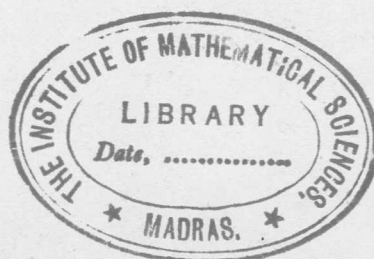# NOTES ON ELEMENTARY PARTICLE TRANSFER PROCESSES IN SOLUTION CHEMISTRY —

ELECTRON TRANSFER REACTIONS.

BY

KOTRA V. KRISHNAMURTY

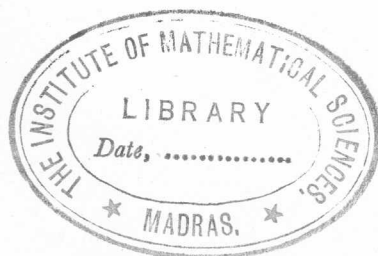THE INSTITUTE OF MATHEMATICAL SCIENCES, MADRAS-4, INDIA.

NOTES ON ELEMENTARY PARTICLES TRANSFER PROCESSES IN SOLUTION CHEMISTRY.

ELECTRON TRANSFER REACTIONS.

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CONTENTS

I. INTRODUCTION

The title of this report is intended to be so especially
when the author has made a small but sincere attempt to survive
under extraordinary circumstances amidst a galaxy of dedicated
workers in the field of Elementary Particle Physics at the
Institute of Mathematical Sciences, Madras. When a chemist
dares to speak of 'elementary particles' he unwittingly refers
to either electron or proton with a sense of smallness about
himself and a feeling of gratitude to the fellow physicist to
whose over-crowded album these particles once belonged almost
exclusively.

Two fundamental transfer processes utilizing the elementary
particles, namely, electrons and protons that are of importance
in the chemical and biological world are the electron transfer
process that includes oxidation-reduction, and the proton trans-
fer process. Since the early days of acid-base theories consi-
derable amount of work has been done on the proton transfers
and they are in a way generally better understood than the elec-
tron transfers. Also with the availability of deuterium inte-
resting studies made on the isotope effects in acid-base reac-
tions have contributed significantly to our knowledge on proton
transfers in recent years.

The study of electron transfers, however, was for a long
time confined to generally experimental observations in the gas
phase and in solids. Their study in solutions, particularly in
aqueous solution, became possible with the advent of radioisoto-
pic tracers. Although several systems, both cationic and anio-
nic, have been explored in good kinetic thoroughness the general

nature of the electron transfer process itself is the least
understood of the fundamental processes in solution chemistry.
Attempts to classify the electron transfer reactions as having
high activation energy and high activation entropy on one hand
and those having high activation energy and low activation en-
tropy on the other have not been as successful as first thought.
More recently, however, the complex theorecical problems associa
ted with the mechanism of electron transfer in solution are re-
cognized and partial solutions attempted by somewhat artificial
division of the electron transfer process itself into three
successive stages, namely, the initial approach of the reactants
the surmounting of the Franck-Condon barrier, and the mechanis-
tic part convincing to the conventional chemist. Great signifi-
cance is therefore attached to the work of Marcus dealing with
the first two aspects of the problem and to that of Halpern and
Orgel on the latter. It is therefore the purpose of this report
to briefly survey the various electron transfer systems in the
periodic table and to comment on the current status of the theo-
retical development of the subject.

II. ELECTRON TRANSFER REACTIONS

A. <u>Electron Transfer in the Gas Phase</u>:

The electron transfer process in the gas phase was first discovered in 1927 in their mass-spectrometric measurements by Smyth, Harnwell, Hogness and Lunn[1]. Kallmann and Rosen [2] apparently were the first to study a process of the type

$$N_2^+ + N_2 = N_2 + N_2^+$$
$$Ar^+ + Ar = Ar + Ar^+$$

in which a positive ion is neutralized upon collision with an atom or molecule resulting in the production of a new positive ion. In view of the historical parallelism between gas phase studies on one hand and solution phase studies on the other and their mutual interplay found in physical chemistry it is interesting to consider first such charge transfer process in the gas phase between simple molecules before taking up a similar study concerning ions surrounded by a solvent dielectric. The latter is more complicated indeed.

Ion-molecule or ion-atom collision cross-sections for reactions of the type cited above are obtained principally from two sources: (a) measurement of the drift velocity of the ion in the parent gas and (b) measurement of the attenuation of the ion beam caused by inelastic collision with the gas molecules. Earlier work in this field has been summarized in the proceedings of a symposium on Electron Transfer Process held at the Univer-sity of Notre Dame in 1952 by Muschlitz and Simons [3], Horn-beck [4] and Holstein [5]. Horn beck compares the hard sphere
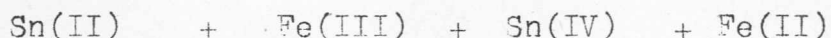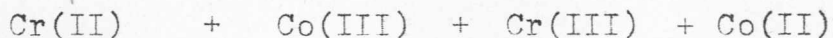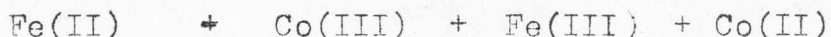
cross-sections obtained from drift velocity measurement with those obtained from velosity measurements for three gases, helium, neon and argon. In all the three cases the hard sphere cross-sections were found to be several times larger than the gas kinetic cross-sections suggesting that ion-atom or ion-molecule collisions involve quantum mechanical symmetry effects than a simple gas kinetic repulsion. Although the quantum mechanical symmetry effects are rigorously inseparable they have been listed as (1) a force of resonance attraction, (2) a force of resonance repulsion and (3) charge transfer. This complicated interaction to a good approximation is treated by the hard sphere model of the kinetic theory. The measured cross-sedtion from drift velocity data might well be called the cross section for resonance charge transfer. The simultaneous transfer of two or more electrons is much less probable than single electron transfers. Gurnee and Magee (6) considered this double charge transfer reactions (Ne^{++} + Ne = Ne + Ne^{++}) and such two electron changes are well-known in solution chemistry e.g. Tl^{+}--Tl^{+++} , Sn^{++} -- Sn^{++++} . Taube (7) gives a brief summary of the recent developments in this field having some bearing on the solution electron transfers.

The importance of the electron exchange is recognized by early investigators (2) in the problem of producing fast atomic and molecular beams. Amdur et al (8), (9) successfully employed this technique for obtaining the fast atom collision cross-sections. The molecular beam method is very useful in the investigation of the fundamental properties of nuclei, atoms and molecules. The electron exchange technique offers an advantage over the conventional oven method for the production

of such beams in that beam that is homogeneous in velocity is
obtained rather than one with a Maxwellian distribution. Elec-
tron exchange is also important in many chemical reactions tak-
ing place in flames, explosions and in gas discharges and in
understanding atomic and molecular structure of complex transi-
ent species.

B. Electron Transfer in Solution Phase:

Simple oxidation-reduction reactions are known to the
chemist for a long time. The following are a few examples:

$$Fe(II) \quad + \quad Co(III) \quad + \quad Fe(III) + Co(II)$$
$$Cr(II) \quad + \quad Co(III) \quad + \quad Cr(III) + Co(II)$$
$$Sn(II) \quad + \quad Fe(III) \quad + \quad Sn(IV) \quad + Fe(II)$$

Many such familiar oxidation-reduction reactions have been
studied from the point of view of their stoichiometry and ther-
modynamics and it is only during the last ten or fifteen years
their kinetics and mechanisms attracted the attention of the
chemists and physicists. New experimental techniques that
were developed since the second world war also contributed
greatly to the study of the kinetics and mechanism of redox
systems. The techniques of isotopic traces, electron paramag-
netic resonance and nuclear magnetic resonance are some of the
more important tools. The isotopic exchange reactions between
two different oxidation states of an element indeed provide most
of the experimental data on electron transfer systems of the
periodic table.

The following examples are self-illustrative:

$$Fe^{2+} + Fe^{*3+} = Fe^{*2+} + Fe^{3+}$$

$$V^{2+} + V^{*3+} = V^{*2} + V^{3+}$$

$$Eu^{2+} + Eu^{*3+} = Eu^{*2+} + Eu^{3+}$$

$$Cu(I) + Cu(II) = Cu(II) + Cu(I)$$

$$V(IV) + V(V) = V(V) + V(IV)$$

$$MnO_4^{=} + \overset{*}{M}nO_4^{-} = \overset{*}{M}nO_4^{=} + MnO_4^{-}$$

$$Fe(CN)_6^{4-} + Fe(CN)_6^{3-} = Fe(CN)_6^{4-} + \overset{*}{F}e(CN)_6^{3-}$$
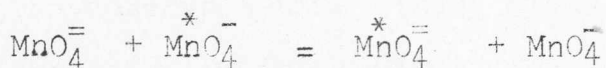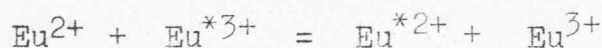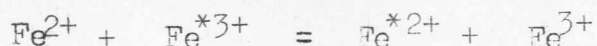
Several reviews devoted to the closely related subject of the isotopic exchange reactions that contain useful information on the electron transfers appeared in literature from time to time and the following sources are of interest: Haissinsky (1950) (10), Wahl and Bonner (1951) (11), Edwards (1952) (12),

. Amphlett (1954) (13), Zwolinsky,Marcus (R.J.) and Eyring(1955) (14), Roginsky (1957) (15) Stranks and Wilkins (1958) (16), Basolo and Pearson (1958) (17), Taube (1959) (7) (18) Marcus R.A. (1959) (19), Stranks (1960) (20), Halpern (1961) (21) and Fraser (1961) (22). It is equally interesting to note that several regional, national and international conferences have been held concerning the topic of electron exchange in solutions in one way or the other during the last decade and a half at several places, the more important being Brookhaven National Laboratory (1948), Paris (1951), University of Notre Dame, Indiana (1952), Memphis (1956), Chicago (1958), Toronto (1958), Gottingen (1959) and Newcastle-upon-Tyne (1960)

C. Experimental Methods:

Broadly speaking great bulk of the data on electron transfer systems in aqueous solutions comes from the isotopic tracer method. It is therefore pertinent to study in detail various experimental methods utilizing this technique. However, other physical methods not involving chemical separations as in the case of isotopic tracer method also deserve mention. For example, measurements of the rate of change of obtical activity have been used to obtain electron transfer rates polarimetrically. In cases where the electron transfer half-times are very small, of the order of seconds and smaller, certain fast reaction techniques involving flow methods in specially designed apparatuses have been used. In addition techniques based on nuclear magnetic and electron paramagnetic resonance are also useful for measuring reaction half-times in the milli and microsecond region and these techniques will be discussed in each case.

Isotopic Exchange Method:

The isotopic exchange method of investigating electron transfer reactions depends on the following factors: (i) the existence of two or more oxidation states of an element which are stable in aqueous solution and soluble over a resonable range for kinetic studies, (ii) the molecular species in solution must be identical except for charge and (iii) a radioisotope of reasonable half-life and known decay characteristics or enriched stable isotope of the element must be available. It would be experimentally convenient if the half-life of the radioisotope is far greater than the half-times of the reaction we are measuring. Otherwise

complicated decay corrections require to be made and this takes
away the beauty of this method.

The isotopic exchange method is now so well established
that it is generally used wherever the above conditions are
satisfied for learning about electron transfer systems. The
kinetics of isotopic exchange can be studied for a system in
which the reactants are uniformly distributed in a single phase
and the exchanging atoms are chemically equivalent more readily
than other complicated situations where two phases and chemically
non-equivalent in the exchanging species. It is by no means
impossible even then, except the observed rate data will be diffi-
cult to interpret meaningfully. In any case it has been shown
(23), (24), (25), (11) that the radioactivity initially present
in a non-equilibrium distribution is transferred from one species
to the other following a first order rate law. This is obvious
from the fact in an isotopic exchange reaction there is no net
chemical reaction and therefore the over-all concentrations of
the reactants remain unchanged. Hence for the process:

$$AX \quad + \quad BX^* \quad = \quad AX^* \quad + \quad BX$$

the enthalpy change, $\Delta H = 0$ and therefore the free energy change
$F = -T\Delta S$. The entropy of the exchanging system at equilibrium
when all the isotopes are uniformly distributed among the reactan
is greater than the entropy of the initial state where the isotop
is deliberately added and so not uniformly distributed. The
increase in entropy of the system is therefore the entropy of
mixing of isotopes and is accompanied by a decrease in the free
energy. This is the driving force for an isotopic exchange reaction

and the rate can be measured by following the growth or loss of
radioacitivty in either of the reacting species by conventional
counting procedures after a chemical separation is performed to
quench the reaction. Several separation methods both physical
and chemical have been discussed at length in many standard text
books (11), (26). In actual practice the specific activity which
is defined as the ratio of the counting rate to unit chemical con-
centration or a function of the chemical concentration, is gene-
rally determined as a function of time. This then gives the
fraction exchanging in a certain time t and the time for half-
exchange $t\frac{1}{2}$ is a very important experimental parameter in kineti
of isotopic exchange.

The "exponential isotopic exchange law" as it is generally
called is derived and discussed below taking a specific chemical
system. The element vanadium has four well-known oxidation state

$$V^{2+}\underline{0.25} \qquad V^{3+}\underline{0.36} \qquad VO^{2+}\underline{\pm 1.0} \qquad VO_2^+$$

purple   green   blue   yellow
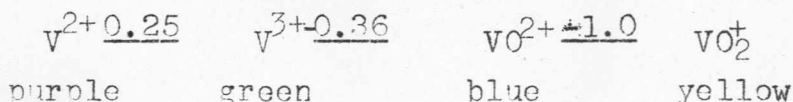
and several isotopes with the following decay characteristics(2

NUCLIDE	HALF-LIFE	DECAY
$_{23}V^{46}$	0.40 s	β^+~6
V^{47}	32 m	β^+1.9
V^{48}	16.2 d	β^+0.69; EC;γ0.99,1.32 1.04
V^{49}	635 d	EC;γ0.119,0.081
V^{50}	$>10^{14}$ y	
V^{51}	most abundant stable	
V^{52}	3.76 m	β^-2.5;γ1.4,
V^{53}	23 h	β^-0.6;γ

It is obvious V^{48} and V^{49} can be used in a study of the iso-
topic exchange between any two oxidation states of the element.
Because of the radiochemical advantage, V^{48} prepared by Ti^{48}
(d, 2n) V^{48} reaction has been used, for example, as a tracer
in the following reaction.

$$V^{II} + V^{*III} = V^{*II} + V^{III}$$

Let the total vanadium (II) concentration be a and the total
vanadium (III) concentration b. Let also x and y represent the
molar concentration of the radioactive atoms of vanadium (II)
and vanadium (III) respectively though negligibly small.

total vanadium (II) = $[V^*(II)]$ + $[V(II)]$ = a, $[V^*(II)]$ = x
total vanadium (III) = $V^*(III)$ + $[V(III)]$ = b, $[V^*(III)]$ = y

At time, t = ∞

$$x = x_\infty \qquad y = y_\infty \qquad \text{and} \qquad x_\infty / y_\infty = /a/b$$

Let the rate of the reaction between vanadium (II) and vanadium
(III) i.e. the rate of electron transfer (at reasonable acidi-
ties when all the ions are present mostly as V^{++} and V^{+++})
in dynamic equilibrium be R and the rate of appearance of x
be some function of a and b. Now,

Rate of appearance of x = Rate of formation of $V^*(II)$
                             - Rate of destruction to go back to $V^*(III)$

$$dx/dt = (R\,y/b)\cdot(a - x)/a - (R\,x/a.)\,(b - y)$$

$$dx/dt = (R/ab)\,(ay - bx)$$

where

y/b is the fraction of reactions occurring with $V^*(III)$

x/a is the fraction of reactions occurring with $V^*(II)$

$(a - x)/a$ is the fraction of reactions occurring with $V(II)$

and $(b - y)/b$ is the fraction of reactions occurring with $V(III)$

From the principle of conservation of radioactivity in an exchanging system we have

$$x_\infty + y_\infty = x + y$$

Substituting for y in the above we have $y = x_a + x_\infty \, b/a - x$

$$dx/dt = R/ab \ (ax_a + bx_\infty - ax - bx)$$
$$= R/ab \ (a + b)(x_\infty - x)$$

This can be written in a form suitable for integration

$$\int dx/(x_\infty - x) = (R/ab)(a + b)\int dt$$

Integrating and evaluating the integration constant by taking $x = 0$ at $t = 0$,

$$- \ln (x_\infty - x) = (R/ab)(a + b)t + C, \text{ where } C = - \ln x_\infty$$
$$- \ln (x_\infty - x) + \ln x_\infty = (R/ab)(a + b)$$
$$- \ln(1 - x/x_\infty) = (Rt/ab)(a + b)$$

If x/x_∞ the fraction exchanging is denoted as F we have the exchange law in the logarithmic and the exponential form

$$R = -ab/(a + b) \quad \ln (1 - F)/t \quad \text{Logarithmic form}$$
$$(1 - F) \quad \exp \left\{ -(a + b)Rt/ab \right\} \quad \text{Exponential form}$$

Since there is no net chemical reaction, R is therefore the rate of randomization of the radioactive tracer and is a function of the reactant concentrations and factors like acidity or pH, solvent composition, ionic strength, temperature, added impurities, light etc. Since in any single experiment R remains fixed it is seen that a plot of $\ln (a - F)$ versus t gives a

straight line. This is called the McKay plot (23.) The
fraction exchange F is obtained conventionally from the specific
activities of one or both the reactants A_0 , A_t and A_∞
being the specific activities at zero-time, at time t, and
at infinite time respectively. Any curvature in the McKay plots

$$F = (A_t - A_0)/(A_\infty - A_0)$$

indicates departure from ideality and they are treated accord-
ingly (11). Figures 1 to 8 illustrate a series of properly
planned experiments for the vanadium (II)-Vanadium(III) system
reported by Krishnamurty and Wahl (27). Figure 1 is a semi
log plot of (1 - F) vs. t from which the $t_\frac{1}{2}$ can be read out.
Figure 2 is a plot of $t_\frac{1}{2}$ vs reciprocal of total vanadium con-
centration and the slope of unity indicates that the half-time
increases linearly with decrease in total vanadium concentration.
Figures 23 and 4 are long-log plots of R vs. V(II) or V(III)
concentrations and unit slope again indicates that the exchange
is first order with respect to teach species. Figure 5 is
a semi log plot of the rate constant, k vs. reciprocal of
temperature, a 1/T (Arrhenius plot). The experimental acti-
vation energy is obtained from the slope by multiplying it
with 2.303 and the gas constant. From the experimental activa-
tion energy, E_a and the observed rate constant the entropy of
activation , refered to a standard state of one mole per liter
of each reacting species can be calculated from the Eyring's
equation (28)

$$k = eKT/h . exp(-E_a/RT) . exp (\Delta S^{\neq}/R)$$

where

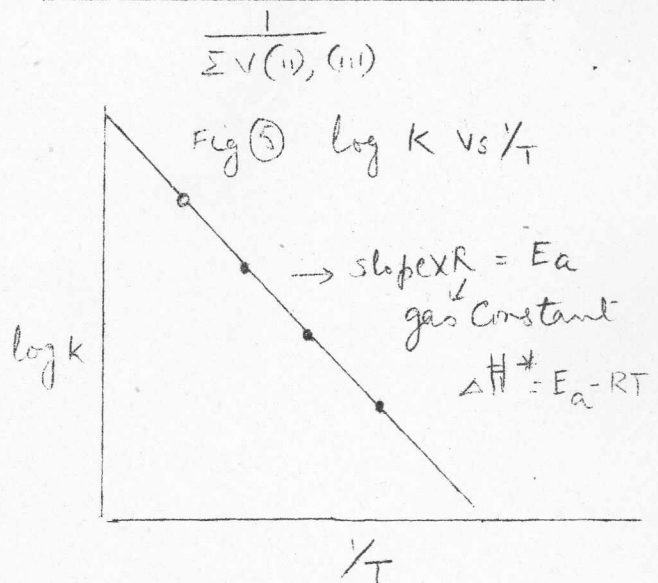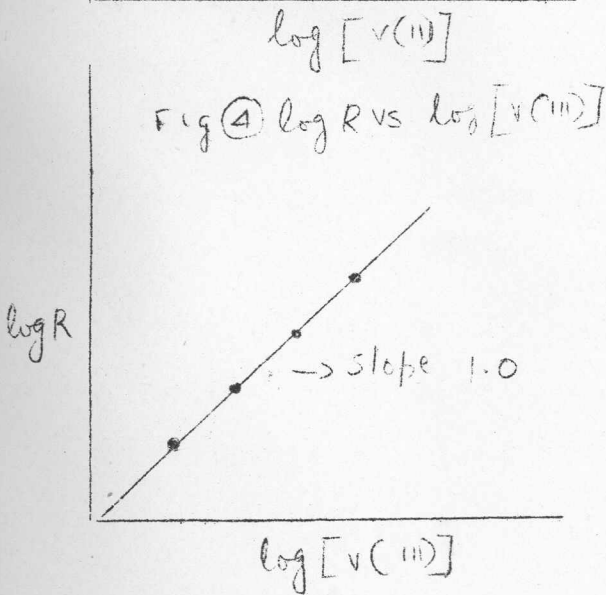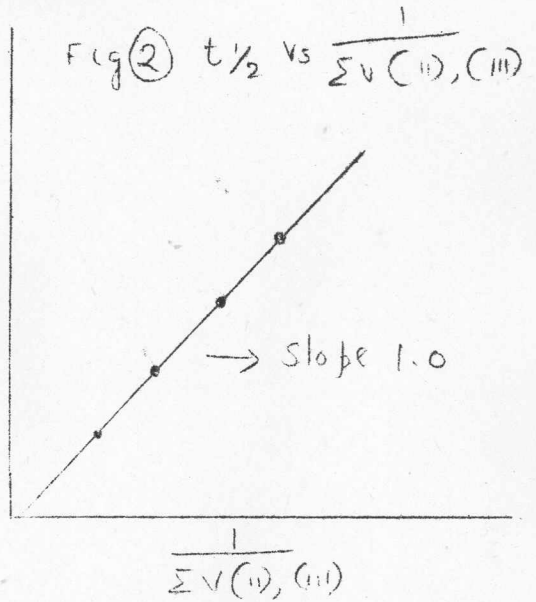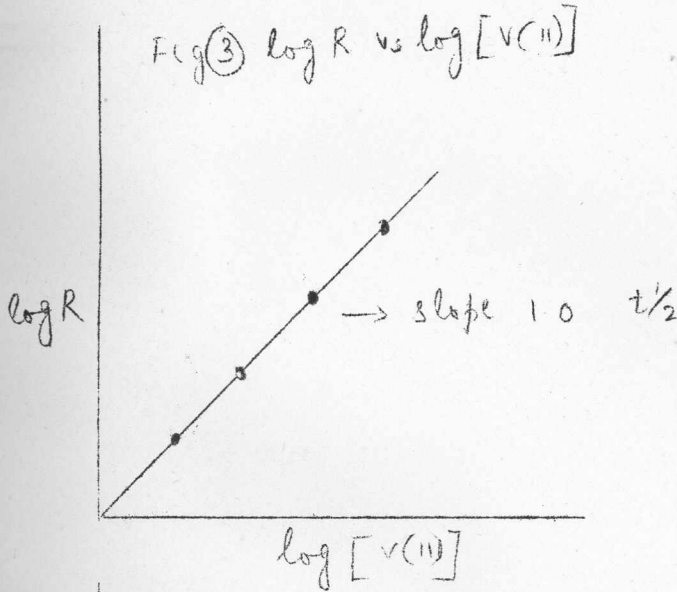k $=$ observed rate constant

e $=$ base of the natural logarithm

k $=$ Boltzmann constant

h $=$ Planck constant

E $=$ experimental activation energy

R $=$ gas constant

T $=$ temperature K

$\Delta S^{\neq}$ $=$ entropy of activation

If the volume change on forming the activated complex from the reactants is assumed to be negligible the enthalpy of activation, $\Delta H^{\neq} = E_a - RT$. From this the free energy of activation, $\Delta F^{\neq}$ can be calculated using the equation

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

Figure 6 is a study of the dependence of the hydrogen ion concentration and shows the plot of k $\underline{vs.}$ $1/(H^+)$ The appearance of an intercept indicates that the exchange takes place by (a) an acid independent path and (b) an acid idependent path. Figure 7 is a study of the dependence of added chloride ion concentration and shows the plot of k $\underline{vs}$ (Cl^-). Here again the intercept gives the rate constant for zero chloride observed in the chloride ion catalysis of the V(II)/V(III) system.

If $F = \frac{1}{2}$ then $t = t\frac{1}{2}$ and the arate of equation becomes the rate $R = \ln 2\ (ab)/(a+b)t\frac{1}{2}$. The rate constant, k therefore is $\ln 2/(a+b)t\frac{1}{2}$ and we obtain the familiar "bimolecular exchange law" $R = k\ (ab)$, i.e. $R = k\ \left[V(II)\right]\ \left[V(III)\right]$ since the molar concentrations of the tracer atoms are negligible.

Fig ① Semi log plot

Fig ⑧ Non-ideal McKay plot

$\rightarrow$ initial slope

Fig ③ $\log R$ vs $\log [V(II)]$

$\log R$ $\rightarrow$ slope 1.0

$\log [V(II)]$

Fig ② $t\frac{1}{2}$ vs $\frac{1}{\Sigma V(II), (III)}$

$t\frac{1}{2}$ $\rightarrow$ Slope 1.0

$\frac{1}{\Sigma V(II), (III)}$

Fig ④ $\log R$ vs $\log [V(III)]$

$\log R$ $\rightarrow$ slope 1.0

$\log [V(III)]$

Fig ⑤ $\log K$ vs $\frac{1}{T}$

$\log k$ $\rightarrow$ slope $\times R = E_a$
gas constant

$\Delta H^{*} = E_a - RT$

$\frac{1}{T}$

Fig ⑥ K vs $\frac{1}{(H^+)}$

Fig ⑦ K''' vs (Cl^-)

K

$K = K_1 + \frac{K_2}{(H^+)}$

→ slope K_2

$\}K_1$

$\frac{1}{(H^+)}$

K'''

→ slope K''

$K''' = K' + K''(Cl^-)$

(Cl^-)
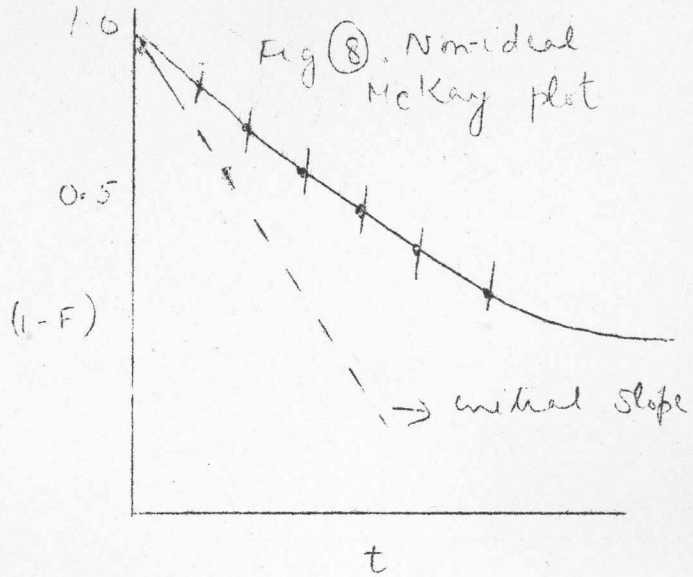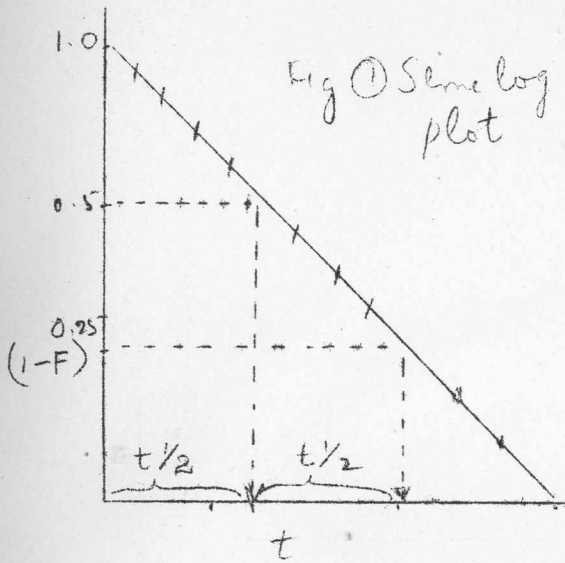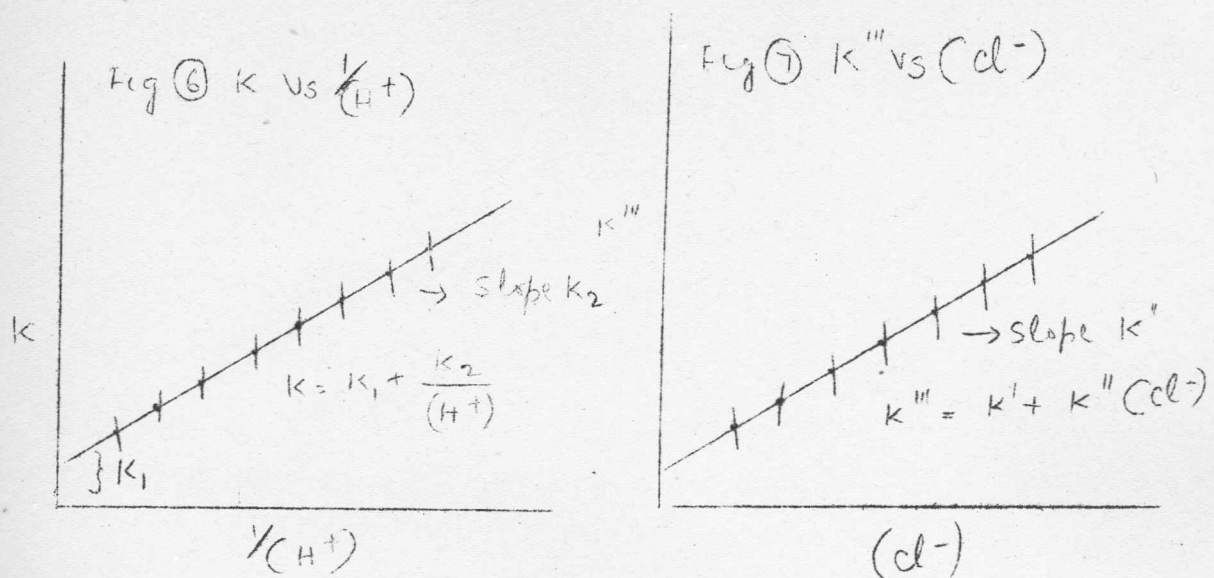
A detailed investigation of the isotopic exchange between
two different oxidation states of an element gives the overall
kinetic rate expression from which mechanistically the electron
transfer part can in principle be separated. We shall now see
the same in the case of vanadium(II)-vanadium(III) how it is
possible. From the numerous diagrams it is obvious the overall
rate law for this exchange is of the form

$$R = \left[V(II)\right]\left[V(III)\right]\left\{k_a + k_b/(H^+) + k_c(Cl^-)\right\}$$

where the first term is independent of the hydrogen-ion and the
chloride-ion concentrations. If we determine the rate in suffi-
ciently acid solutions where the hydrolysis

$$V^{+++} + H_2O = VOH^{++} + H^+ \quad (K_h = 2.0 \times 10^{-4})$$
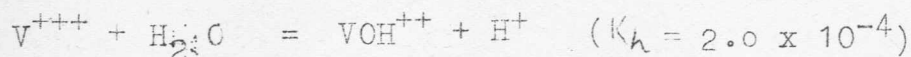
is negligible and also in chloride-free media the observed rate
is just the rate of electron transfer:

$$V^{++} + V^{+++} \longrightarrow$$
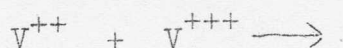
It is therefore advisable while working with any system to study
the overall kinetic behaviour before trying to extract the elec-
tron transfer part that is of interest to us here. This is
particularly so while working with transitional metal ions which
are prone to hydrolyse in solutions of $pH \geqslant$ 3 or 4.

Rapid Mixing and Quenching Techniques:

Whereas the conventional isotopic exchange method can be
applied to reactions whose half-times are greater than one minute
or so, it is necessary in the case of rapid isotopic exchange
reactions reported in earlier literature as "immeasurably fast"
to develop techniques of rapid mixing of the reactants and arrest
the progress of the reaction by a rapid quench-separation tech-
nique. Wahl and coworkers (29), (30), (31), (32) successfully
developed adaptations of the Hartridge and Roughton apparatus (33
to follow the kinetics of $MnO_4^{2-} \text{---} MnO_4^{-}$ exchange, $Ag*(I)--Ag(I$
exchange and the $Fe*(CN)_6^{4-} \text{---} Fe(CN)_6^{3-}$ exchange. The study of
fast reactions in general, including the isotopic exchange ones
is a fascinating subject and a recent international Colloquium
at Gottingen (34), and other sources (35), (36) (37) give invalu-
able collection of techniques since Hartridge and Roughton who
first introduced in 1922 mixing devices to study reactions taking
place in milliseconds rather than minutes.

Optical Activity Method:

Dwyer and Gyarfas (38) and later Eichler and Wahl (39) inde-
pendently followed the rate of electron exchange between large
complex ions like $Os(dipy)_3^{2+}$ and $Os(dipy)_3^{3+}$ polarimetrically
by observing the decrease in optical rotation as a function of
time after mixing $d-Os(dipy)_3^{2+}$ with $l-Os(dipy)_3^{3+}$. Polarimet-
ric measurements are generally restricted to a limited number of
complexes which can be readily resolved and which are not too
highly colored to obscure observation with the conventional
sodium lamp.

Electron Paramagnetic and Nuclear Magnetic Resonance Methods:

Fast electron transfer reactions with half-times 10^{-9} to 10^{-1}
seconds in principle, can be studied by these new techniques which
are introducedonly recently into the kineticist's armoury. The
electron paramagnetic resonance method or the electron spin reso-
nance method as it is also called was particularly adapted by
Weissman and coworkers (40), (41), (42), (43) in the study of
electron transfer in solution between aromatic hydrocarbon nega-
tive ions and neutral aromatic hydrocarbons. This is the first
reported case of direct experimental evidence for electron trans-
fer in solutions. Ward and Weissman (40) have shown recently
that the exchange:

$$C_{10}H_8^- \quad + \quad C_{10}H_8 \quad = \quad C_{10}H_8 \quad + \quad C_{10}H_8^-$$

takes place in tetrahydrofuran or 1,2-dimethoxyethane as solvents.
The naphthalene negative ion has 17 hyperfine components in its
electron spin resonance spectrum extending 27.2 oersteds and
broadening of the lines occurs with added naphthalene. From the

variation of the line breadth with the concentration of added
naphthalene a second order rate constant has been determined in
the range 10^7 -- 10^9 $M^{-1}sec.^{-1}$ depending upon the solvent and
the nature of the positve ion, lithium, sodium, potassium, rubi-
dium or cesium. Similar study has been made by Weissman and
Tuttle (41) with benzene, toluene, ortho-, meta-, and para-,
xylenes, anthracene and their respective negative ions.

McConnell and Weaver (44) were the first to develop the
nuclear magnetic resonance method for measuring the fast elec-
tron transfer reaction between Cu(I) and Cu(II). A detailed
theory for this method has been developed by McConnell and Ber-
ger (45) and in principle the method can be extended to systems
containing an element with a natural isotope having a non-zero
nuclear spin. Though electron spin resonance and nuclear mag-
netic resonance are both paramagnetic phenomena, the former is
observed kin the microwave region. The latter however is obser-
ved in the radiofrequency region requiring only simpler detection
equipment. It was shown that if hyperfine splitting can be obser-
ved in the paramagnetic resonance of a solution containing a
nuclide in both a diamagnetic and a paramagnetic ion, then the
nuclear resonance line width of the nuclide is a direct measure
of the lifetime of the diamagnetic ion. A determination of the
Cu-63 or Cu-65 nuclear resonance line width in concentrated
hydrochloric acid solutions containing both Cu(I) and Cu(II)
chloride leads to an evaluation of the bimolecular rate constant.
$k = 0.5 \times 10^8$ M^{-1} $sec.^{-1}$ This is by far the fastest ex-
change reaction measured in solution. Giulano and McConnell (46)
extended the nuclear magnetic resonance method for measuring the

rate of electron transfer between (vanadium (IV) and vanadium(V)
from a study of V-51 resonance line broadening in .6.5 f acid
solutions. Britt and Yen (47) measured the rate of the MnO_4^{2-}-- Mn
electron transfer reaction by pulsed nuclear magnetic resonance
technique and observed that their results are generally in agree-
ment with these obtained in an isotopic tracer study made earlier
by Sheppard and Wahl (29).

D. Electron Transfer Systems:

In this section are given certain individual electron trans-
fer systems in somewhat arbitrary way following the periodic
table. Other methods of classification as (1) cationinc electron
transfers and anionic electron transfers, (2) electron transfer
between simple ions and between large complex ions, (3) one elec-
tron transfers and two electron or many electron transfers, (4)
outer sphere electron transfer reactions, inner sphere electron
transfers, or electron transfers via bridged activated complex
and reactions by uncertain mechanisms, have been made earlier (48
(7) (21), (22) for grouping the experimental data. Allied to the
electron exchange reactions we have oxidation-reduction reactions
involving net chemical change. These reactions also provide in-
teresting information concerning the electron transfer process
and are discussed under each element at the appropriate place.
Table 10 lists kinetic data and the isotopic exchange between the
elements in two different oxidation states for quick comparison
and in this section each system is discussed in detail.

VANADIUM

$$V \overset{\sim 1.2}{\text{---}} V^{2+} \overset{0.25}{\text{---}} V^{3+} \overset{-0.36}{\text{---}} VO^{2+} \overset{-1.0}{\text{---}} VO_2^+$$
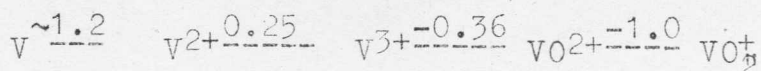
V(II)--V(III): Krishnamurty and Wahl (27) studied the kinetics of this system using V-48 as tracer and a separation method by which V(II) is complexed with 2,2'- dipyridyl and precipitating $V(OH)_3$. In 1.0 f $HClO_4$ and ionic strength 2.0 the rate of exchange is consistent with the law, $R = k \left[V(II) \quad V(III)\right]$ The experimental activation energy is 13.2 kcal/mole, and the activation parameters are $\Delta H^{\ddagger} = $ 12.6 kcal/mole, $\Delta S^{\ddagger} = -24.9$ e.u, and $\Delta F^{\ddagger} = -20.0$ kcal/mole. The rate is unaffected by increase in the surface area of the reaction vessel, by the absence of ordinary diffuse light, by doubling the ionic strength to 4.0 or by replacement of $NaClO_4$ by $LiClO_4$ for adjustment of ionic strength. The rate is however, increased by lowering the hydrogen ion concentration below 0.5 M and by the presence of chloride ion. The rate data are consistent with the expression

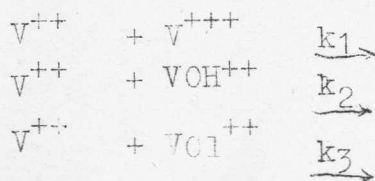$$k = k_1 + k_2/(H^+) + k_3(Cl^-)$$

the values of the constants at 25° being

$$k_1 = 0.61 \ f^{-1} \ min.^{-1}$$

$$k_2 = 0.21 \ min.^{-1}$$

$$k_3 = \sim 85 \ f^{-2} min.^{-1}$$

A plausible interpretation of the three term rate expression is that exchange can occur via the three paths

$$V^{++} + V^{+++} \xrightarrow{k_1}$$
$$V^{++} + VOH^{++} \xrightarrow{k_2}$$
$$V^{++} + VCl^{++} \xrightarrow{k_3}$$

The first path gives the electron transfer path between $+2$ and $+3$ states of vanadium and it would be interesting to compare with other 3d transitional metal ions. Table 1 gives comparision of the systems studied.

TABLE 1

COMPARISON OF KINETIC DATA FOR $M^{2+} - M^{3+}$ SYSTEMS

System			$k, f^{-1} sec.^{-1}$	$E.$, kcal/mole	$\Delta S^{\neq}$,e.u	Ref.
V^{++}	--	V^{+++}	1×10^{-2}	13.2	-25	(27)
Fe^{++}	--	Fe^{+++} 4.2		9.9	-25	(81)
Co^{++}	--	$Co^{+++} \sim 5$		13.2	-13	(100)
Cr^{++}	--	$Cr^{+++} < 2 \times 10^{-5}$		22	-8	((57)

The case of Eu^{++} -- Eu^{+++} is omitted here in the table as the exchanging electron is a 4f electron and the rate of exchange is comparable to Cr^{++} -- Cr^{+++} system. As shown in the table the rate of electron transfer between V^{++} and V^{+++} is greater than the rate of electron transfer between Cr^{++} and Cr^{+++} or between Eu^{++} and Eu^{+++} but less than that between Fe^{++} and Fe^{+++} or Co^{++} and Co^{+++}. The reactions listed here are similar both as to charge type and type of electron transferred. The general mechanism is discussed separately.

V(III)--V(IV):   Furman and Garner (49) studied the kinetics of this system using V-48 as tracer and an ion-exchange method of separation. In 0.5 to 2.0, acid the rate of exchange is consistent with the law, $R = k \left[V(III)\right] \left[V(IV)\right]/\left[H^{+}\right]$. The overall rate constant

$$k = 4.5 \times 10^{12} \exp(-20,700/RT) sec.^{-1}$$

It is V(III) that causes the hydrogen ion dependence arising from the equilibrium

$$V^{+++} + H_2O = VOH^{++} + H^+, \quad K_h \cong 2 \times 10^{-3} \text{ M}$$
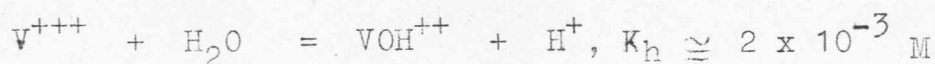
where as the V(IV) will be present as VO^{++} or a hydrated form of this as $V(OH)_2^{++}$. It is thus possible to extract the specific rate constant for the reaction between VOH^{++} and VO^{++}, $k' = k/K$ = 0.29 M^{-1} sec^{-1} at 0° . The experimental activation energy for this exchange reaction is 10.7 kcal/mole and $\Delta S^{\neq}$ = -24 e.u The mechanism might involve in addition to electron transfer, transfer of either hydroxyl group or of protons.

V(IV)--V(V): Giuliano and McConnell (46) studied the kinetics of this system using nuclear magnetic resonance technique described earlier. From a study of V-51 resonance line broadening the rate of electron exchange between paramagnetic vanadium (IV) and diamagnetic vanadium (V) in high acid and chloride concentrations has been measured. It is first order in V(IV), second order in V(V) and the specific rate constant $k = 1.5 \times 10^{-6} M^{-2}$ sec^{-1} in 6.5 f H^+ and 3 M Cl^- . A tentative mechanism includes a rapid monomer-dimer equilibrium involving vanadium (V) prior to the electron exchange as shown below.

$$2 \, V(V) = (V(V))_2$$
$$(V(V))_2 + V(IV) = (V(V))_2 + V(IV)$$
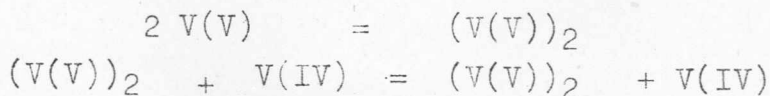
The large excess of chloride in which the electron transfer process was observed provides either chloride bridging or complexing of the V(IV) and V(V) species to account for such high rates.
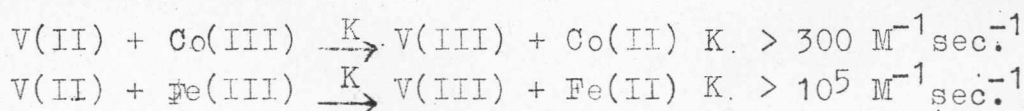
<u>Oxidation-reduction reactions:</u>   Both V(II) and V(III) are power-full reducing agents and considerable kinetic work has been done lately using these ions. King and Garner (50) studied the oxidation of V(II) and V(III) ions by perchlorate ion leading to the following rate laws.

$$-d(V^{++})/dt = k_1 (V^{++}) (ClO_4^-) + 2k_2 (V^{++}) (ClO_4^-)$$

and in the absence of V(II) ion

$$- d(V^{+++})/dt = k_2(V^{+++}) (ClO_4^-)$$

The rate determining step in the V(II)--ClO_4^- reaction is reported to involve an oxygen atom transfer from ClO_4^- to V^{++} or possibly an electron transfer from V^{++} to ClO_4^- Bennett and Sheppard (51) very recently reported approximate rates for the following oxidation reduction reactions.

$$V(II) + Co(III) \xrightarrow{K} V(III) + Co(II) K > 300 \ M^{-1}sec.^{-1}$$
$$V(II) + Fe(III) \xrightarrow{K} V(III) + Fe(II) K > 10^5 \ M^{-1}sec.^{-1}$$

Zwickel and Taub (52) studied the oxidation of V(II) ion by several complex ions of Co(III) and concluded, unlike that of Cr involves an outer-sphere mechanism. Fraser (53) extended this study in great detail.

Rabideau and Kline (54) studied the kinetics of the reaction between Pu(IV) and V(III) inperchlorate media. The rate of the reaction has been found to be first order in Pu(IV) and V(III) each and both inverse first and inverse second order in $[H^+]$. The stoichiometry of the reaction is

$$Pu^{4+} + V^{3+} + H_2O = Pu^{3+} + 2 H^+ + VO^{2+}$$
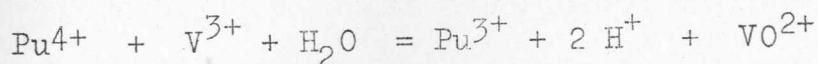
and the rate law is

$$-d\left[Pu(IV)\right]/dt = k\left[Pu^{4+}\right]\left[V^{3+}\right]\left[H^{+}\right]^{-1} = k_2\left[Pu^{4+}\right]\left[V^{3+}\right]\left[H^{+}\right]^{-2}$$

Higginson, Rosseinsky, Stead and Sykes (55) studied the kinetics of the following reactions in $HClO_4$
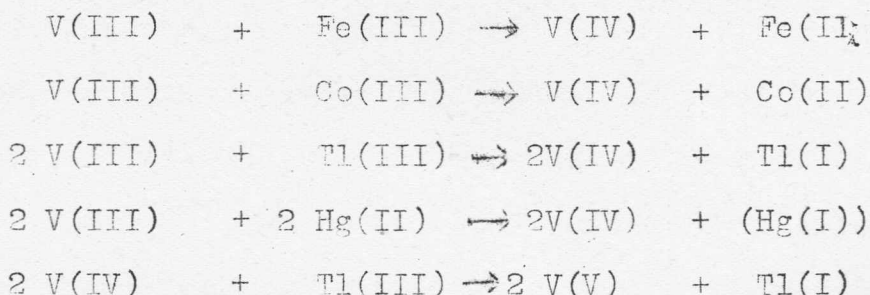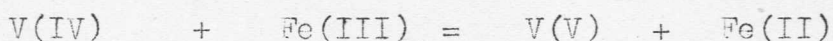
$$V(III) \quad + \quad Fe(III) \rightarrow V(IV) \quad + \quad Fe(II)$$
$$V(III) \quad + \quad Co(III) \rightarrow V(IV) \quad + \quad Co(II)$$
$$2\,V(III) \quad + \quad Tl(III) \rightarrow 2V(IV) \quad + \quad Tl(I)$$
$$2\,V(III) \quad + 2\,Hg(II) \rightarrow 2V(IV) \quad + \quad (Hg(I))$$
$$2\,V(IV) \quad + \quad Tl(III) \rightarrow 2\,V(V) \quad + \quad Tl(I)$$

and the equilibrium constant for

$$V(IV) \quad + \quad Fe(III) = \quad V(V) \quad + \quad Fe(II)$$

Useful correlations between the entropies of activation $\Delta S^{\ddagger}$ found for these bimolecular oxidation-reduction reactions and the charge on the activated complex have been made commenting on the positive value of $\Delta S^{\ddagger}$ found in some cases--see Fig.11

CHROMIUM

$$Cr \xrightarrow{0.91} Cr^{2+} \xrightarrow{0.41} Cr^{3+} \xrightarrow{1.33} Cr_2O_7^{2-}$$
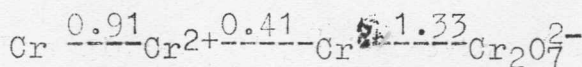
Cr(II)--Cr(III): Plane and Taub (56) in their investigation of the kinetics of exchange of water between solvent and $Cr(H_2O)_6^{3+}$ found Cr^{2+} exerting a marked catalytic effect on the exchange. From these experiments which provided an indirect method of stuyding the rate of electron transfer they given an upper limit for the electron transfer between Cr^{2+} and Cr^{3+} as $0.028\ M^{-1}\cdot min.^{-1}$ Anderson and Bonner (57) studied the kinetics of the Cr(II)--Cr(III) exchange using Cr-51 as tracer and a

novel separation method of converting Cr(II)--Cr(III) exchange chromium(III)-oxalato complex which did not exchange with $Cr(H_2O)_6^{3+}$. The exchange is slow and half-times of the order of hours were reported. No chloride ion catalysis was observed and from the inverse first order dependence of the hydrogen ion concentration a rate law consistent with the data is

$$R = k_1(Cr^{2+})(Cr^{3+}) + k_2(Cr^{2+})(CrOH^{2+})$$ where K_1 and K_2 are given the values

$$k_1 = =0.07 \; f^{-1} \; hr^{-1} \quad and \quad k_2 = 2.5 \times 10^3 \; f^{-1} \; hr^{-1}$$

The large value of K_2 as compared with k is considered as plausible for an atom transfer mechanism for the acid dependent path via the transition state:

$$Cr(H_2O)^{2+} + Cr*OH^{2+} \rightleftarrows \left[\begin{array}{cc} CrO--H--OCr \\ H \qquad H \end{array} \right]^{\ddagger \; 4+} \rightleftarrows \quad CrOH^{2+} + Cr*(H_2O)^2$$
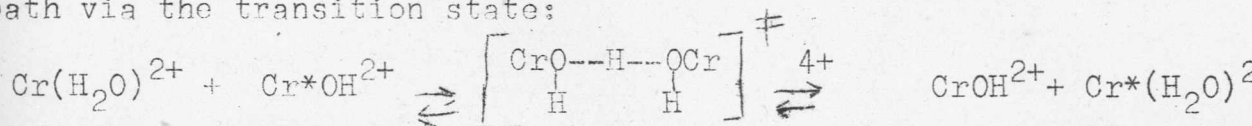
The experimental activation energy is 22 kcal/mole and the entropy of activation -8 e.u.

Ball and King (58) report the rate of electron transfer of Cr(II)--Cr(III)X systems, where X = fluoride, chloride, bromide, thiocyanate and azide and table 2 gives kinetic data along with other related systems.
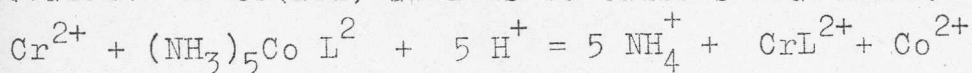
TABLE 2.

G(II)--G(III) ELECTRON TRANSFER SYSTEMS

System	k, M^{-1} sec.$^{-1}$	Ref.
Cr^{2+} -- $Cr*^{3+}$	2×10^{-5} (24.5o)	(57)
Cr^{2+} -- $Cr*OH^{2+}$	0.66 (24.5o)	(57)
$Cr*^{2+}$ -- CrF^{2}	2.6×10^{-3} (0o)	(58)
$Cr*^{2+}$ -- $CrCl^{2+}$	0.15 (0o)	(58)
Cr^{2+} - t -- $CrCl_2^{+}$	~ 2×10^{3} (25o)	(59)
$Cr*^{2+}$ -- $CrBr^{2+}$	> 60 (25o)	(58)
$Cr*^{2+}$ -- CrN_3^{2+}	>1.2 (25o)	(58)
$Cr*^{2+}$ -- C_rNCS^{2+}	1.8×10^{-4} (27o)	(58)
CrU^{2+} -- $Cr*U^{3+}$	8×10^{-5} (methanol) 56o	(60)
(U = urea)		
Cr^{2+} -- $Cr(NH_3)_5 F^{2+}$	2.7×10^{-4} (25o)	(61)
Cr^{2+} -- $Cr(NH_3)_5 Cl^{2+}$	5.1×10^{-2} (25o)	(61)
Cr^{2+} -- $Cr(NH_3)_5 Br^{2+}$	3.2×10^{-1} (25o)	(61)
Cr^{2+} -- $Cr(NH_3)_5 I^{2+}$	5.5 ± 1.5 (25o)	(61)

Cr(III)--Cr(VI):   Altman and King (62) in a very recent study
of this system not only confirmed Menker and Garner (63) that the
exchange between Cr(III) and Cr(VI) in acid solutions is immea-
surably slow but extended the same to measure the rates at 94.8o.
On the basis of the rate law

$$R = \left[Cr(H_2O)_6^{3+} \right]^{4/3} \left[H_2CrO_4 \right]^{2/3} \left\{ k \left[H^+ \right]^{-2} + k' \right\}$$

they assume that the rate-determining step in the exchange is a reaction of Cr(III) and Cr(V), the latter being in equilibrium with Cr(III) and Cr(VI). The exchange between Cr(V) and Cr(VI) is assumed to be relatively rapid compared to the Cr(III) and Cr(VI) exchange. At $94.8°$ and in solutions of ionic strength 0.92 the observed rate constants are $k = 6.6 \times 10^{-7} M\ sec.^{-1}$ and $k' = 1.4 \times 10^{-5}\ M^{-1}\ sec.^{-1}$

Oxidation-reduction reactions: Since Cr(II) is a powerful reducing agent several oxidation-reduction reactions are possible. The most interesting one is the Taube's reactions that has been studied kinetically in detail in recent years. Libby (64) concludes that a sudden change in bond type from ionic for Cr(II) to covalent for Cr(III) applies to Taube's reactions.

$$Cr^{2+} + (NH_3)_5 Co\ L^2 + 5\ H^+ = 5\ NH_4^+ + CrL^{2+} + Co^{2+}$$

Specific rate constants, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in table 3 for various ligands (L) used in the study of Taube's reaction.

TABLE 3.

KINETIC DATA FOR TAUBE'S REACTION

Reaction	$k, M^{-1}\ sec.^{-1}$	temp. °C	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ e.u.	Ref.
Cr^{2+} -- $Co(NH_3)_5\ H_2O^{3+}$	0.5	20	2.9	-52	(65)
Cr^{2+} -- $Co(NH_3)_5\ OH^{2+}$	1.5×10^6	20	4.6	-18	(65)
Cr^{2+} -- $Co(NH_3)_5\ Cl^{2+}$	$> 10^3$	20			(66)
Cr^{2+} -- $Co(NH_3)_5\ O_2CCH_3^{2+}$	0.18	25.1			(67)
Cr^{2+} -- $Co(NH_3)_5\ O_2OCH_2Cl^{2+}$	0.11	29.5			(68)

Reaction	$k, M^{-1} sec.^{-1}$	tem., $^\circ C$	$\Delta H^{\neq}$ (Kcal/mole)	$\Delta S^{\neq}$ e.u	Ref
Cr^{2+} -- $Co(NH_3)_5 O_2 CCHCl_2^{2+}$	0.08	30.5			(68)
Cr^{2+} -- $Co(NH_3)_5 O_2 CCF_3^{2+}$	0.07	30.00			(68)
Cr^{2+} -- $Co(NH_3)_5 (H-succinate)^{2+}$	0.17	14.1			(67)
Cr^{2+} -- $Co(NH_3)_5 (CH_3-succinate)^{2+}$	0.17	25.0			(68)
Cr^{2+} -- $Co(NH_3)_5 (H-fumarate)^{2+}$	0.75	14.3	7.5	-33	(67)
Cr^{2+} -- $Co(NH_3)_5 (CH_3-fumarate)^{2+}$	0.43	2.5			(67)
Cr^{2+} -- $Co(NH_3)_5 (H-phthalate)^{2+}$	0.06	14.2	5.1	-47	(67)
Cr^{2+} -- $Co(NH_3)_5 (H-isophthalate^{2+})$	0.11	14.2	2.6	-56	(67)
Cr^{2+} -- $Co(NH_3)_5 (H-terephthalate^{2+})$	36	16.6			(67)
Cr^{2+} -- $Co(NH_3)_5 (benzoato)^{2+}$	0.16	27			(22)
Cr^{2+} -- $Co(NH_3)_5 (p-aldehydo benzoato)^{2+}$	~500	27			(22)
Cr^{2+} -- $Co(NH_3)_5 H-Oxalate)^{2+}$	>200	25			(69)

In addition to those listed in the table very recently Fraser (22)
obtained second order rate constants ranging from 0.13 to 1.6 $M^{-1}sec.^{-1}$
for the same Taube's reaction with the following ligands, L = p-sulfo-
benzoato, p-hydroxybenzoato, p-cyanobenzoato, phenylterephthalato,
cresylterephthalato, phenylfumarato, cis-cyclopropanedicarboxylato,
trans-cyclopropanedicarboxylato, amidofumarato, and diethylamido-
fumarato.

Whereas the above oxidation-reduction reactions are rightly
classified as innersphere reactions there are, however, reactions
with an outer sphere reductant such as $Cr(dipy)_3^{2+}$ shown in table 4.
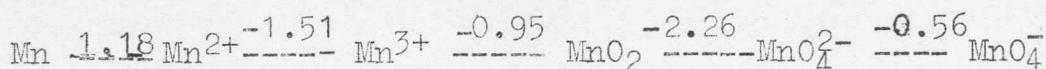The rate is sensititve to changes of pH

TABLE 4

REACTIONS OF $Cr(DIPY)_3^{2+}$ WITH TAUBE'S OXIDIZING AGENTS(70)

Oxidant	$k,\ M^{-1}\ min^{-1}\ x\ 10^{-3}$		temp., $°C$
$Co(NH_3)_5\ H_2O^{3+}$	126		4
$Co(NH_3)_5\ D_2O^{3+}$	48		4
$Co(NH_3)_5\ Cl^{2+}$	630		4
$Co(NH_3)_5\ Br^{2+}$	$>10^3$		4
$Co(en)_3^{3+}$	2.2	$(\mu = 0.1)$	25
$Co(NH_3)_6^{3+}$	41	$(\mu = 0.1)$	24

and ionic strength. Zwickel and Taube (70) made a detailed study of salt, ligand, deuterium isotope effects on this reaction and postulated a quantummechanical tunnelling process for the observed electron transfer reaction. In support of this a general comparison of the rates between $Cr(dipy)_3^{2+}$ -- $Co(en)_3^{3+}$ and $Cr(dipy)_3^{2+}$ -- $Co(NH_3)_6^{3+}$ is made. The bulky size of the ethylenediamine (en) molecule making tunnelling distances greater and consequently lowering the probability for barrier penetration. Hence $Co(en)_3^{3+}$ will react with $Cr(dipy)_3^{2+}$ less rapidly as shown by the magnitude of the specifid rate.costant.

Oxidation-reduction reactions involving Cr.(VI) are well-known and complicated and it is not intended to dwell on this subject here. However, it is interesting to mention the copper catalyzed reaction between molecular hydrogen and dichromate ion studied by Peters and Halpern (71). At 110° the second order rate constant $k = 1.5 \times 10^{-7}$ and the experimental activation energy is 26.6 kcal/mole.

MANGANESE

$$Mn \xrightarrow{\ 1.18\ } Mn^{2+} \xrightarrow{\ -1.51\ } Mn^{3+} \xrightarrow{\ -0.95\ } MnO_2 \xrightarrow{\ -2.26\ } MnO_4^{2-} \xrightarrow{\ -0.56\ } MnO_4^{-}$$

Mn(II)-Mn(III): Adamson (72) repeated some of the experiments done by Polissar (73) in perchloric acid and reported that the Mn*(II)-Mn(III) exchange is rapid but measurable ($t\frac{1}{2}$ ca. 10-20 sec.). No further work has been done on this system and at 25° the second order rate constant is estimated as ~ 4 $M^{-1} sec.^{-1}$ Polissar's observation that the Mn(II)--Mn(III) in oxalic acid medium is fast may well be due to respective oxalato complexes of Mn(II) and Mn(III) participating in the exchange rather than the uncomplexed ions.

Exchange between $Mn(CN)_6^{3-}$ -- $Mn(CN)_6^{4-}$ has also been reported as fast (74)

Mn(VI) -- Mn(VII): Sheppard and Wahl (29), have not only successfully measured the rate of this electron transfer when other investigators failed but with their ingeneous rapid mixing and quenching techniques studied the kinetics in detail. Mn-54 was used as a tracer. The exchange reaction obeys the rate law, $R = k \left[MnO_4^{2-} \right] \left[MnO_4^{-} \right]$ and the rate constant at 0° and in 0.16 M NaOH is 710 $\pm$ 30 $M^{-1} sec.^{-1}$ The experimental activation energy is 10.5 kcal/mole. The rate is very little affected by the presence of anions. However, marked cationic catalysis has been reported and the rate constants follow the order depending upon the cation at constant electrolyte concentration. An extension of the specific cation catalysis

$$k_{CsOH} > k_{KOH} > k_{NaOH} = k_{LiOH}$$

by Gjertsen and Wahl (75) shows that the rate increases linearly with the cesium ion concentration. A suggestion that cesium is the bridging atom in this anionic electron transfer system is made

$$\left[O_3MnO\text{--}Cs\text{--}OMnO_3 \right]^{2-}$$
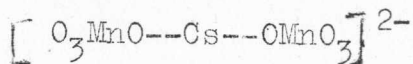
Britt and Yen (47) studied the MnO_4^{2-} --MnO_4^- exchange by pulsed nuclear magnetic resonance technique and reporte almost the same rate constants (within ~30%) as by the isotopic exchange method.

$$k_{nmr.} = (1.23 \pm 0.25) \times 10^3 M^{-1} \text{ sec.}^{-1}$$
$$k_{i.e} = (1.70 \pm 0.22) \times 10^3 M^{-1} \text{ sec.}^{-1}$$

Mn(II)--Mn(VII): No further work has been done on this diffi-cult system since Adamson (72) reported a $r\frac{1}{2}$ of 20 hours in $10^{-3}M$ solutions of the reactants and in 3M Hclo 4. Manganese dioxide is produced in the reaction making measurements not easily repro-ducible. However, a rate law

$$R = k \left[H^+\right]^{1.0-1.6} \left[Mn^{2+}\right]^{1.0-1.6} \left[MnO_4^-\right]^{0.0-0.6}$$

is indicated.

Oxidation-reduction reactions: Since permanganate is a powerful oxidizing agent several oxidation-reduction reactions are possible. In a recent review Ladbury and Cullis summarize all the available data on permanganate oxidations.

IRON

$$Fe \xrightarrow{\underline{0.44}} Fe^{2+} \xrightarrow{\underline{-0.77}} Fe^{3+}$$
$$Fe(CN)_6^{4-} \xrightarrow{\underline{-0.36}} Fe(CN)_6^{3-}$$
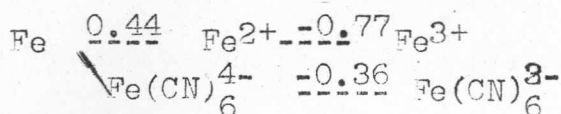
Fe(II)-Fe(III): No other electron transfer exchange system received so much attention as the Fe(II)--Fe(III) system. Earlier work includes conflicting and contradictory reports on the methods of separation and exchange half-times. Using a chemical method of separation Nahinsky (76) reported that the exchange is complete in ~5 sec. whereas Van Alten and Rice (77) using a diffusion method of separation gave a $t_{\frac{1}{2}}$ of 18.5 $\pm$ 2.5 days. Kierstead of (78) using the same diffusion method reported 39 days as the half-time for this exchange Betts, Gilmour and Leigh (79) found that the exchange was complete in one-half hour. Linnenbom and Wahl (80) obtained different results when they repeated Van Alten and Rice diffusion experiments and found the half-time less than 2 hours.

Siverman and Dodson (81) developed an ingeneous chemical method of separation by which Fe(II) is complexed to form $Fe(dipy)_3^{2+}$ while precipitating the Fe(III) as the hydroxide $Fe(OH)_3$. (c.f. the same method was successfully used by Krishnamurty and Wahl in the vanadium (II)-vanadium(III) exchange.). Using Fe-55 as tracer the kinetics of Fe(II)--Fe(III) exchange have been studied in great detail by the same authors. Observed experimental rate data fitted nicely into arate law

$$R = k_1 \left[Fe^{2+}\right] \left[Fe^{3+}\right] + k_2 \left[Fe^{2+}\right] \left[FeOH^{2+}\right]$$

where k_2 is nearly 1000 times larger than k_1 . The first in the rate law can be interpreted as the direct electron transfer path between Fe^{2+} and Fe^{3+} ions and the second term suggesting possible participation of -OH bridge in the electron transfer

process or even a H-atom transfer. About the same time Hudis and and Wahl (82) made a detailed study of the kinetic of the exchange reactions between $Fe(II)$ and the fluoride complexes of $Fe(II)$ FeF^{2+} , FeF_2^+ and FeF_3 . For the path involving Fe^{2+} -- $FeOH$ they suggest H-atom transfer mechanism as more likely. To test the validity of the H-atom transfer mechanism Hudis and Dodson (83) repeated the rate studies in D_2O as solvent for the $Fe(II)$ --$Fe(III)$ system. A deceleration of rate by a factor of 2 in D_2O was noticed for both the reactions:

$$Fe^{2+} \qquad Fe^{3+} \qquad \xrightarrow{K}$$
$$Fe^{2+} \qquad FeOH^{2+} \xrightarrow{K}$$
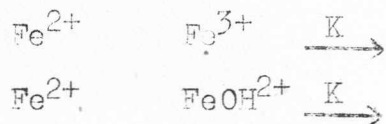
suggesting that atom transfer may be the case in the reactions. In a further examination of this system Sutin, Rowley and Dodson (84) carried out the kinetics of the chloride-catalysed exchange between $Fe(II)$--$Fe(III)$ in light and heavey water and fount that the kinetic isotope effect, $k_{D_2O}/k_{H_2O}/ = 1/2$ nearly the same for all the three reactions.

$$Fe^{2+} \quad + \quad Fe^{3+} \quad \longrightarrow$$
$$Fe^{2+} \quad + \quad FeOH^{2+} \longrightarrow$$
$$Fe^{2+} \quad + \quad FeCl^{2+} \longrightarrow$$
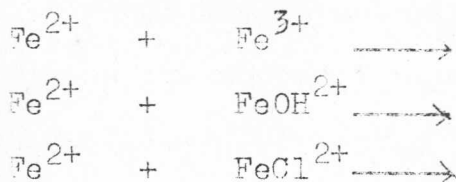
It is concluded that the solvent deuterium isotopic effect is not of much value diagnostically. However, a possibility still exists that all the three reactions might proceed via a common mechanism, perhaps H-atomttransfer. This can be questioned on the following grounds. The equilibrium isotope effect, $k_{D_2O}/k_{H_2O} = 2$ found for the association reaction

$$Fe^{3+} \quad + \quad Cl^- \quad = \quad FeCl^{2+}$$

is of the same order of magnitude as the kinetic isotope effect for the exchange reaction. Since the equilibrium does not involve any net H-atom transfer or proton transfer and secondly similar kinetic isotope effects are noticed in other redox systems (that do not involve H-atom transfer) it is not very likely that H-atom transfer mechanism is the case for Fe(II)--Fe(III) exchange reactions. It can, however, be argued that the observed solvent isotope effects may well be due to some sort of "structure-breaking" action of the various species differently placed in the two solvent

With a view to learn the important part played by the solvent Horne (85) investigated the rate of Fe(II)--Fe(III) exchange in methyl alcohol, ethyl alcohol and n-propyl alcohol, Sutin '86) in isopropyl alcohol and Maddock (81) in nitromethane. The exchange rate was markedly decelerated in the organic solvent as compared to water. From a study of the absorption spectrum of $Fe(ClO_4)_3$ in isopropyl alcohol and in water-isopropyl alcohol mixtures Sutin(86) explains the observed deceleration of the isotopic exchange between Fe(II)--Fe(III) ($k_{H_2O}/k_{i-prop} = 10^8$) due to a variety of causes: (1) complexity of the exchanging species, (2) differences in the solvent reorganization energies for each exchanging species, (3) inability of isopropyl alcohol to play the same role as water and (4) dielectric constant on the equilibrium ---

$$Fe(H_2O)_6^{3+} + H_2O = Fe(H_2O)_5OH^{2+} + H_3O^+$$

Lieser and Schroeder (88) studied the Fe(II)--Fe(III) exchange in solutions containing sulfate ion and report strong catalysis by the sulfate ion. They also interpret the catalysis in terms of a H-atom transfer mechanism.

Horne (89) made an extensive study of the oxalate ion catalysis on this exchange with a view to establish any differences in the activation energies for various anionic-catalyses reported earlier. Oxalate ion was chosen for this study because it is structurally more complex unlike the halide ions whose catalytic effect has been the subject of intense study. The exchange is reported to be catalyzed by silver foil, and by accetate, succinate and phenolate ions.

Available kinetic data on the Fe(II)--Fe(III) exchange are shown in table.5.

$\underline{Fe(CN)_6^{4-} -- Fe(CN)_6^{3-}}$: Wahl and Coworkers (31) (32) successfully measured the rate of this fast exchange reactions using Fe-55 labelled $Fe(CN)_6^{4-}$ ion and a specially designed adaptation of Hartridge-Roughton rapid mixing apparatus resembling the one used earlier for measuring the fast $MnO_4^{2-} -- MnO_4^-$ exchange. Half-times as small as 0.07 sec. were measured reproducibly. Prior to a detailed kinetic study by Deck and Wahl (31) factors causing nearly 100% zero -time exchange and other separation problems have been systematically investigated by Wolfsberg (90). The separation method involves extraction of $Fe(CN)_6^{4-}$ into a chloroform solution of $(C_6H_5)_4 AsCl$ with a stand-in carrier like $Co(CN)_6^{3-}$ ion. Deck (32) investigated the kinetics in KOH solution and the rate law is

$$R = k \left[Fe(CN)_6^{4-} \right] \left[Fe(CN)_6^{3-} \right]$$

In 0.01 M KOH and at 0° the rate constant k has a value 355 M^{-1} sec^{-1} The rate changes sharply with the alkali concentration and there is a specific catalytic effect of k^+ ion. Other small

ions also are found to exhibit the catalytic effect. In an extension of this study King (91) found that as little as 10^{-3} M barium ion concentration increases the rate measurably.

Oxidation-reduction reactions: Oxidation reactions of Fe^{2+} by several oxidizing agents, simple, complex and organic peroxides as well as reduction reactions of Fe^{3+} by several reducing agents are well summarized by Stranks (20) giving relevant kinetic data. Reynolds and Lumry (92) cite several examples of ferrous ion oxidation in water solutions and conclude that water plays an important role in the reaction. In the hydroperoxide oxidation of Fe^{2+} replacement of solvent environment of H_2O by D_2O produces an increase of 0.8 kcal/mole in the $\Delta H^{\ddagger}$ value and this isotope effect is taken as evidence for the participation of a bond containing hydrogen in the rate determining step. The proposed mechanism for Fe(II)--Fe(III) exchange is not a simple and direct electron transfer between the ions when they are in closest proximity. In fact the evidence is in favour of some type of atom or group transfer in addition.

TABLE 5

KINETIC DATA FOR FE(II)--Fe(III) EXCHANGE

System		$k, M^{-1} sec^{-1}$	Temp., $^{\circ}C$	E_a kcal/mole	$\Delta S^{\ddagger}$	Ref.
Fe^{2+} --	Fe^{3+}	0.87	0	9.9	-25	(91)
Fe^{2+} --	$FeOH^{2+}$	1×10^3	0	7.4	-18	(91)
Fe^{2+} --	FeF^{2+}	9.7	0	9.1	(32)
Fe^{2+} --	FeF_2^{+}	2.5	0	9.5	-22	(32)
Fe^{2+} --	$FeCl^{2+}$	9.7	0	8.8	-24	(91)

System	$k, M^{-1} sec^{-1}$	temp., °C	E_a kcal/mole	$\Delta S^{\ddagger}$	Ref.
Fe^{2+} -- $FeCl_2^+$	15	0	9.7	-20	(81)
Fe^{2+} -- $FeBr^{2+}$	4.9	0	8.5	-25	(61)
Fe^{2+} -- $FeBr_2^+$	19	0	14	-3	(85)
Fe^{2+} -- $FeSCN^{2+}$	12.2	0	7.9	-27	(93)
Fe^{2+} -- $Fe(SCN)_2^+$	2.0	0	8.6	-28	(93)
Fe^{2+} -- FeN_3^{2+}	$1.8. \times 10^3$	0	13.7	+6.8	(94)
Fe^{2+} -- $FeC_2O_4^+$	7×10^2	0	9.2	-14	(89)
Fe^{2+} -- $Fe(C_2O_4)_2^{--}$	$\sim 3 \times 10^3$	0	--	--	'89
Fe^{2+} -- $Fe(o\text{-}phen)_3^{3+}$ [1]	3.7×10^4	25	~ 0.8	-37	(36)
Fe^{2+} -- $Fe(EDTA)^-$	$< 4 \times 10^{-4}$	30	--	--	(96)
Fe^{2+} -- $Fe(dipy)_3^{3+}$	2.7×10^4	25	--	--	(37)
$Fe2+$ -- $Fe(dipy)_3^{3+}$	8.5×10^4		--	--	(37)
$Fe(CN)_6^{4-}$ $Fe(CN)_6^{3-}$	3.5×10^2	4	4.7	-32	(32)
$Fe(o\text{-}phen)_3^{2+}$ -- $Fe(o\text{-}phen)_3^{3+}$	$>10^5$	0	--	--	(39)
$Fe(Me_2\text{-}phen)_3^{2+}$ -- $Fe(me_2\text{-}phen)_3^{3+}$	$> 2 \times 10^4$	0	--	--	(97)
$Fe(EDTA)^{2-}$ -- $Fe(EDTA)^-$	$> 10^3$	0	--	--	(95)
$Fe(C_5H_5)_2$ -- $Fe(C_5H_5)_2^+$	$>10^4$	0	--	--	(98)
$Fe(t\text{-}phen)_3^{2+}$ -- $Fe(d\text{-}dipy)_3^{3+}$	$>10^8$	25	--	--	(99)
$Fe(dipy)_3^{2+}$ -- $Fe(D\text{-}phen)_3^{3+}$	$> 10^8$	25	--	--	(99)

dipy = 2,2'-dipyridyl

tripy = 2,2',2"-tripyridyl

d-dipy = 4,4'-dimethyl-2,2'-dipyridyl

o-phen = 1,10-phenanthroline

o-phen = 5-phenyl-1, 10-phenanthroline

t-phen = 3,4,7,8-tetramethyl 1, 10-phenanthroline

EDTA = ethylenediaminetetracetic acid

A very elegant rapid-mixing-flow-technique coupled with spectrophotometric and automatic recording services has been developed very recently by Sutin and Gordon(36) for the study of certain very fast oxidation-reduction reactions. The oxidation of Fe^{2+} by $Fe(o\text{-phen})_3^{3+}$ in 0.5 M $HClO_4$ was shown to be first order in each species with a specific rate constant $k \approx 3.7$ x 10^4 M^{-1} $sec.^{-1}$ at 25°. Interesting correlation between the free energies of activation $(\Delta F^{\neq})$ and the standard free energy changes (ΔF^0) of several oxidation-reduction reactions involving Fe^{2+} is made. Fig.9 shows the linear relationship between $\Delta F^{\neq}$ and ΔF^0.
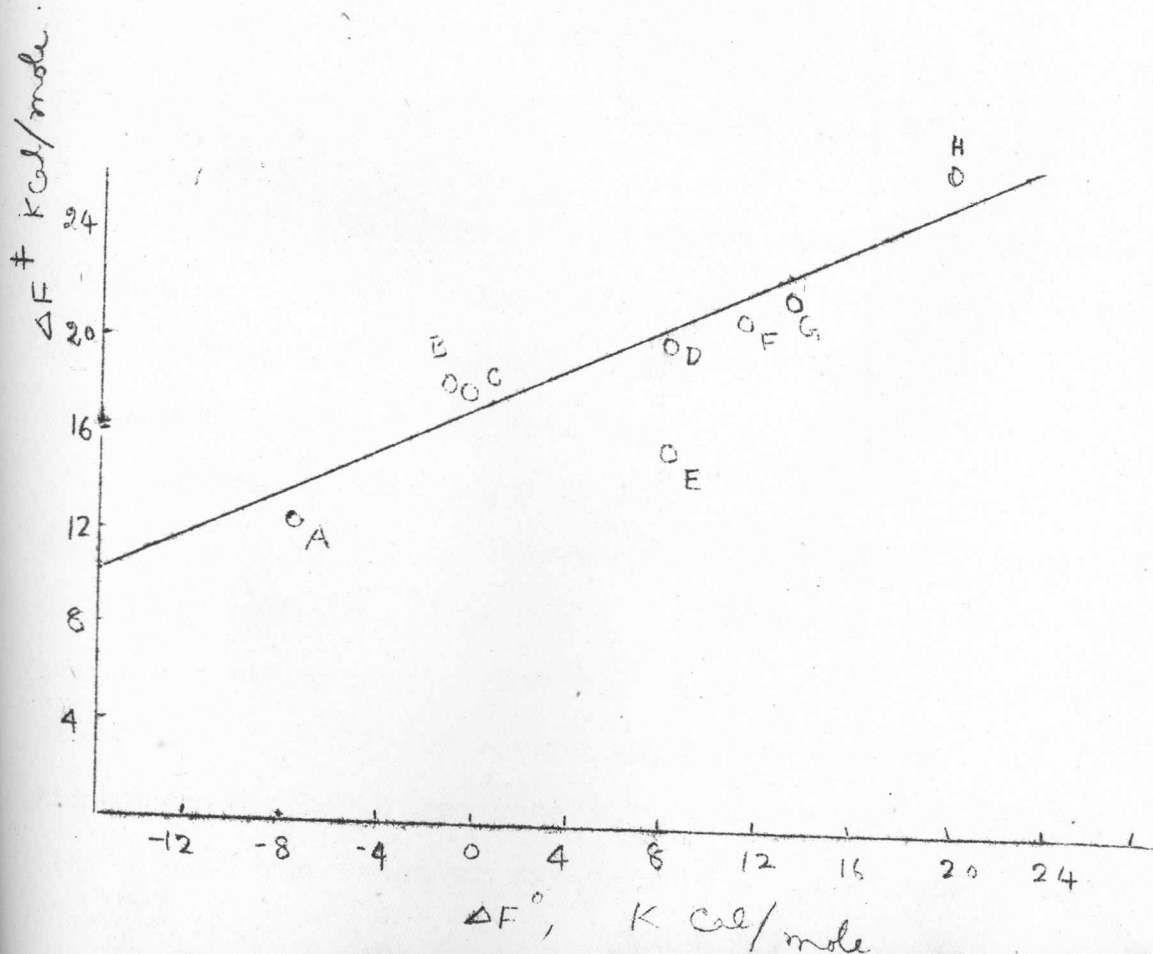
fig.9 -FREE ENERGY OF ACTIVATION vs. STANDARD FREE ENERGY CHANGE

Oxidation of Fe(II) by various oxidizing agents: (A) Fe(o-ph...
(B) $FeCl^{2+}$; (C) Fe^{3+} (D) 2,6-dichlorosemiquinone; (E) $FeOH^{2+}$;
(F) benzosemiquinone;   (G) tolusemiquinone;   (H) durosemiquinone.
Data from Stuin and Gordon (36)

From the linear relation between $\Delta F^{\ddagger}$ and ΔF^{o} it appears
that the reaction of $Fe(H_2O)_6^{2+}$ with $Fe(H_2O)_6^{3+}$ is somewhat slower
than expected while the reaction $Fe(H_2O)_6^{2+}$ with $Fe(H_2O)_5 OH^{2+}$ seems
faster. This has been explained earlier by Hudis and Wahl (82) as
a special case because of the formation of a symmetrical activated
complex resulting in a higher probability of H-atom transfer and
greater exchange rate. In any case $Fe(H_2O)_6^{2+}$ -- $Fe(H_2O)_5 OH^{2+}$
proceeds by a different mechanism.

$$\left[(H_2O)_5 \text{--} Fe^{++} \text{--} O \text{---} H \text{-----} O \text{--} Fe^{*++} \text{--} (OH_2)_5 \right]^{\ddagger}$$
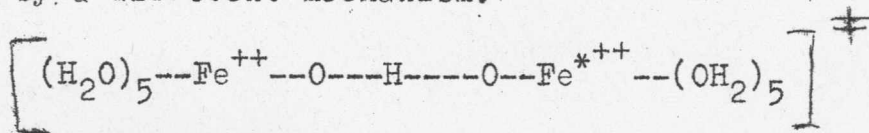
Ford-Smith and Sutin (37) observed similar linear relation
between $\Delta F^{\ddagger}$ and ΔF^{o} for a variety of Fe (II) oxidation reactions
by substituted 1,10-phenanthroline, 2,2'-dipyridyl, 2,2',2"-
tripyridyl complexes of $Fe(III)$.

Gordon, Williams and Sutin ( ) studied the kinetics of the
oxidation of Fe(II) by $Ag(o-phen)_2^{2+}$ $Ag(dipy)_2^{3+}$ $Ru(dipy)_3^{3+}$
$Os(dipy)_3^{3+}$ and $IrCl_6^{2-}$ in $HClO_4$ and H_2SO_4 solutions. Table 6
gives a summary of rate constant data on the oxidation-reduction
reactions of Fe(II) by various oxidazing agents. The reactants
listed in the table are generally substitution inert and it is
likely electron transfer may proceed via outer sphere activated

complexes. It would appear therefore Marcus theory of electron transfers, can be applied in the case (see under theories of electron)

TABLE 6

KINETIC DATA ON OXIDATION-REDUCTION REACTIONS

System	Rate constant k, M^{-1} sec.$^{-1}$ (25°)
Fe^{2+} -- $Ag(o-phen)_2^{2+}$	1.7 x 10^6
Fe^{2+} -- $Ag(dipy)_2^{2+}$	1.4 x 10^6
Fe^{2+} -- $Ru(dipy)_3^{3+}$	7.2 x 10^5
Fe^{2+} -- $Os(dipy)_3^{3+}$	1.4 x 10^3
Fe^{2+} -- $IrCl_6^{2-}$	3.2 x 10^6
$Os(dipy)_3^{2+}$ -- $Fe(o-phen)_3^{3+}$	> 10^3
$Fe(p-phen)_3^{2+}$ -- $Ru(dipy)_3^{3+}$	> 10^8
$Fe(t-phen)_3^{2-}$ -- $Ru(dipy)_3^{3+}$	> 10^8
$Fe(CN)_6^{4-}$ -- $Os(dipy)_3^{3+}$	> 10^8
$Fe(CN)_6^{4-}$ -- $Fe(o-phen)_3^{3+}$	> 10^8
$Fe(CN)_6^{4-}$ -- $IrCl_6^{2-}$	4.8 x 10^5
$Fe(CN)_6^{4-}$ -- MnO_4^{-}	1.3 x 10^4
$Fe(CN)_6^{4-}$ -- $OsCl_6^{2-}$	1.8 x 10^{-1}

dipy = 2,2'-dipyridyl o-phen = ortho phenanthroline or 1,10-ph.

p-phen = 5-phenyl-1, 10-phenanthroline
t-phen = 3,4,7,8-tetramethyl-1, 10-phenanthroline

Data from Gordon, Williams, and Sutin (99)

COBALT

$$Co \xrightarrow{0.28} Co^{2+} \xrightarrow{-1.82} Co^{3+}$$
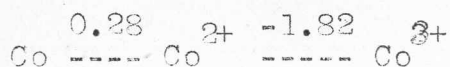
Co(II)--Co(III): Bonner and Hunt in a recent paper (100) report complete kinetic data on this exchange reaction studied earlier by the same authors (101). The tracer used was Co-60. The system resembles very much other M(II)--M(III) systems and the rate law is

$$R = \left[Co(II)\right] \left[Co(III)\right] \left\{ k_1 + K_2 / [H^+] \right\}$$

In 1 f $HClO_4$ at 3.2° and ionic strength unity k_1 and k_2 are $50 M^{-1}$ min^{-1} and $8.3 M^{-1} min^{-1}$ respectively. There is an increase in the rate with ionic strength increase. The experimental activation energy is 13.2 kcal/mole and $\Delta s^{\ddagger} = -13$ e.u The over-all rate is one-half- as fast in D_2O as in H_2O. Other cobalt(II)-cobalt(III) electron transfer systems are listed in table 7 for the purpose of comparison.

TABLE 7

KINETIC DATA FOR Co(II)--Co(III) EXCHANGE

System	$k, M^{-1} sec^{-1}$	temp. $^\circ C$	E_a kcal/mole	$\Delta s^{\ddagger}$	Ref.
Co(II) -- Co(III)	Ca. 5	25	13.2	-13	(100)
$Co(en)_3^{2+}$ -- $Co(en)_3^{3+}$	5×10^{-5}	25	13.7	-39	(102)
$Co(NH_3)_6^{2+}$ -- $Co(NH_3)_6^{3+}$	5.3×10^{-5}	60	13.5	-46	(103)
$Co(NH_3)_6^{3+}$ in liq. NH_3	6×10^{-5}	25	23	-10	(104)

System	k, $M^{-1}sec^{-1}$	temp.$^{\circ}C$	E_a kcal/	$\Delta S^{\ddagger}$	Ref.
$Co(NH_3)_5(HO)^{2+}$ -- $Co(NH_3)_5(H_2O)^{3+}$	7.5×10^{-4}	60	13.3	-43	(105)
$Co(C_2O_4)_3^{4-}$ -- $Co(C_2O_4)_3^{3-}$	9×10^{-7}	25	--	--	(106)
$Co(C_2O_4)_2^{2-}$ -- $Co(C_2O_4)_3^{3-}$	1.4×10^{-5}	25	--	--	(106)
$Co(dipy)_3^{2+}$ -- $Co(dipy)_3^{3+}$	18	45	--	--	(107)
$Co(o-phen)_3^{2+}$ -- $Co(o-phen)_3^{3+}$	4.5	20	--	--	(107)
$Co(EDTA)^{2-}$ -- $Co(EDTA)^{-}$	4×10^{-7}	25	22	-17	(95)

Electron transfer between the ammine complexes of Co(II) and Co(III) has been the subject of intensive and extensive study since 1949 when Lewis, Coryell and Irvin (102) first reported the differences in the exchange rates in the following closely related systems.

(1) $Co(NH_3)_6^{2+}$ -- $Co(NH_3)_6^{3+}$ $t_{\frac{1}{2}} > 80$ days

(2) $Co(en)_3^{2+}$ -- $Co(en)_3^{3+}$ $t_{\frac{1}{2}}$ 2-50 hours

(3) $Co(en)_3^{2+}$ -- $Co(NH_3)_6^{3+}$ $t_{\frac{1}{2}}$ a few minutes

(4) $Co(NH_3)_6^{2+}$ -- $Co(en)_3^{2+}$ $t_{\frac{1}{2}} > 500$ days

Appelman, Anbar and Taube (108) extended this study using $Co(NH_3)_5$ H_2O^{3+} to see if a built-in brdging group might facilitate rapid electron transfer. Very recently, however, Stranks (109) made a significant contribution in explaining the electron exchange between the various systems involving cobalt ammine complexes.

Electron exchange between the oxalato complexes of Co(II) and Co(III) has been summarized in a recent review by Krishna-murty and Harris (110). From a kinetic study of this complica-ted electron exchange process Dainton, Laurence, Schneider, Stranks and Vaidya (106) proposed a mechanism involving 'external electron transfer' to explain the observed isotopic exchange and an 'internal electron transfer' to account for the thermal decomposition of $Co(C_2O_4)_3^{3-}$

Optical activity method of studying the kinetics of elec-tron transfer, described earlier, has been successfully applied by Yong Ae Im and Busch (111), (112) for the system $Co(EDTA)^{2-}$ -- $Co(EDTA)^-$. The second order rate constant for the electron transfer obtained in this study, $k = 1.4 \ M^{-1} \ hr.^{-1}$ at 100° agrees well with the value of $1.1 \ M^{-1} \ hr.^{-1}$ (extrapolated to 100°) reported by Adamson and Vorres (95) earlier by an isotopic exchange method using Co-60 as tracer. Yong Ae Im and Busch (113) extended the optical activity method for measuring the rates of electron transfer to a new system, $Co(PDTA)^{2-}$ --$Co(PDTA)^-$ where PDTA stands for propylenediamine tetra acetate. Useful comparison is made between the above two systems and a novel method of resolution has been suggested. Using the same optical activity method Dwyer and Sargeson (114) very recently studied the kinetics of the slow electron transfer between $Co(en)_3^{2+}$ and $Co(en)_3^{3+}$ which was the subject of intensive investigation by earlier workers using the radioisotopic method.

Oxidation-reduction reactions: The ion Co^{3+} is such a powerful oxidizing agent that it decomposes water readily and the kinetics of this reaction have been studied by Bawn and White [115] in dilute $HClO_4$ solutions. Some hundreds of complexes are known in which the +3 oxidation state of cobalt is found more stable than the corresponding +2 state. Some of the Co(III)-complexes are equally good oxidizing agents and it is fascinating to study the oxidation-reduction reactions that provide wealth of data on the fundamental electron transfer process. Recently Taube and his coworkers reported a number of interesting reactions of $Co(NH_3)_5 L^{2+}$ with such powerful reducing agents as Cr^{2+} , V^{2+} , Eu^{2+}, $Cr(dipy)_3^{2+}$ and $V(dipy)_3^{2+}$ as part of a program to learn about the electron transfer process and the activation effects that accompany the reaction [18], [116], [117] [118], [119]. A few illustrative examples on the oxidation-reduction reactions are shown in table 8. Data on Taube's reaction are given under 'Chromium' in table 3.

TABLE 8

KINETIC DATA ON OXIDATION-REDUCTION REACTIONS

System	$k, M^{-1}sec^{-1}$	Temp. $^{\circ}C$	Ref.
$Co^{3+}-- H_2O$ (0.1M$HClO_4$)	3×10^{-2}	20	(115)
$Co^{3+}-- HO_2^-$	2×10^{12}	20	(120)
$Co^{3+}-- HCHO$	20	22	(121)
$Co^{3+}-- Tl^+$	5×10^{-5}	0	(122)
$Co^{3+}-- Fe^{2+}$	10	0	(51)

System	k, M^{-1} sec.$^{-1}$	temp. $^{\circ}C$	Ref.
$CoOH^{2+}$ -- Fe^{2+}	6500	0	(51)
$Co(III)$ -- $V(II)$	> 300	0	(51)
$Co(III)$ -- $Cr(II)$	> 300	0	(51)
$Co(C_2O_4)_3^{3-}$ -- Fe^{2+}	~1000	20	(123)

RELATIVE RATES

(Data taken from Zwickel and Taube (52))

Oxidizing agent	Cr^{2+}	V^{2+}	$Cr(dipy)_3^{2+}$
$Co(NH_3)^{3+}$	1	1	1
$Co(NH_3)_5H_2O^{3+}$	6.0×10^3	135	91
$Co(NH_3)_5OH^{2+}$	2×10^{10}	$< 10^7$	50
$Co(NH_3)_5Cl^{2+}$	$> 10^5$	1.6×10^3	1.5×10^3

COPPER

$$Cu \overset{-0.52}{------} Cu^+ \overset{-0.15}{-----} Cu^{2+}$$
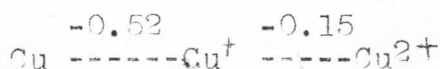
$\underline{Cu(I)--Cu(II)}$:   McConnell and Weaver (44) studied the
electron transfer between $Cu(I)$ and $Cu(II)$ using the nuclear
magnetic resonance method. A determination of the Cu-63 or
Cu-65 (whose natural abundances are 69.1% and 30.9% respectively)
nuclear resonance line width in 12 M HCl containing both $Cu(I)$
and $Cu(II)$ chloride complexes leads to an evaluation of the
second order rate constant, $k = 0.5 \times 10^8$ M^{-1} sec.$^{-1}$. It is

difficult to obtain the rate constant betweent the uncomplexed ions and therefore what is measured in this study apparently refers to internal electron transfer within the interaction complex:
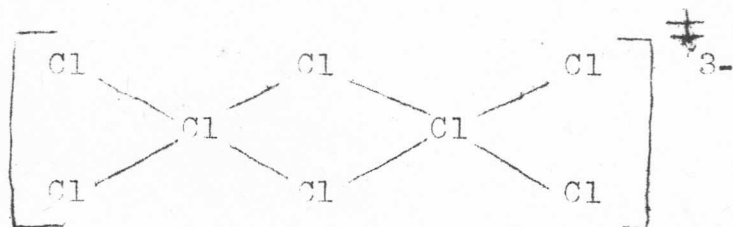

(In 12 M HCl copper ions are present as the chloride complexes: $CuCl_2^-$ and $CuCl_4^{2-}$)

SILVER

$$Ag \overset{-0.80}{-----} Ag^+ \overset{-1.98}{-----} Ag^{2+} \overset{-2.1}{-----} AgO^+$$

Ag(I)--Ag(II): Gordon and Wahl (30) studied the kinetics of this fast exchange using Ag-110m as tracer and a specially designed rapid-mixing, flow, and quenching techniques for measuring half-times in the range 0.1 to 1 sec. In 5.87 M HClO$_4$ the exchange between Ag(I) and Ag(II) obeys the rate law, $R = k \left[Ag(II) \right]^2$. The second order rate constant k $\cong$ 1020 $\pm$ 40 M^{-1}Sec^{-1} at 0° and the experimental activation energy is 12.5 $\pm$ 1.2 kcal/mole. No evidence for direct exchange of electron from Ag(I) to Ag(II) is found and the rate data are best interpreted by the following mechanism:

$$2 Ag(II) \rightleftharpoons Ag(I) + Ag(III)$$
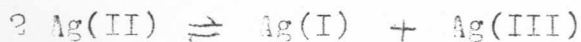
The rate of exchange is therefore the rate of this reaction (in the opposite direction) at equilibrium.

Oxidation-reduction reactions: Noyes and coworkers (124), studied the oxidation of Ag(I) in nitric acid solutions by ozone and the decomposition of water by Ag(II) in acid solutions. In both the studies Ag(III) has been considered as an intermediate.

GOLD

$$Au \xrightarrow[\quad\quad\quad]{-1.68} Au^+ \xrightarrow[\quad\quad\quad]{-1.29} Au^{2+} \xrightarrow[\quad\quad\quad]{-1.29} Au^{3+}$$
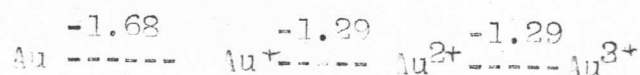
Rich and Taube (125) in their study of the uncatalyzed exchange of Cl^- and $AuCl_4^-$ on the other obtained evidence for the oxidation state Au(II) as responsible for the observed catalysis. It is also postulated that Au(II) may exist in equilibrium with Au(I) and Au(III). By an indirect calculation a lower limit for the Au(II)--Au(III) exchange rate constant is given as $\sim 10^8$ M^{-1} Min^{-1} No further work is available.

MERCURY

$$Hg \xrightarrow[\quad\quad\quad]{-0.79} Hg_2^{2+} \xrightarrow[\quad\quad\quad]{-0.92} Hg^{2+}$$
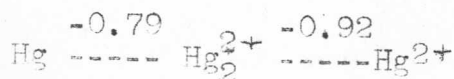
Hg(I)--Hg(II):   Wolfgang and Dodson (126) studied the kinetics of the isotopic exchange Hg(I) between Hg(I) and Hg(II) using Hg-203 as tracer and in the presence of cyanide ion. In $HClO_4$ and in the absence of cyanide ion these authors also noticed complete exchange as reported earlier by Haissinsky and Cottin (127) and by King (128). Using picrolonic acid or chloride as the precipitant for Hg(I) a chemical separation has been developed. In the solutions containing approximately equivalent amount of cyanide to the Hg(II) the rate is found to be first order in

Hg(I) and in Hg(II)   However, it is dependent on the cyanide
ion concentration and very much less on pH in dilute acide solu-
tion. The specific rate constant (for a solution containing
equivalent amounts of Hg(II) and CN⁻) is 5.7×10^3 M^{-1} sec^{-1}
at 0° and the experimental activation energy 14 kcal/mole. The
exchange of uncomplexed Hg_2^{2+} and Hg^{2+} ions is complicated by the
dismutation of Hg_2^{2+}

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} \qquad Hg$$
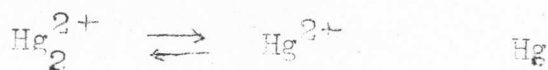
and the exchange is considered to be too rapid for measurement.
A dismutation constant 5.5×10^{-9} has been reported for this
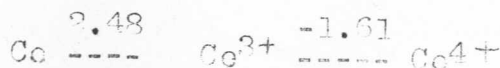equilibrium by Moser and Voigt (129). A dissociative atom trans-
fer mechanism apparently explains the Hg(I)--Hg(II) rapid ex-
change inthe absence of cyanide which causes the deceleration
effect perhaps via complexation.

$$Hg_2^{2+} \longrightarrow Hg^{2+} + Hg$$
$$Hg^{*2+} + Hg \;\; = \;\; (Hg^{*}Hg)^{2+}$$

$$\overline{}$$

$$Hg_2^{2+} + Hg^{*2+} = Hg_2^{*2+} + Hg^{2+}$$

$$\overline{}$$

CERIUM

$$Ce \xrightarrow{\;2.48\;} Ce^{3+} \xrightarrow{\;-1.61\;} Ce^{4+}$$
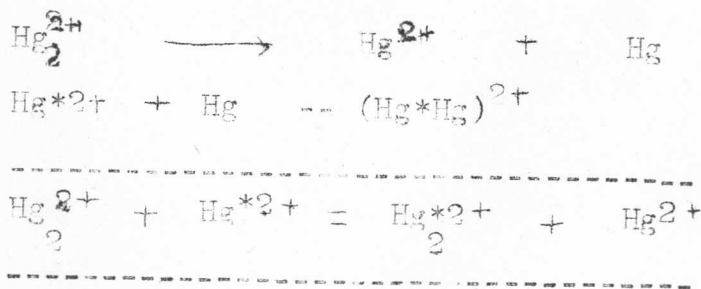
Ce(III)--Ce(IV):   Linnenbom and Wahl (80) using electri-
cal migration methods and Ce-141 as tracer reported that comp-
lete exchange occurred during the time of separation. Gryder

and Dodson (130), noticing complete exchange by a diffusion
method of separation, developed a chemical separation technique
involving the extraction of Ce(IV) from HNO$_3$ solutions into
diethylether. Exchange half-times were found to be of the order
of minutes and in HClO$_4$ and HNO$_3$ kinetic studies were made.

In HNO$_3$ solutions Gryder and Dodson found that the rate of
exchange to be first order in both Ce(III) and Ce(IV) concentra-
tions and inverse second order with respect to the hydrogen ion
concentration. The rate law

$$R = k \left[Ce(III) \right] \left[Ce(IV) \right] = \left\{ k_1 + k_2 / [H] \right\} \left[Ce(III) \right] \left[Ce(IV) \right]$$

and the overall rate constant k (M^{-1} min^{-1}) is given by

$$k = 2.09 \times 10^6 \quad ex(-7700/RT) \quad \frac{2.61 \times 10^{20}}{[H]^2} exp(-24000/RT)$$

It is obvious that the exchange proceeds by (1) an acid indepen-
dent path and (2) an acid dependent path. However, it is not
clear about the nature of the hydrolyzed cerium species that
participate in the second path. In any case it would be interest-
ing to the study the dependence of the exchange rate on the
nitrate ion concentration.

In perchloric acid solutions the acid dependence is not
studied in great detail to permit any reasonable interpretation.
However, the overall exchange rate is first order in Ce(III),
between zero and one in Ce(IV) concentrations and dependent on
the medium, the rate law being

$$R = \left[Ce(III) \right] \left\{ 1.60 \times 10^{13} \quad exp(-19400/RT) + 1.11 \times 10^{13} \left[Ce(IV) \right] exp(-16800/RT) \right\}$$

The fractional order with respect to Ce(IV) is explained in terms
of a dual exchange Ce^{3+} in the ground state and excited state.

At room temperature $10^{-3}\%$ of Ce^{3+} is reported to be in the excited state. On the basis of such an assumption the following mechanism is suggested.

$$Ce(IV) \quad + \quad Ce(III) \xrightleftharpoons{K_1} \quad \text{Exchange}$$

$$Ce(III) \quad + \quad Solvent \xrightarrow{K_2} \quad Ce*(III) \quad solvent$$

$$Ce*(III) \quad + \quad Ce(IV) \xrightleftharpoons[K_4]{K_3} \quad exchange$$
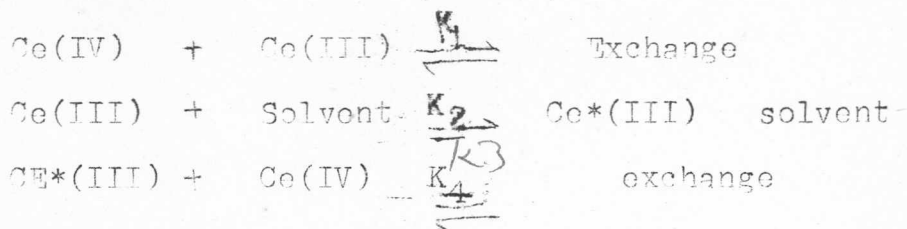
$C*(III)$ is an excited electronic state and this is a forbidden transition and must take place by collision with solvent molecules. Assuming $k_4 \gg k_3$ the following rate law is postulated consistent with the observed rate data.

$$R = k \left[Ce(III)\right] \quad + \quad k' \left[Ce(III)\right] \left[Ce(IV)\right]$$

Hornig and Libby (131) studied the fluoride catalysis of the Ce(III)--Ce(IV) system. The rate was found to be first order in the added fluoride ion concentration and concluded either Ce(III) or Ce(IV) must form a relatively stable bond with F^-. The corresponding chloride catalysis was found to be much smaller than the fluoride case as one might expect the larger ions to be less effective. The apparent activation energy for the fluoride catalyzed Ce(III)--Ce(IV) exchange is 11.7 kcal/mole.

Duke and Parchen (132) in an extension of the work on this system repeated some of the exchange experiments in $HClO_4$ and found that in 6 M $HClO_4$ the relative reactivity of the various hydrolytic monomeric forms of Ce(IV) with respect to electron transfer increases in the following order:

$$Ce(IV) \quad < \quad CeOH^{3+} \quad < \quad Ce(OH)_2^{2+} \quad < \quad Ce(OH)_3^+$$
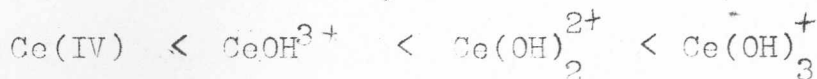
Although OH⁻, F⁻ and Cl⁻ ions catalyze the Ce(III)--Ce(IV)
exchange the following apparently do not have any effect ---
platinum, platinum black, surface, diffuse light or molecular
oxygen.

EUROPIUM

$$Eu \overset{2.41}{----} Eu^{2+} \overset{0.43}{----} Eu^{3+}$$
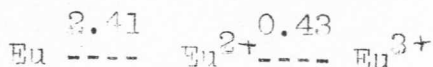
Eu(II)--Eu(III):   Meier and Garner (133), studied the kine-
tics of this exchange using Eu-152 as tracer. In 1.0 M HCl and at
ionic strength 2 the rate is expressed by the equation:

$$R = 6.5 \times 10^{11} \quad exp \; (-20800/\underline{R}T) \quad [Eu(II)][Eu(III)][Cl^-]$$
$$M.Sec.^{-1}$$

The results suggest that a chloride complex $EuCl^{2+}$ might parti-
cipate in the exchange, since halo-complexes of rate earths
have been reported in literature. It is also concluded that the
rate of electron transfer between the uncomplexed ions, Eu^{2+}
and Eu^{3+} is very slow compared to the chloride--catalyzed
exchange.

TIN

$$Sn \overset{0.14}{----} Sn^{2+} \overset{-0.15}{-----} Sn^{4+}$$
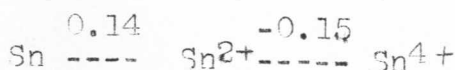
Sn(II)--Sn(IV):   Davidson et al (134) studied the kinetics
of this exchange in 9 M HCl using Sn-113 as tracer. Between 0°
and 25° the rate is given by

$$R = 4.5 \times 10^7 \quad [Sn(II)] \quad [Sn(IV)] \; exp(-10800/\underline{R}T)$$
$$M \cdot min.^{-1}$$

An increase in rate upon irradiation with light of appropriate
wavelength is explained in terms of an interaction complex

forming between the + 2 and + 4 oxidation states.

Meyer and Kahn (135) studied the $SnCl_2$ -- $Sn*Cl_4$ exchange in
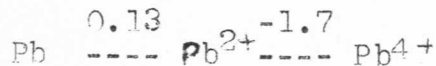ethanol using the 27-hour Sn-121. Half-times of the order
of hours were found and the rate.

$$R = 5.02 \times 10^{16} \left[SnCl_2\right] \left[SnCl_4\right] \exp(-23700/\underline{R}T) \quad M.hr.^{-1}$$

It is likely that a dissociative atom transfer mechanism operates
prior to a two-electron transfer in this case.

Gordon and Brubaker (136) studied the Sn(II)--Sn(IV) exchange
in sulfuric acid.

LEAD

$$Pb \xrightarrow{0.13} Pb^{2+} \xrightarrow{-1.7} Pb^{4+}$$

Pb(II)--Pb(IV):   Hevesy and Rona (137) as early as 1915
performed the first isotopic exchange experiments and later
Hevesy and Zechmeister (138) in 1920 demostrated rapid exchange
between Pb(II) and Pb(IV) in glacial acetic acid using a natural
isotope of lead, Th-B (10-hr. Pb-212).

Evans, Huston and Norris (139) repeated the Pb(II)--Pb(IV)
exchange in glacial acetic acid and found~0.4% exchange in ~ 4
hours at 80°. The species present in acetic acid medium are
mostly covalent acetates of lead and the exchange may well be
due to complicated group transfer mechanism.

ANTIMONY

$$SbH_3 \xrightarrow{0.51} Sb \xrightarrow{-0.21} SbO^+ \xrightarrow{-0.68} Sb_2O_4 \xrightarrow{-0.48} Sb_2O_5$$
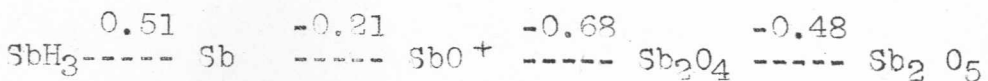
Sb(III)--Sb(V): Bonner (140) studied the kinetics of this complicated exchange reaction in 6M HCl solutions. In a subsequent study Cheek, Bonner and Wahl ( ) extended the investigation from 6 M to 12 M HCl and found that the rate increase with increasing HCl concentrations to a minimum value in approximately 9.3 M HCl, then decreasing between 9.3 M and 12 M. The following rate laws under different experimental conditions are suggestive of the complexity of this system. In the range 4.7 -- 6.1 M HCl, 5.4 -- 6.1 M Cl⁻ , 0.0008 -- 0.040 M Sb(III) and Sb(V), 0 -- 0.8 M Na⁺ and at 25°

$$R = 8.8 \times 10^{11} \left[Sb(III) \right]^{0.6} \left[Sb(V) \right]^{1.1} \left[H^+ \right]^{4} \left[Cl \right]^{9} \quad M.hr^{-1}$$

While not attaching any fundamental significance to the exponents in the rate law satisfactory rate laws are obtained for experiments done in 9.3 M and 11.8 M HCl solutions (141).

(9.3 M) $R = \left[Sb(III) \right] \left[Sb(V) \right] 0.9 \times 1.12 \times 10^{13} exp(-18490/RT)$
$$M.min.^{-1}$$

(11.8M) $R = \left[Sb(III) \right] \left[Sb(V) \right] 1.39 \times 10^{12} exp(-17200/RT)$
$$M.min.^{-1}$$

Complex exchange curves observed in 6.5 M to 8 M region led to postulating two or more species of Sb(V) which exchange at different rates with Sb(III). Bonner and Goishi (142) made a detailed study of the complex exchange curves as also the nature of Sb(V) in HCl solutions.

From this thorough study of the Sb(III) -- Sb(V) system a tentative mechanism is given for the exchange taking place in

54

strongly acid solution via a symmetrical activated complex.

$$Sb^*Cl_6^- + SbCl_4(H_2O)_2 \rightarrow \left[Cl_4Sb^* \diagdown \begin{matrix} Cl \\ Cl \end{matrix} \diagup SbCl_4 \right]^{2-} + 2H_2O \longrightarrow$$
$$Sb^*Cl_4^- (+2H_2O) + SbCl_6^-$$
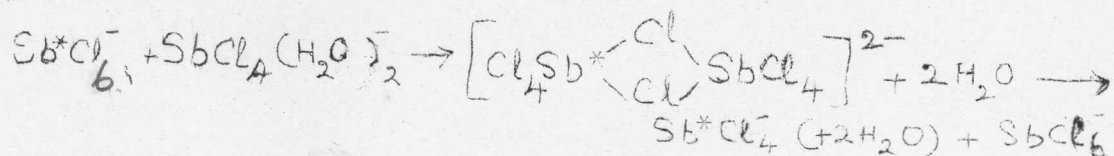
Brubacker and Sincius (143) report that no exchange of antimony occurs in sulfuric acid solutions between 3 M and 12 M. However, when chloride is added exchange occurs and the rate increases with the chloride ion concentration. The observed nonlinearity of the exchange plots indicate complex and competing reactions in sulfuric acid medium also. It may therefore be necessary to form chloride bridges to facilitate electron transfer in the transition state independent of the medium.
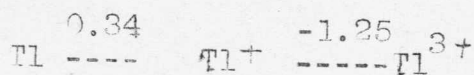
THALLIUM

$$Tl \overset{0.34}{----} Tl^+ \overset{-1.25}{-----} Tl^{3+}$$

Tl(I)--Tl(III):   There has been considerable interest in this two-electron exchanging system. As early as in 1948 Prestwood and Wahl (144) at Washington University and Harbottle and Dodson (146) at Brookhaven National Laboratory simultaneously reported on the kinetics of Tl(I)--Tl(III) exchange in acid solutions. A thorough study of separation-induced exchange made by Prestwood and Wahl (145) revealed the complexities of the precipitation techniques, viz. Tl(III) as $Tl(OH)_3$, and Tl(I) as $TlBr$, Tl_3CrO_4 and Tl_2PtCl_6 . Induced exchange was found to decrease in the order

$$OH^- > Br^- > PtCl_6^{2-} > CrO_4^{2-}$$
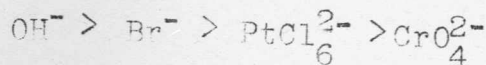
falling from ∼50% to ∼5% . Harbottle and Dodson (147) used the chromate separation and confirmed the low induced exchange reported by Prestwood and Wahl. The experimental results are in good agreement with the two group of workers although there is difference in the interpretation.

Both groups report that the rate of exchange is dependent on the first power of both Tl(I) and Tl(III) concentrations and in $HClO_4$ decreases as the hydrogen ion concentration is increased. When these studies (145), (147), (148) were made an accurate value for the hydrolysis constant of Tl^{3+} was not known and the interpretations were subject to the usual uncertainty whether the observed behaviour is due to acidity effect or medium effect. However Rossotti's analysis (149) supports assumptions of Prestwood and Wahl (   ). In a very recent paper Roig and Dodson measured the exchange at 25° in 3 M $NaClO_4$-$HClO_4$ media at various acid concentrations down to 0.1 M. This study was made with a view to utilize Biedermann's data (150) on the hydrolysis of Tl(III) under more or less same experimental conditions. Roig and Dodson (151) report the following rate law (in contrast to results at higher ionic strengths)

$$R = k_o \left[Tl^+ \right] \left[Tl^{3+} \right] + k_1 \left[Tl^+ \right] \left[TlOH^{2+} \right]$$

where

$$k_o = 0.253 \pm 0.005 \quad M^{-1} \ hr^{-1} \quad (Ea = 17.4 \ kcal/mole)$$
$$K_1 = 0.089 \pm 0.012 \quad M^{-1} \ hr^{-1}$$

Although little evidence is found for the exchange path Tl^+ + $Tl(OH)_2^+ \xrightarrow{k_2}$ an upper limit of 0.1 $M^{-1} hr^{-1}$ is given for the specific rate constant of this reaction.

Gilks and Waind (152) studied the $Tl(I)$--$Tl(III)$ exchange in D_2O and report an isotope effect, $K_{H_2O}/K_{D_2O} = 1.5$ This is further shown under 'Isotope Effects' in comparison with other systems.

Numerous investigations on the anion catalysis of this system are reported in literature. Prestwood and Wahl (145) studied the nitrate ion catalysis in good thoroughness resulting in the following rate law

$$R = \left[Tl(I) \right] \left[Tl(III) \right] \left\{ X + k/\left[H^+ \right] + k'' \left[NO_3^- \right] \right\}$$

where

$$k = 3.8 \times 10^8 \exp (-17600/RT) \ M^{-1} \ sec.^{-1}$$
$$k' = 7.9 \times 10^2 \exp (-10200/RT) \ sec.^{-1}$$
$$k'' = 2.5 \times 10^8 \exp (-16000/RT) \ M^{-2} \ sec.^{-1}$$

Brubaker and Mickel (153), and Wiles (154) studied the $Tl(I)$--$Tl(III)$ exchange in sulfuric acid solutions and found large catalytic effects on the rate.

Chloride (147), (155), (156), Bromide (157), and Cyanide (158) are reported to exhibit similar acceleration effect on the exchange rate. Brubaker and Andrade (159) studied the effects of various oxyacids--oxalic, acetic, succinic, malic and tartaric acid, on the exchange rate and obtained evidence for the reduction of $Tl(III)$ when oxalic, malonic, malic and tartaric acids were added to the exchanging system.

The bromide catalysis data obtained recently by Carpenter, Ford-Smith, Bell and Dodson (157) can be explained satisfactorily by the following rate expression.

$$R = k_0 \left[Tl \right]^+ \left[Tl^{3+} \right] + k_2 \left[TlBr^+ \right] + k_3 \left[TlBr_3 \right] + k_4 \left[Tl \right] \left[TlBr_4^- \right]$$
$$+ k_6 \left[TlBr_2^- \right] \left[TlBr_4^- \right]$$

where the values of the specific rate constants at 30° and at ionic strength 0.5 (upto $[Br^-] = 0.2$ M) are:

$$K_0 = 0.69 \quad M^{-1} \text{ hr.}^{-1}$$
$$k_2 = 8 \times 10^{-3} \quad \text{hr.}^{-1}$$
$$k_3 = 4.5 \times 10^{-3} \quad \text{hr.}^{-1}$$
$$k_4 = 4.6 \quad M^{-1} \text{hr.}^{-1}$$
$$k_6 = 2.37 \times 10^3 \quad M \text{hr.}^{-1}$$

Dodson et al (157) speculate that the faster exchange between Tl^+ and $TlBr_2^-$ may be due to the formation of a symmetrical activated complex of the type
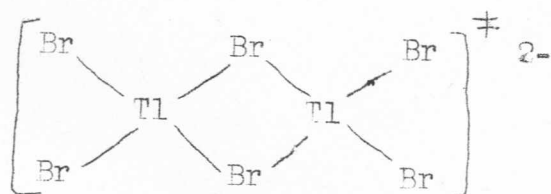
There is some evidence reported by Figgis (160) based on the nuclear magnetic resonance spectrum of Tl-205 that chloride and bromide produce a strong effect on the electronic configuration of Tl(III) as shown by large chemical shifts). This may be conjectured as responsible for some of the halide catalyses effects observed in the Tl(I)--Tl(III) exchange.

Born and Vogg (161), recently revived interest in the separation methods used in Tl(I)--Tl(III) exchange by studying the heterogeneous exchange between Tl(I) and Tl(III)-hydroxide.

Oxidation-reduction reactions: Oxidation reactions of Tl(I) by oxidizing agents like Ce(IV)(55) Co(III) (122), Br_2(157) and several reduction reactions of Tl(III) by Fe(II) (162), Fe(o-phen)$_3^2$ (163) Os(dipy)$_3^{2+}$ (164), Hg(I) (165), V(IV) (55), Cr(II) (166), U(IV) (167), have been studied with a view to learn whether such

redox   reactions take place by a single step- two-electron trans
fer or by successive one-electron transfer steps. The rates of
oxidation-reduction reactions involving a net chemical change and
their kinetic picture in general have a bearing on the general
understanding of the Tl(I)--Tl(III) electron transfer.

Ashurst and Higginson (168) in their study of the kinetics of
the oxidation of Fe(II) By Tl(III)

$$Fe(II) \; + \; Tl(III) \; \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \; Fe(III) \; + \; Tl(II)$$

$$Fe(II) \; + \; Tl(II) \; \overset{K_2}{\rightarrow} \; Fe(III) \; + \; Tl(I)$$

$$2\, Fe(II) \; + \; Tl(III) \; \longrightarrow \; 2\,Fe(III) \; + \; Tl(I)$$
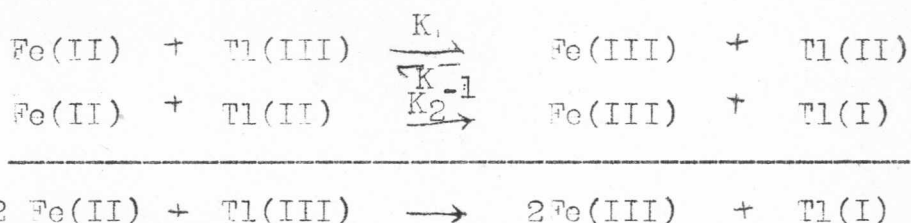
postulate the above mechanism invoking Tl(II) as an intermediate
oxidation state between Tl(I) and Tl(III) in accordance with the
following rate law they obtained.

$$R = k_1 k_2 \; \left[Fe(II)\right]^2 \; \left[Tl(III)\right] / \left\{ k_{-1}\left[Fe(III)\right] + k_2 \left[Fe(II)\right] \right\}$$

Similar mechanisms have been offered for the oxidation of Tl(I)
by Co(III) (182), and for the reduction of Tl(III) by V(IV)

$$2\, Co(III) \; + \; Tl(I) \; \longrightarrow \; 2\, Co(II) \; + \; Tl(III)$$

$$2\, V(IV) \; + \; Tl(III) \longrightarrow \; 2\, V(V) \; + \; Tl(I)$$
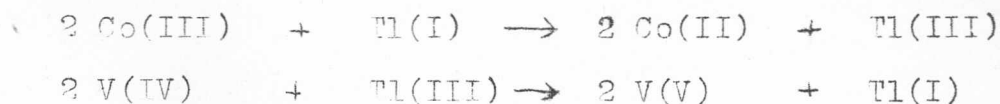
Harkness and Halpern (167) from a kinetic study of the reac-
tion

$$U(IV) \; + \; Tl(III) \; \overset{K}{\longrightarrow} \; U(VI) \; + \; Tl(I)$$
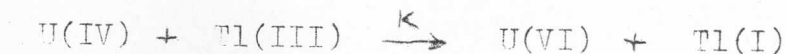
obtained a simple bimolecular rate law

$$R \; = \; k \; \left[U(IV)\right] \; \left[Tl(III)\right]$$

and this is consistent with either a single step two-electron as above or two successive one-electron transfer steps:

$$U(IV) + Tl(III) \xrightarrow{K} U(V) + Tl(II)$$

$$U(V) + Tl(II) \xrightarrow{Fast} U(VI) + Tl(I)$$
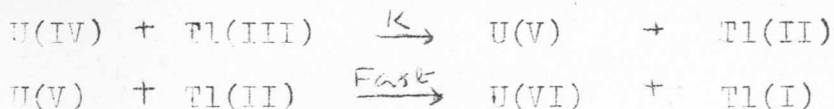
The intermediate oxidation state U(V) has been invoked earlier in the kinetic study of the reaction (162):

$$U(IV) + 2 Fe(III) \longrightarrow U(VI) + 2 Fe(II)$$

The intermediate oxidation state Tl(II) mechanistically invoked for the oxidation reduction reactions is also postulated for the Tl(I)--Tl(III) electron transfer discussed earlier.

Armstrong and Halpern (166) in their kinetic study of the oxidation of Hg(I) by Tl(III) in $HClO_4$ obtained the rate law

$$R = k \; [Hg_2^{2+}][Tl(III)] \, / \, [Hg(II)]$$

consistent with the following mechanism.

$$Hg_2^{2+} + ClO_4^- \rightleftharpoons Hg_2 ClO_4^+ \qquad \text{rapid equilibrium}$$

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0 \qquad \text{rapid equilibrium}$$

$$Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^+ \qquad \text{rapid equilibrium}$$

$$Hg^0 + TlOH^{2+} \longrightarrow Hg^{2+} + Tl^+ + OH^- \qquad \text{RATE DETERMI-NING}$$

$$H^+ + OH^- \rightleftharpoons H_2O$$
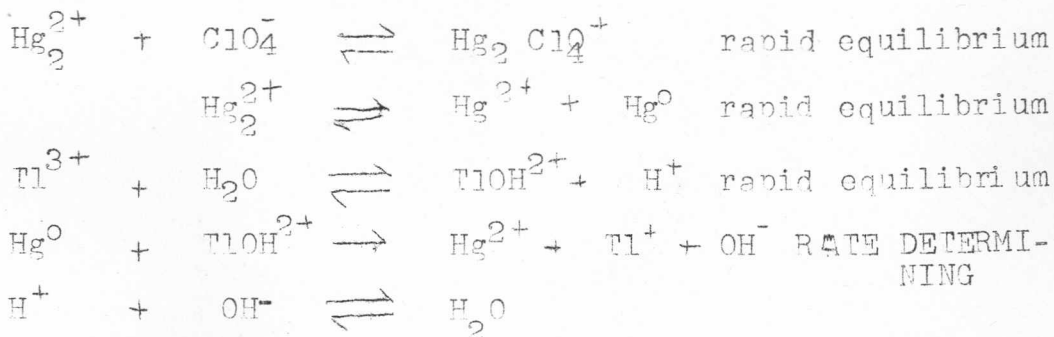
The Hg atoms invoked here reacting with the reactive $TlOH^{2+}$ species come from the dismutation of Hg_2^{2+} as shown above. This system is particularly interesting because Hg^0 is iso-electronic with Tl^+ and a comparison of the rate determining steps in (1) Hg(I)--Tl(III) and (2) Tl(I)--Tl(III) shows that neutral atoms of mercury react with $TlOH^{2+}$ much faster than the isoelectronic Tl^+ ion. Under comparable conditions the rate

constants for these two allied systems are several orders of
magnitude different.

(1) $Hg^0 + TlOH^{2+} \rightarrow Hg^{2+} + Tl^+ + OH^-$ (k = 1 x 10 M^{-1} sec.$^{-1}$

$\Delta s^{\ddagger} = +13 \pm 10$ e.u.)

(2) $Tl^+ + Tl*OH^{2+} \rightarrow Tl^{3+} + Tl*^+ + OH^-$ (k ranges between
2.5 x 10^{-5} -- 3.3 x 10^{-4}

M^{-1} sec. $\Delta S^{\ddagger} = -20$ e.u)
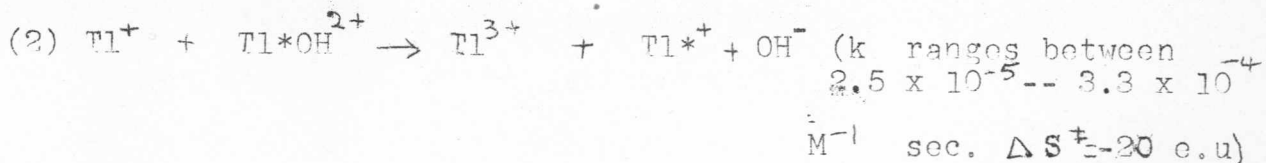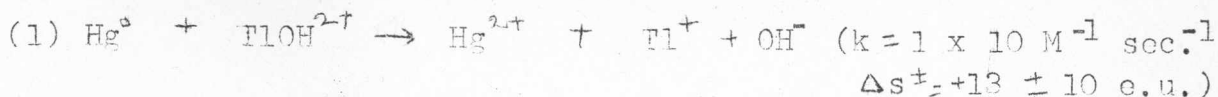
It is therefore obvious that Hg reacts 10^9 to 10^{10} times faster
with $TlOH^{2+}$ than Tl^+. This is explained in terms of the un-
usually high positive value for $\Delta S^{\ddagger}$ in (1).

<div align="center">URANIUM</div>

$$U \overset{1.80}{----} U^{3+} \overset{0.61}{----} U^{4+} \overset{0.62}{----} UO_2^+ \overset{-0.05}{----} UO_2^{3+}$$

$$-0.33$$
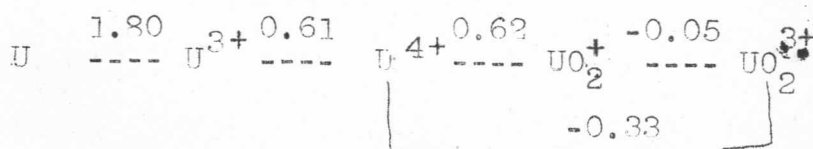
U(IV)--U(VI): Measurable exchange rates have been reported
in a number of earlier investigations (170) on this system in
aqueous solutions. Betts (171) studied the exchange in sul-
furic acid under thermal and photochemical conditions, and
King(172) in perchloric acid solutions. Rona (173) reports
the following rate law in hydrochloric acid medium at pH 0.85--
1.6

$$R = k \left[U(IV) \right]^2 \left[U(VI) \right] \left[H^+ \right]^{-3}$$

with an overall activation energy 33.4 kcal/mole. No evidence
for any chloride ion catalysis or specific salt effect was
reported. Because of various hydrolytic equilibria and the
disproportionation equilibrium involving U(V), the intermediate
oxidation state, the detailed mechanism is not, however, clear.
More recently masters and Schwartx (174) employed U(IV)--U*(VI)
exchange as a means to investigate the reaction

$$U(IV) + U(VI) \rightleftharpoons 2 U(V)$$
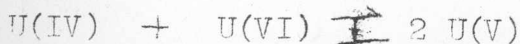
under conditions of chemical equilibrium in perchlorate media.
Specially prepared reactant solutions made from spectrochemica-
lly analyzed uranium oxide which had been depleted with respect
to the naturally occurring isotopes U-234 and U-235 were used.
Labelled U(VI) solutions were prepared (with an isotopic enrich-
ment 2%)using U-233.

Two parallel exchange paths, one occurring at a rate pro-
portional to $[U(IV)]$ with an activation energy of 38 kcal/mole
the other showing a higher order $[U(IV)]$ dependence with an
activation energy of 28 kcal/mole. Since the latter path is
analogous to Rona's (173) observations more attention was paid
to the elucidation of the first path of exchange by Masters and
Schwartz (174). The following rate law is consistent with their
data

$$ R = K \frac{[U^{4+}][UO_2^{2+}]}{[H^+]^3} = K \frac{[U(IV)][U(VI)]}{[H^+]^3 + K_h[H^+]^2} $$
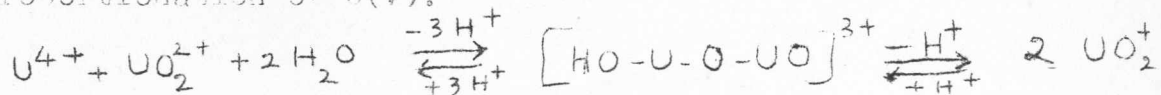
where $k = 4.14 \times 10^{-6}$ M^{-2} sec.$^{-1}$ at 39.4° and ionic strength
2.0 and

$$ K_h = \frac{[UOH^{3+}][H^+]}{[U^{4+}]} $$

(the value of K_h at 39.4° is 0.0560).

This study includes(a) U(IV) dependence, (b) U(VI) depen-
dence (c) Hydrogen ion dependence (d) Ionic strength dependence
and (e) Effect of Ultraviolet Irradiation. The reaction between

U^{4+} and UO_2^{2+} to form UO_2^+ is described to pass through the same activated complex identical with the one formed in the disproportionation of U(V).

$$U^{4+} + UO_2^{2+} + 2 H_2O \underset{+3 H^+}{\overset{-3 H^+}{\rightleftharpoons}} \left[HO-U-O-UO \right]^{3+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} 2\ UO_2^+$$

Amis and coworkers (175), (176), (177) (178) studied the U(IV)--U(VI) exchange in both water-acetone mixtures containing hydrochloric acid and in ethyleneglycol-water mixtures containing hydrochloric acid. Results of an earlier study of this exchange in water-alcohol mixtures by Mathews, Hefley and Amis (175) are shown in table 9 to illustrate the complexity of the kinetics of U(IV)--U(VI) electron transfer.

TABLE 9

U(IV)--U(VI) EXCHANGE IN WATER-ALCOHOL (175)

Percent Ethanol	Order in $\left[U(IV) \right]$	Order in $\left[U(VI) \right]$	Order in $\left[(H^+) \right]$
0	2.0	1.0	-3.0
30	0.93	1.4	-1.74
60	0.87	1.08	-0.97
90	2.89	0.10	-1.06
100	0	2.70	-1.26

The zero order in U(IV) in 100% ethanol obviously suggests that the hydrolytic species of this are not of much consequence in the course of this exchange.

Oxidation-reduction reactions: Newton and Rabideau (179) summarize several oxidation reactions of U(IV) with Fe^{3+}, $CeOH^{3+}$, PuO_2^{2+}, etc. Baker and Newton (180) recently reported the reaction between U(IV) and H_2O_2 with the following chain carriers.

$$U(IV) + H_2O_2 = U(V) + HO$$

$$U(V) + H_2O_2 = U(VI) + HO$$

$$U(IV) + HO = U(V) + H_2O$$

$$U(V) + HO = U(VI) + H_2O$$

$$HO + H_2O_2 = HO_2 + H_2O$$

$$U(IV) + HO_2 = U(V) + H_2O_2$$

$$U(V) + HO_2 = U(VI) + H_2O_2$$

$$HO + HO_2 = H_2O + O_2$$

$$U(V) + O_2 = U(VI) + HO_2$$
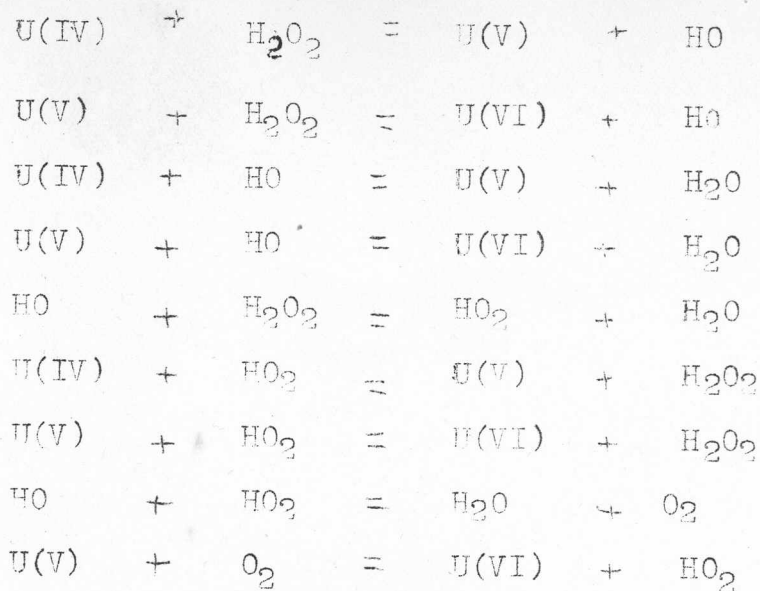
Some of the steps in the above scheme derive support from an independent kinetic study by Halpern and Smith (181) made earlier on the oxidation of U(IV) by O_2.

NEPTUNIUM

$$Np \xrightarrow{1.86} Np^{3+} \xrightarrow{-0.15} Np^{4+} \xrightarrow{-0.75} NpO_2^+ \xrightarrow{-1.15} NpO_2^{2+}$$

Np(IV)--Np(V): Sullivan, Cohen and Hindman (182) studied this exchange using Np-239 and their data fit the rates law

$$R = k_1 \left[NpO_2^+ \right]^2 \left[H^+ \right] + k_2 \left[Np^{4+} \right]^{1.5} \left[NpO_2^+ \right]^{0.5} \left[H^+ \right]^{-1}$$
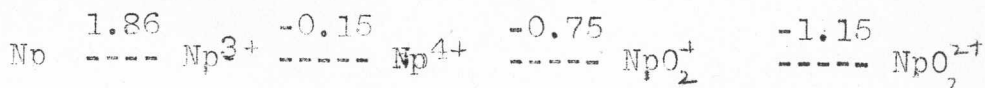
where

$$k_1 = 1.10 \times 10^{-5} \quad M^{-2} \quad sec^{-1} \quad at \quad 25^\circ \quad and$$

$$k_2 = 6.45 \times 10^8 \quad M \quad sec^{-1} \quad at \quad 25^\circ$$

The mechanism suggested for high acid range is

$$2 Np^*O_2^+ + H^+ \rightleftarrows [X^*]^{3+} \rightleftarrows Np^*O_2^{2+} + Np^*O_2H^+ \quad (DISPROPORTIONATION)$$

$$Np^*O_2H^+ + Np(OH)_2^{2+} \rightleftarrows Np O_2H^+ + Np^*(OH)_2^{2+}$$
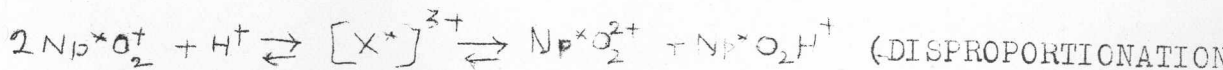
and for the low acid range

$$Np^{4+} + Np^*O_2^+ \rightleftarrows Np^*O_2^{2+} + Np^{3+}$$

$$Np^{4+} + 2 H_2O \rightleftarrows Np(OH)_2^{2+} + 2 H^+$$

$$Np(OH)_2^{2+} + Np^*O_2^{2+} \rightleftarrows [Y^*]^{4+} \rightleftarrows Np^*(OH)_2^{2+} + NpO_2^{2+}$$
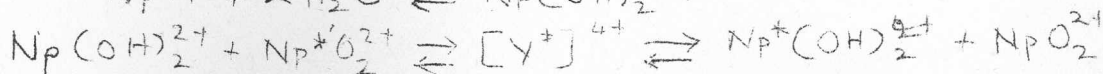
The existence of a disproportionation path via Np(V) also derives from an independent study by Hindman, Sullivan and Cohen (183) on the reaction

$$Np(IV) + Np(VI) \longrightarrow 2\,Np(V)$$

The disproportionation of the +5 state in the solution chemistry of the actinide elements, U(V), Np(V), Pu(V) and Am(V) has been shown to play an important role in the study of simple electron transfer reactions as well as oxidation-reduction reactions involving the actinide ions.

Np(V)--Np(VI): Cohen, Sullivan and Hindman (184) studied this exchange thoroughly in aqueous solutions, in presence of chloride and nitrate and in heavy water as solvent. In an extension of this study Cohen, Sullivan, Amis and Hindman, repeated [185] the experiments in ethyleneglycol-water and sucrose-water of varying composition and found that the electron transfer exchange to be independent of the composition and of the gross properties, dielectric constant, refractive index, viscosity of two mixed solvents.

In presence of chloride and in dilute acid solutions the rate law for Np(V)--Np(VI) exchange can be written

$$R = K_1 \left[NpO_2^+ \right] \left[NpO_2^{2+} \right] + K_2 \left[NpO_2^+ \right] \left[NpO_2^{2+} \right] \left[H^+ \right] + K_3 \left[NpO_2^+ \right] \left[NpO_2C\ell \right.$$

$$+ K_4 \left[NpO_2^+ \right] \left[NpO_2C\ell_2 \right]$$

where

$$k_1 = 73.5 \quad M^{-1} \quad sec^{-1} \text{ at } 4.5^\circ$$

$$k_2 = 15 \quad M^{-2} \quad sec^{-1} \text{ at } 4.5^\circ$$

$$k_3 = 330 \quad M^{-1} \quad sec^{-1} \text{ at } 4.8^\circ$$

$$K_4 = 160 \quad M^{-1} \quad sec^{-1} \text{ at } 4.8^\circ$$

Oxidation-reduction reactions: The reaction between U(IV)
and Np(VI) has been reported by Zielen, Sullivan and Hindman(186)
recently.   Since Np(VI) is a good oxidizing agent it should be
possible to study other oxidation-reduction reactions.

PLUTONIUM

$$Pu \xrightarrow{2.03} Pu^{3+} \xrightarrow{-0.97} Pu^{4+} \xrightarrow{-1.15} PuO_2^+ \xrightarrow{-0.93} PuO_2^{2+}$$
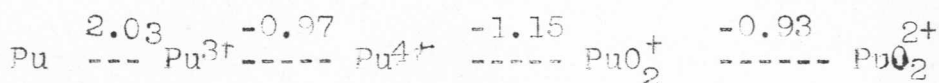
Pu(III)--Pu(IV):   Keenan (187) studied the kinetics of Pu(III
Pu(III)--Pu(IV) exchange using Pu-238 tracer and found the
following rate law:

$$R = k_1 \left[Pu^{3+}\right]\left[Pu^{4+}\right] + k_2 \left[Pu^{3+}\right]\left[PuOH^{3+}\right]$$

where

$$k_1 = 20 \ M^{-1} \ sec^{-1} \ at \ 25° \quad (Ea = 7.7 \ kcal/mole)$$
$$k_2 = 2.0 \times 10^{-4} \ M^{-1} \ sec^{-1} \ at \ 25° \ (Ea = 2.8 \ kcal/mole)$$

Keenan (187) suggests a OH^*group transfer as plausible mechanism
in the Pu(III)-Pu(IV) exchange rather than H-atom transfer.   No
work is done on the exchange between other oxidation states
except some studies on the disproportionation reaction of Pu(V)
by Rabideau(188).

MISCELLANEOUS SYSTEMS

In this section are included (1) those electron transfer
reactions whose kinetic details and complexities are not yet
known and (2) certain important anionic systems where mechanisms
like atom or group transfer are more likely than simple electron
transfer itself.   The grouping is therefore somewhat arbitrary.

+ 2 and +3 Oxidation states: Eichler and Wahl (39) in their study of certain fast electron-exchange reactions between large complex cations obtained the rates of electron transfer for $Os(dipy)_3^{2+}$ ---- $Os(dipy)_3^{3+}$ ($k > 10^5$ M^{-1} sec^{-1} at 0° and in 3 M H_2SO_4) by the isotopic exchange method using Os-185 and by the optical activity method. This study also includes net oxidation-reduction reactions involving several dipyridyl and o-phenanthroline complexes of Fe, Os, and Ru.

+3 and +4 Oxidation states: Sloth and Garner (189) studied the exchange of Ir-192 between $IrCl_6^{3-}$ and $IrCl_6^{2-}$ and obtained a second order rate constant (assuming the rate law:

$$R = k \left[IrCl_6^{3-} \right] \left[IrCl_6^{2-} \right] ?) \quad k > 83 \quad M^{-1} \quad sec^{-1} \text{ at } 0^\circ \text{ and in}$$
1 M HCl

+4 and +5 Oxidation states: Wolfgang (190) studied the exchange of Mo-99 between $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ and obtained a second order rate constant (assuming the rate law:

$$R = k \left[Mo(CN)_8^{4-} \right]\left[Mo(CN)_8^{3-} \right] \quad k > 10^3 \quad M^{-1} \quad sec^{-1} \text{ at } 2^\circ$$

and in solutions containing cyanide.

Goodenow and Garner (191) studied the exchange of W-185 between $W(CN)_8^{4-}$ and $W(CN)_8^{3-}$ and Weissman and Garner (192) followed the same exchange by the nuclear magnetic resonance method observing W-183 n.m.r. spectrum. In both cases assuming a rate law of the type

$$R = k \left[W(CN)_8^{4-} \right] \left[W(CN)_8^{3-} \right]$$

lower and upper limits were measured.

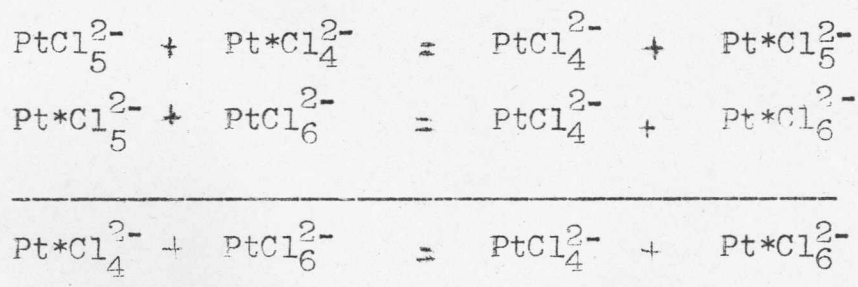|	Isotopic Exchange Method	Nuclear Magnetic Resonance Method
k (M^{-1} Sec^{-1})	$> 4 \times 10^4$	$\leq 4 \times 10^8$

It would be interesting to recall that the exchange of a metal ion in the cyanocomplexes is generally fast. Adamson et al (74) finds manganous

finds manganese exchange between $Mn*(CN)_6^{4-}$ and $Mn(CN)_6^{3-}$ fast.

+ 2 and +4 Oxidation states: Rich and Taube (193) in their detailed study of the chloride exchange with $PtCl_6^{2-}$ postulate a catalytic species of an unusual oxidation state of +3 for platinum in chloride media as $PtCl_5^{2-}$. They observed a slow exchange of Pt-191 between $PtCl_4^{2-}$ and $PtCl_6^{2-}$ which is accelerated by exposure to ultraviolet light. Assuming a rate law of the type

$$R = k \left[PtCl_4^{2-} \right] \left[PtCl_6^{2-} \right]^2$$

in 0.01 M HCl $25°$ Rich and Taube report values 1.9×10^{-2} M^{-1} sec.$^{-1}$ and 0.2 M^{-1} sec.$^{-1}$ for k in diffuse day light and on irradiation by ultraviolet light respectively. The following mechanism seem to explain the observed exchange of platinum.

$$PtCl_5^{2-} + Pt*Cl_4^{2-} = PtCl_4^{2-} + Pt*Cl_5^{2-}$$
$$Pt*Cl_5^{2-} + PtCl_6^{2-} = PtCl_4^{2-} + Pt*Cl_6^{2-}$$

$$\overline{Pt*Cl_4^{2-} + PtCl_6^{2-} = PtCl_4^{2-} + Pt*Cl_6^{2-}}$$

Iodine-Iodate Exchange: Myers and Kennedy (194) made a thorough investigation of this system which was reported by several workers earlier as slow. This is the first known system where activity coefficient data are introduced to account for the behaviour of the weak acid, HIO_3. The exchange rate is represented by

$$R = 2.1 \times 10^{-2} \left[\gamma_{HIO_3} \right]^{3.6} \left[I_2 \right]^{0.6} \left[H^+ \right]^{1.8} \left[IO_3^- \right]^{1.8}$$

where γ_{HIO_3} represents the activity coefficient of iodic

acid. It is assumed the exchange proceeds via iodide-iodate reaction

$$5 \; I^- + IO_3^- + 6 \; H^+ = 3 \; I_2 + 3 \; H_2O \qquad (k \sim 2 \times 10^{47})$$
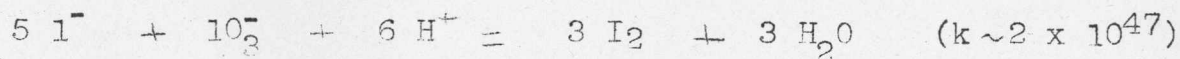
and the plausible mechanism suggested is based on transfer of two electrons between the ions IO_2^+ and I^- within the activated complex which also contains H^+ and any negative ion (like ClO_4^-, NO_3^- or IO_3^-) A^-.
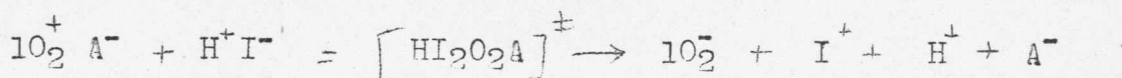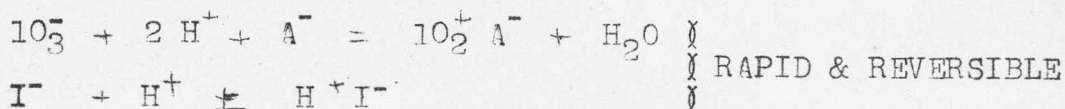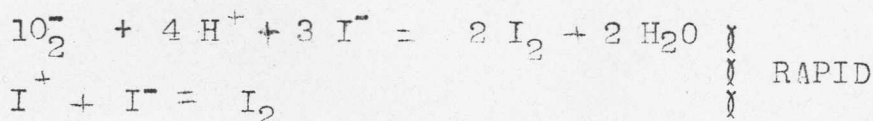
$$IO_3^- + 2 \; H^+ + A^- = IO_2^+ A^- + H_2O \quad \Big\}$$
$$I^- + H^+ \rightleftharpoons H^+ I^- \qquad\qquad\qquad \Big\} \text{ RAPID \& REVERSIBLE}$$

$$IO_2^+ A^- + H^+ I^- = \left[HI_2O_2A \right]^{\pm} \longrightarrow IO_2^- + I^+ + H^+ + A^-$$

RATE DETERMINING STEP

$$IO_2^- + 4 \; H^+ + 3 \; I^- = 2 \; I_2 + 2 \; H_2O \quad \Big\}$$
$$I^+ + I^- = I_2 \qquad\qquad\qquad\qquad \Big\} \text{ RAPID}$$

System	Isotope	Half life	Rate Law	Specific* rate const.	Conditions medium, temp., & ionic strength	Ref.
M(I)---M(II)						
a. Cu(I)-Cu(II)	$Cu^{63/65}$	stable	$k(Cu^I)(Cu^{II})$	0.5×10^8	12 f HCl	(44)
b. Ag(I)-Ag(II)	Ag^{110m}	253 d	$k(Ag^{II})2$	10^2	6 f $HClO_4$, 0°	(30)
Hg(I)-Hg(II)	Hg^{203}	48 d	$k(Hg^I)(Hg^{II})$	>1000 5.7×10^3	$HClO_4$, 0°, 0.125 CN-	(126)
M(II)---M(III)						
Ti(II)-Ti(III)	Ti^{44}	10^3 y	-----	-----	-----	
V(II)-V(III)	V^{48}	16 d	$k(V^{2+})(V^{3+})+k'(V^{2+})(VOH^{2+})$	1.0×10^{-2} ~ 1.8	1 f $HClO_4$, 25° 2.00	(27)
Cr(II)-Cr(III)	Cr^{51}	28 d	$k(Cr^{2+})(Cr^{3+})+ (Cr^{2+})(CrOH^{2+})$	$<2 \times 10^{-5}$ ~ 0.7	1 f $HClO_4$, 25° 1.0	(57)
Mn(II)-Mn(III)	Mn^{54}	300 d	$k(Mn^{II})(Mn^{III})$?	>4	$\sim$1 f $HClO_4$ R.T.	(72)
Fe(II)-Fe(III)	Fe^{55}	2.6 y	$k(Fe^{2+})(Fe^{3+})+k'(Fe^{2+})(FeOH^{2+})$	4.2 3200	0.55 f $HClO_4$ 25°, 0.55	(81)
Co(II)-Co(III)	$Co^{60}-$	5.2 y	$(Co^{II})(Co^{III})\{k +k/(H^+)\}$	0.83;0.14	1 f $HClO_4$ 3.2°,1.0x	(100)
Ru(II)-Ru(III)	Ru^{103}	40 d	-----	-----	-----	
Rh(II)-Rh(III)	Rh^{102}	220 d	-----	-----	-----	
Sm(II)-Sm(III)	Sm^{145}	340 d	-----	-----	-----	
Eu(II)-Eu(III)	Eu^{152}	13 y	$(Eu^{II})(Eu^{III})\ k+k'(Cl^-)$	$<1 \times 10^{-4}$ 3.7×10^{-4}	1 f HCl,25°, 2.00	

				K_c		
Yb(II)-Yb(II)	Yb^{169}	31 d	-----		-----	
b.Os(II)-Os(III)	Os^{185}	93 d	k(Os-dipy$_3^{2+}$)(Os-dipy$_3^{3+}$) ?	>10^5	2,2'-dipyridyl complexes, 0°	(39)
M(III)----M(IV)						
Ti(III)-Ti(IV)	Ti^{44}	10^3 y	-----	----	-----	
V(III)-V(IV)	V^{48}	16 d	k(V^{III})(V^{IV})(H$^+$)$^{-1}$	2.6x10^{-3}	0.5 f HClO$_4$, 25°, 2.5	(49)
Ce(III)...(IV)	Ce^{144}	285 d	k(Ce^{III})(Ce^{IV})+k'(Ce^{III})(Ce^{IV})(H$^+$)$^{-2}$			
			k(Ce^{III})(Ce^{IV})+k'(Ce^{III})(Ce^{IV})2	1.4,16.6 Complex dep. on H$^+$	6 f HNO$_3$,0°	(130)
			(Ce^{IV})2		6 f HClO$_4$,0°	(132)
Pr(III)-Pr(IV)	Pr^{143}	14 d	-----	----	----	
Tb(III)-Tb(IV)	Tb^{160}	73 d	-----	----	----	
Ir(III)-Ir(IV)	Ir^{192}	74 d	k(IrCl$_6^{3-}$)(IrCl$_6^{2-}$)	> 83	1 f HCl, 1°	(189)
U(III)-U(IV)	U^{233}	1.62 x 10^5 y	-----	----	----	
Np(III)-Np(IV)	Np^{239}	2.35 d	----	----	----	
Pu(III)-Pu(IV)	Pu^{238}	86.4 y	k(Pu^{3+})(Pu^{4+})+k'(Pu^{3+})(PuOH^{3+})	20, 2.0 x 10^{-4}	0.5 f HClO$_4$, 25°, 2.0	(187)
M(IV)--M(V)						
V(IV)-V(V)	V^{48}	16 d	k(V^{IV})(V^{V})2 ?	1.5 x 10^6	6.5 f HCl	(46)
Mo(IV)-Mo(V)	Mo^{99}	66 h	k(Mo(CN)$_8^{4-}$)(Mo(CN)$_8^{3-}$) ?	>10^3	CN$^-$ 2°	(190)

Reaction	Isotope	Half-life	Rate law	Rate constant	Conditions	Ref.
a. W(IV)-W(V)	W185 W183	73 d stable	$k(W(CN)_8^{4-})(W(CN)_8^{3-})$?	$> 4 \times 10^4$ $< 4 \times 10^8$	CN^-, 2°	(191) (192)
Np(IV)-Np(V)	Np239	2.35 d	$k(Np(2\cdot))^2(H^+)+k'(Np4+)1.5 (NpO_2^{\pm})^{0.5}(H^+)^{-2}$	1.10×10^{-5} 6.45×10^{-8}	0.04 f HClO$_4$, 25°, 1.2	(182)
M(V)---M(VI)						
Np(V)-Np(VI)	Np239	2.35 d	$k(NpO_2^+)(NpO_2^{2+})+$ $k(NpO_2^+)(NpO_2^{2+})(H^+)$	73.5 15	1 f HClO$_4$, 4.5° 3.0; 25°, 1.2	(184)
M(VI)---M(VII)						
b. Mn(VI)-Mn(VII)	Mn54	300 d	$k(MnO_4^{2-})(MnO_4^-)$	710	0.16 f NaOH, 0°	(29)
M(I) -- (M(III)						
Tl(I)-Tl(III)	Tl204	3.5 y	$k(Tl^+)(Tl^{3+})+k'(Tl^+)(TlOH)^{2+}$	0.154, 1.22	0.8 f HClO$_4$, 25°, 3.68	(145)
M(II)---M(IV)						
Sn(II)--Sb(IV)	Sn113	119 d	$k(Sn^{II})(Sn^{IV})$	6.3×10^{-3} 6.2×10^{-5}	9 f HCl, 25° C_2H_5OH, 25°	(134) (135)
Pb(II)-Pb(IV)	Pb212	10.6 h	$k(Pb(OAc)_2)(Pb(OAc)_2)$?	0.4% ex. in $\sim$ 4 hrs.	17 f HOAc, 80°	(138) (139)
Pt(II)-Pt(IV)	Pt191	3.0 d	$k(PtCl_4^{2-})(PtCl_8^{2-})$?	1.9×10^{-2} 0.2	0.01 f HCl, 25° UV light	(193)
M(III)---M(V)						
Nb(III)-Nb(V)	Nb91m	62 d	----	-----	-----	

sb(III)--Sb(V)	Sb^{124}	60	d $k(Sb^{III})^{0.6}(Sb^{V})^{1.1}(H^{+})^{4}(Cl^{-})^{9}$	2.4×10^{-14}	5 f HCl, 25°	(140)

M(IV)----M(VI)

U(IV)_U(VI)	U^{233}	1.62×10^{5} y	$k(U^{IV})^{2}(U^{VI})(H^{+})^{-1/3}$	2.7×10^{-3}	HCl, pH 0.85-1,6, 25° ~ 1.0	(173)

M(III)----M(VI)

Cr(III)-Cr(VI)	Cr^{51}	28	d $k(Cr^{III})(Cr_{2}O_{7}^{2-})$? $\left\{ k(H^{+})^{-2} + k^{1} \right\} (Cr(H_{2}O)_{6}^{3+})^{4/3}(H_{2}O_{4})^{2/3}$	$\sim 9 \times 10^{-6}$ 6.6×10^{-7} 1.4×10^{-5}	0.05 f $HClO_{4}$, 45^{o}(63) 94.8^{o}	(62)

* Units of the specific rate constant are not the same where a simple second order rate law is not indicated.

a. NMR method used; b. Rapid-mixer used.

E. Theories of Electron Transfer:

Electron transfer theories for reactions in solution have been mostly qualitative until recently. During the last ten years, however, there has been such an advancement in techniques and in general increased attention paid to the study of electron transfer exchange reactions that we now have quantitative theories to explain and predict rates in a given system. The following chronological survey gives an idea of the development of the theories of electron transfer in solution.

1933	Shaffer	"Equi-Valence Change" hypothesis
1934	Weiss	"Coulombic Repulsion hypothesis'
1936	Gorin	"Coulombic Repulsion" hypothesis
1937	Michaelis	"One-step electron transfers
1947	Remick	Developed Shaffer's hypothesis
1948	Duke	Developed Gorin-Weiss hypothesis
1951	Myers & Prestwood	List all factors governing electron transfer reactions
1952	Adamson	Magnetic susceptibility sum-difference product correlation with exchange half-times
1952	Libby	Application of Franck-Condon Principle
1953	Hindman, Cohen and Sullvian	Correlation of partial molal entropies
1954	Weiss	Electron tunnelling theory
1954	Marcus, Zwolinsky and Eyring	Electron tunnelling mechanism developed for electron exchange reactions.
1954	Taube & Myers	Bridge activated complexes
1956	Marcus (R.A.)	Quantitative theory of electron transfer formulated

1956	Orgel	Application of ligand field theory
1957	Marcus (R.A.)	Quantitative theory of electrochemical electron transfers formulated and free from arbitrary assumptions
1959	Marcus (R.A.)	Theory well-developed, applied for MnO_4^{2-}/MnO_4^- and $Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}$ systems.
1939	Laidler	Electron transfer theory based on the theory of diffusion controlled reactions.
1960	Marcus (R.A.)	Marcus theory developed for treating solvent ligand and inert salt effects.
1960	Halpern & Orgel	Theory of electron transfer between metal ions in bridged systems.

Shaffer-Remick "Equi-Valence" Hypothesis: The equivalence
change hypothesis proposed by Shaffer (195) in 1933 and modified
by Remick (196) in 1947 predicts that oxidizing and reducing
agents which gain or lose the same number of electrons should
react rapidly.   More recently Halpern (81) made a thorough exa-
mination of the equivalence principle and found only limited
validity when applied to certain oxidation reduction and electron
transfer reactions--(1) oxidation of metal ions by oxygen re
(2) reduction metal ions by hydrogen and (3) electron transfer
between transfer between metal ions.

Gorin-Weiss-Duke "Coulombic Repulsion" Hypothesis:

The coulombic repulsion hypothesis was first suggested by
Gorin (197) and Weiss (198) and later by Duke (48). It predicts
that if the reactants have like charges, coulombic repulsion
should make the reaction go slow. The slowness of the Tl(I)--
Tl(III) and Ce(III)-Ce(IV) are some examples that are consistent

with the theory. Duke (48) discusses this hypothesis qualita-
tively and concludes that the charge on the ions may well be an
important factor in predicting the course of the reaction.

Michaelis' Principle of "Compulsory Univalent Oxidation Steps"
Michaelis (199) proposed that electron transfer reactions must
proceed in one-electron steps. This is partly true when we
apply totthe transitional metals which generally ehi bit oxida-
tion states that differ by one electron and react with each
other by 1-equivalent steps. In recent years the detection of
unusual oxidation states as intermediates in certain reactions
lends support to this principle in a way. For example, Sn(III),
Fe(IV), Tl(II), Cr(IV), Cr(V), Mn(V), U(V), Cl(VI) and some
others are highly probable and these perhaps account for the
rapid reaction rates. At the same time there are many two-equi-
valent redox reactions which proceed in one step through the
transfer of a H^--ion or O-atom.

Meyers and Prestwood (11): Summarize all the factors gover-
ning the rates of electron-transfer reactions as follows:
(1) the number of electrons transferred (2) the binding energy
and the type of electron transferred (3) coulombic attraction or
repulsion (4) structure and composition of the reactants and (5)
environment of the reactants.

This concludes to some extent much of the earlier think-
ing on the theories of electron transfers in solution and all
of them naturally are qualitative in their scope. About this
time a symposium on Electron Transfer and Isotopic Reactions
held in 1952 at the University of Notre Dame stimulated interest
in developing semi-quantitative and near-quantitative theories

of electron transfer in solutions and we shall now examine some
of the attempted correlations between the exchange half-times
and certain physical parameters.

Adamson (200)   Attempted a correlation between the exchange
half-times and the magnetic susceptibilities of the exchanging
ions.   To illustrate this correlation actually the product of the
sum and differences of the magnetic susceptibilities is shown in
table 11. along with the half-times for exchange reported.

TABLE 11

EXCHANGE HALF-TIMES VS MAGNETIC SUSCEPTIBILITIES

Electron Exchange Pair	Magnetic Susceptibilities		(Sum x difference)	Order of half-time
$Eu(II)--Eu(III)$	8	3.5	52	1 hr
$Co(en)_3^{2+}-- Co(en)_3^{3+}$	4.9	0	24	2 -- 50 hr
$Co(NH_3)_6^{2+}-- Co(NH_3)_6^{3+}$	4.9	0	24	>80 d
$Mn(II)--Mn(III)$	5.9	5.0	10	< 1 min
$Ce(III)--Ce(IV)$	3.5	0	6	10 min
$Fe(II)--Fe(III)$	5.2	5.7	6	20 sec
$V(II)--V(III)$	3.9	2.8	7	5 5 min
$Os(bipy)_3^{2+}-- Os(bipy)_3^{3+}$	(0)	(1.7)	3	seconds
$Fe(CN)_6^{4-}-- Fe(CN)_6^{3-}$	0	1.7	3	Fast
$MnO_4^{2-}-- MnO_4^{-}$	1.7	0	3	Fast
$Co(TPP)--Co(Tpp)^{+}$	1.7	0	3	Fast

TPPP   tetraphenylporphine

It is obvious that the larger the sum-difference product of the susceptibilities the slower the exchange. This prediction seems to hold good in the case of observed fast electron transfers between the Co(II)- and Co(III)-TPP complexes in benzene solution. Dorough and Dodson (201) noticed fast exchange between Co(TPP) and Co(TPP)$^+$. Cl$^-$ with $t_\frac{1}{2} \sim 500$ sec. Krishnamurty and Dorough (202) found that the exchange between Co(TPP) and Co(TPP)$^+$ Br$^-$ even faster with $t_\frac{1}{2} \sim 50$ sec. This observed fast exchange is in keeping with the low susceptibilities product reported.

Another prediction is the net oxidation-reduction between the diamagnetic Hg(II) and the paramagnetic Fe(II) which goes slow eventhough simple electron transfers between Fe(II) and Fe(III) and between Hg(I) and Hg(II) are known to be fast.

$$Hg(II) + Fe(II) = Hg(I) + Fe(III)$$

Adamson clearly confirmed this observation by following the reaction spectrophotometrically at 270 mμ at which wavelength Fe(III) has a large absorbance. The half-times found were of the the order of several days.

The hitherto uninvestigated Sm(II)-Sm(III) and Yb(II)-- Yb(III) systems might prove extremely interesting since their magnetic susceptibility sum and difference product (Sm: 9.3; Yb: 21) seem to suggest exchange half-times comparable to those of V(II)--V(III) and Eu(II)--Eu(III) exchange systems respectively Not even preliminary work has been done on either Sm(II)--Sm(III) exchange or Yb(II)--Yb(III) exchange and it would be interesting to study these 4-f electron transfer processes.

Hindman, Cohen and Sullivan (203) have shown interesting correlation between the exchange rates of electron transfer reactions and the difference in partial molal entropies of the exchanging ions in aqueous solution $\Delta \bar{S}^o = \left| \bar{S}_i^o -- \bar{S}_j^o \right|$. For small values of $\Delta \bar{S}^o$ rapid exchange seem to be the case. Small values of $\Delta \bar{S}^o$, however, indicate great deal of similarity in structure of the exchanging species hence minimun Frank-Condon restrictions (204), (205), for electron transfer. Application of Franck-Condon principle to the case of electron transfer reactions is discussed later.

The exchange between NpO_2^+ and NpO_2^{2+} ions is fast, k being $\geqslant 810$ M^{-1} sec.$^{-1}$ and the small value for $\Delta \bar{S}^o = 8$ e.u seem to explain the correlation. Another example is the slowness of the exchange between Np^{4+} and NpO_2^+, k being $\sim 10^{-7}$ M^{-1} sec.$^{-1}$ and $\Delta \bar{S}^o = 80$ e.u. indicating some type of complex exchange mechanism other than simple electron transfer.

Libby's Theory of Electron Transfer: Libby(204) in 1952 developed a theory of electron transfer applicable to solutions by way of Franck-Condon principle. The theory specifies that the electron merely jumps from reductant to oxidant and is based on calculated probabilities of 'electron-jump' as a function of distance between the oxidant and reductant. Libby divides the problem into two parts:

(1) quantum mechanics of the electron exchange itself H_2^+, hydrogen molecule ion as model (in vacuum), and

(2) the application of Franck-Condon principle to the case of aqueous solutions.

Libby calculates the 1s exchange frequencies for H_2^+ and concludes that even the 1s wave function gives high rates of .

exchange at distance of 10 Å and larger. Repeating the calculations for the generalized H_2^+ in which the two positive nuclei have charges of + Ze, the exchange of 3d electrons was shown to be even more frequent at large internuclear distances. The following diagram (Fig.10) shows Libby's plot of exchange frequency vs internuclear distance calculated for the 1s and $3d_{z2}$ wave functions.

Fig (10) EXCHANGE FREQUANCY Vs INTERNUCLEAR DISTANCE.
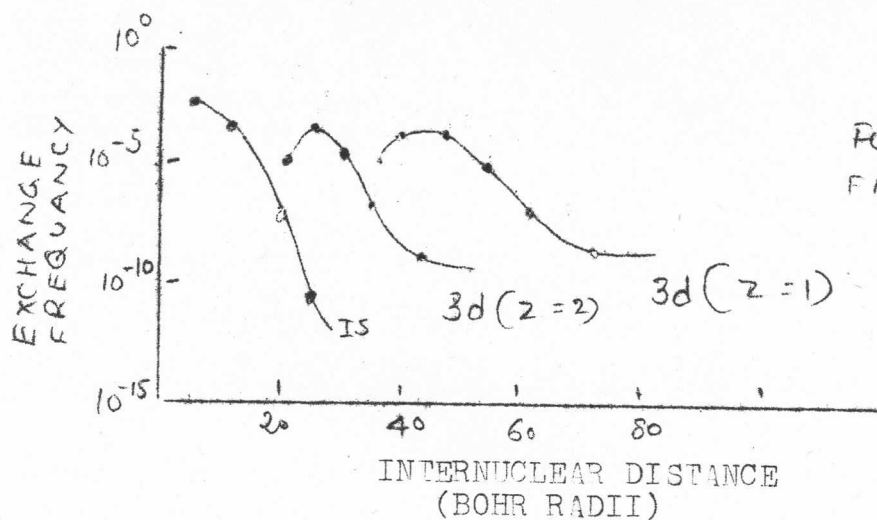
Simple electron transfer process therefore cannot be the slow step and Libby finds alternative explanation to account for the slowness observed in certain electron transfer reactions in aqueous solution by considering the changes in the environment of each reactant. Libby concludes that large symmetrical complex ions like $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ or MnO_4^{2-} and MnO_4^{-} should exchange rapidly as these ions are surrounded by fixed coordination sphere Experimentally this prediction is borne out, however.

Franck-Condon principle states that during an electronic transition in a molecule the nuclei do not significantly alter their relative positions or velocities. This principle finds wide application in spectroscopy and is invoked here to explain

the problem of electron transfer in aqueous solution. When an
electron jumps from the reductant to the oxidant instantaneously,
the transit time is smaller and atoms do not have sufficient time
to change their positions. The coordination spheres therefore
must adjust themselves to their new environments and this cons-
titutes the energy barrier to the electron transfer process.
This has been illustrated in the case of Fe^{2+}_{aq} and Fe^{3+}_{aq}
exchange where the initial ferrous environment is occupied by a
ferric ion after the electron jump and the ferric environment
even ferrous ion. The extra energy of hydration stored at the
ferrous environment eventually leaks to the ferric environment
by a slow collisional process. However, the differences in the
instantaneous rate of electron jump and the slow rate of hydra-
tion energy moments constitute the socalled activation energy
for electron transfer. It is also assumed that the electron has
no time for solvation. In the case of small cations with water
molecules in their first coordination sphere there exists a
large energy barrier resulting in slow rates. On the other
hand large complex ions like MnO_4^{2-} and MnO_4^{-} are so symmetric
in their structure no prior rearrangement is necessary to effect
the electron transfer process and hence exchange rapidly. The
part played by small anions like Cl^{-} in accelerating the rate of
electron transfer in M^{2+} -- M^{3+} systems is explained in terms
of symmetrizing structures, matching energies and minimizing
coulombic repulsions prior to electron transfer process.

Marcus (R.J.), Zwolinsky and Eyring (206): Postulate an
electron tunnelling hypothesis for electron transfer reactions in
aqueous solution. They assume a form of potential energy
barrier over which the electron must pass from the reductant
to the oxidant. The possibility of leakage through the barrier
in a non-classical sense is a well-known quantum mechanical
phenomenon and Mott and Sneddon (207) state electrons penetrate
freely through potential barriers about ten atomic diameters
thick and few electron-volts high. It is therefore clear that
electron transfer can take place at distances considerably greater
than would correspond to actual collision of the reactants. The
problem is reduced to calculation of the critical intercationic
tunnelling distance in the activated complex and is discussed by
Marcus(R.J.), Zwolinsky and Eyring (206).

In their extensive theoretical analysis (1) the probability of an
electronic transition is considered as a transmission coefficient
(k_e) in the expression for the specific rate constant and (2)
the free energy of activation ($\Delta F^{\dagger}$) for the electron exchange
reaction is considered to be a sum of the free energy of rearrange-
ment of the hydration. and coordination shells of the cations,
and electrostatic repulsion energy.

Using a triangular potential barrier ( ) an approximate
expression for the transmission coefficient is obtained as

$$K_e = \exp \left[- \frac{8\pi}{3 h} \delta_{ab} \left(2m (V - W) \right)^{\frac{1}{2}} \right]$$

where

V = height of the electron barrier

W = kinetic energy of the tunnelling electron

r_{ab} = tunnelling distance

m = electron mass

h = planck's constant

The terms V and W are independently considered in the theoretical treatment and are given by the following expressions:

$$V = e^2 \; Z*/r_0 \quad - \quad e^2 \; f(n)/D \; r_{ab}$$

$$W = e^2 \; Z*/2 \; r_0$$

The expression for the transmission coefficient, based on the above approximations can now be written as

$$K_e = \exp \left\{ -\frac{8\pi}{3h} r_{ab} \left[2 \, me^2 \left(\frac{Z}{2 \, r_0} - \frac{f(n)}{D \, r_{ab}} \right) \right]^{1/2} \right\}$$

According to the transition state theory ( ) the specific rate constant is given by

$$K = K_e \, KT/h. \; \exp(-\Delta F /RT)$$

Substituting K_e in this equation the specific rate constant for the electron exchange reaction is therefore

$$K = \frac{KT}{h} \exp \left\{ -\frac{8\pi}{3h} \, r_{ab} \left[2 \, me^2 \left(\frac{Z}{2 \, r_0} - \frac{f(n)}{D \, r_{ab}} \right) \right] - \frac{\Delta F^{\ddagger}_r}{RT} - \frac{e^2 \, n_a \, n_b}{RT \, D \, r_{ab}} \right\}$$

The symbols used in obtaining the above expressions have the following significance.

k	specific rate constant
k	Boltzmann constant
h	Planck's constant
r_{ab}	tunnelling distance
m	electron mass
e	electronic charge
Z^*	positive charge on the central atom of the reductant
r_o	radius of electronic orbit
f(n)	$n_a \left[(1+\gamma)^2 \right] -- n_b \right]$
	where $\gamma^2 = n_b/n_a$
n_a	charge on cation 'a'
n_b	charge on cation 'b'
D	dielectric constant
$\Delta F_r^{\neq}$	reorganization free energy of activation
R	gas constant
T	absolute temperature

This formulation of the specific rate constant expresses compe-
tition between the two mechanisms--(1) the "easy" path of low
repulsive energy leading to larger r_{ab} and (2) the "hard" path
of closest approach i.e. $K_e \longrightarrow 1$. At some definite value of r_{ab}
these two counter-balance each other and there will be a critical
intercationic distance in the activated state at which the rate
will be maximum. This distance denoted by r^*_{ab} is derived by
Eyring et al from the specific rate constant expression as

$$r^*_{ab} = \sqrt{\frac{3 e^2 n_a n_b h r_o^{\frac{1}{2}}}{8 \pi e K D T (mZ^*)^{\frac{1}{2}}}}$$

Having derived the optimum tunnelling distance the authors calculate the free energy of activation as a contribution of three terms

$$\Delta F^{\ddagger} = -\underline{R}T \ln K_e + \Delta F^{\ddagger}_{rep} + \Delta F^{\ddagger}_r$$

where $\Delta F^{\ddagger}_{rep}$ is the coulombic repulsion term and $\Delta F^{\ddagger}_r$ the solvent reorganization term. Data are presented for various systems in table 12. However, it must be pointed out the authors used a value of 8.1 kcal/mole for $\Delta F^{\ddagger}_r$ obtained from consideration of Fe^2 -- Fe^3 exchange data although a priori calculation of this term would be made the theory complete. Sheppard and Wahl(29) report that the electron tunnelling hypothesis is not a reasonable model for MnO_4^{2-} -- MnO_4^{-} exchange.

TABLE 12

COMPARISON OF ELECTRON TUNNELLING MODEL WITH EXPERIMENTAL DATA

System	r^*_{ab}, Å	$-\underline{R}T \ln K_e$	$\Delta F^{\ddagger}_{rep}$	$\Delta F^{\ddagger}_r$	$\Delta F^{\ddagger}_{total}$	$\Delta F^{\ddagger}_{obsd}$
$Co(en)_3^{2+}$ -- $Co(en)_3^{3+}$	5.9	4.38	4.32	8.1	16.8	23.5
Tl^+ -- $TlOH^{2+}$	3.3	2.63	2.57	8.1	13.3	23.9
VOH^{2+} -- VO^{2+}	4.4	4.00	3.86	8.1	16.0	17.2
Fe^{2+} -- Fe^{3+}	6.0	4.37	4.25	8.1	16.7	16.7
Fe^{2+} -- $FeOH^{2+}$	4.9	3.57	3.47	8.1	15.1	12.2
Fe^{2+} -- $FeCl^{2+}$	4.9	3.57	3.47	8.1	15.1	15.3
Fe^{2+} -- $FeCl_2^+$	3.4	2.48	2.50	8.1	13.1	15.1
Ce^{3+} -- Ce^{4+}	9.3	5.52	5.48	8.1	19.1	18.0
MnO_4^{2-} -- MnO_4^- ($Z^* = 6$)	2.6	2.9	2.9	6.6	12.4	12.4
MnO_4^{2-} -- MnO_4^- ($Z^* = 3$)	3.1	2.5	2.4	7.5	12.4	12.4
MnO_4^{2-} -- MnO_4^- ($Z^* = 1$)	4.0	1.8	1.9	8.7	12.4	12.4
Fe^{2+} -- Fe^{3+}	6.0	4.4	3.8	8.5	16.7	16.7

All energy values are in kcal/mole and D = 78 in all cases except the last four rows where it is 88.
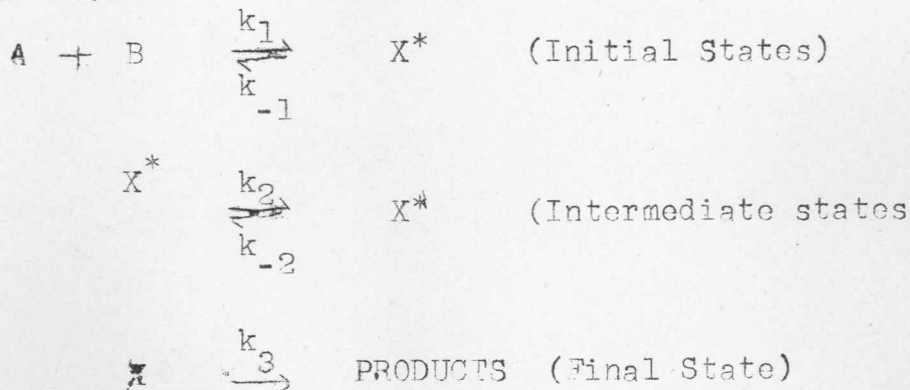
Data taken from Marcus (R.J.), Zwolinsky and Eyring (206), and Sheppard and Wahl (29).

Marcus Theory of Electron Transfer:

Marcus (208) formulated a quantiative theory of electron transfers in solution for the first time free from "arbitrary assumptions" and "adjustable parameters" to make a priori calculation of the free energy of activation $\Delta F^{\pm}$ from first principles in the case of simple electron transfer reactions. In most chemical reactions, appreciable changes in various inter-atomic distances and bond angles occur as a result of collisions and passing through a 'critical collision' or an 'activated complex' corresponding to the hump in the potential energy diagram for the reaction. A detailed knowledge of this activated complex enables calculation of the reaction rate. When such a reaction occurs very often there is a transfer of atoms, radicals, groups or even ferrying of a whole molecule resulting in a case of strong interaction of the electronic structures in the activated complex or transition state. Thus considerable spatial overlap of the electronic orbitals would result before a chemically significant reaction takes place via an activated complex. However, there are reactions, for example, the electron transfer type where the transfer merely involves an electron between the reactants. Only a slight overlap of the electronic orbitals is necessary to effect this process. Marcus theory therefore is developed primarily for such cases where there is only weak interaction that may be sufficient to electronically couple the the two ions or molecules and allow electron transfer to take place.

In the formulation of the theory two assumptions are made in addition to the special case of weak interaction or small over- lap of the electronic orbitals in the activated complex. (1) The reactants are treated as rigid spheres inside which no change in atomic configuration takes place during the reaction. In the case of a metal ion its coordination shell also is included for consideration as a rigid sphere whose radius will not be eugal to sum of the crystallographic radius of the bare ion and the dia- meter of water molecule (or any ligand). The surrounding medium of the rigid sphere is treated as a continuous unsaturated di- electric the reorganization of which contribute to the free energy of reorganization, $\Delta F_r.^{\ddagger}$.(2) The distance over which the electron jumps is taken as the distance of closest approach of the rigid spheres. In other words, in the case of a reaction like M_{aq}^{++} -- M_{aq}^{+++} his distance is equal to the sum of the crystallographic radii of the bare reactant ions plus twice the diameter of a water molecule.

Kinetic Formulation: The following reaction scheme is written assuming two successive intermediate states X^* and X, which have the same atomic configurations but different elec- tronic configurations.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^* \qquad \text{(Initial States)}$$

$$X^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X^* \qquad \text{(Intermediate states}$$

$$X \xrightarrow{k_3} \text{PRODUCTS} \quad \text{(Final State)}$$

The formulation of twosuccessive intermediate states in a way is in accordance with the Frnak-Condon principle. Electronic motion is so rapid that the solvent molecules lag behind and so the reaction has to proceed via two successive intermediate states of which X^* is closer to the reactant configuration and X to the product configuration. The overall rate of the reaction is written as

$$\text{Rate} = k_{bi} \; C_A \; C_B = k_3 \; C_X$$

where k_{bi} , C_a , C_b are the observed rate constant, the concentration of A and the concentration of B respectively. The rate is also given by $k_3 C_X$ where k_3 is the rate constant for the last step and C_X the concentration of X.

Applying the steady-state approxiamtions for the intermediate states X^* and X we have

$$\frac{dC_{X^*}}{dt} = 0 \qquad k_1 C_A C_B - (k_{-1} + k_2) C_{X^*} + k_{-2} C_X$$

$$\frac{dC_X}{dt} = 0 = k_2 C_{X^*} - (k_{-2} + k_3) C_X$$

Substituting for C_X in the overall rate equation k_{bi} is expressed as

$$k_{bi} = \frac{k_1 k_2 k_3}{(k_{-1} k_{-2} + k_{-1} k_3 + k_2 k_3)}$$

$$= \frac{k_1}{1 + (1 + k_{-2}/k_3) k_{-1}/k_2}$$

Marcus makes a thorough examination of the various rate constant

estimating each one and finds that k_{-1} is essentially equal to k_2

and k_2 the same as k_{-2}. Therefore, when k_2 and k_{-1} are of

the same order of magnitude it can be shown (neglecting a factor

of about two)

$$k_{bi} \cong k_1$$

and k_1 was shown earlier as equal to $Z \exp(-\Delta F^*/RT)$, where the

second order rate constant k_1 is in units of c.c. $mole^{-1} sec^{-1}$

and Z is the collision number in solution given as 10^{16} c.c.

$mole^{-1} sec.^{-1}$ at room temperature. ΔF^* represents the change in

free energy of ion-ion and ion-solvent interactions accompany-

ing the formation of the activated complex from the reactants

and is given by (209) (210)

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

where

$$2m + 1 = -\left[\Delta F^0 + (e_1 e_2 - e_1^* e_2^*)/D_s e\right]/\lambda$$

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right)(\Delta e)^2$$

e_1^* and e_2^* are the reactant charges, e_1 and e_2 are the product of

charges and ΔF^0 is the standard free energy change in the elec-

tron transfer step. In these equations $(\Delta e) = (e - e_1^*) = $

$(e_2^* - e_2^*)$, n is the refractive index of the solvent and D_s is

the dielectric constant of the medium. The factor r, distance

between the centres of the reactants is set equal to its minimum

value $(a_1 + a_2)$ where a_1 and a_2 are the effective radii of

the reactants.

For electron exchange reactions where $\Delta F = 0$, $e_2 = e_1^*$, $e_1 = e_2^*$, $a_1 = a_2 = a$ the above equation reduces to

$$\Delta F^* = \frac{1}{2a} \left[\frac{e_1 e_2}{D_s} \quad \frac{(\Delta?)^2}{4} \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \right]$$

The quantity ΔF^* termed 'excess free energy of activation' by Marcus is related to the usual free energy of activation $\Delta F^{\neq}$ thus,

$$\Delta F^{\neq} = \Delta F^* \quad --- \quad 13.3 \, T \quad cal/mole$$

Marcus theory therefore can be used for calculating the rate of a any redox reaction from ionic radii and standard free energy chan of a reaction from first principles. Reasonable agreement with experimental data can be seen in table 13.

TABLE 13.

COMPARISON OF MARCUS THEORY F^* VALUES WITH EXPERIMENT

ELECTRON TRANSFER REACTIONS

Reaction	a (Å)	Temp. °C		ΔF^* (expt)	ΔF^* (calc)	Ref
$MnO_4^{2-} -- MnO_4^-$	2.9	1	0.17	12.8	9.2	(210)
$Fe(CN)_6^{4-} -- Fe(CN)_6^{3-}$	4.5	4	1.0	12.7	10.1	(210)
$Mo(CN)_8^{4-} -- Mo(CN)_8^{3-}$	4.8	2	--	12.6	9.5	(210)
$Fe^{2+} -- Fe^{3+}$	3.4	0	0.5	16.3	9.8	(210)
$Co^{2+} -- Co^{3+}$	3.4	0	0.5	16.4	9.9	(210)
$Fe^{2+} -- FeF^{2+}$	3.4	0	0.33	14.3	8.7	(20)
$Fe^{2+} -- FeF_2^+$	3.4	0	0.17	15.0	7.6	(20)
$Fe(C_5H_5)_2 - Fe(C_5H_5)_2^+$	4.1	-75	--	6.0	5.3	(109)
$Fe(C_5H_5)_2 - Fe(C_5H_5)_2^+$	3.5	-75	--	6.0	6.1	(109)
$V^{2+} -- V^{3+}$	3.5	25	0.56	20.6 c	10.0	(211)

OXIDATION REDUCTION REACTIONS

$Fe(CN)_6^{4-}$ -- $IrCl_6^{2-}$	a_1 (A)	a_2 (A)	ΔF^0	ΔF^* (expt)	ΔF^* (calc)	
$Fe(CN)_6^{4-}$ -- $IrCl_6^{2-}$	4.5	4.3	-15.2	9.2	4.2	d(99)
$Fe(CN)_6^{4-}$ -- $IrCl_6^{2-}$	4.5	4.3	- 7.8	9.8	2.4	d(99)
$Fe(CN)_6^{4-}$ -- $OsCl_6^{2-}$	4.5	4.2	- 1.6	18.5	8.5	(99)
$Os(dipy)$ -- $IrCl_6^{2-}$	4.3	7	- 5.3	6.5	2.0	(99)
$Os(dipy)_3^{2+}$ -- $Fe(Phen)_3^{3+}$	7	7	- 5.3	6.5	1.2	(99)
$Os(dipy)_3^{2+}$ -- $Ru(dipy)_3^{3+}$	7	7	-10.1	6.5	0.2	(99)

$\alpha = . \Delta F^*_{repulsion} / \Delta F^*_{reorganization}$. All free energy values
in kcal/mole.

c $F^*(expt)$ is the overall value for V(II)--V(III) exchange
in 1 M $HClO_4$

d In H_2O

e In 0.5 M $HClO_4$

The similarity between solution electron transfers and elec-
trochemical electron transfers has been recognized throughout in
the Marcus theory and the various theoretical expressions with
suitable modifications have been used with success. An interest-
ing paper by Marcu(212) in the Transactions have been used with
succelectrode Processes summarizes the status of electrochemical
electron transfer theory1 More recently, however, Marcus(213)
extended his theory for treating contributions from solvents,
ligands and inert salts in the case of solution electron transfers.

Among other quantitative theories of electron transfer Laidler (214) developed a theoretical treatment appropriate to the Fe(II)--Fe(III) system based on the theory of diffusion controlled processes. The total free energy of activation calculated as contributions due to diffusion, repulsion and tunnelling is found to pass through a minimum at a separation of 4 $\overset{o}{A}$ and is 15.4 kcal/mole in good agreement with the experimental value of 16.8 kcal/mole. Marcus (215), however, finds one of Laidler's assumptions in the formalism as incorrect. In any case the theory has not been applied to other than Fe(II)-Fe(III) system.

Orgel (216) discussed the theory of electron transfers from the point of view of the ligand field theory. The mechanism of electron transfers via bridge activated complexes have been examined by Taube and Myers (217) and by George and Griffith (218) and recently by Halpern and Orgel (219).

Halpern and Orgen (219) developed a se i quantitative study of the role of bridging groups in promoting electron transfers between metal ions in solution treating it as a case of 'strong interaction' where considerable orbital overlap and interaction between orbitals of the metal ions through those of the bridging groups give two types of exchange mechanisms-- direct double exchange and super exchange. Expressions for the exchange frequencies for these two different types of exchange are derived using the time-dependent perturbation theory. Hush (220) developed a quantitative treatment of electron transfer assuming "strong interaction and adiabatic transfer" corresponding

to real situation commonly met in chemical reactions. Halpern
(21) summarizes the quantitative theories of electron transfer
as (1) a case of non-adiabatic electron transfer, (2) adiabatic
transfer--weak interaction and (3) adiabatic transfer--strong
interaction.
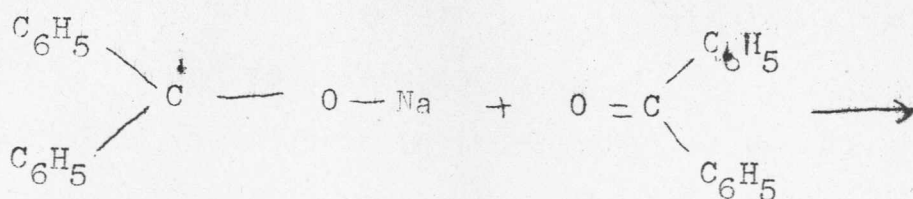
F. Mechanism of Electron Transfer:

The mechanisms of direct electron transfer can be broadly
treated by three types as has been described by Taube (7) and
more recently by Halpern(21):

1. Reactions via the outer sphere activated complex
2. Reactions via the inner sphere activated complex
3. Reactions via unknown mechanisms

Kinetic studies described earlier undoubtedly give insight into
the nature of electron transfer but always a few crucial experi-
ments demonstrate the probable mechanism. Electron transfer
occurs in the case of $Co(en)_3^{2+}$ -- $Co(en)_3^{2+}$, $Fe(CN)_6^{4-}$ -- $Fe(CN)_6^{3-}$
and MnO_4^{2-} -- MnO_4^{-} for example, through an extended activated com-
plex in which the first coordination sphere is practically un-
affected. The other kinetic reason may well be that the substi-
tution in these complex ions is slower compared to the electron
exchange. A remarkable sensitivity by the presence of Cs^+ ions
has been reported in the MnO_4^{2-} -- MnO_4^{-} exchange by Gjertsen and
Wahl (75). An outer sphere bridge activated complex of the type

$$\left[O_3MnO - Cs - OMnO_3 \right]^{3-}$$
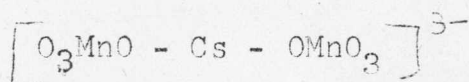
has been postulated to explain the linear behaviour of caesium
ion catalysis observed in this exchange. Similar role of cations
in the $Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-}$ is predicted. Using the electron spin
resonance technique Adam and Weissman (43) report in the case of
Na-ketyle of benzophenone and benzophenone system in 1,2-dimetho-
xyethane that each electron seem to carry its sodium nucleus,
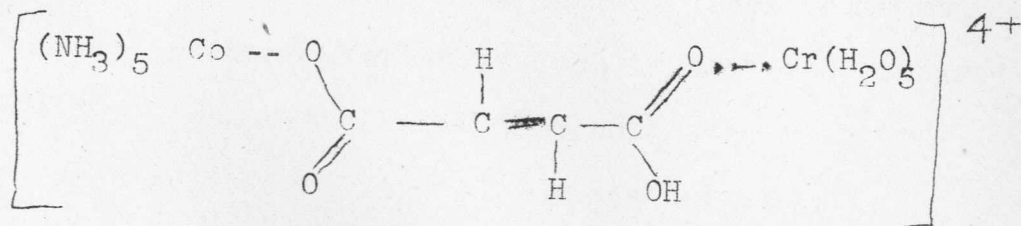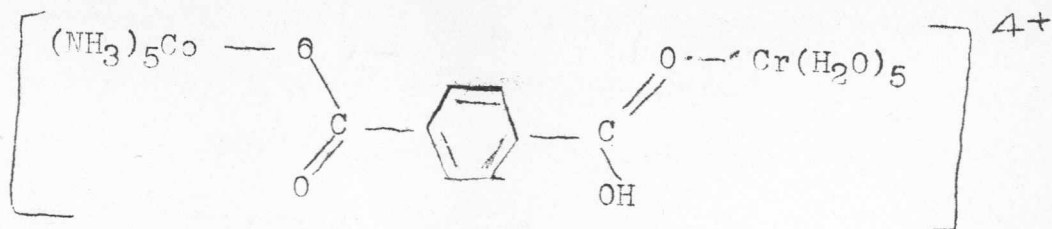in other words a type of Na-atom transfer process.

$$
\begin{array}{c}
C_6H_5 \\
\hspace{1em} \searrow \\
\hspace{2em} \overset{\bullet}{C} \longrightarrow O \longrightarrow Na \quad + \quad O = C \hspace{-0.5em} \begin{array}{l} \nearrow C_6H_5 \\ \searrow C_6H_5 \end{array} \longrightarrow \\
C_6H_5 \nearrow
\end{array}
$$

Taube and coworkers have made significant contribution in the
area of _inner sphere reactions_ which occur via the _inner sphere
activated complex_ (or bridge activated complex.). The best
example is the mechanism operating in the Taube's reaction des-
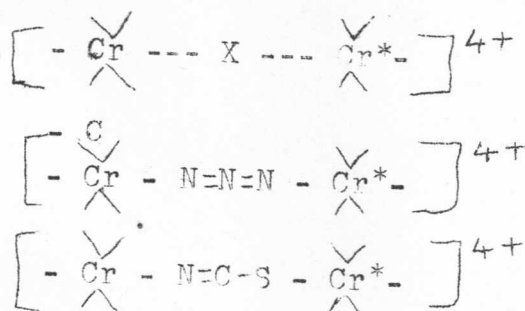cribed earlier. The structure of the activated complex is

$$
\left[(NH_3)_5 \text{--} Co^{III} \quad \text{--} X \text{--} \quad Cr^{II}(H_2O)_5 \right]^{4+}
$$
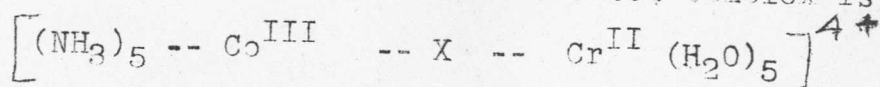
where X may be F^-, Cl^-, Br^-, CNS^-, N_3^-, SO_4^{2-}, PO_4^{3-}, $P_2O_7^{4-}$,
acetate, butyrate , fumarate crotonate, oxalate, succinate, male-
ate, phthalate, isophathalate, terephthalate, benzoate, p-alde-
hydo benzoate, etc. The high rates of terephthalate and fumarate
compared to other carboxylic acids have been interpreted in terms
of a bridge activated complexes such as

$$
\left[(NH_3)_5 \; Co \text{--} O \underset{O}{\overset{\displaystyle C}{\big|}} \text{---} \underset{H}{\overset{H}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}} = C \text{---} \underset{OH}{\overset{O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}}} \text{.--.} Cr(H_2O)_5 \right]^{4+}
$$

$$\left[(NH_3)_5Co - O \quad \cdots \quad O \cdots Cr(H_2O)_5 \right]^{4+}$$

The two metal ions are coordinated to different carboxyl groups
and the electron is transferred by some conduction mechanism
through the conjugated π-electron system. Several accompany-
ing activation effects in electron transfer reactions have been
reported by Taube and coworkers (18), (116), (117), (118), (119).

Ball and King (58) report in their study of the exchange
reactions of Cr(II) and Cr(III)X the following bridge activated
complexes:

$$\left[- \underset{\wedge}{\overset{\vee}{Cr}} --- X --- \underset{\wedge}{\overset{\vee}{Cr}}*- \right]^{4+}$$

$$\left[- \underset{\wedge}{\overset{C}{\underset{}{\overset{\vee}{Cr}}}} - N=N=N - \underset{\wedge}{\overset{\vee}{Cr}}*- \right]^{4+}$$

$$\left[- \underset{\wedge}{\overset{\vee}{Cr}} - N=C-S - \underset{\wedge}{\overset{\vee}{Cr}}*- \right]^{4+}$$

From a kinetic study they suggest the following order of effi-
ciency of the bridging groups for electron transfer between
Cr(II) and Cr(III)' The symmetrical nature

$$Br^-, N_3^- > Cl^- > OH^- > F^- > NCS^- > H_2O$$
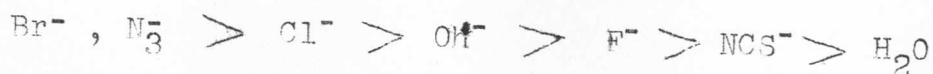
of the azide ion seen to facilitate far more rapid electron
transfer via bridge mechanism as is seen in the rate compared to
the related NCS$^-$ ion as the bridging group. The rate in
presence of the azide ion is $\sim 10^4$ times larger.

More recently Chia and King (221) report in their study of electron transfer between Cr^{2+} and cis- CrF_2^+ that $[(H_2O)_4F --Cr---F--Cr(H_2O)_5]^{3+}$ is the bridge activated complex rather than a symmetrical species:

$$\left[(H_2O)_4 Cr \diagdown_{F}^{F} Cr^*(H_2O)_4 \right]^{5+}$$
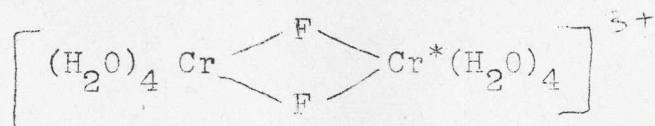
In the area of reactions with uncertain mechanism the exchange of Fe(II)--Fe(III) is the foremost in spite of the fact several investigators studied various aspects of this exchange. Often comparison is made with reactions of known mechanism, for example the relative rates of oxidation of V(II), Cr(II) and $Cr(dip)_3^2$ by $Co(NH_3)_5 X^2$ obtained by Zwickel and Taube (52). For many reactions unequivocal evidence, whether the reaction belongs to the inner sphere activated type or the outer sphere activated type, is not available and more work seem to be in order.

Higginson (222), Newton and Rabideau (179) have tried correlations involving the entropy of activation _vs_ the charge on the activated complex. Fig.11 is an illustration by Halpern (21) based on the data of Higginson _et al_ (   ). Since $\triangle S^{\neq}$
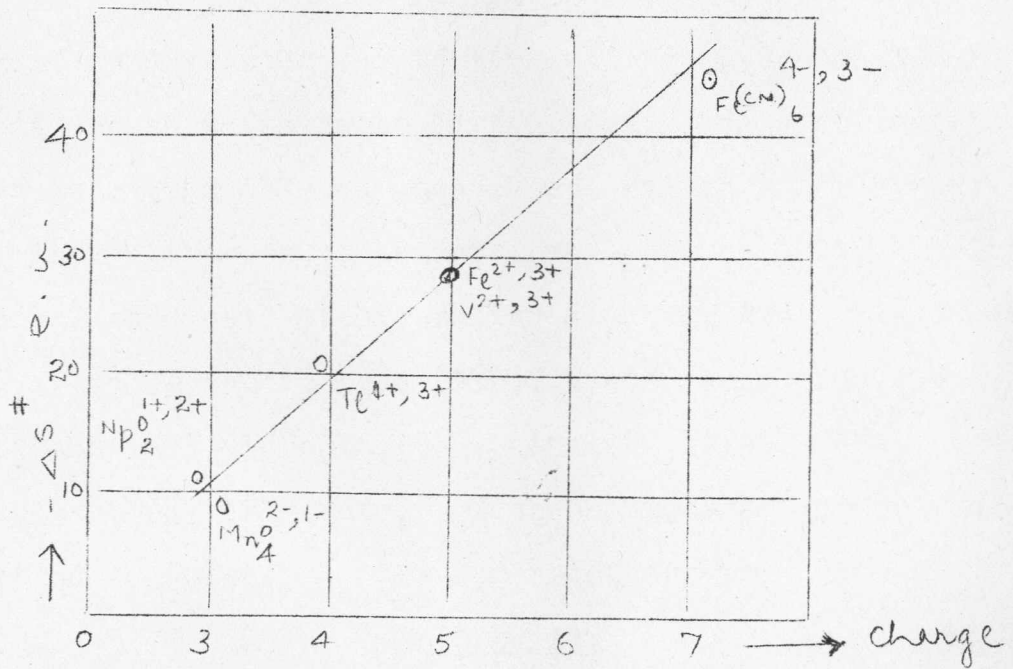
Fig 11   ENTROPY OF ACTIVATION vs
CHARGE ON ACTIVATED COMPLEX

is a useful kinetic parameter providing information about the structure of the activated complex in related systems it will be worthwhile for a comparison with reactions of known mechanism. Likewise other kinetic parameters should be useful such as $\Delta H^{\ddagger}$ and $\Delta V^{\ddagger}$.

Since electron exchange systems are often studied in water as solvent a change in solvent is usually included in the study of several systems, particularly in D_2O. The D_2O isotope effects are shown in table 14. In many cases solvent isotope effect is unable to give unequivocal evidence for a specific mechanism. Other solvents have been used only in a limited number of studies: liquid sulfur dioxide (223), liquid amonia (104), glacial acetic acid (139), acetic anhydride (139), nitromethane (87) alcohols (86), ethylene glycol (185), benzene (202), acetone (177), etc. Much needs tobe done on the solvent effect on the electron transfer reactions.

TABLE 14.

SOLVENT DEUTERIUM ISOTOPE EFFECTS IN OXIDATION-REDUCTION REACTIONS

Reaction	k_{H_2O} / k_{D_2O}	Ref.
$Fe^{2+} -- Fe^{3+}$	2	(83)
$Co^{2+} -- Co^{3+}$	2	(101)
$Tl^{+} -- Tl^{3+}$	~ 1.5	(152)
$NpO_2^{+} -- NpO_2^{2+}$	1.4	(184)
$Fe^{2+} -- FeOH^{2+}$	2	(83)
$Fe^{2+} -- FeCl^{2+}$	2.5	(224)
$Fe^{2+} -- FeN_3^{2+}$	1.5	(94)

Reaction	k_{H_2O} / k_{D_2O}	Ref.
$V^{2+} -- Co(NH_3)_6^{3+}$	1.7	(52)
$V^{2+} -- Co(NH_3)_5Cl^{2+}$	2.2	(52)
$Cr^{2+} -- Co(NH_3)_6^{3+}$	1.3	(52)
$Cr^{2+} -- Co(NH_3)_5OH$	3.8	(65)
$Cr^{2+} -- Co(NH_3)_5OH_2^{3+}$	2.6	(65)
$Cr^{2+} -- Co(NH_3)_5Cl^{2+}$	1.3	(66)
$Cr^{2+} -- Co(NH_3)_5(H-fumarate)^{2+}$	~ 1	(67)
$Cr(dipy)_3^{2+} -- Co(NH_3)_5OH_2^{3+}$	2.6	(70)
$Cr(dipy)_3^{2+} -- Co(NH_3)_6^{3+}$	1 *	(70)

* Zwickel and Taube ( ) report a 30% reduction in the
rate of this reaction if $Co(ND_3)_6^{3+}$ is used as the oxidant.

OTHER KINETIC ISOTOPE EFFECTS

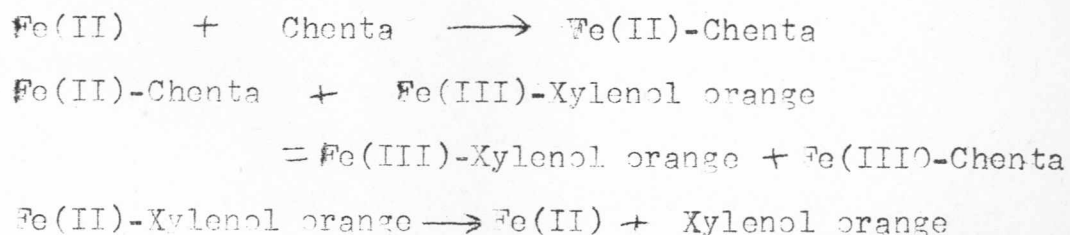|	$k (O16)/k (O^{18})$	$k(N^{14})/k (N^{15})$	
$Cr^{2+} -- Co(NH_3)_5OH_2^{3+}$	1.035	1.003	(225)

Murmann, Taube and Pausey (225) interpret the oxygen iso-
tope effect in the oxidation complex. Cr^{2+} by $Co(NH_3)_5OH_2^{3+}$
as weakening of the Co--O bond in the activated complex. The
smaller isotope effect for nitrogen is also indicative of slight
weakening of the Co--N bonds in the activated complex.

G. Application of Electron Transfer:

The field of inorganic reaction mechanisms has been
all along a neglected one with but a handful of workers inte-
rested in applying the techniques of organic reaction mechanisms
to explain the behaviour of certain coordination compounds.

However, since the second world war a new interest began with the advent of tracers and novel techniques resulting in almost unbelievable amount of work. The study of electron transfer reactions is one example in modern inorganic chemistry. The applications of this in preparative chemistry have already provided short and elegant methods for preparing complexes of metals in substitution-inert oxidation state. Beck (226) gives a novel method for the preparation of a Fe(III)--complex of cyclohexane-1,2-diamine tetraacetic acid (Chenta) using an electron transfer exchange reaction .

$$Fe(II) \quad + \quad Chenta \quad \longrightarrow \quad Fe(II)\text{-}Chenta$$

$$Fe(II)\text{-}Chenta \quad + \quad Fe(III)\text{-}Xylenol\ orange$$

$$= Fe(III)\text{-}Xylenol\ orange + Fe(IIIO\text{-}Chenta$$

$$Fe(II)\text{-}Xylenol\ orange \longrightarrow Fe(II) + Xylenol\ orange$$

Yong Ae Im and Busch (113) report a novel method of resolution through electron transfer in the system Co(PDTA)$^-$ --Co(PDTA)$^{2-}$ (PDTA propylenediamine tetraacetic acid). An equilibrium mixture containing nearly 80% of one of the isomers has been obtained in this study.

In conclusion it may be said the field of electron transfer is just beginning and with the concerted efforts of physical chemists, organic chemists, biochemists and physicists it should be possible to develop an understanding of the more complex systems encountered in biological electron transfers.

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