the former much more readily than the latter. Magnetic data show that in all these complexes the bonding is predominantly ionic, so that once again the importance of structural factors is apparent.

The iron complexes have been studied in greater detail by Jones and Long.[98] Ferrous iron and the ferrous complex undergo instantaneous exchange, presumably by dissociation, at pH 1·5—4·7 and $\mu = 0{\cdot}14$—$0{\cdot}22$; the exchange between ferric ion and the ferric complex has a half-time of several hours at 25° and $\mu = 1{\cdot}10$, in 0·01M-solution. The rate is dependent upon acidity, and by carrying out experiments over a range of acidities three terms were obtained in the rate expression, with hydrogen-ion exponents of 3, 0, and -1. If the inverse power is assumed to arise by participation of $FeOH^{2+}$ at low acidities, the overall rate expression at $\mu = 1{\cdot}1$ becomes:

$$R\ (\text{mole l.}^{-1}\ \text{min.}^{-1}) = 0{\cdot}47[FeY^-][H^+]^3 + 0{\cdot}015[FeY^-][Fe^{3+}] + 0{\cdot}14[FeY^-][FeOH^{2+}]$$

This agrees well with the observed results except around 0·1M-hydrogen ion, which may indicate another acid-dependent term. The mechanism suggested for the exchange involves three independent paths, *viz.*:

$$FeY^- + 2H^+ \rightleftharpoons H_2FeY^+;\quad H_2FeY^+ + H^+ \xrightarrow{k_1} Fe^{3+} + H_3Y^-$$

$$FeY^- + \overset{*}{F}e^{3+} \xrightarrow{k_2} Fe^{3+} + \overset{*}{F}eY^-$$

$$FeY^- + \overset{*}{F}eOH^{2+} \xrightarrow{k_3} FeOH^{2+} + \overset{*}{F}eY^-$$

It should be noted that the ion $FeOH^{2+}$ undergoes exchange ten times as rapidly with the complex ion as does aquo-ferric ion, despite its smaller net charge. Taube has pointed out[99] that since the rate-determining step involves removal of a chelating group, exchange should be facilitated by ions which associate with Y^{4-}, and he suggests studying the exchange in the presence of an ion which will do this without partaking in the exchange, *e.g.*, Al^{3+}.

Miscellaneous Exchange Reactions

The Table summarises briefly the available data on systems not mentioned above; the information is mostly fragmentary, and the extent and

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[97] Long, Jones, and Burke, BNL-C-8, 106 (1948).

[98] Jones and Long, *J. Phys. Chem.*, 1952, **56**, 25.

[99] Taube, *ibid.*, p. 32.

accuracy often do not warrant calculation of rate constants or half-times. It should be remembered also that the distinction between a very slow exchange and no exchange at all is not a precise one, and may depend upon the conditions and duration of the experiment. Very full tables of exchange data up to 1950 will be found elsewhere.[1d]

The following systems have been reported to show no appreciable exchange: tellurous acid–telluric acid;[100] trimetaphosphate–hexametaphosphate;[101] phosphorous acid–phosphoric acid;[102] sulphate–persulphate;[103] sulphite–sulphate;[76, 78] sulphide–sulphate;[76b, 78] sulphide–thiocyanate;[104] cyanide–thiocyanate;[104b] chlorine dioxide and perchlorate, chlorate, chloride, or chlorine;[105] chlorate and either chloride or chlorine;[105, 106] Cr^{3+} and either $Cr(en)_3{}^{3+}$ or $Cr(urea)_6{}^{3+}$.[110]

System	Conditions	Remarks †	Ref.
Fe^{2+}–$Fe\ ph_3{}^{2+}$	0·05N-H^+	35% in 1 hr.	5
Fe^{2+}–$Fe\ dipy_3{}^{2+}$	0·04N-H^+	23% in 2 hr.	5
Ni^{2+}–$Ni\ dipy_3{}^{2+}$	—	Complete in ~ 100 min.	83
Ni^{2+}–$Ni\ en_3{}^{2+}$	—	Complete in 5 min.	83
Cr^{3+}–$Cr_2O_7{}^{2-}$ Cr^{3+}–$CrO_4{}^{2-}$	0·01N-Cr^{III}, 0·005N-Cr^{VI}, 0·05N-$HClO_4$ or -HNO_3	$t_{\frac{1}{2}} = 60$ days, 45°; 430 days, 25°	107–109
Cr^{3+}–$Cr(CN)_6{}^{3-}$	0·001N, pH 3—4	71% in 72 days	107
Cr^{3+}–$CrF_3(H_2O)_3$	0·1—1·0N-HNO_3	Slow exchange, decreasing with increasing acidity	110
$NpO_2{}^+$–$NpO_2{}^{2+}$	1·0M-$HClO_4$	Complete in 1 min.	111
M^{3+}–$M^{III}(S_2O_3)_3{}^{3-}$	2N-HCl	Rates increase in order As < Sb < Bi	112
Cu^{2+}–$Cu^{II}(S_2O_3)_2{}^{2-}$	0·5N-HCl	30% in 10 min.	112
$IO_3{}^-$–$IO_4{}^-$	0·5N-HNO_3	$t_{\frac{1}{2}} \sim 150$ hr.	75
ClO_2–$ClO_2{}^-$	Acid or alkaline solution	$k > 10^4$ l. mole^{-1} min.$^{-1}$	105
$Co(NH_3)_4CO_3{}^+$–$HCO_3{}^-$	0·03M; 0·01M-Na_2CO_3	$t_{\frac{1}{2}} \approx 7$ hr.	113

† Unless otherwise stated, the results refer to room temperature.

Some General Considerations regarding Exchange

Most exchange reactions, whether they involve transfer of an electron or of an atom or group, proceed by one of two mechanisms. The rate-determining step may be dissociation, *e.g.*, AB $\rightleftharpoons$ A + B, followed by rapid

[100] Haissinsky and Cottin, *Analyt. Chim. Acta*, 1949, **3**, 226.

[101] Vogel and Podall, *J. Amer. Chem. Soc.*, 1950, **72**, 1420.

[102] Wilson, *ibid.*, 1938, **60**, 2697.

[103] Riesebos and Aten, *ibid.*, 1952, **74**, 2440.

[104] (*a*) Heisig and Holt, *ibid.*, p. 1597; (*b*) Adamson and Magee, *ibid.*, p. 1590.

[105] Taube and Dodgen, BNL-C-8, 143 (1948); Dodgen and Taube, *J. Amer. Chem. Soc.*, 1949, **71**, 2501.

[106] McCallum and Holmes, *Canad. J. Chem.*, 1951, **29**, 696.

[107] Menker and Garner, *J. Amer. Chem. Soc.*, 1949, **71**, 371.

[108] Muxart, P. Daudel, R. Daudel, and Haissinsky, *Nature*, 1947, **159**, 538; Burgus and Kennedy, *J. Chem. Phys.*, 1950, **18**, 100.

[109] Ogburn and Brenner, *Trans. Electrochem. Soc.*, 1949, **96**, 348.

[110] King and Garner, *J. Amer. Chem. Soc.*, 1952, **74**, 5534.

[111] Cohen, Sullivan, and Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 352.

[112] Scoffier, *Compt. rend.*, 1948, **227**, 63.

[113] Harris and Stranks, *Trans. Faraday Soc.*, 1952, **48**, 137; Stranks, *ibid.*, p. 911.

exchange between, say, A and A* ; alternatively the exchange may proceed by an association mechanism such as AB + A* $\rightleftharpoons$ ABA* $\rightleftharpoons$ A + BA*. In the first case, the rate will be of the first order in concentration of AB and independent of A ; in the second case it will be of the first order in both species. Examples of both these types have been given in the preceding sections ; it is not proposed to discuss them further, since excellent reviews are available.[1a, 1b, 1d]

Electron-transfer reactions provide an example of the second class, since the first step is assumed to be the formation of a transition complex in which the transfer can take place. Some of the factors affecting electron transfer have already been discussed, and we shall now consider certain other features which have been observed in a study of such reactions.

Magnetic Factors.—Adamson[114] has drawn an interesting correlation between exchange rates and magnetic properties for a series of one-electron transfer reactions. Exchange is slow between species possessing large magnetic moments, particularly if the two moments differ appreciably, and a remarkable correlation appears if we tabulate exchange half-time on the one hand, and the product of the sum and difference of the moments on the other. The theoretical basis of this is at present obscure, but the method is of obvious value for predicting systems which would be worthy of study.

Factors influencing Electron-transfer within the Transition Complex.—From the experimental data on exchange reactions, together with results obtained from inorganic redox reactions, it is possible to appreciate some of the factors involved. Seaborg[115] originally suggested that exchange would be favoured if the two species formed symmetrical structures, *e.g.*, MnO_4^- and MnO_4^{2-}, since this would involve the minimum disturbance to the structures when the electron is transferred. Libby[116] has extended this concept on the basis of ideas analogous to the Franck–Condon principle. Owing to the fact that the transfer of an electron is much faster than the transfer of water molecules in solution, the two newly-formed species in an exchange between simple hydrated ions in aqueous solution will find themselves in incorrect environments as far as their hydration atmospheres are concerned ; *e.g.*, in the exchange between ferrous and ferric ion, the newly formed ferrous ion is initially located in an environment typical of a ferric ion, and *vice versa.* Excess of hydration energy is thus stored initially at the *original* ferrous ion site, and can only leak across to the *final* ferrous ion site by a slow collisional process. Thus, although the *net* heat change is zero, there will be a barrier to exchange which results in an energy of activation comparable to the difference in heats of hydration. Libby has attempted to calculate the height of the barrier by considering the difference in the energies required to assemble charges, initially at infinity, on to ions of radius r and charges Z and $(Z + 1)$. It is tempting to compare the result of 10·8 kcal. for an ion of radius 1 Å with the observed experimental activation energy of $\sim$ 10 kcal. common to many single-electron transfer reactions, but

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[114] Adamson, *J. Phys. Chem.*, 1952, **56**, 858.

[115] Seaborg, *Chem. Reviews*, 1940, **27**, 250.

[116] Libby, *J. Phys. Chem.*, 1952, **56**, 863.

the derivation is subject to uncertain factors, and the agreement must be regarded as fortuitous.

Effects of this type are likely to be much smaller for large, strongly-co-ordinated complexes, particularly if the two species are symmetrical within the amplitude of their zero-point vibrations. Owing to the large ionic radius, differences in hydration energy will be small, and there may be no strongly-bound water in the complex. Libby considers that this explains why the apparently more complex systems such as MnO_4^{2-}–MnO_4^- and $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ undergo exchange much more rapidly than the systems Fe^{2+}–Fe^{3+}, etc. The slow exchange in the system $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$, which appears to be an exception to this rule, is readily understood when we compare the Co–N distances in the two states ; [117] the two complexes are so far from being symmetrical that a considerable barrier to exchange is present. Several authors have tended to describe the complexing shell as either insulating or conducting, depending on whether the net charge at the periphery is positive or negative, and to conclude that the latter type will favour electron-transfer while the former will undergo only slow exchange.[20, 86] On this view, amine and water complexes would undergo exchange more slowly than cyanide or oxygen complexes. Libby, however, does not believe that the distinction is very great ; he points out that, in a complex involving water molecules, the electron moves too rapidly to become solvated, so that the energy required may actually be only slightly different from the gaseous ionisation potential. Approximate calculations based on 3*d* wave-functions for the ion H_2^+ (since exchange in the transition elements is frequently assumed to involve 3*d* electrons) indicate that the electron may penetrate several layers of water molecules, so that the insulating power of the latter may be much less than is sometimes supposed.

Libby suggests that in addition to specific catalysis, by negative ions, of exchange involving two positively charged ions (*e.g.*, the catalysis by hydroxyl or chloride ion of the exchange between ferrous and ferric ions), there is the possibility of general catalysis. Specific catalysis may arise because of the difference in reactivity of the species present, *e.g.*, $FeOH^{2+}$ may be more reactive than Fe^{3+} ; general catalysis may result from a reduction in the repulsive forces between the two species of like charge, owing to the presence of the oppositely charged ion between them. If a symmetrical linear complex of the form $M^{n+}\cdot X^-\cdot M^{(n+1)+}$ can be formed, in which the two positive ions are sufficiently close for their hydration shells to overlap, the energy barrier for exchange may be reduced considerably ; the smaller the negative ion, the greater the expected catalytic effect. In some cases this type of catalysis may be obscured by a larger, negative specific effect, *e.g.*, in the effect of traces of chloride ion on the thallium system. Some discussion has centred around the point whether the complex is formed from the two positive ions and the negative ion, or from the positive ion of smaller charge and the complex formed by the other with the negative ion.[118] This distinction is somewhat finely drawn, and does not appear capable of resolution at this stage. The catalytic effect of chloride ion is, of course, well-known in certain

[117] Brown, *J. Phys. Chem.*, 1952, **56**, 868.

[118] See discussion following ref. 116.

inorganic reactions, *e.g.*, the reduction of ferric ion by stannous ion.[119] The role of chloride ion in facilitating electron transfer between ferrous and ferric ions also receives support from the work of McConnell and Davidson,[120] who found optical interaction absorption in mixed solutions of these ions in 6—12N-hydrochloric acid (cf. the work on antimony and tin referred to above), which they attribute to electron transfer in bridged complexes of mixed valency. The colours developed when precipitates of ferrous hydroxide are oxidised in air have been attributed to a ferrous–ferric electron transfer through hydroxyl-ion bridges, since the colours weaken and finally disappear if the distance between ferrous and ferric ions is gradually increased [121] by the incorporation of other ions such as Al^{3+}. We would expect *a priori* to observe interaction absorption in solutions of ferrous and ferric ions in the presence of hydroxyl ion also, but the anion concentration required appears to be greater than that required for precipitation of ferric ion.[122] Brown has pointed out that two factors appear to determine the catalytic efficiency of negative ions,[123] namely size and electron affinity. The former determines its bridging power, smaller ions being more effective, and the latter its ability to conduct electrons. Thus, the bridging efficiency will probably decrease in the order $OH^- > F^- > Cl^- > Br^- > I^-$, and the conduction in the reverse order $I^- > Br^- > Cl^- > OH^- > F^-$ In principle, the balance between these two factors could be derived from a study of electron-transfer rates in the presence of the various ions. The complexity of anion catalysis is illustrated by recent work of Hudis and Wahl on the exchange between ferrous ion and fluoride complexes of ferric ion.[124] Although the fluoride ion is much smaller than the chloride ion, the two are found to exert comparable catalytic effects. These authors consider that this may indicate that exchange in the ferrous–ferric system proceeds not by electron transfer, but rather by proton transfer, a suggestion which had previously been made by Dodson and Davidson (see p. 249) ; an alternative explanation might be that the results reflect a combination of both general and specific catalytic effects, since fluoride ion is much more effective than chloride ion in catalysing exchange between cerous and ceric ions. The role of oppositely charged ions, as well as the factors influencing formation of the transition state, have also been discussed by Haissinsky.[11]

The alternative mechanism to that proposed above for electron transfer, namely, solvation of an electron followed by transfer, is rejected by Libby on energetic grounds and also because a free electron should reduce water. Wolfgang [125] has pointed out that the Franck–Condon principle, as applied by Libby to these reactions, should be less restrictive in non-polar solvents, since no dipolar reorientation is required, and the small energy for electronic redistribution is probably easily supplied, *e.g.*, by inversion of the solvent

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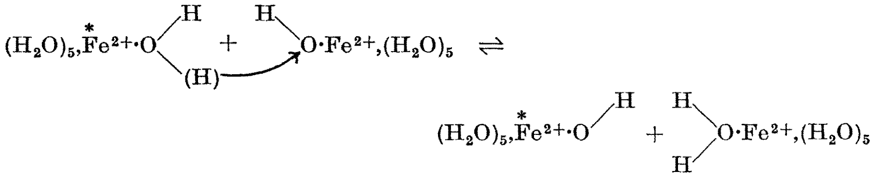
[119] Duke and Pinkerton, *J. Amer. Chem. Soc.*, 1951, **73**, 3045.
[120] McConnell and Davidson, *ibid.*, 1950, **72**, 5557.
[121] Shively and Weyl, *J. Phys. Chem.*, 1951, **55**, 512.
[122] Amphlett and (Mrs.) Davidge, unpublished work.
[123] Brown, *J. Phys. Chem.*, 1952, **56**, 852.
[124] Hudis and Wahl, *J. Amer. Chem. Soc.*, 1953, **75**, 4153.
[125] Wolfgang, *J. Phys. Chem.*, 1952, **56**, 867.

molecule in liquid ammonia solutions ; this suggests a possible field for further work.

Dodson and Davidson [126] have proposed an interesting alternative to electron transfer in the iron system, which may also apply to other similar cases. Under conditions where the ferric species is partly converted into the complex $FeOH^{2+}$, exchange may occur by proton transfer from the hydration shell of the ferrous ion :



They suggest that this might be tested by carrying out the exchange in deuterium oxide solution, where exchange by this mechanism would be much slower ; a large isotope effect would not be expected for the alternative mechanism :

$$(H_2O)_6,Fe^{2+} + OH^- + Fe^{3+},(H_2O)_6 \rightleftharpoons 2H_2O + (H_2O)_5,Fe^{2+}\cdot OH^-\cdot Fe^{3+},(H_2O)_5$$

Their mechanism, if correct, might explain the much greater efficiency of hydroxyl ion relative to chloride ion as a catalyst ; in the latter instance neither mechanism is as simple as the proton transfer postulated above. It has been suggested elsewhere [127] that the reduction of ferric ion in aqueous solution by X-rays may involve completion of a hydration shell by the analogous reaction $(H_2O)_5Fe^{2+}\cdot OH + H \longrightarrow Fe^{2+},(H_2O)_6$; this would explain why the reduction is favoured by decreasing acidity.

Finally, we may note briefly that since exchange reactions are examples of simple oxidation–reduction systems, they will offer much information regarding factors likely to influence the behaviour of the latter in general. It will be obvious from the examples chosen that no simple rules exist which would enable such behaviour to be predicted, and that each system must be treated on its merits.[128]

Further studies, in particular the acquisition of precise quantitative data, will serve a two-fold purpose ; they should help in the elucidation of oxidation–reduction mechanisms, and they should provide information on the structure and reactivity of ions in solution.

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[126] Dodson and Davidson, *J. Phys. Chem.*, 1952, **56**, 866.

[127] Amphlett, *Nature*, 1953, **171**, 690.

[128] Gryder, *Trans. N.Y. Acad. Sci.*, ser. II, 1949, **12**, 18.