

*Advances in*  
**INORGANIC CHEMISTRY**  
AND  
**RADIOCHEMISTRY**

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EDITORS

H. J. EMELEÚS

A. G. SHARPE

VOLUME 1

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H. J. EMELEÚS

A. G. SHARPE

*University Chemical Laboratory  
Cambridge, England*

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## PREFACE

The world-wide interest in inorganic chemistry and radiochemistry has created a keen demand for articles by experts which review the fields of current interest to research workers and which serve, also, to inform the nonspecialist of recent progress. It is with this in mind that the editors venture to commend this series of volumes to the reader. It is hoped that, in the succeeding volumes, the topics presented will, in a relatively short period of time, cover many of the major fields. Thereafter, there will, of necessity, be other articles which bring these topics up to date. The editors are most grateful to those who have contributed to this volume and to others who have promised contributions for later volumes. They are particularly glad that the response has been international, since they feel that the subject has an unusually wide appeal and each country has much to learn from the approach of workers in others.

Perusal of the material presented in this volume will show that the definition of inorganic chemistry adopted here is a broad one. Modern inorganic chemistry depends for its very existence on the application of physical and physicochemical principles to chemical phenomena, and it is intended that the integration of structural, kinetic, and thermodynamic data with descriptive chemistry shall be one of the main features of this series.

H. J. EMELÉUS  
A. G. SHARPE

*January, 1959*

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# MECHANISMS OF REDOX REACTIONS OF SIMPLE CHEMISTRY

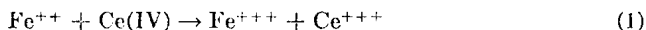
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## I. Introduction

The principal concern in this chapter will be the mechanism of reaction of metal ions in which a change of oxidation state takes place on reaction. These reactions, of which



may be taken as typical, are part of the material of instruction in general and analytical chemistry and as such are familiar to anyone with training in chemistry. Nevertheless, fundamental questions as to the means by which the change in oxidation state takes place were until recently not formulated, let alone answered.

The general subject includes as a proper part problems of specific chemistry such as are encountered in the reaction, for example, of  $\text{Fe}^{++}$  with  $\text{MnO}_4^-$ : What are the steps by which the system proceeds to the final products, and what are the properties of the intermediate oxidation states of Mn (or of Fe) which must be involved for such a complex over-all reaction? Important for inorganic chemistry as such questions are, for the most part they have been set aside, and attention is directed rather to the description of the individual steps. Given a process of simple order, we shall consider questions such as these: What is the closest distance of approach of oxidant and reductant? What is the arrangement of other groups besides the reactant metal ions in the activated complex? What motions of these groups are necessary to consummate the reaction? How are the

rates dependent on the nature of the metal ions and on the other groups which may be present in the activated complex? These questions will be given a more specific formulation when we consider the various proposals which have been made describing the "electron transfer" process.

## II. Electron Transfer in the Gas Phase

It is instructive to consider some features of the data on charge-transfer processes in the gas phase between simple molecules before considering the systems as they are complicated by the interactions of the central atoms with molecules of the solvent or other groups. The earliest experimental evidence for the occurrence of electron transfer between species in the gas phase was obtained from mass spectroscopic measurements (120). Data on the cross sections for such reactions are derived principally from two sources: measurement of the drift velocity of ions in various gases and measurements of the attenuation of ion beams brought about by inelastic collisions with molecules. The cross section for charge transfer is dependent on the kinetic energy of ions, so that the data on the drift velocity, involving speeds more nearly those of thermal energies, will be considered first.

The subject of drift velocities, particularly as it pertains to inert gas systems, was discussed by Hornbeck (58) (experimental results) and Holstein (57) (theoretical) as part of the program for a symposium on Electron Transfer Processes in general, held at Notre Dame in 1952. The significant observation is that the drift velocity of an ion such as  $\text{He}^+$  is much less than is expected if account is taken only of the usual processes for energy transfer, including polarization of He by the positive ion. Similar effects are noted for the other inert gas ions and have been recorded also for  $\text{N}_2^+$  in  $\text{N}_2$  (90). The effective collision cross section is increased by symmetry effects which include electron transfer as a component. Table I

TABLE I  
COMPARISON OF CROSS SECTION FOR ELECTRON TRANSFER  $T_i$   
WITH GAS KINETIC CROSS SECTION  $T_a$

	$T_i \times 10^{16} \text{ (cm}^2\text{)}$	$T_a \times 10^{16} \text{ (cm}^2\text{)}$
He	54	15
Ne	65	21
A	134	42

presents the data taken from Hornbeck's paper comparing the cross section for charge transfer with the "normal" cross section for ion-molecule interaction including atom polarization.  $T_i$  considerably exceeds  $T_a$ , and

is large enough so that electron transfer over nuclear separations as large as 5-8 Bohr radii must be invoked. For  $N_2^+$  in  $N_2$  the effect on drift velocity is smaller than is observed for the inert gases, and the mobility is only 7.5% less than the normal gas kinetic mobility. The difference between an inert gas on the one hand and a more complex molecule on the other can be attributed to the circumstance that the equilibrium internuclear separations for  $N_2^+$  and  $N_2$  are different, as are the separations of the vibrational levels. Since the electron transfer process is adiabatic, the energies at the two sites must match closely to make transfer possible.

During the Notre Dame Symposium, Muschlitz and Simons (93) summarized work on the cross sections for inelastic scattering of protons by various gases. The cross sections for 100-volt protons on He, Ne, Kr, and A are in the ratios 0, 1.5, 48, and 28 (52); for a complex molecule such as  $C_2H_6$ , a value of 112 is observed; there is a decrease in the cross section for inelastic scattering as the kinetic energies of the ions increase (118). The interesting qualitative features are: the maximum in the cross section for the inert gas as atomic number increases and the large cross section for  $C_2H_6$  (and other complex molecules). Presumably, the large cross section for complex molecules undergoing electron transfer to  $H^+$  comes about because, by using vibrational states, these molecules can provide many ways of bringing about the energy matching.

Since shielding by other electrons at large distances for a test electron is complete, and since the cross sections for electron transfer when simple atoms are involved are large compared to atomic dimensions, hydrogen-like wave functions can be used to describe the electron distribution at the large radii in question. Thus calculations of the probability of electron transfer, at least in simple cases, meet with a fair degree of success. Such calculations have been made by Holstein (57) for the symmetrical inert gas systems, using Hartree-Fock wave functions for the outermost shells. Gurnee and Magee (48), dealing with the same systems, have used the Slater wave functions (119) and have chosen in each case a value for the parameter  $\alpha$  (which in the hydrogen-like case would be  $(2I)^{1/2}$  where  $I$  is the ionizing potential) such that the one-electron wave function is approximately satisfied for the range of distances in question. Satisfactory agreement of calculated and experimental cross sections for  $Ne + Ne^+$  and  $He + He^+$  is obtained. The treatment of Gurnee and Magee also includes double charge transfer reactions; the theory and observations made for such reactions (141) are germane to the issue of 1 versus 2e changes in redox reactions. Experimentally, the cross section for  $Ne^{++} + Ne = Ne + Ne^{++}$  is about  $1/4$  of that for the 1e process in the same system, while for A, the ratio is about  $1/2$ . Theory (48) suggests a ratio of about  $1/2$  for both sets of reactants. For the discussion of charge transfer in diatomic mole-

cules, Gurnee and Magee used Heitler-London functions for the electronic part of the wave functions and harmonic oscillator and rigid rotator functions for the internal motions. Of the internal motions, only the vibrational part affects the probability of electron transfer. Gurnee and Magee have tabulated values of the vibrational overlap integrals for  $\text{H}_2\text{-H}_2^+$ ,  $\text{HD-HD}^+$ ,  $\text{D}_2\text{-D}_2^+$ , and  $\text{N}_2\text{-N}_2^+$ —these range from 0.195 for  $\text{D}_2\text{-D}_2^+$  to 0.940 for  $\text{N}_2\text{-N}_2^+$ . The case of widest application is that for which the energies of the initial and final states differ. At small relative velocities, the probability of transfer decreases sharply as the energy difference increases; for an energy difference as small as 0.05 eV, electron transfer is possible only when relative velocities are of the order of  $10^6$  cm sec $^{-1}$  or larger (48).

### III. Interaction of Reactant Ions with Environment

For the systems with which we are concerned, other molecules are always in close proximity to the species undergoing charge transfer. Since even in a solvent of low dielectric constant the energy of interaction with the medium of a charge residing on a sphere of atomic dimensions amounts to several tens of kilocalories per mole, and since a redistribution of charge always occurs in the reactions of present interest, due consideration must be given to these interactions. These interactions are often discussed in a way that glosses over structural features, as is done for example in the application of the Born equation. But from a chemist's point of view it is necessary to inquire into the structure of the solvent surrounding the ions, especially in a solvent containing polar molecules, and in particular to distinguish groups in the first coordination sphere from those further out which may also be influenced by the electric field of the central ions. This distinction is natural, not only because the forces binding the first layer are greater than for those further out, but also because the residence time for a solvent molecule adjacent to a cation of high charge may be considerably greater than for solvent having only solvent as neighbor. The forces that give individuality to the different ions, whether we consider the influence of the ligands on the central ion or vice versa, are largely expended in the first coordination sphere, so that differences in the interaction which two ions such as  $\text{Al}(\text{OH}_2)_6^{+++}$  and  $\text{Fe}(\text{OH}_2)_6^{+++}$ , having the first coordination spheres completed, have with the surrounding medium can be understood largely as differences that arise from the slightly different radii of the two central ions. The distinction between groups in the first coordination sphere and other groups may become unsharp in certain cases [of which  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  may be an example] in which not all the groups in the first coordination sphere are equivalent. However, even in most such cases, the less firmly bound solvent molecules experience a much greater electric

field than do those in the second sphere of coordination, so that the distinction can still be maintained.

Several aspects of solvation phenomena will be considered: solvation of cations, interaction of cations with other groups, and phenomena of electrolytic dissociation. The essential general features will be covered if we consider on the one hand a solvent of high dielectric constant, such as water, and on the other, remark on the differences in the state of an electrolyte produced by dissolving it in solvents of low dielectric constant. Special emphasis will be given to the subject of hydration of ions, because most of the work on redox reactions has been done with water as solvent.

Over the last 15 years great progress has been made in understanding hydration of cations. The existence of well-defined hydrates of cations in crystals leads naturally to the supposition that cations in solutions will also be hydrated. Certainly the energies of hydration of cations with water are great enough (ranging from approximately 60 kcal mole<sup>-1</sup> (73) for Cs<sup>+</sup> to > 10<sup>3</sup> kcal for a tripositive cation such as Al<sup>+++</sup>) so that it is not unreasonable to expect cations and water in the first sphere of coordination to constitute definite chemical species. In spite of the force which such general considerations may have, hydrated cations have not been part of the careful chemist's vocabulary of molecules, and for good reasons. With only evidence of the kind cited for the existence of hydrated ions in solution, questions can be raised as to their existence as definite species. In the solid, species of particular formula may be stabilized by the forces producing the ordered arrangement. In the liquid, several different configurations may have approximately the same energy; even when the energy differences for different configurations are appreciable, the residence time of a particular set of water molecules in the first coordination sphere may be so short that the concept of the hydrated cation as a molecule loses significance. In a program for the study of hydration of ions, the experimenter seeks to establish the formulae of the hydrated ions, their labilities and the energy differences between states of different coordination numbers.

Most of the classical physicochemical methods for the study of hydration of ions fail to distinguish between water in the first coordination sphere and water more remote from the central ion which also comes under the influence of its charge. Some of the methods more recently applied have provided a clearer picture. The oxygen isotope exchange method, where applicable, not only can define the composition of the first coordination sphere but also can be used to measure the lability of the aquo ion. Thus it has served to establish Cr(OH<sub>2</sub>)<sub>6</sub><sup>+++</sup> (64); (NH<sub>3</sub>)<sub>5</sub>Co(OH<sub>2</sub>)<sup>+++</sup> (114); and (NH<sub>3</sub>)<sub>4</sub>Co(OH<sub>2</sub>)<sub>2</sub><sup>+++</sup> (105) as well-defined species in solution and also to fix the half-time for exchange of

these species ( $t_{1/2}$  of the order of 20 to 40 hr at 25°). In a further development (10) of this method, which makes accessible shorter sampling times, it has been shown that  $\text{Al}^{+++}\text{aq.}$  can indeed be represented as  $\text{Al}(\text{OH}_2)_6^{+++}$ , and that the half-time for the exchange of bound water exceeds 0.005 sec. Experiments on the effect which cations exert on the relative fugacities of  $\text{H}_2\text{O}^{16}$  and  $\text{H}_2\text{O}^{18}$  have served to indicate that even cations which form labile hydrates (for example,  $\text{H}^+\text{aq.}$ ) nevertheless form definite hydrates (40).

Perhaps the greatest progress has been made in the subject of hydration of cations by the studies of the electronic spectra of transition metal ions. The theoretical developments on the influence of ligand fields on the energy levels of ions, which culminated in the work of Penney and Schlapp (102) and of Van Vleck (133) on magnetic properties of ions, have been applied by Hartmann and co-workers (51, 65), as well as others (91), to the problem at hand. The theoretical ideas can be applied in two ways. In one application the spectrum of an ion in solution is compared with that in a solid in which the composition and constitution of the hydrated ion are known. However unsatisfactory the simple application of crystal field theory may be in predicting quantitatively the energy levels of the ion in a hydrate, it can in many cases nevertheless be trusted to indicate the magnitude of the changes in spectrum which can be expected to accompany a change in coordination number. In another application, less empirical but also less dependable, an analysis of the spectrum of the ion, applying the principles of crystal field theory, can be used to determine the symmetry of the ligand field. Difficulties can be encountered in the second application arising from the incomplete resolution of the electronic bands and from unresolved questions of intensities. The work on the electronic spectra has, however, served to establish the formulae of the hydrates of most colored transition metal ions in water.

A relatively new technique (139) for measuring the substitution labilities of hydrated paramagnetic cations is observation of the line broadening of the nuclear magnetic resonance absorption of ligand nuclei caused by the central ion. The effect of the line broadening is particularly marked for ions which permit rapid exchange of water in the first coordination sphere and is much weaker for an ion such as  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ . This technique has been applied by Wertz (139) to  $\text{Cl}^-$  substitution and by Connick (30) to  $\text{H}_2\text{O}$  substitution in hydrated cations. There has been a revival of interest (22) in the application of X-ray diffraction to a study of aqueous solutions, and further significant progress can be expected in the near future using this technique.

Specific hydration of anions is not dealt with here, not because the energy of hydration is not large but because there is greater question of

the existence of definite species in the sense implied in the discussion of the cations. The hydration of anions is different in this sense, that simple ion dipole (hydrogen bond) interactions come into question, and it is likely that the residence time of a particular water molecule adjacent to an anion will not be much longer than for water adjacent to water.

Conventional physicochemical methods, the most powerful of which depend on the application of the mass law, can be used to establish the composition of a complex ion with respect to a nonsolvent ligand. Even when the composition with respect to nonsolvent ligands is established, many questions remain which are particularly hard to answer for substitution labile systems. Thus when an ion of formula  $\text{FeCl}_4^-$  is proposed, one can ask, how many molecules of water in addition to the  $\text{Cl}^-$  comprise the first coordination sphere? If the formula is  $\text{FeCl}_4(\text{H}_2\text{O})_2^-$ , what is the ratio of the *cis* to *trans* form at equilibrium? Furthermore, for oppositely charged ions of high charge, the distribution between two forms must be considered, in only one of which is there a direct bond of the ligand to central ions. Thus the studies on hydration of cations need to be extended also to complex ions which are coordinatively unsaturated with respect to nonsolvent ligands. Studies with complex ions which are not labile to substitution help greatly in assessing the importance of outer-sphere<sup>1</sup> forms. For the system  $(\text{NH}_3)_5\text{CoOH}_2^{+++} + \text{SO}_4^{=}$ , inner-sphere and outer-sphere forms are of about equal stability (131). The outer-sphere affinity of  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  for  $\text{Cl}^-$  is very small. This latter conclusion, based on the careful work of Gates and King (43), casts doubt on the strong outer-sphere association of halides and tripositive ions indicated by the work of Linhard (78) and of Evans and Nancollas (39).

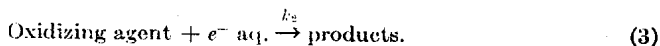
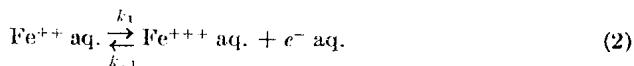
The incomplete dissociation of ion pairs which are coordinatively independent, observed for ions of opposite and high charge, even in water, is a common phenomenon in solvents (71) of low dielectric constant ( $D$ ). In liquid  $\text{NH}_3$  with  $D = 27$  at  $-60^\circ$ , strong electrolytes such as  $\text{NaNO}_3$  or  $\text{NH}_4\text{Cl}$  have dissociation constants of the order of  $10^{-3}$ . When dioxane is the solvent ( $D = 2.18$ ), a salt such as  $\text{Bu}_4\text{NClO}_4$ , though comprised of large ions of low charge, has a dissociation constant of the order of  $10^{-18}$ . For such solutions the model of an ion atmosphere surrounding each ion collapses to one in which the electrolyte exists as ion pairs, but with the further complication that at reasonable concentrations of electrolyte association of the ion pairs takes place (41).

<sup>1</sup>The term requires definition. It refers to regions beyond the first coordination sphere of a cation considered as center, but not to anions considered as centers. Thus, for the system  $\text{Al}^{+++} \text{aq.} - \text{Cl}^- \text{aq.}$ , the distinction is between  $\text{AlCl}^{++} \text{aq.}$  and  $\text{Al}(\text{OH}_2)_6^{+++} \cdot \text{Cl}^-$ , and the question of the hydration of  $\text{Cl}^-$  is not raised (for example, no distinction is made between structures such as  $\text{Al}^{+++}(\text{OH}_2)_6 \cdot \text{Cl}^-$  and  $\text{Al}^{+++}(\text{OH}_2)_6 (\text{OH}_2)_n \text{Cl}^-$ ).

#### IV. General Consideration of the Electron Transfer Process in Solution

Let us consider first some general features of electron transfer between ions in solution without specific, detailed discussions of individual systems. The conditions which must be met to make electron transfer between two ions possible are matching the energy of the electron at the two sites and sufficient orbital overlap between the two sites to provide for a reasonable probability of transfer (76, 104). Various factors are involved in meeting these conditions, and these are considered qualitatively in the present section discussing mainly reactions in media of high dielectric constant but also referring briefly to media of low dielectric constant.

The mechanism of the electron transfer itself has been given considerable discussion, and attention has been directed to it as a barrier penetration phenomenon (84, 104, 137). This emphasis is justified only to the extent that other reasonable possibilities exist. Let us examine at the outset one such alternative process which has also come up for consideration, namely one in which the electron spends sufficient time in the solvent to be solvated. For a reaction with  $\text{Fe}^{++}$  as reducing agent, the mechanism corresponding to this process would be formulated as follows:



A mechanism of this kind, consisting of discrete steps, can be rejected on the basis of kinetic evidence for all systems which have thus far been studied in detail (although it would be dangerous to reject it as a possibility for very powerful reducing agents in water or liquid ammonia). For if reaction (2) forward is slow compared to (3), the rate of reaction will be independent of the concentration of oxidizing agent, while if (2) is maintained as an equilibrium with (3) rate determining, the rate of reaction will be inverse in the concentration of  $\text{Fe}^{+++}$ . Such rate laws have not been observed for the systems of simple chemistry which we are discussing. However, the feature that the rates can be inverse in the concentration of the product formed from the reducing agent has frequently been observed for systems of complex chemistry. In every such case, this kinetic feature can reasonably be attributed to the formation of an intermediate oxidation state.

If the model is modified by postulating that the electron is strongly affected by the presence of the oxidizing agent, the conditions for barrier penetration are also met, and it is difficult to see what experimental criteria would distinguish the two cases, whether the electron surmounts a



barrier the shape and magnitude of which is affected by the reactant ions, or whether it penetrates such a barrier. An answer would be given if the energy levels of the electron in the activated complex were known and if the shape and height of the barrier could be calculated. Knowledge of the distribution of electrons in the complex molecules in question is not sufficiently quantitative to settle the issue at present.

The suggestion (34) analogous to that contained in Eqs. (2) and (3), but having the oxidizing agent remove electrons from the solvent, can be rejected in many systems for reasons similar to those advanced for the electron in the solvent. In any case, such processes would seem to be reasonable possibilities only for the strongest oxidizing agents—for  $\text{H}_2\text{O} = \text{HO} + \text{H}^+ + e^-$  lies at approximately  $-2.8$  volts (72)—and there is no evidence that an oxidizing agent such as  $\text{Co}^{++}\text{aq.}$  with  $E^0$  at  $-1.8$  volts makes use of a solvent-hole mechanism.

The limited conclusions reached in the preceding paragraph should not be taken to imply that the description of these processes as barrier penetration phenomena is always apt. It is useful to consider the extreme mechanisms: in one the geometries of the oxidized and reduced forms, at least as regards the first sphere of coordination, are the same, and substitutions in the first coordination sphere are not readily accepted; in the other there are important changes in the first coordination sphere accompanying the electron transfer, and further, at least one of the species readily accepts substitution, and the coordination spheres interpenetrate in the activated complex. It will be noted that more than one condition has been specified for each case. The conditions are not necessarily combined as they appear here, and other cases can arise. The particular combinations have been chosen to provide the greatest contrast in behavior which can be expected.

The systems of the first class afford the closest approach to a simple barrier penetration process, and perhaps they more readily respond to a theoretical analysis. It can reasonably be supposed that for these systems orbital overlap for the two ions is small, so that the frequency of the electronic transition is small, and there is no substantial binding between the two exchanging centers. A model of this kind presumably corresponds to the "weak overlap" cases as defined and discussed by Marcus (82). In attempting to calculate the rates of these reactions, besides the problem of the shape and height of the barrier for the electron transfer, electrostatic interaction of the reactants must be dealt with and the energy necessary to distort the solvent and ionic atmosphere about each ion to make the energy of the electron equal at the two sites. Different workers have emphasized different ones of these factors, and serious differences of opinion are recorded.