

On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. II. Applications to Data on the Rates of Isotopic Exchange Reactions*

R. A. MARCUS

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York

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The rates of some homogeneous isotopic exchange reactions in solution are considered in the light of a recently developed quantitative theory of redox processes (Part I). The relative importance of several factors influencing the rates of these reactions is discussed. These factors include the Coulombic repulsion between the ionic reactants and the extent of solvation of the ions. Free energies and entropies of activation of various reactions are calculated from the theory without the use of any adjustable parameters. The agreement with the experimental data is considered to be satisfactory.

On the basis of the theory and of earlier experiments in heavy water an experimental method is tentatively suggested for distinguishing electron and atom transfer mechanisms. This method applies to halide-catalyzed exchange reactions of metal aquo-ions, and to other anion-catalyzed reactions of this type not involving breakable OH bonds.

INTRODUCTION

DURING the past decade a considerable number of experimental studies have appeared¹ on the rates of isotopic exchange redox reactions between ions differing only in their valency. Such reactions constitute the simplest type of oxidation-reduction reaction. For this reason their study has proved very useful in yielding information on some of the molecular properties which may affect the rate of redox reactions in general. Sufficient data have been accumulated so that a number of generalizations about the behavior of these isotopic exchange reactions can be drawn. Various suggestions have been advanced²⁻⁷ on the detailed mechanism of these reactions. These were either qualitative or semi-empirical in origin. Two of these interesting papers^{3,7} described a quantitative theory of the transfer of an electron between the two reactants. The work of R. Marcus, Zwolinski, and Eyring⁸ was primarily concerned with the problem of the tunneling of an electron from one reactant to the other through a solvent barrier. These authors also pointed out that a reorganization of the solvent molecules had to occur prior to the tunnelling. Though the corresponding free energy term for this reorganization was not calculated

a priori, an empirical adjustable parameter was introduced for it and was chosen in such a way as to obtain the best agreement with the data. The slightly earlier work of Weiss⁷ represented a first attempt to evaluate some of the factors affecting the rates of electron transfer reactions. However, the portion of the work dealing with solvation problems is invalidated because of errors in a number of its basic arguments and equations.

Recently a quantitative theory of electron transfer reactions has been formulated⁸ from first principles plus assumptions which we consider reasonable on *a priori* grounds. The theoretical equation deduced contains no adjustable parameters and relates the reaction rate to the ionic charges and radii of the reactants and to the standard free energy of reaction. In the present paper the expression is applied to some available data on simple isotopic exchange reactions which involve electron transfer. The nature of the agreement obtained is considered satisfactory.

THEORETICAL

Theoretical Equations

In Part I of this series⁸ the following equation was derived for the bimolecular rate constant, k_{bi} , of an electron transfer step, using some recently established⁹ expressions for the properties of systems having non-equilibrium electrical polarization. As in Part I, this equation for k_{bi} is to be multiplied by an electron-tunneling factor which preliminary considerations indicate to be of the order of magnitude of unity.¹⁰

⁸ R. A. Marcus, J. Chem. Phys. 24, 966 (1956), hereinafter referred to as Part I.

⁹ R. A. Marcus, J. Chem. Phys. 24, 979 (1956).

¹⁰ This factor is the reciprocal of the denominator in Eq. (7) of Part I, and has a maximum value of unity. It can be calculated by various methods discussed there. For example, using some preliminary electron-tunneling computations⁸ to evaluate one of the terms it was tentatively concluded⁸ that the factor was of the order of unity within the error of those calculations. Even if the factor were as low as 0.01 the values of ΔF_{calc}^* in Table I would only have to be increased by $kT \ln 100$ or 2.5 kcal mole⁻¹ at 0°C.

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¹ See review articles: Zwolinski, Marcus, and Eyring, Chem. Revs. 55, 157 (1955); C. B. Amphlett, Quart. Revs. 8, 219 (1954); O. E. Myers and R. J. Prestwood, *Radioactivity Applied to Chemistry*, edited by Wahl and Bonner (John Wiley and Sons, Inc., New York, 1951), Chap. I; Betts, Collinson, Dainton, and Ivin, Ann. Repts. Progr. Chem. (London) 49, 42 (1952); R. R. Edwards, Ann. Rev. Nuclear Sci. 1, 301 (1952); M. Haissinsky, J. chim phys. 47, 957 (1950); and recent reviews in Ann. Rev. Phys. Chem.

² W. F. Libby, J. Phys. Chem. 56, 863 (1952), and the accompanying discussion of this paper.

³ R. Marcus, Zwolinski, and Eyring, J. Phys. Chem. 58, 432 (1954).

⁴ R. Platzman and J. Franck, Z. Physik 138, 411 (1954).

⁵ A. W. Adamson, J. Phys. Chem. 56, 858 (1952).

⁶ H. Taube and H. Meyers, J. Am. Chem. Soc. 76, 2103 (1954).

⁷ J. Weiss, Proc. Roy. Soc. (London) A222, 128 (1954).

We have ^{8,11} for k_{bi}

$$k_{bi} = Z \exp(-\Delta F^*/RT) \quad (1)$$

where Z is the collision number in solution and ΔF^* is given by Eqs. (2) to (4).

$$\Delta F^* = m^2\lambda + e_1^*e_2^*/D_s r, \quad (2)$$

where

$$2m+1 = -[\Delta F^0 + (e_1e_2 - e_1^*e_2^*)/D_s r]/\lambda \quad (3)$$

and

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) (\Delta e)^2. \quad (4)$$

In these equations, e_1^* and e_2^* are the charges of the reactants and e_1 and e_2 are those of the products. As a result of reaction the change in charge of reactant 1, Δe , is $(e_1 - e_1^*) = (e_2^* - e_2)$. The effective radii of the reactants a_1 and a_2 are discussed later. The standard free energy change of the electron transfer step in the reaction is ΔF^0 . The value which should be employed for r , the distance between the centers of the reactants in the collision complex, has been discussed in Part I. For reasons outlined there, r will be set equal to its minimum value $(a_1 + a_2)$. D_{op} is the square of the refractive index, while D_s is the static dielectric constant.

It will be useful also to write the rate expression, Eq. (1), in terms of the energy of activation E_a , defined in the usual way as $-R\partial \ln k_{bi}/\partial(1/T)$, and in terms of the entropy term, ΔS^* , defined in Eq. (5).

$$\Delta S^* = -\partial \Delta F^*/\partial T. \quad (5)$$

Introducing Eq. (1) into the definition of E_a and neglecting the slight temperature dependence of Z , one finds

$$k_{bi} = Z \exp(\Delta S^*/R) \exp(-E_a/RT). \quad (6)$$

The terms ΔF^* and ΔS^* defined in this paper are not quite the same as the well-known free energy and entropy of activation,¹² ΔF^\ddagger and ΔS^\ddagger , but are readily related to them.¹³ The terms ΔS^* and ΔF^* will be termed the excess entropy of activation and the excess free energy of activation. They have a simple physical interpretation. The quantity ΔF^* is the free energy of

¹¹ In Eq. (3) a term ΔS_e , has been omitted [see Eq. (40) of reference 8]. This term is the contribution to the entropy of reaction arising from any difference between the electronic degeneracy of the reactants and the products. Depending upon the reaction, it is either zero or negligible.

¹² See Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

¹³ The terms ΔF^\ddagger and ΔS^\ddagger are defined by the relations

$$k_{bi} = (kT/h) \exp(-\Delta F^\ddagger/RT) \\ = e(kT/h) \exp(\Delta S^\ddagger/R) \exp(-E_a/RT).$$

At room temperature the term kT/h equals 10^{13} sec^{-1} while Z , the collision number in solution, is¹⁷ about equal to $10^{10} \text{ cc mole}^{-1} \text{ sec}^{-1}$. When the standard state in ΔS^\ddagger corresponds to 1 mole cc^{-1} of each reactant and of the activated complex, then the units of this Eyring expression for k_{bi} become $\text{cc mole}^{-1} \text{ sec}^{-1}$. When Eq. (6) is equated to this equation for k_{bi} we then obtain $\Delta S^\ddagger = \Delta S^* - R + R \ln 1000 = \Delta S^* + 11.8 \text{ cal deg}^{-1} \text{ mole}^{-1}$ and $\Delta F^\ddagger = \Delta F^* - RT \ln 1000$.

formation of the intermediate state from the reactants, in excess of what it would be if the state were simply the usual transient collision complex of two neutral, non-reactive particles in a solution. Similarly, ΔS^* is the corresponding entropy term.

EFFECTIVE RADII

In the derivation of Eq. (2) for ΔF^* each ion was treated as being surrounded by a sphere of radius a inside of which the dielectric medium, i.e., the solvent, is saturated and inside of which it is unsaturated. Similar models have been used¹⁴ extensively in calculating the free energy of solvation of ions.

As discussed in Part I if, as is usually assumed, the innermost hydration layer around monatomic ions is largely saturated it will not contribute to ΔF^* , and a then equals the sum of the crystallographic radius of the ion and of the diameter of a water molecule. Polyatomic ions such as $\text{Fe}(\text{CN})_6^{-3}$ and MnO_4^- , being rather large, would not be expected to cause dielectric saturation of the solvent as readily as the smaller monatomic ions, since the electric field of the ion, which is responsible for the saturation, falls off roughly as the square of the distance from the center of the ion. Thus, one would expect that a for the cited polyatomic ions would be approximately the actual crystallographic radii. This is also consistent with the assumption that only the first layer of water molecules about a monatomic ion is saturated, since a hydrated monatomic ion has about the same radius as these polyatomic ions.

When a is slightly different for an ion when it is a reactant and when it is a product it was suggested that a mean value for a be adopted. As noted later, a refinement of the theory could take the effect of this variation on the rate into account.

ATOM VS ELECTRON TRANSFER

Isotopic exchange redox reactions may occur by the alternative mechanisms of atom transfer and of electron transfer. For example, in the chloride ion catalyzed¹⁵ isotopic exchange reaction of ferrous and ferric ions, one of the reactions involves the reaction of a Fe^{+2} ion with a FeCl^{+2} ion. The reaction can occur either via the transfer of an electron to produce Fe^{+3} and FeCl^+ ions, or by a transfer of a chlorine atom to produce, respectively, a FeCl^{+2} and a Fe^{+2} ion. It has not yet proved possible to establish which path occurs in this case. Similar remarks apply to the reaction¹⁵ of Fe^{+2} with a hydrolyzed ferric ion, FeOH^{+2} . Here, the reaction could occur by an electron transfer, or alternatively by the transfer of a hydrogen atom¹⁶ from the

¹⁴ See J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* 1, 515 (1933); D. D. Eley and M. G. Evans, *Trans. Faraday Soc.* 34, 1093 (1938); E. J. W. Verwey, *Rec. trav. chim.* 61, 127 (1942); R. W. Atrec, *Dissertation Abstr.* 13, 481 (1953).

¹⁵ J. Silverman and R. W. Dodson, *J. Phys. Chem.* 56, 846 (1952).

¹⁶ R. W. Dodson and N. Davidson, *J. Phys. Chem.* 56, 866 (1952).

hydrated ferrous ion to the hydrolyzed ferric ion, FeOH^{+2} . Another reaction in the ferrous-ferric reaction involves the oxidation of a ferrous ion by the uncomplexed ferric ion.¹⁵ Such a process seems more likely to occur by an electron transfer.

The $\text{Cr}^{+2}-\text{CrCl}^{+2}$ isotope exchange reaction has been shown to possess an atom transfer mechanism.¹⁷ Because of the difference in behavior of Cr^{+3} and Fe^{+3} ions one cannot immediately conclude that the chloride ion catalyzed $\text{Fe}^{+2}-\text{Fe}^{+3}$ isotope exchange reaction also has an atom transfer mechanism.

Taube and co-workers have shown that many other inorganic redox reactions of Cr^{+2} possess an atom or group transfer mechanism.¹⁸ On the other hand, reasonable evidence⁶ was obtained for a bridged-activated complex electron transfer mechanism for the reduction of IrCl_6^{-3} and of $\text{Fe}(\text{CN})_6^{-4}$ by Cr^{+2} . It may be remarked that the theory developed in Part I does not apply, in its present form at least, to bridged-complex electron transfer reactions nor, of course, to atom or group transfer reactions. In the present paper *a priori* reaction rates are calculated for reactions for which a bridged-activated complex seems less likely.

THEORETICAL EQUATIONS FOR ISOTOPIC EXCHANGE REACTIONS

With one possible exception we shall consider here isotopic exchange reactions in which the products in the elementary electron transfer step in the reaction are chemically indistinguishable from the reactants in that step, though they are distinguishable in some physical property such as radioactive behavior. In such reactions, the standard free energy change of the elementary step, ΔF^0 , is zero, while $e_1^* = e_2$ and $e_2^* = e_1$. Introducing these values into Eq. (3), we find that m equals $-\frac{1}{2}$. Again, it was observed previously that the radius a_1 , say, is the mean value calculated for reacting particle 1 as a reactant and as a product. Since, in the present case, reacting particle 1 as a product is the same as 2 as a reactant, and conversely, we have $a_1 = a_2$ and will denote these by a . Since r is taken to equal $(a_1 + a_2)$ it therefore equals $2a$. Introducing these relations into Eq. (2) we obtain for ΔF^*

$$\Delta F^* = \left[\frac{e_1^* e_2^*}{D_s} + \frac{(\Delta e)^2}{4} \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \right] \frac{1}{2a} \quad (7)$$

The free energy change, ΔF^* , is seen to be composed of two terms. The first, $e_1^* e_2^* / D_s 2a$, is the contribution of the Coulombic repulsion or attraction of two reactants whose distance of approach to each other is $2a$. The second is actually the contribution which would arise from the reorganization of the solvent molecules in order to form the nonequilibrium activated state

from an equilibrium state at the same distance of approach, $2a$. This term is seen to increase as the ionic radius a decreases and as the amount of charge transferred Δe increases. This is as expected. The greater the difference in the equilibrium degree of orientation of the solvent molecules about an ion when it is a reactant as compared to this difference when it is a product, the greater will be the necessary reorganization of the solvent molecules in order to form the intermediate state, and therefore the greater will be ΔF^* . This difference in degree of orientation will increase with increasing difference Δe in the charge of the ion when it is a product and when it is a reactant, and will increase with increasing ability of the ions to become solvated. This ability increases as a decreases.

Since D_{0p} is essentially independent of temperature it follows from Eqs. (2) and (5) that ΔS^* is given by

$$\Delta S^* = -\frac{1}{2a} [e_1^* e_2^* - (\Delta e)^2 / 4] \frac{\partial(1/D_s)}{\partial T} \quad (8)$$

When only one electron is transferred the term $(\Delta e)^2 / 4$ will generally be appreciably less than $e_1^* e_2^*$ and we would then have

$$\Delta S^* \cong \frac{e_1^* e_2^*}{2a} \frac{\partial(1/D_s)}{\partial T} \quad (9)$$

The first term of Eq. (8), $-(e_1^* e_2^* / 2a) \partial(1/D_s) / \partial T$, is the usual entropy change which occurs when two ions approach each other under equilibrium conditions, the distance of approach r being $2a$. The second term of Eq. (8) is the entropy change resulting from the reorganization of the solvent molecules which would accompany the formation of the nonequilibrium state from this equilibrium state at the same r . This second term was seen, in the derivation of Eq. (9) from Eq. (8), to be small. This is so because accompanying this solvent reorganization there is a decrease in entropy of solvation around one ion which is approximately cancelled by an increase around the other. The solvent near the more highly charged ion of the two reactants becomes less "frozen" or oriented and that near the other ion becomes more oriented in the reorganization process. This conclusion, that the entropy of reorganization is a small contribution to ΔS^* , is contrary to what has been assumed in one explanation³ of the observed values of ΔS^* .

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

(a) Excess Free Energy of Activation

From the experimental value of the bimolecular rate constant, k_{bi} , an experimental value of ΔF^* is calculated with the aid of Eq. (1). In this equation the collision number in solution, Z , is¹⁹ equal to 10^{16} cc

¹⁷ H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

¹⁸ H. Taube, *J. Am. Chem. Soc.* **77**, 4481 (1955) and references cited therein.

¹⁹ A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (John Wiley and Sons, Inc., New York, 1953), Chap. 7.

TABLE I. Excess free energy of activation ΔF^* of isotopic exchange reactions.

Reaction	a (Å)	Temperature (°C)	ΔF_{expt}^* (kcal mole ⁻¹)	ΔF_{calc}^* (kcal mole ⁻¹)
MnO ₄ ²⁻ —MnO ₄ ⁻	2.8 _d	1	12.8 ^a	9.2
Fe(CN) ₆ ⁴⁻ —Fe(CN) ₆ ³⁻	4.5	4	12.7 ^b	10.1
Mo(CN) ₆ ⁴⁻ —Mo(CN) ₆ ³⁻	4.8	2	<12.6 ^c	9.5
Fe ²⁺ —Fe ³⁺	3.4 _d	0	16.3 ^d	9.8
Co ²⁺ —Co ³⁺	3.4 _d	0	16.4 ^e	9.9
Tl ⁺ —Tl ³⁺	...	24.9	18.8 ^f	...

^a J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.* 75, 5133 (1953);
^b A. C. Wahl and C. F. Deck, *ibid.*, 76, 4054 (1954); ^c R. L. Wolfgang, *ibid.*,
 74, 6144 (1952); ^d J. Silverman and R. W. Dodson, *J. Phys. Chem.* 56, 846
 (1952); ^e N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.* 74, 1866 (1952);
^f R. J. Prestwood and A. C. Wahl, *ibid.*, 71, 3137 (1949); ^g F. J. C. Rossotti,
J. Inorg. Nuclear Chem. 1, 159 (1955). The radii a are taken from the
 appendix.

mole⁻¹ sec⁻¹. Values of ΔF^* obtained in this way are listed as ΔF_{expt}^* in Table I. These values are known quite accurately, since ΔF^* depends only on the logarithm of k_{bi} . Thus an error of a factor of 2 in k_{bi} introduces an error of only 0.4 kcal mole⁻¹ in the ΔF^* values listed in Table I. The temperatures at which these experimental values of k_{bi} were measured are also given in the table. However, these ΔF_{expt}^* have not been corrected for salt effects, and the actual values at infinite dilution (where ΔF_{calc}^* applies) would be slightly higher.

Theoretical values of ΔF^* were calculated at these temperatures using Eq. (7), together with the radii a obtained from the appendix and the literature values²⁰ of the dielectric constant D_s at the various temperatures. The square of the refractive index of water, D_{op} , which also appears in Eq. (7) equals 1.8.

In the light of the usual accuracy of prediction of free energies of activation of reactions in general, the agreement between the calculated and experimental values of ΔF^* in Table I is considered to be encouraging, no adjustable parameters having been introduced into the calculations. The difference between ΔF_{expt}^* and ΔF_{calc}^* is largest for the Fe²⁺—Fe³⁺ and Co²⁺—Co³⁺ reactions. It is quite possible that the innermost hydration layer of these ions is not completely dielectrically "saturated" as assumed. Just as the reorganization of the solvent outside the "saturated" layer, prior to the electron jump, was responsible for the ΔF^* given by Eq. (2), there would be in this case an additional contribution to ΔF_{calc}^* arising from any changes which may have to occur in interatomic distances in this innermost hydration layer, prior to the electron jump, in order to form the activated state. This idea can be shown to offer an explanation for some recent data²¹ on the relative rate of one of these reactions in water and in heavy

²⁰ J. Wyman, *Phys. Rev.* 35, 623 (1930).

$D_s = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2]$ where t is in degrees centigrade.

²¹ J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.* 78, 911 (1956). It was observed that the rate constants of the uncatalyzed and hydroxyl ion catalyzed Fe²⁺—Fe³⁺ exchange reaction were each twice as great in water as they were in heavy water. They proposed an atom transfer explanation.

water.²² Computations on this additional contribution to ΔF^* , arising from any changes in interatomic distances within the spheres of radius a , are in progress.^{22a} This contribution will be small for tightly-knit ions, such as, perhaps, the complex cyanide and the manganate ions.

Other possible reasons for a difference between ΔF_{expt}^* and ΔF_{calc}^* can, of course, be suggested. For example, the electron-tunneling factor discussed in reference 10 may be somewhat less than unity. However, such a factor would not be temperature-dependent and would not therefore enter into any comparison between experimental and calculated values of the activation energy. The former is¹⁵ 9.9 kcal mole⁻¹ and the latter is readily computed to be 5.5 kcal mole⁻¹. This difference is not much less than that in the ΔF^* 's. We infer that this electron-tunneling factor is probably not the major contribution to the difference in ΔF^* 's, although it may be a contributing factor.

The thallos-thallic exchange reaction in Table I may occur either by two successive one-electron transfers or one two-electron transfer. Because of the uncertainty of mechanism, no ΔF_{calc}^* is given in Table I.

The relative magnitude of the two contributions to ΔF^* in Eq. (3), the Coulombic repulsion and the solvent reorganization free energy, is of some interest. We find these terms to be generally of the same order of magnitude. The ratio of the Coulombic to the second term is calculated to be 0.50 for the Fe²⁺—Fe³⁺ reaction, 0.50 for the Co²⁺—Co³⁺ reaction, 1.0 for the complex cyanide reactions and 0.17 for the manganate reaction. Using these results, it may be inferred from Table I that no simple correlation between the reaction rate and the size of the Coulombic term would be expected. No such correlation has in fact been found.

One reaction which is of some interest but which has not been included in Table I is the isotopic exchange reaction between cobaltous and cobaltic amines.²³ The CoN bond distance in these two compounds is very different²⁴ and, as previously mentioned, the theory does not apply in its present form to reactions in which

²² Any changes in interatomic O—H distances in the innermost hydration layer needed to form the activated state are easier for O—H bonds than for O—D bonds since the former have a higher zero-point energy. Incidentally, the difference in rates in the two solvents cannot, according to Eq. (2), arise from the dielectrically unsaturated part of the medium since the solvents do not differ appreciably in their D_s or D_{op} . Some experimental data of Lange and Martin [*Z. Elektrochem.* 42, 662 (1936)] are also of particular interest in this regard. For many salts these authors found appreciable differences in the free energy of solution of a salt in H₂O and D₂O. Since the D_s and D_{op} of the two solvents are essentially the same, these differences in free energy of solvation presumably arise from differences in atomic polarization of the dielectrically saturated innermost solvation layer.

^{22a} Note added in proof.—Some preliminary classical mechanical results on this aspect of the problem are noted briefly in *Trans. N. Y. Acad. Sci.*, March 1957. This paper also presents some other developments in the theory of the rate of electron transfers in solution and at electrodes.

²³ Lewis, Coryell, and Irvine, *J. Chem. Soc.* 1949, Suppl. Issue No. 2, S386.

²⁴ See H. C. Brown, *J. Phys. Chem.* 56, 868 (1952).

appreciable changes in bond lengths occur. Using the refinement of the theory mentioned earlier, it is planned to calculate a free energy of activation for this reaction.

(b) Excess Entropy of Activation

Of the reactions listed in Table I, the temperature dependence of only the ferrous-ferric reaction appears to have been carefully studied. From this the experimental value of excess entropy of activation may be computed with the aid of Eq. (6) to be $-23 \text{ cal mole}^{-1} \text{ deg}^{-1}$ at 0°C . The theoretical value ΔS^* is found from Eq. (8) to be $-14 \text{ cal mole}^{-1} \text{ deg}^{-1}$. Considering the experimental errors that always accompany a measurement of ΔS^* and considering the assumptions of theory, the experimental and calculated values agree reasonably well.

REACTION RATES IN HEAVY WATER—A POSSIBLE CRITERION OF MECHANISM

Using the theory outlined in this paper, an experimental method can be proposed for distinguishing between different mechanisms in certain cases, based upon $\text{D}_2\text{O}-\text{H}_2\text{O}$ isotope effects. As a concrete example the $\text{Fe}^{+2}-\text{Fe}^{+3}$, $\text{Fe}^{+2}-\text{FeOH}^{+2}$ and $\text{Fe}^{+2}-\text{FeCl}^{+2}$ reactions will be considered.

If these reactions have a small-overlap electron transfer mechanism, that is, if there is but a small overlap of the electronic orbitals of the two reactants in the activated complex, then a basic assumption of the present theory⁸ is fulfilled. In this case, more or less comparable $\text{D}_2\text{O}-\text{H}_2\text{O}$ isotope effects would be expected for each rate constant, for reasons given earlier.²² Since the $\text{Fe}^{+2}-\text{Fe}^{+3}$ and $\text{Fe}^{+2}-\text{FeOH}^{+2}$ rate constants were twice as great²¹ in H_2O as they were in D_2O , this mechanism would predict an effect of similar magnitude for the $\text{Fe}^{+2}-\text{FeCl}^{+2}$ reaction.

If a reaction has an atom transfer mechanism, then a $\text{D}_2\text{O}-\text{H}_2\text{O}$ effect would probably be expected only if that atom were hydrogen. Thus, an isotope effect could occur for the $\text{Fe}^{+2}-\text{Fe}^{+3}$ and $\text{Fe}^{+2}-\text{FeOH}^{+2}$ reactions, but not for the $\text{Fe}^{+2}-\text{FeCl}^{+2}$ reaction if it involves a chlorine atom transfer.²⁵ This is quite different from the predicted behavior of the small-overlap electron transfer mechanism. For similar reasons the two mecha-

²⁵ This expected absence of isotope effect in a chlorine atom transfer process can, of course, be tested by measuring the rate constant of the atom transfer $\text{Cr}^{+2}-\text{CrCl}^{+2}$ reaction in the two solvents.

nisms could be distinguished in other reactions between metal aquo ions if no breakable OH bonds are involved.

If a reaction has a large-overlap electron transfer mechanism, then it can be shown that the present theory^{8,22} does not apply. The isotope effect would be that calculated from the usual theoretical expressions. No isotope effect would be expected unless the OH vibration frequencies in the hydration shells change appreciably when the activated complex forms. If any such effect does occur it would probably be rather similar for the $\text{Fe}^{+2}-\text{FeOH}^{+2}$ and $\text{Fe}^{+2}-\text{FeCl}^{+2}$ reactions.

APPENDIX. IONIC RADII

The following data were used for estimating the polarizing radii in Table I in accordance with the suggestions made earlier.

The crystallographic radii of Fe^{+2} , Fe^{+3} , Co^{+2} , and H_2O are²⁶ 0.75, 0.60, 0.72 and 1.38 Å. The mean of the first two is 0.68 Å, and by analogy that of Co^{+2} and Co^{+3} is 0.03 Å less.

In the permanganate ion the MnO bond length is about²⁷ 1.46 Å. The van der Waals' radius of this oxygen atom was estimated from data²⁸ on many oxyanions to be about 1.4 Å.

In the $\text{Mo}(\text{CN})_6^{-4}$ ion the MoC and CN bond lengths are²⁹ 2.15 and 1.15 Å. The van der Waals' radius of this nitrogen was estimated from the data²⁷ to be about 1.5 Å. In the iron cyanide ions the FeC distance was assumed to be 1.85 Å, its value in²⁴ $\text{Fe}(\text{CNCH}_3)_6^+$. The radius of an iron cyanide ion along an FeCN axis is 4.5 Å when inferred from these data. This is in reasonable agreement with a value of 4.35 Å which we have estimated from lattice parameters³⁰ of various iron cyanide crystals.

²⁶ A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950).

²⁷ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. II. This is the shortest and therefore presumably least polarized MnO bond in AgMnO_4 .

²⁸ W. Huckel, *Structural Chemistry of Inorganic Compounds* (Elsevier Publishing Company, New York, 1951).

²⁹ J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.* 61, 2853 (1939).

³⁰ J. F. Keggin and F. D. Miles, *Nature* 137, 577 (1936); Weiser, Mulligan, and Bates, *J. Phys. Chem.* 46, 99 (1942). Because of "interlocking," it may be remarked parenthetically, the distance between centers of these complex ions in a crystal is 7.2 Å, which is somewhat less than 2×4.35 Å. The use of an a equal to 7.2/2 rather than 4.35 or 4.5 would have improved slightly the agreement in Table I, but would probably be somewhat less consistent with the basic assumptions.