INORGANIC OXIDATION-REDUCTION REACTIONS IN SOLUTION

ELECTRON TRANSFERS[1]

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I. GENERAL CONSIDERATIONS

For decades the detailed chemistry of inorganic reactions in aqueous media has been limited to observations of their stoichiometry. Interpretation has usually involved thermodynamic considerations and has neglected time dependence entirely. Here and there authors guardedly made statements to the effect that in some particular systems equilibrium is slow in being attained and that a judicious choice of catalysts is necessary to speed the attainment of equilibrium. In all other cases the assumption was made that reactions involving ions occurred rapidly and went on to completion. The simple stoichiometry of gaseous chem-

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ical systems served admirably as the basis for development of our knowledge of the theory of chemical kinetics. Later, organic chemistry attracted kineticists in droves. Only a few hardy souls remained to marvel at the complexities and subtleties of inorganic reaction systems in solution. More recently the development of new techniques of kinetic observation, such as those involving the polarograph, the oscilloscope, measurements with both stable and radioactive isotopes, and recording spectrophotometers, has led to a concerted attack on the solution chemistry of inorganic systems. This review is limited to a comprehensive view of inorganic oxidation–reduction reactions in aqueous systems—especially those involving an electron transfer between the reactants. It is nevertheless hoped that this effort may stimulate interest in this somewhat neglected field of chemical theory—inorganic kinetics.

II. Oxidation–Reduction Reactions Involving Electron Transfer

Classical definitions of oxidation and reduction reactions in terms of oxygen content were in time broadened to include all reactions in which materials either gain or lose electrons.

In most reactions, obviously, a redistribution of electrons occurs. In many cases this *electron loss* (oxidation) or *electron gain* (reduction) might be interpreted by the assignment of fractional oxidation states to chemically bound elements. In systems where chemical change results in the formation of new covalent bonds, interpretation is made not in terms of integral numbers of electrons, but in terms of changes in atomic electron densities, namely, electronegativity values. Such concepts are discussed in recent texts by Ingold (41) and Moeller (54) and will not be pursued further here. This review will deal only with oxidation–reduction systems which are clearly characterized by a complete electron transfer between an oxidant (electron acceptor) and a reductant (an electron donor) and will not be concerned with acidity and basicity in the sense proposed by G. N. Lewis.

In the past ten years extensive experimental research has been done on a class of oxidation–reduction systems involving electron transfers with no chemical change, i.e., the standard free-energy change is zero—the reacting species being identical with the products. As an example, consider the ferrous–ferric reaction in aqueous solution (the asterisk denotes a second isotope, either radioactive or stable).

$$Fe^{+2} + Fe^{*+3} \rightarrow Fe^{*+2} + Fe^{+3} \qquad \Delta F^0 = 0 \quad (1)$$

All ionic symbols used in this report omit specific reference to solvation. These "electron-exchange" reactions serve as a useful model for extending our general knowledge of inorganic oxidation–reduction systems.

The reader is referred for background information to the excellent discussion by Taube (68) of the labile and inert ionic complexes, Uri's (73) thorough review of inorganic free radicals in solution, and Baxendale's (7) discussion of oxidation–reduction reactions involving hydrogen peroxide. Partial listings of electron-exchange reactions have been given by Gryder (30) and by Meyers and

Prestwood (53). Haissinsky (32) included a few electron-exchange processes in his general review on isotopic or atom-exchange reactions. While this manuscript was in preparation there appeared a brief discussion by F. Duke (20) of the nature of electron-exchange reactions.

In addition to electron-exchange reactions, some attention will be directed to inorganic oxidation–reduction systems in which $\Delta F^0 \neq 0$, i.e., the electron transfer occurs in systems whose reactants and products are chemically identifiable. The question of one- or two-electron steps in the course of oxidation and reduction was recently discussed by Westheimer (80) and will be excluded from this review. The weight of modern evidence, experimental as well as theoretical, seems to favor the concept that only one electron is transferred at a time in the kinds of reactions to be discussed in this paper.

III. EXPERIMENTAL INFORMATION

A. KINETIC ANALYSIS

Rate measurements, as a function of acidity and anion concentrations and augmented by thermodynamic data on equilibrium constants, permit one, in some cases, to unravel the steps contributing to the overall kinetics. Silverman and Dodson's (66) paper on the electron-exchange reaction between the two oxidation states of iron in acid aqueous solutions provided an interesting analysis. The radioactive ferric isotope Fe^{55} was used in this study. They found that the reaction velocity was first order in both oxidation states of iron. However, the variation of the velocity as a function of acid concentration and chloride concentration suggested that four simultaneous reaction paths for ferrous ion were involved: (*1*) the unhydrolyzed ferric ion, Fe^{+3}, (*2*) the $FeOH^{+2}$ ion, and the two chloride complexes (*3*) $FeCl^{+2}$ and (*4*) $FeCl_2^{+1}$. These particular oxidation–reduction reactions are unique in that the reactants and products are identical except for negligible isotope effects. This implies an equilibrium constant of unity and thus equal specific rate constants for the forward and reverse reactions.

B. CLASSIFICATION OF REACTIONS

It proves convenient to group all kinds of oxidation–reduction reactions in the fields of chemistry and biology in two classes, based on the existence or absence of thermodynamically stable intermediates in the chain of events leading from the initial to the final state of the reaction. Reactions not admitting of stable intermediates are defined as Class I and are obviously limited to a single step, i.e., a dismutation of the activated complex. The Class II oxidations, which admit of the existence of thermodynamically stable intermediates, are not basically different from any other chemical kinetic systems proceeding by a series of primary and secondary steps. This particular scheme has been emphasized by Weiss (77) in his interpretation of oxidation–reduction phenomena. It is obvious that the rate-determining step of a Class II reaction will be entirely analogous to a Class I reaction; thus any mechanism which can be derived for Class I will equally well apply to Class II, supplemented by the previously

TABLE 1

Class I reactions; cations

Reaction	ΔE	$\Delta S^\ddagger$	Separation Method	Solvent	μ	$\Delta F^\ddagger_{obs}$	$\Delta F^\ddagger_{calc}$	Reference
	kcal./mole	*cal./deg.-mole*				*kcal./mole*	*kcal./mole*	
$Co(en)_3^{+2}$–$Co(en)_3^{+3}$	14.3	−33	Extraction	HCl	1.0	23.5	16.8	(43)
$Co(NH_3)_6^{+2}$–$Co(NH_3)_6^{+3}$	Slow		Extraction	HCl	—	—	—	(43)
				NaOH	—	—	—	(49)
Fe^{+2}–Fe^{+3}	9.9	−25	Precipitation	$HClO_4$	0.55	16.7	16.7**	(66)
Fe^{+2}–$FeOH^{+2}$	7.4	−18	Precipitation	$HClO_4$	0.55	12.2	15.1	(66)
Fe^{+2}–$FeCl^{+2}$	8.8	−24	Precipitation	$HClO_4$	0.55	15.3	15.1	(66)
Fe^{+2}–$FeCl_2^+$	9.7	−20	Precipitation	$HClO_4$	0.55	15.1	13.1	(66)
Fe^{+2}–FeF_2^+	9.1	−20	Precipitation	$HClO_4$	0.5	14.2	15.1	(40)
Fe^{+2}–FeF_2^{+2}	9.5	−22	Precipitation	$HClO_4$	0.5	14.9	13.1	(40)
Ce^{+3}–Ce^{+4}	7.7	−40	Extraction	HNO_3	6.18	18.0	19.1	(31)
Ce^{+3}–$Ce^{+4}[H^+]^{-2}$	24.0	+25	Extraction	HNO_3	6.18	16.6		(31)
NpO_2^+-NpO_2^{+2}	8.3	−24	Extraction	$HClO_4$	1.0	14.3	14.6	(15)
VOH^{+2}–VO_2^{+2}	10.7	−24	Ion exchange	$HClO_4$	2.5	17.2	16.0	(26)
$Os(bipy)_3^{+2}$–$Os(bipy)_3^{+3}$	Fast		Optical activity	$HClO_4$	—	—	—	(23)

** Fitted value.

TABLE 2

Class I reactions; anions

Reaction	Rate Law	Separation Method	Solvent	Temperature	Reference
				°C.	
MnO_4^{-2}–MnO_4^-	Complete within 35 sec.	Extraction	4 *M* KOH	0	(38)
	Complete	Precipitation	—	—	(44)
	Complete within 5 sec.	Extraction	2 *M* NaOH	−1	(8)
	$k' = 650$ moles/l.-sec.	Extraction	9.15 *M* NaOH	1	(65)
$Fe(CN)_6^{-4}$–$Fe(CN)_6^{-3}$	Complete within 4 hr.	Diffusion	10^{-3} *M* HCl	25	(14)
	Complete within 5 hr.	Electrophoresis	H_2O	25	(14)
	Complete within 4 min.	Ion exchange	H_2O	25	(14)
	Complete within 1 min.	Precipitation	1 *M* HCl Neutral 0.05 *M* NaOH	25	(72)
	$k' \sim 10^3$ moles/l.-sec.	Precipitation	H_2O	4	(75)
$Mo(CN_8)^{-4}$–$Mo(CN)_8^{-3}$	Complete within 5 sec.	Precipitation	0.01 *M* NH_4ClO_4	2	(82)

mentioned secondary steps. Class I reactions are listed in tables 1 and 2, respectively, the choice depending on whether both reactants are cations or anions. All the electron-transfer reactions where the identity of the reactant species is in doubt or where the standard free-energy change is not zero are listed together as Class II reactions in table 3. Additional kinetic information is required to reveal whether the reported Arrhenius energies of activation refer to the overall reaction consisting of a series of primary and secondary steps as emphasized by Weiss (77) or to a single chemical transformation. The reactions of Class II involving different oxidation states of the same element, as, for example, the thallium, tin, europium, antimony, and uranium systems, will probably become identified with the Class I reactions once the chemical species involved in the electron transfer are identified.

TABLE 3

Class II reactions

Reaction	ΔE	$\Delta S^{\ddagger}$	Separation Method	Solvent	μ	$\Delta F^{\ddagger}_{obs}$	Other Orders	Reference
	kcal./mole	*cal./deg.-mole*				*kcal./mole*		
Tl^{+}-$TlOH^{+2}$	14.7	−33	Precipitation	$HClO_4$	6.0	23.9	—	(34)
Sn^{+2}–Sn^{+4}	10.8	−34	Precipitation	HCl	10.0	23.3	—	(12)
$SnCl_2$–$SnCl_4$	23.7	−16	Precipitation	Absolute alcohol	—	18.3	—	(52)
Sb^{+3}–Sb^{+5}	27.0	−32	Precipitation	HCl	6-12	35.9	$(H^{+})^{4}(Cl^{-})^{9}$	(9)
Eu^{+2}–Eu^{+3}	20.8	−3	Precipitation	HCl	2.0	21.0	(Cl^{-})	(51)
$Fe(OH)_2^{+}$-Sn^{+2}	22.6	+4	—	$HClO_4$	—	20.7	—	(29)
Fe^{+3}-Np^{+4}	35.0	+51	—	$HClO_4$	1.0	19.2	$(H^{+})^{-3}$	(39)
Fe^{+2}–HQ^{-}	20.2	+53	—	$HClO_4$	—	3.8	—	(6)
U^{+4}–U^{+6}	33.4	+31	Precipitation	HCl	>1	23.6	$(H^{+})^{-3}$	(62)
Fe^{+2}–$TlOH^{+2}$	18.4	−7	—	$HClO_4$	3.0	20.0	—	(41a)
Fe^{+2}-HO_2^{-}	28.0	+50	—	$HClO_4$	—	12.4	—	(5)

C. EXPERIMENTAL DETAILS

For Class I reactions where the reacting species are identical with the products ($\Delta F^0 = 0$), unless some other than chemical characteristic of the system, such as optical activity (23) (see table 2), can be found to follow the change, radioactive tracers must be employed. This can be easily visualized: if ferrous ions interact with ferric ions, and only ferrous ions are "tagged" with a radioactive tracer, then the amount of radioactivity appearing in the ferric form after a given period of time will be proportional to the number of times a ferrous ion gave up its electron and became a ferric ion. This technique was introduced by Hevesy and Zechmeister (36) in 1920, who found complete exchange between plumbous and plumbic ions in boiling glacial acetic acid. The availability of radioactive isotopes of many elements in the last decade has placed a considerable body of experimental information in our hands.

The majority of the reactions reported herein have been studied by radioactive tracer techniques. This means that one of the reacting species was prepared from the radioactive isotope and the other from an inactive isotope of the same element. The appropriate concentrations, *a* and *b*, of these reactants are then mixed to make a solution of known ionic strength and pH. Aliquots are withdrawn from the solution from time to time and the two different valence forms of the element are separated. The amount of activity appearing in the originally unlabeled form is then an indication of the progress of the reaction. Analytically this is given by the expression

$$\ln\left(1 - \frac{x}{x_\infty}\right) = -Rt\,\frac{(a + b)}{ab} \tag{2}$$

first derived by McKay (50), in which x is the activity of the originally inactive material at time t and x_∞ is the same quantity when the exchange is complete. The rate of the electron exchange is given by

$$R = k'a^{\alpha}b^{\beta} \tag{3}$$

where k' is the specific reaction rate constant, and α and β are the orders of the reaction with respect to the components a and b, respectively, expressed in number of equivalents of exchangeable atoms. The order of the reaction is found by independent variations of the concentrations of the reactants a and b. If the reaction system admits of more than one electron-exchange reaction, i.e., several different chemical species are participating in the electron exchange, then R is the overall rate expression for electron exchange and can become a relatively complicated function of several rate constants, equilibrium constants, and anion and acid concentrations. Several typical examples are taken up by Meyers and Prestwood (53).

Since most of the electron-exchange reactions are quite rapid, special precautions must be taken in the choice of a method of separation for the two oxidation states of the element in order to minimize exchange effects during the separation. For this reason, the separation technique is specified for each reaction system listed in the tables. The separation technique becomes especially critical for very fast reactions such as those involving anions as reactants. The separation procedure which involves precipitation of one of the reactants is the one considered most likely to induce exchange because of surface effects. Such effects were tested for in all reactions studied by this method and were taken into account in calculating values. It has been shown (58) that these effects will not change calculated rates provided the effects are reproducible.

D. SUMMARY OF KINETIC DATA

In reviewing the data on electron-exchange reactions listed in tables 1 and 3, the following detailed information has been included to serve as a background for the theoretical discussions to follow: the Arrhenius energy of activation ($\Delta E \simeq \Delta H^{\ddagger} + RT$, since $\Delta V^{\ddagger}$ is negligible for reactions in solution), the entropy of activation ($\Delta S^{\ddagger}$), the observed free energy of activation at 25°C. ($\Delta F^{\ddagger}_{\text{obs}}$), the supporting aqueous electrolyte medium (a point of importance when the anion effect is discussed in the next section), and the ionic strength (μ). The rate information for practically all Class I reactions involving cations was obtained from a detailed analysis of the corresponding overall reactions; thus, the quoted Arrhenius energies refer to the *rate-determining* step in each case. (For details of these analyses the reader is referred to the original references listed.) A column of calculated free energies of activation ($\Delta F^{\ddagger}_{\text{calc}}$) for electron transfer is included in table 1 for all reactions characterized by negative entropies of activation. These values were calculated on the basis of the electron tunnelling hypothesis advanced by the authors (47). In table 3, where the detailed mechanism of the overall reaction is less certain, the reported Arrhenius energies of activation represent apparent instead of true energies of activation. Where effects of foreign anions and pH were studied, the orders observed are given in a separate column. The antimony system, with an admitted ninth-order dependence on chloride-ion concentration, will bear further investigation.

IV. THEORETICAL INFORMATION

A. SURVEY OF PAST WORK

One of the more difficult facts to explain about electron-exchange reactions is how two highly charged ions can overcome their mutual repulsion and approach closely enough to form an activated complex. The charge of some cations involved in these reactions is occasionally reduced by hydrolysis of the hydrated cation, forming a hydroxyl intermediate, or by ion-pair formation (73) with some anion (most frequently a halide ion). However, the reactants in these cases are still cations, even with reduced charges. The electrostatic repulsive force between such cations when forced together closely enough to form an activated complex is usually quite large. The coulombic repulsion between ions of charge p_a and q_b at a distance r_{ab} will be $p_aq_be^2/r_{ab}$. Suppose a ferrous ion is made to approach within 2 Å. of a ferric ion. The coulombic repulsion alone will amount to

$$\frac{2 \times 3 \times (4.8 \times 10^{-10})^2 \times 6.02 \times 10^{23}}{2 \times 10^{-8} \times 4.186 \times 10^{10}} = 994 \text{ kcal./mole} \qquad (4)$$

In addition, it will require a considerable amount of energy to adjust the hydration shells of the two ions. Some amount of ingenuity has been expended in explaining why these reactions proceed despite such seemingly unfavorable energy requirements.

The first suggestions which were made in this direction were rules of thumb, designed to predict which reactions would be fast and which would be slow. One of these was Shaffer's equivalent change principle (63, 64), which states that oxidation–reduction reactions in solution will be fast only if the donor and acceptor molecules each exchange a like number of electrons. Thus, reactions like

$$A^{+2} + B^{+} \rightarrow A^{+} + B^{+2} \qquad (5)$$

and

$$A^{+3} + B^{+} \rightarrow A^{+} + B^{+3} \qquad (6)$$

will be fast, whereas reactions of the type

$$A^{+3} + 2B^{+} \rightarrow A^{+} + 2B^{+2} \qquad (7)$$

will be slow. According to Shaffer, the slow velocity of the last type of reaction is due to the necessity for a three-body collision to initiate the reaction. The catalytic effect on slow reactions like reaction 7 of substances such as dyes or manganese compounds is explained by Shaffer as being due to their ability to react in one-electron stages. The equivalence principle applies, of course, to all electron-exchange reactions where $A \equiv B$.

Remick (60, 61) supplemented the equivalence theory of Shaffer by the additional consideration of "potential humps." This idea had been introduced by Bancroft and Magoffin (3, 4). According to Remick, oxidation–reduction reactions in which two electrons are exchanged would not have to surmount an energy barrier, whereas the velocity of those reactions in which only one electron is exchanged is inversely proportional to the height of the barrier, which in turn he assumed was related to the E.M.F. of the reaction. This particular rule has no bearing on the limiting case of electron exchange ($A \equiv B$), where the E.M.F. is of course zero. Sufficient evidence has been accumulated in recent years to indicate that these unfamiliar oxidation states, such as Mg^+, Sn^{+3}, Cr^{+4}, are not of unusually high energy value as Remick believed, but rather are present in sufficient concentrations in aqueous solution to provide an easier path for the electron exchange in some instances (56).

Gershinowitz (27) has correlated Conant's (16, 17) data on the kinetics of oxidation–reduction reactions of quinones and amines by defining an E.M.F. for the equilibrium between reactants (i) and activated complexes:

$$F^{\ddagger} - F_i = -n\mathfrak{F}(E_0^{\ddagger} - E_{0i}) \qquad (8)$$

where $F^{\ddagger}$ and F_i represent the free energies of species i in the activated and ground states, respectively, and $E_0^{\ddagger}$ and E_{0i} the E.M.F.'s for the same states. The $E_0^{\ddagger}$'s can only be related to E_0's for compounds which are members of a homologous series and when each member of such a series reacts with the same oxidant or reductant.

Weiss (77) also supplemented the equivalent change principle by extending Shaffer's concept of catalysis of electron-exchange reactions by dyes. Weiss noted that reactions of the type represented by equation 7 would be fast in which A existed also in a valence state intermediate between the ones in which A exists as reactant and as product. This is consistent with the assumption of the principle of compulsory univalent oxidation.

Another contribution of Weiss to the theory of oxidation–reduction reactions is the suggestion (78) that these may proceed by coupling with another system of suitable E_0. One such system suggested by Weiss is the molecular oxygen–oxygen ion system; this reaction is visualized as follows:

$$M^{+n} + O_2 \rightarrow M^{+n+1} + O_2^- \qquad (9)$$

$$M^{+n+1} + O_2^- \rightarrow M^{+n} + O_2 \qquad (10)$$

Another system involves the hydroxyl ion

$$M^{+n} + OH \rightarrow M^{+n+1} + OH^- \qquad (11)$$

$$M^{+n+1} + OH^- \rightarrow M^{+n} + OH \qquad (12)$$

Many of the authors cited in the previous section have tested for an oxygen effect on the rates of electron-exchange reactions; usually none was found, or where one was found it arose from the slow oxidation of the reactant ion of lower valence. Nevertheless, such tests are not decisive in rejecting the possibility of the existence of an equilibrium such as shown in equations 9 and 10, since a sufficient amount of oxygen may always exist in solution to establish such an equilibrium. The situation with respect to an equilibrium such as shown in equations 11 and

12 and corresponding equilibria with the halide ions is clearer. Uri (74) has pointed out that in these cases it is more likely that an ion-pair will be formed.

$$\mathrm{M}^{+n+1} + \mathrm{OH}^- \rightarrow \mathrm{MOH}^{+n} \qquad (13)$$

It is true that such ion-pair formation occurs quite frequently in Class II reactions. In this respect this suggestion reduces to the one of Weiss (77) referred to previously. On the other hand, the reaction according to equation 12 would require an intramolecular charge transfer of the following kind:

$$\mathrm{M}^{+n+1} + \mathrm{OH}^- \rightarrow [\overset{\xleftarrow{\;1e^-\;}}{\mathrm{M}^{+n+1} \cdots \mathrm{OH}^-}] \rightarrow \mathrm{MOH}^{+n} \qquad (14)$$

Such a charge transfer bears some resemblance to the light-absorption studies reviewed by Rabinowitch (59). These spectral changes have been called electron-transfer spectra; at the present time it is not known whether such changes occur in the course of oxidation–reduction reactions when there is no external source of electromagnetic radiation.

Adamson (1) has presented an interesting correlation of exchange half-time as a function of the magnetic susceptibilities of the reactant ions. This function is the product of the sum and the difference of the magnetic susceptibilities, i.e., $(\kappa_A + \kappa_B)(\kappa_A - \kappa_B)$. The smaller this product, the faster the exchange reaction seems to proceed. Adamson does not give any particular reason for this correlation.

Theoretical discussions of electron-exchange reactions based on the electron tunnelling hypothesis have recently been given independently by Weiss (79) and by Marcus, Zwolinski, and Eyring (47). A discussion, based on electron exchange between two nuclei as in the hydrogen molecule-ion and involving the Franck–Condon principle, was given by Libby (46). Other contributions to the theory of oxidation–reduction reactions involving electron transfers, such as the role of intermediates proposed by Duke (19, 20) and the bridged activated complexes of Taube and coworkers (69–71), will be covered under the appropriate headings below.

B. ANION AND SOLVENT EFFECTS AND THE BRIDGED ACTIVATED COMPLEX

One manner in which the high repulsion energy of two cations can be reduced is by the introduction of an anion between them. This has been proposed by several authors (15, 33, 37, 46, 70, 71). The effect of the introduction of a univalent anion c on the repulsion energy $e^2(p_aq_b/r_{ab} - p_a/r_{ac} - q_b/r_{bc})$ can be shown by the following oversimplified calculation: suppose a ferrous ion is located 2 Å. from a chloride ion, which in turn is located 2 Å. from a ferric ion; the potential energy for the linear complex is now attractive:

$$\frac{(4.8 \times 10^{-10})^2 \times 6.02 \times 10^{23}}{10^{-8} \times 4.186 \times 10^{10}} \left[\frac{2 \times 3}{4} - \frac{2}{2} - \frac{3}{2}\right] = -308 \text{ kcal./mole}$$

Since we are primarily interested in relative values, here, as in the previous calculation, we chose to omit the dielectric constant of the solvent. This calculation is certainly not accurate, but serves to indicate the tremendous change in the electrostatic repulsive energy that occurs when a suitable anion is introduced into the activated complex.

Before proceeding to examine the role of anions and solvent molecules, an enumeration of possible mechanisms of electron transfer may be instructive. Disregarding the effect of solvent and anions, the following reactions require consideration:

1. Reactions between oppositely charged particles

$$A^+ + B^- \rightleftarrows [A^+ \cdots B^-] \rightarrow A + B \tag{15}$$

Such reactions are rarely, if ever, slow, because the electrostatic attraction makes it easy to acquire the activation necessary to approach near enough for the electron to pass across the intervening space within the duration of most collisions.

2. Reactions between an ion and a neutral particle

(i)

$$A^+ + B \rightarrow [A^+ \cdots B]^\ddagger \rightarrow A + B^+ \tag{16}$$

or

$$A + B^- \rightarrow [A \cdots B^-]^\ddagger \rightarrow A^- + B \tag{17}$$

Such reactions are reasonably common in gaseous systems provided the ionization potentials of the two particles are almost equivalent. They are commonly referred to as charge transfers and have been thoroughly discussed by Massey (48). Their importance in radiation chemistry has been assessed by Burton and Magee (13). In reference to electron transfers in oxidation–reduction systems, Weiss (79), Gorin (29), and Duke (21) proposed mechanisms involving neutral intermediates as given above to explain the reaction of like-charged ions. In principle one other possible reaction between an ion and a neutral particle can be written,

(ii)

$$A + B^+ \rightarrow [A \cdots B^+]^\ddagger \rightarrow A^- + B^{+2} \tag{18}$$

involving further ionization of the reductant. Such a case was brought up by Weiss (79). The formation of oppositely charged products is highly unlikely. This reaction represents an earlier suggestion of Weiss on mechanisms in oxidation–reduction systems where A is molecular oxygen and B^+ is a cation, i.e., the oxygen effect.

3. Reactions between like ions

$$A^p + B^q \rightarrow [A^p \cdots B^q]^\ddagger \rightarrow A^{p-1} + B^{q+1} \tag{19}$$

where for either cations or anions, $p = \pm 1, \pm 2, \cdots$, and $q = \pm 1, \pm 2, \cdots$, respectively. Reactions between ions of similar charges, i.e., where $p = q$, are to be excluded, for in such reactions electron transfers are usually strongly endothermic. Cases where the species are equivalent, $A \equiv B$, and the charges on the ions dissimilar, $p \neq q$, are the common electron-exchange reactions given in tables 1 and 2.

Electron transfers by way of intermediates call for consideration (see also Duke (20)).

4. Electron solvation

Denoting the solvent by the symbol S, the electron-transfer mechanism can be written as

$$\begin{gathered} \mathrm{A} + \mathrm{S} = \mathrm{A}^+ + \mathrm{S}^- \\ \mathrm{S}^- + \mathrm{B} \rightarrow [\mathrm{S}^- + \mathrm{B}]^\ddagger \rightarrow \mathrm{S} + \mathrm{B}^- \end{gathered} \tag{20}$$

where the equality sign denotes an equilibrium condition and the activated complex defines the rate-determining step. If this is true, then the solvent can be regarded as a *new oxidant* once the equilibrium is established and the situation reduces to one of the direct electron-transfer reactions considered above. Although electron solvation in liquid ammonia solutions occurs readily, it is rather unlikely that electron attachment will occur in aqueous solution without reducing the water (46). As examples we may cite the reducing action on water of inorganic salts like $\mathrm{Co^{II}(CN)_6^{-4}}$ or electronically excited $\mathrm{Ce^{+3}}$ (35). A case that comes to mind is Platzman and Franck's recent analysis of the absorption spectra of halide ions in water (57). In calculating the positions of the absorption bands of the aqueous halide ions, they proposed a rather unique intermediate with a half-life of less than 10^{-13} sec. The light absorption removes one of the outer p electrons on a halide ion into a discrete quantum state where it is bound in the resultant field of the halogen atom, of the immediate neighboring water molecules of hydration, and of the external polarized dielectric. Thus, this represents a distinct situation which one can hardly regard as electron solvation.

Cases are certainly known where a sufficiently powerful oxidizing agent will undergo reduction by decomposing water, leading to the evolution of oxygen, e.g., in an aqueous solution of $\mathrm{Co^{+3}}$.

5. The anion effect

In view of the importance that the anion effect has assumed in studies of oxidation–reduction systems, it seems desirable to discuss it in some detail. Several proposals have been made about the particular role that the anions play. We briefly mention systems where the anion is actively engaged in the reaction scheme as a reductant. Such systems have been investigated by Duke and his coworkers (19, 22), who found that for the $\mathrm{Ce^{+4}}$–$\mathrm{Tl^{+1}}$ reaction in the presence of chloride and the $\mathrm{Fe^{+3}}$–$\mathrm{Sn^{+2}}$ reaction in the presence of iodide, the halide ions set up an intermediate oxidation–reduction system. They in turn are oxidized and then reduced.

For electron-exchange reactions in particular, the anion effect has been interpreted in terms of a catalytic effect and a bridge transfer mechanism; the former is due to Libby (45) and the latter is primarily due to Taube and coworkers (69, 70, 71). These suggestions have many points of similarity.

(a) Catalytic effect

Certain anions, particularly halide ions, catalyze electron-exchange reactions; for example, marked chloride catalysis was found in the europous–europic reaction and in the ferrous–ferric system. Libby also demonstrated catalysis by fluoride ion of the cerous–ceric electron exchange (37). In several studies where detailed kinetic analyses of this effect were carried out, thermodynamically stable ion-pairs or halide complexes were identified. The exchange with these ion-pair species represents essentially a new path along which the reaction may proceed, and the usual kinetic parameters can be evaluated for these paths just as they are evaluated for the path involving the unassociated ions (74).

A particularly good example of this provision of different reaction paths is the halide catalysis of the ferrous–ferric exchange. When this reaction is carried out in perchlorate solutions, Fe^{+2} exchanges with Fe^{+3} and with $FeOH^{+2}$, the latter arising from the hydrolysis of Fe^{+3} which can be determined from the hydrogen-ion effect on the rate of exchange (66). When chloride is added to the reaction mixture, Fe^{+2} also exchanges with both $FeCl^{+2}$ and $FeCl_2^+$ (66). In turn, when fluoride is added to the reaction mixture, Fe^{+2} exchanges with both FeF^{+2} and FeF_2^+ (40). Similar analyses of the rate have not yet been carried out for the fluoride catalysis of the cerous–ceric exchange (37) and for the chloride catalysis of the thallous–thallic exchange (34). The latter offers an interesting example of the reaction velocity being lowered by an initial addition of the bridge-building anion, the velocity then increasing again upon continuing addition of chloride. A closer examination of experimental conditions is warranted.

To avoid complexing of the "exchange" species and to simplify the kinetic analyses, many investigators have resorted to the use of perchlorate salt media. A large number of the cation electron-exchange studies listed in table 1 were carried out in perchlorate solutions. Here direct electron transfers were observed, as is also true for the anion reactions listed in table 2. No catalysis by the perchlorate ion has ever been observed (66). It is interesting to note that Bonner (2), in a recent study of the Cr^{+2}–Cr^{+3} exchange in perchloric acid solution, found no evidence of chloride catalysis as reported by Taube (71).

The distinction between Class I and Class II reactions can be advantageously made at this point. Thus, consider the two expressions for the rate of reaction

$$R = k'[Eu^{+2}][Eu^{+3}][Cl^-] = k''[Eu^{+2}][EuCl^{+2}] \tag{21}$$

If a substantial amount of the trivalent europium is present as $EuCl^{+2}$, we must consider the equilibrium

$$Eu^{+3} + Cl^- \leftrightarrows EuCl^{+2} : K \tag{22}$$

Further, for the total trivalent europium, $[Eu^{+3}]_0$, we write

$$[Eu^{+3}]_0 \equiv [Eu^{+3}] + [EuCl^{+2}] = [Eu^{+3}] + K[Eu^{+3}][Cl^-] \tag{23}$$

thence

$$[Eu^{+3}] = \frac{[Eu^{+3}]_0}{1 + K[Cl^-]} \tag{24}$$

whence

$$R = \frac{k'[Eu^{+3}]_0}{1 + K[Cl^-]}[Eu^{+2}][Cl^-] \tag{25}$$

Clearly, $k'/(1 + K[\mathrm{Cl}^-])$ will not behave like a simple rate constant unless $K[\mathrm{Cl}^-] \ll 1$. Thus, until K is known, this chemical reaction cannot be put into the category of Class I.

(b) Bridge transfer mechanism

The bridge transfer mechanism was invoked by Taube and his associates in an effort to provide a more detailed mechanism for the process of electron transfer between an oxidant and a reductant. The essential feature of the bridged activated complex is that an added group, whether neutral or charged, is coördinated in a symmetrical fashion between the oxidant and the reductant, providing a more "accessible path for the flow of electrons." It also serves to explain the anomaly that exists for electron exchanges where the reactant species are chemically dissimilar but identical with the products. For instance, consider the following reaction:

$$\mathrm{Fe^{+2} + Fe^{*}OH^{+2} \rightarrow FeOH^{+2} + Fe^{*+2}} \tag{26}$$

Consider, as a possible activated complex, $[\overrightarrow{\mathrm{Fe^{+2}} \cdots (\mathrm{HO})^{-1} \cdots \mathrm{Fe^{+3}}}]^{\ddagger}$. It may be supposed that coincident with a solvation–desolvation process which makes the $\mathrm{Fe^{++}}$ and $\mathrm{Fe^{+++}}$ interchangeable energetically the hydroxyl radical moves to the left, accepting an electron from $\mathrm{Fe^{++}}$ at the same time that it abandons its electron to the $\mathrm{Fe^{+++}}$ on the right. The complicated maneuvering which must precede the actual electron transfer should not obscure the fact that the electron only jumps when there will be no free-energy change unless, as rarely happens, energy is exchanged with the radiation field. When the preparation for electron transfer involves only a small free energy of activation, the process is apt to be immeasurably fast.

Experimental studies indicate that the effectiveness of various ligands in speeding electron exchange by bridge formation runs parallel to their effectiveness in complex formation (70). Increased availability of electron pairs in the outer electronic shell of key elements of the ligand facilitates bridging. Taube and Myers (70), by judicious selection of an oxidation–reduction system, demonstrated directly the formation of a bridged activated complex. They studied the oxidation of $\mathrm{Cr^{+2}}$ with oxidizing agents of the type $\mathrm{Co(NH_3)_5X^{+2}}$ and found a quantitative transfer of X to the reducing agent. Although $\mathrm{Cr^{+2}}$ is labile to substitution, both the cobalt reducing agents used and the resulting $\mathrm{Cr^{+3}}$ complexes preserve their identity for periods of time long compared with the rate of oxidation of $\mathrm{Cr^{+2}}$. Therefore, a group combined with $\mathrm{Cr^{+3}}$ could not have combined with it after the act of oxidation. For the system in which $\mathrm{X^-}$ is $\mathrm{Cl^-}$, it was shown that the group transfer occurs without exchange with the free radioactive chloride ion in solution. Taube carefully points out that although bridge formation will provide an easier path for an electron transfer, the transfer of the bridging group is not an essential feature. Whether a group transfer occurs or not, he believes, will depend on the substitution ability of the reactant ions before and after the electron transfer. The latter is only true, however, when a net chemical change occurs, as in the chromium–cobalt system cited above.

The equivalence of speaking of catalytic effect or bridge formation by an ion is obvious. The complexing establishes more favorable conditions energy-wise, i.e., a new reaction path, to accelerate the overall process leading to electron transfer.

C. THE ENTROPY OF ACTIVATION

A previous paper by the present authors (47) pointed out that there are two possible reaction paths for electron exchange: one with low activation energy (~7–15 kcal./mole) and a relatively large negative entropy of activation (low frequency factor); the other with a high activation energy (~20–35 kcal./mole) and an equivalently large positive entropy of activation (high frequency factor). One of the reactions (cerous–ceric) is able to proceed by either path; for all other reactions one or the other of these paths is definitely favored. The total entropy change for a reaction involving charged species in solution can be attributed to at least six factors, which may be represented by equation 27:

$$\Delta S^{\ddagger}_{\mathrm{exptl}} = \Delta S^{\ddagger}_{T} + \Delta S^{\ddagger}_{R} + \Delta S^{\ddagger}_{h} + R \ln \kappa_{e} + \Delta S^{\ddagger}_{\mu} + \Delta S^{\ddagger}_{D} \tag{27}$$

where $\Delta S^{\ddagger}_{T}$ = translational loss,
$\Delta S^{\ddagger}_{R}$ = rotational loss,
$\Delta S^{\ddagger}_{h}$ = rearrangement of coördination shell, i.e., internal degrees of freedom, which includes changes in polarization of the medium (the electrostriction effect) and in the orientation effect if the reactants possess permanent dipoles,
$R \ln \kappa_{e}$ = transmission coefficient (tunnelling contribution where R is the molar gas constant),
$\Delta S^{\ddagger}_{\mu}$ = electrostatic effects (Debye–Hückel), and
$\Delta S^{\ddagger}_{D}$ = temperature coefficient of dielectric constant at constant ionic strength μ.

It can be shown (28) that

$$\frac{\Delta S^{\ddagger}_{\mu}}{\Delta S^{\ddagger}_{D}} \approx -1.45 \frac{\mu^{\frac{1}{2}}}{r^{\ddagger}} \tag{28}$$

For probable values for the radius of the activated complex ($r^{\ddagger}$) and values of the ionic strength (μ) encountered in electron transfer, this entropy ratio is approximately unity. Thus, these contributions cancel each other within the limits of applicability of the Debye–Hückel and the Born equations. Most electron-exchange studies were made in a range of ionic strength values where the simple Debye–Hückel law does not apply and where this entropy cancellation is incomplete. However, since two classes of bimolecular reactions are being compared, the relative and not the absolute entropy values are of more significance.

For any two reactions taken from the two classes defined on the basis of the positive and negative entropies of activation, the translational loss and the rotational loss are of the same order of magnitude and therefore these cannot account for the large differences found in the entropy of activation. There remain the entropy due to rearrangement of the coördination shell and the contribution of the transmission coefficient. It is assumed that the latter contribution has to be significant; otherwise, the entropy of hydration certainly cannot explain the entropy difference of 60 units observed for the two groups of reactions.

The positive entropies of activation can be explained on the basis of a high electronic transition probability between the two reactant ions so that the contribution of the term $R \ln \kappa_e$ is small. This means that parts of the hydration spheres of these ions have to be rearranged to a greater extent, and the magnitudes of the positive entropies show that from six to ten molecules of water are unfrozen in the formation of each activated complex. This assumes that each freeing of a water molecule from a solvation layer liberates 5 E.U., as in melting. In such cases the high positive activation entropy is associated with a correspondingly high energy of activation to give a moderate value of the free energy of activation.

It might be supposed that the negative entropies of activation could be explained by the reverse mechanism—the freezing of water onto the activated complex. However, inasmuch as the reactants already have maximum amounts of hydration, it appears unlikely that the activated complex with a smaller surface could hydrate to a greater extent. On the basis of this analysis, the magnitudes of the observed negative entropies of activation are best accounted for as extremely small electronic transmission coefficients.

D. THE FRANCK-CONDON PRINCIPLE AND ELECTRON TRANSFERS IN SOLUTION

The limitations that the Franck-Condon principle imposes on radiationless electronic transitions in or between molecular ionic aggregates in solution was recognized only recently. Discussions of this point have been given by Franck (25), Libby (46), and by the authors (47) in connection with electron-exchange reactions. The latter in particular have shown how the application of this principle leads to an adiabatic process for electron-exchange reactions in solution requiring electron tunnelling. The Franck-Condon principle states that the motion of nuclei is negligible during the time required for an electron transfer. The actual electron transfer is always considered to be a fast process; even so, the rate of a reaction involving an electron transfer may be quite slow, since the probability term for electron penetration through the electronic barrier may be much less than unity ($\kappa_e \ll 1$). Therefore, one common misinterpretation of the Franck-Condon principle when applied to electron-exchange reactions in solution is that after an electron is transferred from one hydrated ion to another hydrated ion, the hydration spheres of the two ions are "wrong" for their new charges and have to readjust slowly. It was this readjustment of hydration spheres subsequent to electron transfer which was thought to require an energy of activation.

The Franck-Condon principle implies that, since the nuclei do not move during an electronic transition, the electronic states of the reactants must be made equal before electron transfer can occur. Conservation of energy requires energetic equality of the electronic states of the activated complex during electron transfer. It stands to reason that in preparation for electron transfer some rearrangement of the electronic structures of the interacting complex ions will take place, and that this process is one which may require a considerable amount of energy. Marcus, Zwolinski, and Eyring (47) have designated this part of the free energy of activation required for reaction as $\Delta F_r^\ddagger$.

When any electron is transferred from one part of an activated complex to another, without absorption of radiation, the total energy (as stated previously) must be conserved. This means that the energy required to remove an electron from its initial position must be exactly supplied by the energy of binding the electron to its final position. Thus, for the kind of symmetrical reactions here considered, the half-transferred electron must be unable to distinguish between the system it is leaving and the one it is approaching. Further, since during the electron's swift passage the atoms have no time to move, it follows that both of the ions which are parties to a transfer in the activated complex must reorganize to the identical best intermediate configuration before the electron can start its journey. A corollary of these considerations is that the more different the structures of the oxidized and the reduced states of the ions are, the greater is the reorganizational free energy which will be required to form the intermediate configurations of the activated state.

The difference that one would expect in the rate of exchange between $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ on one hand, and $Fe(aq)^{+2}$ and $Fe(aq)^{+3}$ on the other hand, is thus primarily given by differences in the factor $\Delta F_r^\ddagger$. The magnitude of this term seems to be governed by the amount of similarity of structure in the coördination shells of the two reactant ions. Thus, the octahedral structure of the complex cyanides is the same for the two oxidation states, resulting in a very small $\Delta F_r^\ddagger$, while the structures of the two hydrated ions are probably different in the two oxidation states, resulting in an appreciable value of $\Delta F_r^\ddagger$. Among the exchange reactions of oxyanions these two cases are represented by the MnO_4^{-2}–MnO_4^- reaction (38) (fast; similar structure) and the AsO_4^{-3}–AsO_3^{-3} reaction (81) (slow; dissimilar structure). The fact that the electron exchange among complex ions like MnO_4^{-2}–MnO_4^- is still governed by the remaining two terms of the electrostatic model postulated by the authors (the probability factor $-RT \ln \kappa_e$ and the electrostatic repulsion term $\Delta F_{rep}^\ddagger$, together with a small value of $\Delta F_r^\ddagger$) is demonstrated by the recent finding (65) that the exchange rate in this system is measurable, though very fast. The fact that $\Delta F_r^\ddagger$ depends primarily on the first coördination shell, and not on hydration *per se*, is emphasized by the fast exchange in the cationic system $Os(bipy)_3^{+2}$–$Os(bipy)_3^{+3}$ (23). The anomaly in the cobalt-ammine systems, where the structures differ in the two reactant ions, will be discussed in the following section.

The importance of complex formation in oxidation–reduction reactions is seen to be a double one. In the first place there exists the possibility that the charge product of the two reactant ions can be reduced by using a complexing agent of opposite charge. The other effect of complexing is the one on the activation free energy of rearrangement, $\Delta F_r^\ddagger$. When both ions are complexed, the effect on $\Delta F_r^\ddagger$ is of a larger order of magnitude, essentially determining whether the reaction will be very fast or very slow, corresponding to similarity or dissimilarity of the complex structures of the two ions.

E. THE ELECTRON TUNNELLING HYPOTHESIS

That the probability for penetration of an electron through a barrier could be a determining factor in regulating electron-exchange reactions in solution was recognized by Libby (46) and more fully developed by Weiss (79) and by Marcus, Zwolinski, and Eyring (47). The probability of particles penetrating potential barriers is a fundamental peculiarity of quantum theory. To estimate the specific rate constant, k', the authors calculated the number of encounters per second

$$k_0 = \kappa_a \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \tag{29}$$

between reacting ions which achieved the favorable configuration at which the electrons transfer. This factor should then be multiplied by κ_e, which is the product of the average chance of an electron penetrating the barrier per electronic vibration into the number of these electronic vibrations per above ionic collisions. Because the probability of an electron being able to transfer is much greater if there is very close matching of energy for the initial and final states, the approximation was made of neglecting the transfers on all but the most favorable try. The results should probably be increased by a factor of a few times unity from this cause. Thus, the rate constant is found to be $k' = k_0\kappa_e$.

The relationship between k_0 and κ_e in terms of potential energy profiles is shown in figure 1. For each point along the atomic reaction coördinate there exists a whole set of values of the potential energy of the transition electron, varying with position along the electronic coördinate. Thus, one must find a "best" distance along both coördinates where the rate of electron transfer will be fastest. To achieve this, the rate constant is maximized so that it represents the best possible compromise between close approach of the reactant ions with a high energy of activation, as compared with reaction at large interionic distances with an accompanying large resistance to electron transfer.

Since the term κ_a is probably close to unity, the apparent overall free energy of activation becomes

$$\Delta F^{\ddagger}_{\text{app}} = -RT \ln \kappa_e + \Delta F^{\ddagger}_{\text{rep}} + \Delta F^{\ddagger}_{r} \tag{30}$$

In this first approximation only two factors are assumed to contribute to the free energy of activation of k_0: namely, $\Delta F^{\ddagger}_{\text{rep}}$ arising from the Coulombic interaction of the charges on the two reacting ions and the term, $\Delta F^{\ddagger}_{\text{rep}}$, representing the energy required for rearrangement of the coördination shells of the interacting ions as discussed in the preceding sections. The activity coefficients of the ions and the activated complex which represent the contribution of external factors to the free energy of activation are included in the $\Delta F^{\ddagger}_{\text{rep}}$. In any one case $\Delta F^{\ddagger}_{\text{rep}}$ would be very difficult to calculate. We tried taking it as a constant for all reactions. Although various kinds of collisions may contribute in some degree to electron transfer, the important ones will be those for which the apparent free energy, $\Delta F^{\ddagger}_{\text{app}}$, is a minimum.

Before the limiting value of $\Delta F^{\ddagger}_{\text{app}}$ can be found, an explicit expression has to be used for V, the height of the electronic potential barrier. The authors used a simple electrostatic model. If one approximates the shape of the electronic potential barrier by a triangular barrier, the probability for an electron to penetrate this barrier can be represented by the Gamow factor (18, 55)

$$\kappa_e = e^{-(8\pi r_{ab}/3h)[2m(V-W)]^{\frac{1}{2}}} \tag{31}$$

where V = the height of the electron barrier,
W = the kinetic energy of the electron,
r_{ab} = the width of the barrier at the height of penetration, and
m = the electron mass.

Proceeding in this manner, the following explicit expression was found for the critical intercationic tunnelling distance (r_{ab}^*) in the activated complex

$$r_{ab}^{*2} \simeq \frac{3e^2 p_a q_b h r_0^{\frac{1}{2}}}{8\pi ekDT(mZ^*)^{\frac{1}{2}}} \tag{32}$$

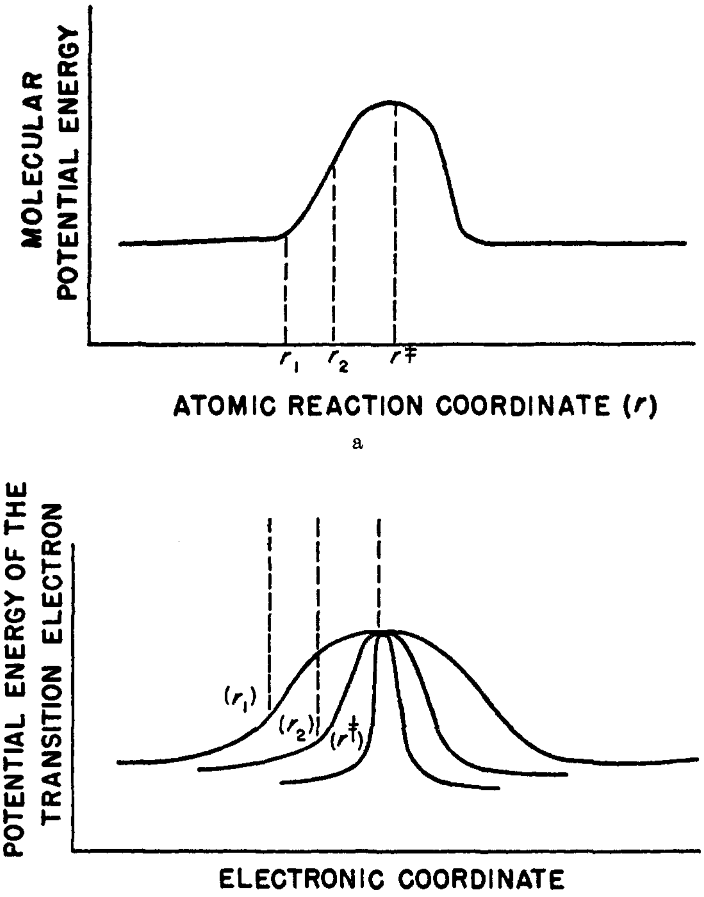

FIG. 1. The relationship between k_0 and κ_e in terms of potential energy profiles

where p, q = the surface electrostatic charges,
Z^* = the positive charge on the central atom of the reductant,
r_0 = the radius of the classical orbit of the exchanging electron in the reductant ion, and
D = the dielectric constant.

On the basis of this relation, the correlative features of the electrostatic model for electron-exchange reactions have been discussed previously (47). These concern the effect on the speed of electron-exchange reactions of the principal and orbital quantum number of the exchanging electron, the dielectric constant of the medium, the charge product of the two reacting ions, and the oxidation state of the central ion.

To compare this model with experimental data for the purpose of correlating apparent total free energies of activation ($\Delta F^{\ddagger}_{\mathrm{app}}$) with the observed values, the empirical constant $\Delta F^{\ddagger}_{r}$ needs to be evaluated. The ferrous–ferric reaction yielded a value of 8.1 kcal./mole. Assuming this value to be a constant for all those reactants whose primary coördination shells consist of water molecules, total free energies of activation were calculated for the cation reactions in table 1. Table 1 includes results of calculations on some recent experimental studies not included in the earlier publication. Considering the crudeness of the model and the approximations made, the agreement between calculated and observed values is interesting. Among the Class I cation reactions listed in table 1, the neptunium reaction (NpO_2^{+}–NpO_2^{+2}) and the iron reaction (Fe^{+2}–Fe^{+3}) have only water in their coördination shell. Here the calculated free energy of activation checks the experimental value within 0.3 kcal.

The assumption used in the estimation of $\Delta F^{\ddagger}_{r}$, that the primary coördination shell is composed solely of water molecules, is badly vitiated when that shell consists solely of ligands other than water. For instance, in the $Co(en)_3^{+2}$–$Co(en)_3^{+3}$ system, the ligand is ethylenediamine. In these cases $\Delta F^{\ddagger}_{r}$ is modified. In the particular case of the cobalt reaction the value of $\Delta F^{\ddagger}_{r}$ is complicated by the fact that the configuration of the coördination shell is different in the divalent and in the trivalent complexes, as is evident from the difference in the carbon–nitrogen bond lengths (11, 67).

The nature of the activated complex must be considered for electron-transfer reactions of the type Fe^{+2}–$FeCl^{+2}$, in which a group which is a member of the primary coördination shell, in this case chloride, is transferred from one central ion to another in order to insure $\Delta F^0 = 0$. The quantity $\Delta F^{\ddagger}_{r}$ measures the energy which is needed to make the electronic states of both reactant ions alike except for charge prior to electron transfer. The atomic arrangement must now be as nearly symmetrical as is economical with respect to both kinds of ligands—water as well as the group which is a member of the reacting ion pair and which is to be transferred. This process may take more or less energy than the rearrangement of water molecules alone. In the case of transfer of a hydroxyl group, it seems to take less energy. From an examination of the data reported in table 1 the various groups which may take part in electron-transfer reactions may be arranged in the following approximate order of increasing $\Delta F_r^{\ddagger}$: OH, H_2O, F, Cl, en, NH_3 (see also 10, 70, 71). The transfer of two groups in general takes more energy than does the transfer of one. This is exemplified by the Fe^{+2}–$FeCl_2^{+1}$ and Fe^{+2}–FeF_2^{+1} reactions, in which the rate is slower than predicted.

This kind of group exchange is necessary for a Class I reaction if the products are to be identical with the reactants. Consider the model shown in figure 2 for the structure of the activated complex. Here two polyatomic hydrated complex ions form the activated complex by sharing two or more coördinated groups through formation of bonds f_1 and f_2. The shared groups X_1 and X_2 may be either water molecules, small ions, or radicals and need not necessarily be identical. On dissociation of the activated complex, scission of the d_1 and d_2 bonds can occur, leading to the formation of the correct product species to insure $\Delta F^0 = 0$ for the overall process.

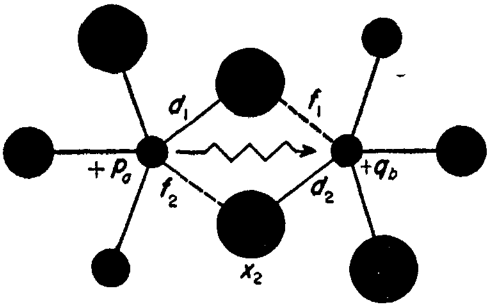

FIG. 2. Model for the structure of the activated complex

Although this model for the activated complex for electron-transfer reactions has many features in common with the bridged activated complex proposed by Taube, prime emphasis is placed on the perturbing effect of the coördinating groups in determining the shape and height of the electronic potential barrier. Only in this sense is it meaningful to speak of the coördinating groups providing a more accessible path for electron transfer.

F. SECOND METHOD FOR TRANSITION PROBABILITIES IN NON-ADIABATIC REACTIONS

Besides barrier leakage we may treat electron transfer by the method of crossing potential surfaces (24, 42, 79, 83, 84).

Figure 3 indicates qualitatively the nature of the process under consideration. Thus the oxidizing and reducing ions must collide with each other. This corresponds to moving toward the left, as indicated by the arrows in figure 3. As the ions approach each other, the total number of solvating ions $m + n$ will change. In three-dimensional space there are not enough degrees of freedom to indicate the change in $m + n$; rather, figure 3 is the reaction rate section in many-dimensional space chosen to keep $\Delta F_{\text{app}}^{\ddagger}$ as low as possible. Although $\Delta F_{\text{app}}^{\ddagger}$ is sharply defined only at stationary points, this diagram should not lead to misunderstanding. Besides colliding, the ions in the course of reaction adjust the relative number of solvating ions, $m - n$, from a negative number through

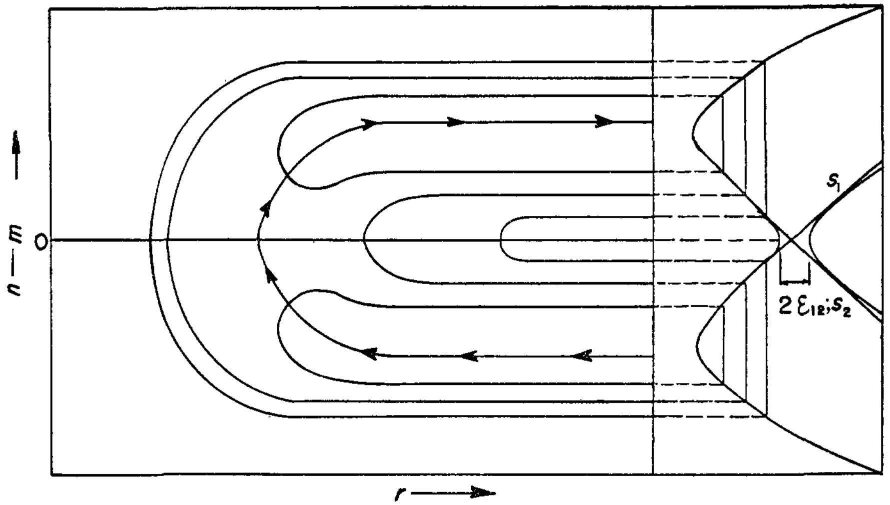

FIG. 3. The surface for $\Delta F^{\ddagger}_{\text{app}}$ for the reaction

$$M^{+p}(H_2O)_m + N^{+(p+1)}(H_2O)_n \rightarrow M^{+(p+1)}(H_2O)_m + N^{+p}(H_2O)_n$$

Here r is the distance between the two isotopic ions, and m and n are the numbers of coordinated molecules.

zero to a positive value. In a successful collision the electron jumps near the line $m - n = 0$. If at this line the electron fails to jump, then the potential surface instead of descending into the valley for products will continue to rise uniformly onto a higher surface, which is indicated in the vertical section on the extreme right of figure 3.

An order of magnitude calculation will now be given. Thus, when the probability of electron transition per collision is small, as in this case, we can write

$$\kappa_e = 1 - e^{-4\pi^2 E_{12}^2/h\bar{v}|s_1 - s_2|} = \frac{4\pi^2 E_{12}^2}{h\bar{v}\,|\,s_1 - s_2\,|} \tag{33}$$

where $2E_{12}$ is the smallest distance between, and $|\,s_1 - s_2\,|$ is the difference of slopes of, the crossing potential surfaces at $n - m = 0$. Here the mean velocity, $\bar{v}$, of moving along the reaction coördinate across the line $m - n = 0$ is $\bar{v} = \sqrt{2kT/\pi m^{\ddagger}}$. If the reduced mass $m^{\ddagger}$ is estimated as half the mass of an iron atom, as it would be were two iron atoms colliding, the average velocity, $\bar{v}$, can be calculated. Since the free energies of activation are around 11 kcal., this suggests that the rate of energy rise, s_1, for the lower surface is about 11 kcal. per 0.5 Å. If s_2 is taken to be equal to $- s_1$, $|\,s_1 - s_2\,|$ is about 2 v. per Ångström unit. Now, in order that κ_e shall have the value 5×10^{-4} estimated from experiment for reaction 1 (66), we require that the resonance energy for the electron between the initial and final positions, E_{12}, should have the value of 7 cal. per mole. E_{12} can readily be calculated from a potential surface for electron displacement. However, this discussion should suffice to show how estimates of κ_e can be refined by this method.

G. COMMENTS ON ELECTROLYSIS OF MAGNESIUM

Water plays a rather special role as a complexing agent in these reactions. One consequence of this special role is lack of knowledge about the amount and the structure of hydration of cations. Another is the disappearance of the separation between coördination and solvent effects, since now complexing agent and solvent are the same. An instructive example of the effect of hydration is the electrolysis of magnesium. When magnesium is oxidized anodically (56), one would expect only Mg^{+2} ions to be formed, because univalent magnesium ions are unstable. Yet more magnesium is lost from the anode than can be accounted for by assuming the formation of Mg^{+2} only. This means that some Mg^+ ions must be formed. It is also noted in this experiment that a quantity of hydrogen is formed at the anode which corresponds to the reaction

$$Mg^+ + H_2O \rightarrow MgOH^+ + \tfrac{1}{2}H_2 \qquad (34)$$

Other oxidizing agents than water were found to produce similar reactions. The small but finite lifetime of the unipositive magnesium ion was indicated by these two facts: as much as 20 per cent of the reducing activity remained after the end of the electrolysis, and the reducing activity could be collected in a separate vessel when a flow system was used for the electrolysis. The tremendous effect of hydration is evident here; the difference of 250 kcal. in ionization potential between the two different oxidation states of magnesium is overcome by the large hydration energy of the dipositive ion (671 kcal.). Yet the unipositive ion must also be stabilized by hydration to a great extent in order to exist as long as it does.

A schematic diagram of the process in configuration space would look much like figure 4. In that diagram the position *a* corresponds to the solid magnesium atom of the electrode, which may go to any of the five possible positions to the extreme right. If water is present, the ions start adding a hydration layer as they

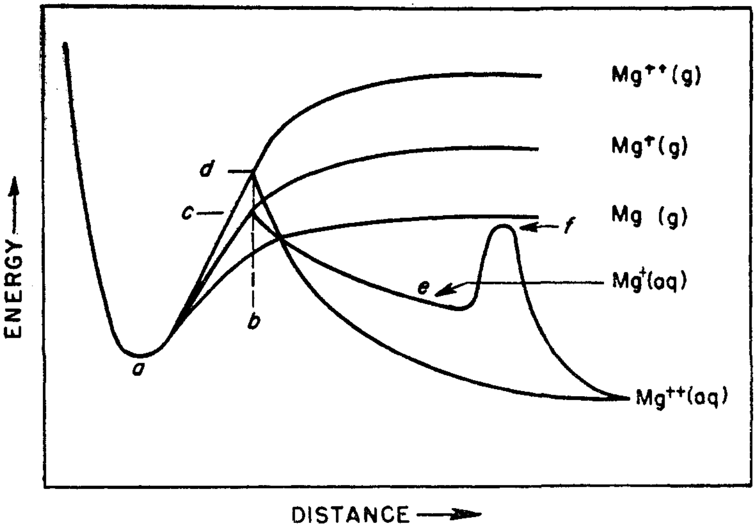

FIG. 4. Schematic diagram in configuration space of the electrolysis of magnesium

cross the Helmholtz double layer at the points *d* and *c*. Actually, there will be a rounding off of the surface at the activated state. If material is present in solution to combine with Mg^+ across the low barrier *f* as fast as it is formed across the *c*, Mg^+ will be formed somewhat faster than Mg^{++}. This effect of environment on the state of ionized magnesium is particularly interesting in the case of chlorophyll.

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