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REORGANIZATION ENERGIES OF OPTICAL ELECTRON TRANSFER PROCESSES

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I. Introduction

Electron transfer reactions and spectroscopic charge-transfer transitions have been extensively studied, and it has been shown that both processes can be described with a similar theoretical formalism. The activation energy of the thermal process and the transition energy of the optical process are each determined by two factors: one due to the difference in electron affinity of the donor and acceptor sites, and the other arising from the fact that the electronically excited state is a nonequilibrium state with respect to atomic motion (Franck–Condon principle). Theories of electron transfer have been concerned with predicting the magnitude of the Franck–Condon barrier; but, in the field of thermal electron transfer kinetics, direct comparisons between theory and experimental data have been possible only to a limited extent. One difficulty is that in kinetic studies it is generally difficult to separate the electron transfer process from the complex formation

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and rearrangement processes that precede it; another is that quite small energy differences can wholly change the course of a reaction, so that errors of, say ± 10 kcal in the theoretical estimate of an activation energy can lead to entirely wrong predictions. So far, therefore, theory has been used mainly to rationalize comparisons between closely related reactions, and not to predict reaction rates absolutely.

The purpose of this review is to assemble the data in the area of spectroscopy for comparisons between theory and experiment. It seems at first sight that the data are simpler to evaluate than are those of kinetics, and certainly the energies involved are larger, which is an advantage where absolute predictions are required. The main obstacle to progress hitherto has been the lack of thermodynamic electron-affinity data for the systems of interest. There is, however, a growing number of systems for which both the spectroscopic and the thermodynamic data are sufficiently accurate to encourage attempts to calculate the Franck–Condon energy.

In Section II, we shall collect the relevant data and calculate values of the Franck–Condon energies; and we shall attempt to rationalize them qualitatively by making suitable comparisons between related systems. In Section III we shall briefly review the electrostatic theories of solvation and reorganization, and in Section IV we shall make some preliminary comparisons between theory and experiment.

A. DEFINITIONS

A thermal electron transfer reaction between complex ions in solution may be written schematically as

$$\underset{p}{(A^{+}\cdots B)(\text{env})} \rightarrow \underset{s}{(A\cdots B^{+})(\text{env})} \tag{1}$$

in which A and B denote atoms each of which possesses two valence states differing by one electron, and the (+) sign denotes the higher of the two valences. This notation will be used throughout for the sake of simplicity, regardless of the actual valences and ionic charges involved. Systems $(A^{+}\cdots B)$ and $(A\cdots B^{+})$ may be binuclear complexes of more-or-less fixed geometry, or they may be reactive pairs in systems undergoing a bimolecular reaction. We shall refer to them in general as the *precursor* (p) and *successor* (s) states. The state symbol (env) denotes the total ligand and solvent environment of the reacting ions, at thermal equilibrium.

The optically excited electron transfer process may then be written

$$\underset{p}{(A^{+}\cdots B)(\text{env})} \xrightarrow{h\nu_{\text{CT}}} \underset{s^{*}}{(A\cdots B^{+})(\text{env}^{*})} \tag{2}$$

in which the product s^* has an electronic configuration similar to that of s, but, by the Franck–Condon principle, the ligand and solvent molecules are in the same positions as in p.

Without attempting any justification, we shall ascribe thermodynamic properties to the state s^*, so that a thermodynamic cycle may be written

$$\begin{tikzcd} & s^* \\ p \arrow[ur, "\Delta Y_{CT}"] \arrow[r, "\Delta Y_{PS}"'] & s \arrow[u, "\Delta Y_{FC}"'] \end{tikzcd} \tag{3}$$

giving

$$\Delta Y_{CT} = \Delta Y_{PS} + \Delta Y_{FC} \tag{4}$$

where symbol Y denotes energy (U), enthalpy (H), Gibbs free energy (G), or entropy (S). Thus ΔG_{PS} is the standard free-energy change associated with the thermal process [Eq. (1)]; and ΔG_{FC} is the reorganizational free energy, i.e., the work done in reversibly distorting the atomic configuration of the successor state into a configuration typical of the precursor state. We shall, moreover, assume* that the entropy change ΔS_{CT} associated with the optical absorption process is zero (unless there is a change in multiplicity, which however we shall ignore). The absorption frequency ν_{CT} then measures the molar energy, enthalpy, and free energy of process Eq. (2):

$$Lh\nu_{CT} = \Delta U_{CT} = \Delta H_{CT} \cong \Delta G_{CT} \tag{5}$$

(the quantities ΔY are molar quantities, L being the Avogadro constant). We note that, by our assumption,

$$\Delta S_{FC} = -\Delta S_{PS} \tag{6}$$

For the reverse electron transfer process, we may write

$$\underset{s}{(\mathrm{A}\cdots\mathrm{B}^+)\mathrm{env}} \xrightarrow{\Delta Y_{CT}'} \underset{p^*}{(\mathrm{A}^+\cdots\mathrm{B})(\mathrm{env}^*)} \tag{7}$$

giving the cycle

$$\begin{tikzcd} p^* & \\ p \arrow[u, "\Delta Y_{FC}'"] \arrow[r, "\Delta Y_{PS}"'] & s \arrow[ul, "\Delta Y_{CT}'"'] \end{tikzcd} \tag{8}$$

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* This assumption was first made explicit by Treinin (*127f*).

with

$$\Delta Y_{CT}' = -\Delta Y_{PS} + \Delta Y_{FC}' \tag{9}$$

which, on combining with Eq. (4) yields

$$\Delta Y_{CT} - \Delta Y_{CT}' = 2\Delta Y_{PS} + (\Delta Y_{FC} - \Delta Y_{FC}') \tag{10}$$

$$\Delta Y_{CT} + \Delta Y_{CT}' = \Delta Y_{FC} + \Delta Y_{FC}' \tag{11}$$

whereas from Eq. (6) we have

$$\Delta S_{FC} = -\Delta S_{FC}' \tag{12}$$

It will be seen in the following that under certain conditions the free-energy terms in parentheses in Eq. (10) cancel, i.e., $\Delta G_{FC} = \Delta G_{FC}'$ [Eq. (74), Section III,B].

B. VALENCY STATES

The foregoing discussion is restricted to cases in which the valencies in the binuclear complexes are localized, so that, for example, the ground state of p can properly be described as $(A^+ \cdots B)$ without appreciable mixing of the state $(A \cdots B^+)$. The range of possible variations, from zero to complete mixing, is shown in Fig. 1, following a discussion by Mayoh and Day (*96*). Ordinate U is the energy of the wave function of the transferring electron (assumed separable from the wave functions of all other electrons in the system), and abscissa x is a "reaction coordinate" describing the course of the reaction $p \rightarrow s$.

Figure 1a shows the case of a complex that is symmetrical as regards the component atoms (i.e., $A \equiv B$) but not necessarily symmetrical in its electronic configuration. If states $(A^+ \cdots A)$ and $(A \cdots A^+)$ do not mix, the energies are given by the zero-order curves (0,0). (According to the theories outlined in Section III, these curves are parabolas.) States p and s at the two minima are mixed-valence complexes of the Robin and Day "Class I" (*119a*). The excitation $p \rightarrow s^*$ has a probability of zero. For a weak interaction, the curves (1,1) differ significantly only at the crossing point. The complexes have localized valences, but are designated Class II, because the $p \rightarrow s^*$ transition produces an observable "intervalence transfer" band in the spectrum. The extent of interaction and, thus, the resonance energy H at the crossing point, can be estimated from the transition dipole moment (*96*). With stronger interactions, the ground states also can have appreciable mixing of

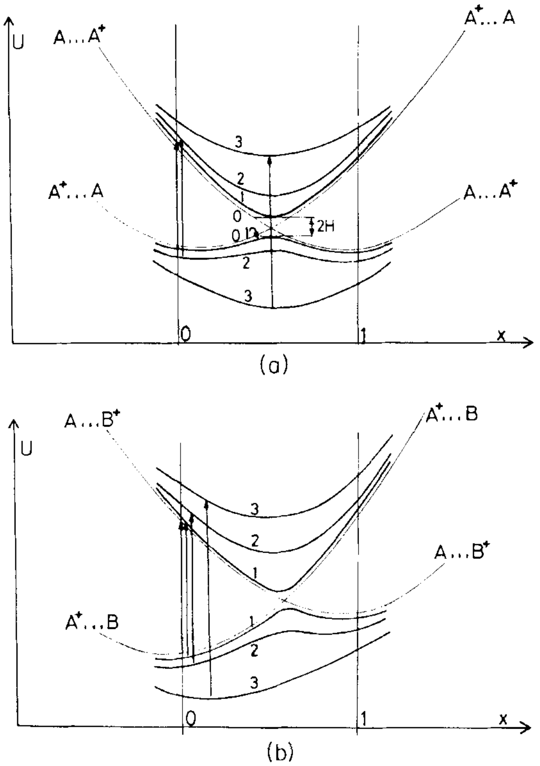

FIG. 1. Idealized energy-level diagrams showing intervalence-type charge-transfer transitions in mixed-valence binuclear complexes. (a) Symmetrical case ($\Delta G_E = 0$), after Mayoh and Day (*96*). The fine lines are parabolas representing the energies of zero-order wave functions for the electronic configurations $A^+ \cdots A$ and $A \cdots A^+$. The bold lines 1, 1; 2, 2; 3, 3 show ground and excited electronic states of the mixed-valence complexes with (1) weak interaction, (2) moderate interaction, (3) strong interaction. The vertical transitions shown by the arrow have intervalence charge-transfer character ($p \rightarrow s^*$) in cases 1 and 2 but not in case 3. (b) Unsymmetrical case ($\Delta G_E > 0$). The labeling of the curves corresponds to that of the symmetrical case (a), but it is seen that even with strong interaction the ground- and excited-state curves (3, 3) have minima at difference abscissas x, hence the vertical transitions retain some charge-transfer character.

the ($A^+ \cdots A$) and ($A \cdots A^+$) configurations (curve 2,2) and, finally, if the resonance energy exceeds a certain critical value (*11*, *67*) states p and s coalesce into a single minimum (curves 3,3) giving a wholly delocalized Class III complex, which should now be termed an "average-valence" rather than a "mixed-valence" complex. There is still a characteristic electronic transition, but it no longer has intervalence charge-transfer character (*11*).

Figure 1b shows the corresponding situations for unsymmetrical complexes. Similar comments apply, except for the fact that even in the case of strong interaction, when the ground state has only one minimum, the optical transition retains some charge-transfer character.

There are now well-attested examples of all the degrees of interaction represented in Fig. 1, some of which will be mentioned in the following. On the other hand, by no means all complexes showing charge transfer have yet been classified. In this review we shall concentrate on complexes with weak interaction, but others will also be considered with appropriate caution, as discussed especially in Section II,F.

It must be stressed that diagrams of the type of Fig. 1 contain other major assumptions, which, however, we shall not discuss here. One assumption is that a single reaction coordinate can be used to characterize the energy changes in the ground and excited states. In fact, the vibrational modes associated with the thermal activation processes are almost wholly unknown, and the interactions between vibrational and electronic excitations are only beginning to be explored, for example by the resonance Raman technique (*22*). Another assumption is that the excited states produced by charge transfer from the ground state s do, in fact, correlate with the precursor p. There are many other possibilities, as has been made clear from studies of photochemical reaction mechanisms (*6*). A classification of mechanisms based on the mixing or nonmixing of reactants and products' ground- and excited-state wave functions has been proposed by Endicott (*45*). In his terminology, only Class I and Class I′ processes are relevant to the present study; but we shall discuss one of the alternative kinds of process in Section II,C.

C. Inner- and Outer-Sphere Energy Terms

The total reorganization energy ΔG_{FC} will in general be made up of three components, which we may call the bonding, the ligand, and the solvent terms:

$$\Delta G_{\mathrm{FC}} = \Delta G_{\mathrm{FC}}^{\mathrm{bond}} + \Delta G_{\mathrm{FC}}^{\mathrm{ligand}} + \Delta G_{\mathrm{FC}}^{\mathrm{solvent}} \qquad (13)$$

The bonding term arises whenever the donor and acceptor atoms are close enough to interact directly, and may be positive or negative depending on whether the excited state s^* is subject to a repulsive or an attractive internuclear force. The ligand term is due to differences in the equilibrium positions of the ligands directly bonded to the two atoms. Experience from kinetic studies suggests that this contribution is likely to be significant for highly ionic complexes with ligands such as H_2O or NH_3, but insignificant for strongly π-bonded complexes with ligands such as CN^- or 2:2′-bipyridyl. The solvent term is the free energy of reorganization of solvent molecules. In this review we shall use the commonly accepted terminology, grouping the bond and ligand terms as the *inner-sphere* component and calling the solvent term the *outer-sphere* component:

$$\Delta G_{FC} = \Delta G_{FC}^{in} + \Delta G_{FC}^{out} \tag{14}$$

The same subdivision is used in the qualitative discussion of ionic solvation energies, and it is found that the outer-sphere part is satisfactorily predicted by electrostatic continuum theories (as reviewed in Section III), whereas the inner-sphere part is best obtained by considering the distortion of individual bonds, using force constants from vibrational spectroscopy.

II. Review of Data

A. SINGLE-ION PROCESSES (PHOTOEMISSION)

The process of ionization of an atom or molecule A in the gas phase may be written

$$A(g) \rightarrow A^+(g) + e^-(g) \tag{15}$$

where the state symbol (g) denotes a free species *in vacuo*, having zero translational kinetic energy. An analogous equation *(111)* may be written for a process in solution:

$$A(env) \longrightarrow A^+(env) + \{e^-\}_{env} \tag{16}$$

where the state symbol (env) denotes the total solvent environment at thermal equilibrium with the species in question, and the symbol $\{e^-\}_{env}$ denotes an electron delocalized throughout the bulk of the solvent (and, hence, not specifically interacting with any chemical species present), but having zero kinetic energy.* Such an electron has been called "quasi-free" *(36)* or "dry" *(40)*; in quantum-mechanical language, it is at the lowest continuum energy level of the system.

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* Notation $\{e^-\}_{aq}$, $\{-\}_{aq}$ is based on that of Noyes, whose paper *(111)* should be consulted for a clear discussion of the problems of definining transfer energies of charged species.

If, however, we specify that the ionization process is instantaneous, so that all atoms and solvent molecules remain in the positions characteristic of the ground state, we may write

$$\mathrm{A(env)} \xrightarrow{\Delta U_{\phi}} \mathrm{A^{+}(env^{*})} + \{\mathrm{e^{-}}\}_{\mathrm{env}} \tag{17}$$

by analogy with Eq. (2) This type of ionization was first explicitly discussed by Platzman and Franck in 1952 (*116*); but it did not become accessible to direct measurement until some 20 years later. Photoemission spectra have now been reported for a variety of chemically reducing species in solution, notably the ferrocyanide ion (*4*, *7*), the solvated electron (*8*, *40*), and a number of other organic and inorganic species (*109*). The mechanism of emission has been analyzed theoretically (*35*) in terms of two consecutive processes: generation of electrons in unbound states and the escape of electrons into the gas phase. Sometimes the energy ΔU_{ϕ} is close to a peak in the photoemission spectra, but equations have been given from which ΔU_{ϕ} can be calculated when this is not the case (*35a*).

Combining equation (*17*) with expressions for the standard reduction of $\mathrm{A^{+}(env)}$ and for the formation and hydration of the proton, we obtain the Franck–Condon parameters as follows:

$$\begin{array}{rll}
\mathrm{A(env)} \rightarrow \mathrm{A^{+}(env^{*})} + \{\mathrm{e^{-}}\}_{\mathrm{env}} & \Delta Y_{\phi}(\mathrm{A}) & (17)\\
\mathrm{A^{+}(env)} + \tfrac{1}{2}\mathrm{H_2(g)} \rightarrow \mathrm{A(env)} + \mathrm{H^{+}(env)} & \Delta Y_{\mathrm{E}}(\mathrm{A^{+}}) & (18)\\
\left.\begin{array}{r}
\mathrm{H^{+}(env)} + \{\mathrm{e^{-}}\}_{\mathrm{env}} \rightarrow \mathrm{H^{+}(g)} + \mathrm{e^{-}(g)}\\
\mathrm{H^{+}(g)} + \mathrm{e^{-}(g)} \rightarrow \mathrm{H(g)}\\
\mathrm{H(g)} \rightarrow \tfrac{1}{2}\mathrm{H_2(g)}
\end{array}\right\} & \Delta Y_{\mathrm{H}} & \begin{array}{r}(19)\\(20)\\(21)\end{array}\\
\\
\mathrm{A^{+}(env)} \rightarrow \mathrm{A^{+}(env^{*})} & \Delta Y_{\mathrm{FC}}(\mathrm{A^{+}}) & (22)
\end{array}$$

It will be noted that Eq. (*19*) is written[†] so as to avoid transferring any net charge across the liquid–vacuum interface (*111*). Values of ΔG_{H}, ΔH_{H}, and ΔS_{H} for aqueous medium are calculated in Table I.

The reverse process, of electron transfer from the continuum to the oxidized ion,

$$\mathrm{A^{+}(env)} + \{\mathrm{e^{-}}\}_{\mathrm{aq}} \rightarrow \mathrm{A(env)^{*}} \qquad \Delta Y_{\phi}(\mathrm{A^{+}} + \mathrm{e^{-}}) \tag{23}$$

has apparently not been studied. By a similar argument, it would

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[†] Throughout this review, we use the units cal = 4.184 J; kK = 10^{3} cm^{-1}. Electric potentials and equilibrium constants reported in the literature have been converted to standard free-energy changes by means of the expressions $-\Delta G^{\ominus} = -zFE^{\ominus} = 2.303\,RT \log K$, where $F = 23.060$ kcal mole^{-1} volt^{-1}, $2.303\,RT = 1.359$ kcal mole^{-1}, at 25°C. Wave numbers of optical transitions reported in the literature have been converted to energy changes by means of the expression $\Delta U = Lhc^{-1}\nu^{-1}$, where $Lhc^{-1} = 2.862$ kcal mole^{-1} kK^{-1}.

TABLE I

CALCULATION OF THERMODYNAMIC PARAMETERS[a] FOR THE ION $H^+(aq)$

Reaction	ΔH (kcal mole^{-1})	ΔG (kcal mole^{-1})	$T\Delta S$ (kcal mole^{-1})	ΔS (cal K^{-1} mole^{-1})
$H^+(aq) + Cl^-(aq) \rightarrow H^+(g) + Cl^-(g)$	348.8^b	333.6^c	—	51.0^b
$\{e^-\}_{aq} + Cl^-(g) \rightarrow Cl^-(aq) + e^-(g)$	-88.7^d	-84.2^d	—	-15.0^d
Subtotal:				
$\{e^-\}_{aq} + H^+(aq)' \rightarrow H^+(g) + e^-(g)$	$260.1^{e,f}$	249.4^e	10.74	36.0^c
$H^+(g) + e^-(g) \rightarrow H(g)$	-315.0^b	-315.0^c	0.00^g	0.0^g
$H(g) \rightarrow \frac{1}{2}H_2(g)$	-52.1^b	-48.6^b	-3.57^b	-11.8^b
Total:				
$\{e^-\}_{aq} + H^+(aq) \rightarrow \frac{1}{2}H_2(g)$	-107.0	-114.2	7.14	24.2

[a] All temperature-dependent parameters relate to $T = 298$ K.

[b] Calculated from data in Ref. 108.

[c] Calculated from the other parameters using $\Delta G = \Delta H - T\Delta S$.

[d] W. M. Latimer *et al.* (*83*).

[e] Sum of the above two parameters.

[f] A value 260.7 kcal mole^{-1} has been obtained (*58*) using somewhat different assumptions to those of Latimer *et al.* (*83*).

[g] Assumed.

yield the Franck–Condon parameters for the process,

$$A(env) \rightarrow A(env)^* \qquad \Delta Y_{FC}(A) \tag{24}$$

where A(env*) denotes a species having the electronic configuration of A(env) but the atomic configuration of A^+(env). If Eq. (74) (see Section III,B) is valid, we have

$$\Delta G_{FC}(A) = \Delta G_{FC}(A^+) \tag{25}$$

Calculations of the Franck–Condon energy ΔG_{FC} for three species are shown in Table II. One complication in the use of the data at this early stage is the variety of solvent systems used; another is the fact that, in the case of $Fe(CN)_6^{4-}$ ion, different salts have been used, and in the less polar media the nature of the cation may be expected to be significant. It is worth noting, however, that, again in the case of $Fe(CN)_6^{4-}$, the photoemission data of Ballard and Griffith (*4*),

TABLE II

SINGLE IONS: FREE-ENERGY PARAMETERS ΔG_{ϕ} FOR THE PHOTOEMISSION PROCESS $A(env) \rightarrow A^+(env^*) + \{e^-\}_{aq}$

Emitting complex (A):	$Fe(CN)_6^{4}$	I^-	$Fe(C_5H_5)_2$
Solvent (env):	aq[a]	Tetraglyme	Tetraglyme
Temperature (°C):	1.2	25	25
Radius of complex A^+ (10^{-10} m)	4.3[h]	1.33[i]	3.8[j]
ΔG (kcal $mole^{-1}$):			
$A(env) \rightarrow A^+(env^*) + \{e^-\}_{env}$	137[b]	143[e]	143[e]
$A^+(aq) + \frac{1}{2}H_2(g) \rightarrow A(aq) + H^+(aq)$	−8[c]	−31.1[f]	−8.0[g]
$\{e^-\}_{aq} + H^+(aq) \rightarrow \frac{1}{2}H_2(g)$	−114[d]	−114.2[d]	−114.2[d]
Totals:	15	2	21

[a] A value for 0.25*M* $Fe(CN)_6^{4}$ in water (cation not specified).

[b] Delahay (*35a*).

[c] Using ΔG ($T = 298$ K) values from Hanania (*59*). ΔH is calculated from the following data (ΔH in units of kcal $mole^{-1}$): $Fe(CN)_6^{4-}(aq) + \frac{1}{2}Br_2(l) \rightarrow Fe(CN)_6^{3-}(aq) + Br^- \cdot aq$ (−4.2), $\frac{1}{2}Br_2(aq) \rightarrow \frac{1}{2}Br_2(l)$ (0.6); $Br^-(aq) + H^+(aq) \rightarrow \frac{1}{2}Br_2(aq) + \frac{1}{2}H_2(g)$ (28.8) (Refs. *61*, *108*, *107*, respectively).

[d] Table I.

[e] Delahay (*37*).

[f] Calculated from the following data (ΔG in units of kcal $mole^{-1}$, at 298 K): $\frac{1}{2}I_2(s) + \frac{1}{2}H_2(g) \rightarrow I^-(aq) + H^+(aq)$ (−12.3); $\frac{1}{2}I_2(aq) \rightarrow \frac{1}{2}I_2(s)$ (−2.0); $I(aq) \rightarrow \frac{1}{2}I_2(aq)$ (assumed same as for gas phase, −16.8) (Refs, *126*, *134*, *108*, respectively).

[g] Kolthoff and Thomas (*77*).

[h] Estimated.

[i] Phillips and Williams (*114*, p. 109).

[j] Average of maximum and minimum estimated radii of $Fe(C_5H_5)_2$ (*128*).

obtained for glycerol media, are evidently continuous with those of Delahay *et al.* (*7*), for aqueous media.

It is interesting to note that the two complexes $Fe(CN)_6{}^{4-}$ and $Fe(C_5H_5)_2$, of somewhat similar dimensions, give similar values of ΔG_{FC}. On the other hand, the negative value found for I^- is clearly incorrect. The error may be due to the use of data from different solvent systems, and it might be expected that the I^- ion, with its smaller radius, would be more sensitive to changes of solvent than the other two ions. But it is difficult to discuss this without more comparative data.

Ballard (*4*) points out that, below the energy of the band maximum, the photoemission current varies exponentially with photon energy, which is evidence that the band width is due to thermal occupation of vibrational levels in the electronic ground state, $Fe(CN)_6{}^{4-}$(env). The threshold energy was found to be approximately 119 kcal mole^{-1} (*4b*) [118.3 kcal mole^{-1} by another method (*7b*)], i.e. about 18 kcal mole^{-1} lower than ΔU_ϕ. It seems likely that the low-energy threshold of the spectrum represents emission from those $Fe(CN)_6{}^{4-}$ ions which happen to have solvent environments similar to those that characterize the ground state of $Fe(CN)_6{}^{3-}$.

B. Donor–Acceptor Pairs

Transfer of charge between localized reducing and oxidizing sites is well known. In a general case, with oxidant A^+ and reductant B , situated at infinite distance apart, we may write

$$A^+(\text{env}) + B(\text{env}) \xrightarrow{h\nu} A(\text{env})^* + B^+(\text{env})^* \tag{26}$$

and the thermodynamic parameters will be given by

$$\Delta Y_{CT} = \Delta Y_{FC}(A) + \Delta Y_E(A^+) + \Delta Y_{FC}(B^+) - \Delta Y_E(B^+) \tag{27}$$

Thus, the Franck–Condon barrier for the oxidant–reductant pair is given by

$$\begin{aligned} \Delta Y_{FC}^{\text{pair}} = \Delta Y_{FC}(A) + \Delta Y_{FC}(B^+) &= \Delta Y_{CT} - \{\Delta Y_E(A^+) - \Delta Y_E(B^+)\} \\ &= \Delta Y_{CT} - \Delta Y_0 \end{aligned} \tag{28}$$

where ΔY_0 denotes the energy, enthalpy, etc., change associated with the equilibrium:

$$A^+(\text{env}) + B(\text{env}) \rightleftharpoons A(\text{env}) + B^+(\text{env}) \tag{29}$$

In principle, the converse charge-transfer process* should also be observable:

$$\mathrm{A(env)} + \mathrm{B^+(env)} \xrightarrow{h\nu'} \mathrm{A^+(env)^*} + \mathrm{B(env)^*} \tag{30}$$

with

$$\Delta Y_{\mathrm{CT}}' = \Delta Y_{\mathrm{FC}}(\mathrm{A^+}) - \Delta Y_{\mathrm{E}}(\mathrm{A^+}) + \Delta Y_{\mathrm{FC}}(\mathrm{B}) + \Delta Y_{\mathrm{E}}(\mathrm{B^+}) \tag{31}$$

If, as predicted by Eq. (74) (see Section III,B), $\Delta G_{\mathrm{FC}}(\mathrm{A^+}) = \Delta G_{\mathrm{FC}}(\mathrm{A})$ and $\Delta G_{\mathrm{FC}}(\mathrm{B^+}) = \Delta G_{\mathrm{FC}}(\mathrm{B})$, then, as before, we obtain

$$\Delta G_{\mathrm{CT}} - \Delta G_{\mathrm{CT}}' = 2\{\Delta G_{\mathrm{E}}(\mathrm{A^+}) - \Delta G_{\mathrm{E}}(\mathrm{B^+})\} = 2\Delta G_0 \tag{32}$$

As yet there are no data for charge transfer over long distances, defined by Eq. (26), although there are some results for intramolecular electron transfer in systems where the donor and acceptor are, if not independent, at least only weakly coupled. Nor have we any data for the variation in charge-transfer energy as a function of distance, except in systems where the coupling between donor and acceptor is evidently strong. The possibility that thermal electron transfer between like-charged ions in solution may take place over large distances has been discussed several times, and some of the quantitative theories involve integration of the rate of reaction over all possible distances (*93*); other theories, however, assume that the bulk of electron transfer takes place between ions in contact (*93*), as discussed in the following.

C. Ion Pairs

When the oxidant and reductant occur in complexes of opposite charge, the assumption that charge transfer occurs mainly between contact pairs becomes reasonable; and, in addition, the free energy of formation of the contact pair can often be estimated. Sometimes, indeed, the study of the charge-transfer spectrum has proved to be the most useful method of obtaining the free energy of formation. In the reaction scheme,

$$\begin{tikzcd}
\mathrm{A^+(env)} + \mathrm{B(env)} \arrow[r, "\Delta Y_{\mathrm{w}}"] \arrow[d, "\Delta Y_0"] & \underset{}{\mathrm{A^+{\cdot}B(env)}} \arrow[r, "\Delta Y_{\mathrm{FC}}'(\mathrm{A^+{\cdot}B})"] \arrow[d, "\Delta Y_{\mathrm{PS}}", "p"'] \arrow[dr, "\Delta Y_{\mathrm{CT}}"' near start] & \underset{p^*}{\mathrm{A^+{\cdot}B(env^*)}} \\
\mathrm{A(env)} + \mathrm{B^+(env)} \arrow[r, "\Delta Y_{\mathrm{w}}'"] & \underset{s}{\mathrm{A{\cdot}B^+(env)}} \arrow[r, "\Delta Y_{\mathrm{FC}}(\mathrm{A{\cdot}B^+})"] \arrow[ur, "\Delta Y_{\mathrm{CT}}'"' near end] & \underset{s^*}{\mathrm{A{\cdot}B^+(env^*)}}
\end{tikzcd} \tag{33}$$

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* Reversible, optical electron transfer has been observed in the solid state, between the ions $\mathrm{Eu^{2+}}$ and $\mathrm{Sm^{3+}}$ doped into crystalline $\mathrm{CaF_2}$ (*143a*).

formula $A^+ \cdot B(env)$ denotes the precursor complex p in which A^+ and B have the same inner-sphere ligands as $A^+(env)$ and B(env), respectively, and the remaining solvent molecules are appropriately rearranged; $A \cdot B^+(env)$ is the successor complex s similarly related to A(env) and $B^+(env)$. Thermal electron transfer reactions of the type $p \rightarrow s$ have been extensively discussed (*93*), and in a few instances, directly measured (*50*). One of the current goals of research in this field is to measure the reaction rate and the total free-energy change ΔG_{PS} for the same system. So far this is still to be achieved.

From Eq. (33) we have

$$\begin{aligned}\Delta Y_{FC}(A \cdot B^+) &= \Delta Y_{CT} - \Delta Y_{PS} \\ &= \Delta Y_{CT} + (\Delta Y_W - \Delta Y_W') - \Delta Y_0 \end{aligned} \tag{34}$$

where ΔY_W and $\Delta Y_W'$ are "work terms" (*93*) for the formation of the precursor and successor complexes, and ΔY_0 is the same as before. At the present time there are no cases in which ΔY_W and $\Delta Y_W'$ are known for the same system, but, in some cases, at least the free-energy terms may be estimated from data on analogous complexes, since it is evident that these do not vary greatly between outer-sphere systems of similar charge type (*12*).

If the algebraic difference in charge between the complexes A^+ and B happens to be +1 [as in the pairs Fe^{3+}, Cr^{2+}; $Fe(C_5H_5)_2{}^+$, $Fe(C_5H_5)_2$; $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$], the two work terms may be expected to cancel; but no spectrum has yet been measured for such a pair (cf. Table IV).

If the redox potentials are not too different, it should be possible to measure spectra for both complexes, $A^+ \cdot B$ and $A \cdot B^+$; however, this again has still to be achieved. From Eq. (33), we find

$$\Delta Y_{FC}'(A^+ \cdot B) = \Delta Y_{CT}' + \Delta Y_{PS} \tag{35}$$

and the energies of the two spectra are related by

$$\Delta Y_{CT} + \Delta Y_{CT}' = \Delta Y_{FC}(A \cdot B^+) + \Delta Y_{FC}'(A^+ \cdot B) \tag{36}$$

$$\Delta Y_{CT} - \Delta Y_{CT}' = 2\Delta Y_{PS} + \{\Delta Y_{FC}(A \cdot B^+) - \Delta Y_{FC}'(A^+ \cdot B)\} \tag{37}$$

On the basis of the electrostatic theory outlined in the following, the braced terms in Eq. (37) will cancel provided that the Groups A and B in the complex have similar geometry. (See Section III,B).

Calculations of ΔG_{FC} based on Eq. (34) are shown in Table III. The values of ΔG_W and $\Delta G_W'$ used are only approximate, because they are based on data for various ionic strengths. But this is not a serious error since they are all small—certainly small enough to justify the assumptions made in the foregoing. Data for cobalt(III) complexes have been included in the Table III, but they cannot be used for calculations of ΔG_{FC} because the cobalt(III) product of the optical redox

TABLE III

CONTACT ION PAIRS: ENERGY PARAMETERS FOR THE CHARGE-TRANSFER PROCESS $(A^+ \cdot B) \rightarrow (A \cdot B^+)$

A^+(env)	B(env)	ΔG_{CT}	$-\Delta G_E(A^+)$	$\Delta G_E(B)$	ΔG_W	$-\Delta G_W'$	$\Delta G_{FC}(A \cdot B^+)$
$Ru(NH_3)_6^{3+}$	Cl^-	97.3	2.3[h]	−57.4[j]	−1.6[a]	0.0[m]	40.6
$Ru(NH_3)_6^{3+}$	Br^-	88.6	2.3[h]	−45.0[j]	−1.4[a]	0.0[m]	44.5
$Ru(NH_3)_6^{3+}$	I^-	71.2	2.3[h]	−31.5[j]	−1.4[a]	0.0[m]	40.6
$Ru(NH_3)_6^{3+}$	NCS^-	88.2	2.3[h]	−39.6[k]	−1.4[m]	0.0[m]	49.5
$Ru(NH_3)_6^{3+}$	$S_2O_3^{2-}$	71.0					
$Ru(en)_3^{3+}$	I^-	63.6[c]	4.9[h]	−31.5[j]	−0.9[n]	0.0[m]	36.1
$Co(NH_3)_6^{3+}$	I^-	106.8[d]	2.3[i]	−31.5[j]	−2.3[o]	0.0[m]	—
$Co(en)_3^{3+}$	I^-	100.2[e]	−2.6[i]	−31.5[j]	−1.8[p]	0.0[m]	—
$Co(en)_3^{3+}$	NCS^-	100.2[f]	−2.6[i]	−39.6[k]	−1.8[m]	0.0[m]	
$Co(en)_3^{3+}$	$S_2O_3^{2-}$	109.9[f]					
$Co(en)_3^{3+}$	$Fe(CN)_6^{4-}$	64.9[g]	−2.6[i]	−8.2[l]	−4.3[q]	3.8[r]	—

[a] Waysbort *et al.* (*143*).

[b] Armor (*3a*).

[c] Elsbernd and Beattie (*43*).

[d] Yokoyama and Yamatera (*152*).

[e] Schmidtke (*122*).

[f] Yoneda (*153*).

[g] Larsson (*81*).

[h] Meyer and Taube (*98a*).

[i] Martell and Sillén (*94*).

[j] Berdnikov and Bazhin (*14*).

[k] Wilmarth (*147*).

[l] Hanania *et al.* (*59*).

[m] Assumed.

[n] Estimated from $Ru(NH_3)_6^{3+} + I^-$, by analogy with pairs of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ complexes (*12*). On the other hand, Elsbernd and Beattie (*43*) found $\Delta G_W \geq +1.8$ kcal mole^{-1}.

[o] Estimated by analogy with $Co(NH_3)_6^{3+} + X^-$ (X = Cl, Br) (*12*).

[p] Estimated from $Co(NH_3)_6^{3+} + I^-$ by analogy with other pairs of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ complexes (*12*).

[q] Assumed to be same as for $Co(NH_3)_5OH_2^{3+} + Fe(CN)_6^{4-}$ (*50*), by analogy with the pair of complexes $Co(NH_3)_5OH_2^{3+} \cdot SO_4^{2-}$ and $Co(en)_3^{3+} \cdot SO_4^{2-}$.

[r] Assumed by analogy with various $M^{2+} \cdot Fe(CN)_6^{3-}$ complexes (*94*).

process is believed to be the low-spin state, whereas the thermodynamic data relate to the high-spin state. Thus the optical process for the complex $Co(NH_3)_6{}^{3+}\cdot I^-$ is

$$Co(NH_3)_6{}^{3+}(aq)\cdot I^-(aq) \xrightarrow{\Delta G_{CT}} Co[t_{2g}{}^6e_g{}^1](NH_3{}^*)_6{}^{2+}(aq^*)\cdot I(aq^*) \qquad (38)$$

where the asterisks are used to show that, in the excited state, both the NH_3 molecules and the solvent molecules are in positions characteristic of the cobalt(III) complex.

If we define an excitation energy ΔG_{ex} for the process,

$$Co[t_{2g}{}^5e_g{}^2](NH_3{}^*)_6{}^{2+}(aq^*)\cdot I(aq^*) \xrightarrow{\Delta G_{ex}} Co[t_{2g}{}^6e_g{}^1](NH_3{}^*)_6{}^{2+}(aq^*)\cdot I(aq^*) \qquad (39)$$

then Eq. (34) need only be modified by the addition of $-\Delta G_{ex}$ on the right-hand side. Provided ΔG_{ex} is the same for complexes with different anions, it is possible to make valid comparisons between the data.

Examining first the optical transition energies ΔG_{CT}, we see that, for $Ru(NH_3)_6{}^{3+}$ complexes, these decrease in the order $Cl^- > Br^- > NCS^- > I^- \approx S_2O_3{}^{2-}$; and for $Co(en)_3{}^{3+}$ the order is similar, $NCS^- > I^- = S_2O_3{}^{2-} > Fe(CN)_6{}^{4-}$. The differences in ΔG_{CT} for the hexammine- and *tris*ethylenediamine metal complexes, with I^- as anion, are similar for cobalt(III) and ruthenium(III). The difference between $Ru(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ is similar for iodide and thiosulfate, but somewhat less for thiocyanate. Except for this last observation, which may have a bearing on the mode of bonding of NCS^- in the outer sphere, these comparisons agree with the additive model of Eq. (34) and provide some support for it. The difference in ΔG_{FC} between the pairs $Co(en)_3{}^{3+}\cdot Fe(CN)_6{}^{4-}$ and $Co(en)_3{}^{3+}\cdot I^-$ can be calculated from the data of Table III provided we assume that the excitation energies ΔG_{ex} cancel. The result, 11 kcal mole^{-1}, may be compared with the apparent difference between ΔG_{FC} for the single species $Fe(CN)_6{}^{3-}$ and I, namely 17 kcal mole^{-1} (Table II). Furthermore the value of ΔG_{ex} itself can also be roughly estimated. From the data for the $Co(NH_3)_6{}^{3+}\cdot I^-$ pair (Table III), we may deduce $\Delta G = 64.3$ kcal mole^{-1} for the process

$$Co(NH_3)_6{}^{2+}[t_{2g}{}^5e_g{}^2](aq) \rightarrow Co(NH_3{}^*)_6{}^{2+}[t_{2g}{}^6e_g{}^1](aq^*) \qquad (40)$$

and if the contribution due to Franck–Condon factors, such as bond compression and solvent reorganization, is the same as for $Ru(NH_3)_6{}^{2+}\cdot(aq) \rightarrow Ru(NH_3)_6{}^{2+}(aq^*)$, then we have $\Delta G_{ex} = 34.7$ kcal mole^{-1}. It is interesting to compare this with the energy of the lowest d-d band in the spectrum of $Co(NH_3)_6{}^{2+}$ ion, which may be ascribed to the transition

$$Co(NH_3)_6{}^{2+}[t_{2g}{}^5e_g{}^2](aq) \rightarrow Co(NH_3)_6{}^{2+}[t_{2g}{}^4e_g{}^3](aq) \qquad (41)$$

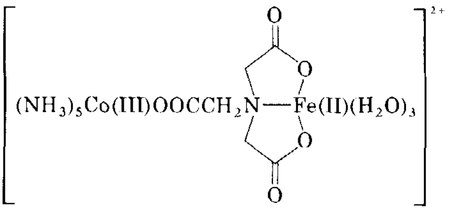
i.e., $\Delta G = 25.8$ kcal mole^{-1} (*5*). The corresponding figures for the *tris*ethylenediamine complexes are 28 and 26.9 kcal mole^{-1}. It should be noted that the equilibrium configuration of low-spin cobalt(II) would be expected to be strongly distorted toward a tetragonal structure, whereas these calculations apply to octahedral systems. Hence the equilibrium

$$\mathrm{Co(NH_3)_6^{2+}}[t_{2g}{}^5e_g{}^2](\mathrm{aq}) \rightleftharpoons \mathrm{Co(NH_3)_6^{2+}}[t_{2g}{}^6e_g{}^1](\mathrm{aq}) \qquad (44)$$

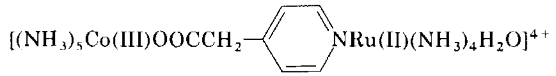
would actually be more favorable than these calculations suggest.

D. Linked Pairs

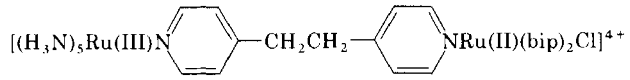
By *linked pairs* we denote oxidant–reductant pairs that are joined by a chain of atoms serving to fix the mutual distance between certain limits but not interacting electronically with either of the reacting centers, as exemplified in structures **I** to **IV**.



(I)



(II)



(III)

$[(\mathrm{C_5H_5})\mathrm{Fe(III)C_5H_4{\cdot}CH_2{\cdot}C_5H_4Fe(II)(C_5H_5)}]^+$

(IV)

Complexes **I** (*20*) and **II** (*68*) are unstable with respect to internal electron transfer, and the rates of the thermal reactions have been measured; complex **III** (*2e*) is stable with respect to electron transfer. Complex **IV** is symmetrical and presumably subject to rapid internal transfer (*103*). Optical charge transfer has not been detected in any of these systems. In the case of the two cobalt(III) complexes, comparison with the data of Table III suggests that the bands should be in the visible or near ultraviolet region, and, for complex **III**, at still lower energy. The intensities, however, would be low in view of the weak metal–metal orbital interaction. Complexes of this type are important models for the outer-sphere electron transfer process and further study of analogous systems would be worthwhile. In particular, they could be used to study the dependence of ΔG_{FC} on internuclear distance, by varying the chain length while keeping the same oxidant and reductant ions and the same inner-sphere ligand environments. It seems evident that, as the interionic distance is decreased, ΔG_{FC} will decrease, but so far neither theoretical nor experimental data are available. In the limit of infinite separation, ΔG_{FC} is expected to approach the sum of the two single-ion reorganization energies [Eq. (28)].

E. BRIDGED BINUCLEAR COMPLEXES

In Tables IV–VI are listed spectral data for binuclear complexes in which the metal ions are joined through a single ligand atom or through a bridging molecule that may be expected to modify the electronic structures of oxidant, reductant, or both. These systems may conveniently be classified according to the degree of certainty of the information that may be deduced from them.

TABLE IV

MISCELLANEOUS BINUCLEAR COMPLEXES: CHARGE-TRANSFER SPECTRA

Complex ($B{\cdot}X{\cdot}A^+$)	Medium	$\nu_{\mathrm{CT}}/10^3\ \mathrm{cm}^{-1}$	Ref.
U(V)—U(VI)	0.1*M* $HClO_4$	13.6	(*110*)
Ti(III)—Ti(IV)	12*M* HCl	14.9, 20.1	(*70*)
Ti(III)—Ti(IV)	20% H_2SO_4	21.2	(*52*)
$(NC)_6V(II)OHV(III)(CN)_5{}^{7-}$	CN^-(aq)	17.0	(*13*)
Fe(II)—Fe(III)	12*M* HCl	Ca. 12.5–18	(*88*)
Cu(I)—Cu(II)	10*M* HCl	Ca. 17	(*38, 39, 87, 142*)
Cu(I)—Cu(II)	CH_3OH, OAc^-	11.1	(*125*)
Sn(II)—Sn(IV)	12*M* HCl	Ca. 25–30	(*146a*)
Sb(III)—Sb(V)	HCl	Ca. 20	(*146b*)[a]
Sn(II)—U(IV)	6*M* HCl	>24	(*101*)
$Cl_5W(III)OW(V)Cl_5{}^{4-}$	12*M* HCl	19.5	(*79*)
Cu(I)—Cu(II)	NH_3(aq)	No interaction	(*87*)
$Fe(CN)_6{}^{4-}$—$Fe(CN)_6{}^{3-}$	aq (?)	No interaction	(*87*)

[a] For further references and discussions, see Robin and P. Day (*119a*), and Allen and Hush (*119b*).

TABLE V

BINUCLEAR COMPLEXES: ENERGY PARAMETERS FOR THE CHARGE-TRANSFER PROCESS $(A^+ \cdot X \cdot B) \rightarrow (A \cdot X \cdot B^+)$

Complexes							
$B \cdot X$	A^+	ΔG_{CT}	$\Delta G_E(B^- \cdot X)$	$-\Delta G_E(A^-)$	ΔG_W	$-\Delta G_W'$	ΔG_{FC}[a]
$(NC)_5Fe(II) \cdot CN^{4-}$	$(H_2O)Fe(III)(CN)_5{}^{2-}$	22.0[b]	−8.2[c]	+9.5[d]	—	—	Ca. 20[e]
B	$X \cdot A^+$	ΔG_{CT}	$\Delta G_E(B^-)$	$-\Delta G_E(X \cdot A^-)$	ΔG_W	$-\Delta G_W'$	ΔG_{FC}[a]
Ag^+	$MnO_4{}^-$	71.5[f]	−46.0[g]	12.8[h]	−1.2[i]	3.1[j]	30.2
Fe^{2+}	$Mo(V)(CN)_6{}^{3-}$	34[k]	−17.6[l]	~17[m]	−4[n]	5.6[k]	36
Cr^{3+}	$CrO_4{}^{2-}$	41[o]	−50 ± 10[p]	7.5 ± 1.5[q]	−7[o]	—	—

[a] See text and Eq. (*45*).

[b] Glauser *et al.* (*51*).

[c] Hanania (*59*).

[d] Malik and Om (*91*).

[e] Assuming $\Delta G_W \sim \Delta G_W'$ (see text, Eq. 45).

[f] Symons and Trevalion (*133*).

[g] Noyes (*112*).

[h] Carrington and Symons (*21*).

[i] Assumed to be the same as for $K^+ \cdot TcO_4{}^-$ (*124*).

[j] Assumed by analogy with $Zn^{2+} \cdot SO_4{}^{2-}$ (*94a, b*).

[k] Malik and Ali (*90*).

[l] Zielen and Sullivan (*154*).

[m] Kolthoff and Tomsicek (*78*).

[n] Assumed by analogy with various $M^{2-} \cdot Fe(CN)_6{}^{3-}$ complexes (*94a, b*).

[o] King and Neptune (*75*).

[p] Haight *et al.* (*56*).

[q] Using $E^{\ominus}$ $(HCrO_4{}^- + 2H^+ \rightleftharpoons H_3CrO_4) = 0.575 \pm 0.075$ volt (*56*) and assuming same acid dissociation constants for H_3CrO_4 as for H_3PO_4 (*94a, b*).

TABLE VI

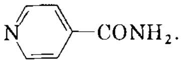
SYMMETRICAL BRIDGED MIXED-VALENCE COMPLEXES

Complex[a] $A \cdot X \cdot A^+$	Medium	ΔG_{CT} (kcal mole^{-1})	Ref.
$(phen)_2V(II) \cdot OH \cdot V(III)(phen)_2^{4+}$	$SO_4^{2-}(aq)$	—	(*106*)
$(phen)_2Mn(III)(O)_2Mn(IV)(phen)_2^{3+}$	CH_3CN	—	(*115*)
$(NC)_4Fe(II)\langle{}^{CN}_{NC}\rangle Fe(III)(CN)_4^{5-}$	aq	22.2	(*44*)
$(C_5H_5)Fe(II)(C_5H_4—C_5H_4)Fe(III)(C_5H_5)^+$	CH_3CN	15.0	(*26, 73*)
$Fe(II)(C_5H_4—C_5H_4)_2Fe(III)^+$	CH_3CN	18.5, 25.1	(*105*) [cf. (*27*)]
$(C_5H_5)Fe(II)C_5H_4C{\equiv}CC_5H_4Fe(III)(C_5H_5)^+$	CH_2Cl_2	18.3	(*84*)
$Fe(II)(C_5H_4—CH_2—C_5H_4)_2Fe(III)^+$	CH_3CN	38.0	(*102*)
$(NC)_5Fe(II)(pyz)Fe(III)(CN)_5^{5-}$	$C_6H_5NO_2$	20.3, 24.3	(*144*)
$L_2Co(I)(Ph_2PCH{:}CHPPh_2)Co(II)L_2^-$	CH_2Cl_2	19.6	(*41*)[b]
$L_2Co(I)(Ph_2PCH{:}CHPPh_2)Co(II)L_2^-$	CH_2Cl_2	21.0	(*41*)[c]
$(H_3N)_5Ru(II)NC \cdot CNRu(III)(NH_3)_5^{5+}$	D_2O	20.0	(*136*)
$(H_3N)_5Ru(II)(pyz)Ru(III)(NH_3)_5^{5+}$	D_2O	19.5	(*29a, d*)
$py(H_3N)_4Ru(II)(pyz)Ru(III)(NH_3)_4py^{5+}$	D_2O	17.3	(*29d*)
$L(H_3N)_4Ru(II)(pyz)Ru(III)(NH_3)_4L^{5+}$	D_2O	17.3	(*29d*)[d]
$(bip)(H_3N)_3Ru(II)(pyz)Ru(III)(NH_3)_3(bip)^{5+}$	D_2O	16.6	(*29d*)
$(bip)_2ClRu(II)(pyz)Ru(III)Cl(bip)_2^{3+}$		22.6	(*18*)
$(H_3N)_5Ru(II)(py\text{-}py)Ru(III)(NH_3)_5^{5+}$	D_2O	27.5	(*137*)

[a] Abbreviations: bip = 2:2′-bipyridyl; phen = 9:10-phenanthroline; py = pyridine; py-py = 4:4′-bipyridyl; pyz = pyrazine.

[b] $L^{2-} = S(CF_3)C{:}C(CF_3)S^{2-}$

[c] $L^{2-} = S(CH_3)C{:}C(CH_3)S^{2-}$

[d] L = 

1. *Labile Complexes of Unknown Structure*

Some of the earliest observations on optical charge transfer were made on solutions containing a metal in two different valency states: interaction colors were observed that could not be attributed to either of the metal ions separately. In most cases, it has been ascertained that only one ion of oxidant and one of reductant is present in the complex, since the intensity of the relevant absorption band is proportional to the concentrations of each. Evidence of the bridging group is indirect but generally convincing; for example, where the medium is shown as hydrochloric acid, it has been found that replacement of chloride ion by some other, noncomplexing, anion discharges the color, and, similarly, with the copper(II)–copper(I) color in methanol, the presence of acetate ion is essential (Table IV). Again, in some cases it has been shown that the addition of other more powerful complexing agents discharges the color, presumably by breaking the binuclear complex down into mononuclear complexes. Thus, the titanium(III)–titanium(IV) system in sulfuric acid is decolorized by the addition of phosphoric acid, and the copper(I)–copper(II) system in methanol is decolorized by acetonitrile.

The actual numbers of anions involved in these complexes have not been determined, and the arrangement of ligands around the two metal ions can only be conjectured. In most cases, it seems likely that the structures are unsymmetrical because the coordination preferences of the metal ions in their two valency states are generally different. Formula $[TiCl^{2+}][TiCl_6{}^{2-}]$ has been suggested for the titanium(III)–titanium(IV) complex in hydrochloric acid; on the other hand, for the copper(I)–copper(II) acetate complex in methanol, a symmetrical structure has been suggested. (In Table IV, the references for all these investigations are cited.)

2. *Complexes with Inert Chromophores*

When the constituent metal ions occur in complexes that exchange their ligands only slowly or when their coordination preferences for the medium in question are well established, the structure of the binuclear complex can be written down with some confidence. This appears to be the case for the complex formed by mixing the ions $Fe(II)(CN)_6{}^{4-}$ and $Fe(III)(CN)_5OH_2{}^{2-}$. A strong interaction color is observed, which implies the formation of a bridged species, since no such color is seen on mixing $Fe(CN)_6{}^{4-}$ and $Fe(CN)_6{}^{3-}$; and the rate of formation of the complex is rapid compared with the rates of replacement exchange of cyanide ligands in either of the two monomers. Hence the most likely structure is one with a single cyanide group connecting the two metals.

Other binuclear complexes with clearly defined structures have been characterized as products of bridged electron transfer reactions, as for example $(NC)_5Fe(II)CNCo(III)(edta)^{4-}$ from the reaction of $Fe(CN)_6{}^{3-}$ and $Co(II)(edta)^{2-}$ (*63*), and $(H_2O)_5Cr(III)ClIr(III)Cl_5$ from $Cr^{2+}\cdot$ aq and $IrCl_6{}^{2-}$ (*132*). Charge transfer spectra and photo-electron transfer reactions have recently been reported (*141a*).

The chromium(III)–chromium(VI) complex listed in Table V almost certainly contains octahedrally coordinated chromium(III) and tetrahedral chromium(VI), as in the separate ions $Cr(H_2O)_6{}^{3+}$ and $CrO_4{}^{2-}$. It is formed rapidly and reversibly on mixing the solutions of these ions, but the actual rate of formation has not been measured, and since the chromium(VI) ion, but not the chromium(III) ion, is known to undergo substitution rapidly, the experiment does not distinguish between the alternative outer- and inner-sphere structures,

$[Cr(H_2O)_6{}^{3+} \cdot CrO_4{}^{2-}]$ and $[(H_2O)_5Cr(III)OCr(VI)O_3]^+$. Similar ambiguities apply to the complexes $Ag^+ \cdot MnO_4{}^-$ and $Fe^{2+}[Mo(V)(CN)_8{}^{3-}]$ in Table V, in which the cations are labile to substitution whereas the anions are inert.

The energetics of these systems may again be described by the general equation (4), and the unknown ΔG_{PS} may again be estimated by means of a thermodynamic cycle involving separated complexes. There are, however, different versions of this cycle, depending on the treatment of the bridging group X. If X is associated with the metal atom A in both its reduced and oxidized forms, we obtain

$$\begin{tikzcd}
A^+ \cdot X(env) + B(env) \arrow[r, "\Delta Y_W'"] \arrow[d, "\Delta Y_0"] & A^+ \cdot X \cdot B(env) \arrow[r, "\Delta Y_{CT}"] \arrow[d, "\Delta Y_{PS}"] & A \cdot X \cdot B^+(env^*) \\
A \cdot X(env) + B^+(env) \arrow[r, "\Delta Y_W'"] & A \cdot X \cdot B^+(env) \arrow[ur, "\Delta Y_{FC}"] &
\end{tikzcd} \qquad (45)$$

with

$$\Delta Y_0 = \Delta Y_E(A^+ \cdot X) - \Delta Y_E(B^+) \qquad (46)$$

but if X is associated with atom B in both forms, we obtain the analogous cycle with

$$\Delta Y_0 = \Delta Y_E(A^+) - \Delta Y_E(B^+ \cdot X) \qquad (47)$$

The available data are listed in Table V. In the case of complex $(NC)_5Fe(II)CNFe(III)(CN)_5{}^{6-}$, the natural choice of reference complexes is the pair $Fe(CN)_6{}^{3-}$ and $Fe(CN)_5OH_2{}^{2-}$, corresponding to $B^+ \cdot X$ and A of Eq. (47). It happens that the standard potentials of the corresponding redox couples are very nearly the same, i.e., $\Delta G_0 \approx 0$; and, although neither of the two work terms is known, it seems likely that they too will approximately cancel.* If so, the observed charge transfer energy is largely a measure of the Franck–Condon barrier. For the systems $Ag^+ \cdot MnO_4{}^-$, both work terms are unknown and, for $Fe^{2+} \cdot Mo(CN)_8{}^{3-}$, the term ΔG_W is unknown, but these can be estimated by analogy with other complexes, and in both cases the uncertainty in so doing is clearly much smaller than the final estimate of ΔG_{FC}. Data for the Cr(III)—Cr(VI) complex are less satisfactory

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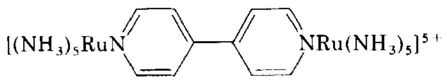
* In partial support of this suggestion, we note the small value of the equilibrium constant, $\log K \cong -1$, for the reaction $(NC)_5Co(III)NCFe(II)(CN)_5{}^{6-} + Fe(III)(CN)_6{}^{3-} \rightleftharpoons (NC)_5Co(III)NCFe(III)(CN)_5{}^{5-} + Fe(CN)_6{}^{4-}$ (*56a*).

but more interesting: there is considerable uncertainty in the Cr(IV)/Cr(III) reduction potential, and it is difficult to estimate the work term $\Delta G_W'$ for the equilibrium $\mathrm{Cr(IV)} + \mathrm{Cr(V)} \rightleftharpoons \mathrm{Cr(IV)\cdot Cr(V)}$. We can, however, conclude that $\Delta G_{FC} + \Delta G_W' = -10 \pm 12$ kcal mole^{-1}, so that if ΔG_{FC} is similar to the other values recorded in Table V, $\Delta G_W'$ must be substantially negative, e.g., $\Delta G_W' \leq -20$ kcal mole^{-1}. This argues strongly for an inner-sphere formulation of the successor complex, $[(H_2O)_5Cr(IV)OCr(V)O_3]^+$. It is only because of the stability of this complex that the charge-transfer absorption appears in the visible region at all. No other examples of Cr(III) → Cr(VI) charge transfer seem to be known.

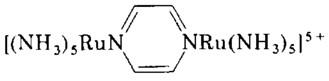
3. Symmetrical Inert Complexes

In recent years several complexes have been prepared that contain oxidant and reductant ions of the same element, with the same inner-sphere ligand environment and a symmetrical bridging group (Table VI). In the most-studied cases, analogous compounds with one more and one less electron are known, forming a redox series $A^+\cdot X\cdot A^+$(env), $A^+\cdot X\cdot A$(env), $A\cdot X\cdot A$(env), and the electronic spectrum of the mixed-valence species contains a unique band in addition to the bands characteristic of the separate $A^+\cdot X$ and $A\cdot X$ chromophores.

When the first complex of this type was reported, it was thought that the energy of the lowest observable electronic transition gave a direct measure of the Franck–Condon energy barrier, but it is now recognized that this is not necessarily the case: it depends on the degree of interaction between the zero-order states, as shown in Fig. 1. The three possibilities of weak, moderate, and strong interaction can be neatly distinguished in the series of complexes **V** to **VII**, respectively.



(V)



(VI)

$[(NH_3)_5RuN{\equiv}C{-}C{\equiv}NRu(NH_3)_5]^{5+}$

(VII)

Complex **V** (*136*) has the characteristic low-energy absorption band, with the predicted half-width, and subject to strong solvent shifts as expected for a long-range charge transfer process; but in the ground state there is evidently very little interaction between the ruthenium atoms. The equilibrium constant K_{con} for the conproportionation reaction among the three members of the redox series,

$$(\text{A·X·A}) + (\text{A}^+\text{·X·A}^+) \xrightleftharpoons{k_{\text{con}}} 2(\text{A·X·A}^+) \tag{48}$$

has been shown to be close to the statistical value, $K_{\text{con}} = 4$.

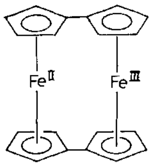
Complex **VI** (*29*) has the low-energy band, but it is relatively narrow and not appreciably solvent-dependent, and there is evidence of appreciable delocalization in the ground state, with $K_{\text{con}} \cong 1.3 \times 10^6$. The exact state of this complex is still controversial. There is no doubt that the valencies are subject to a rapid thermal exchange reaction,

$$[\text{Ru(II)} - \text{Ru(III)}]^{5+} \xrightleftharpoons{k_{\text{ex}}} [\text{Ru(III)} - \text{Ru(II)}]^{5+} \tag{49}$$

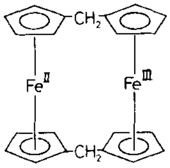
The photoelectron spectrum was initially interpreted (*29e*) in terms of trapped valencies; but a theoretical study by Hush (*67*) has shown that a delocalized description is equally consistent with the data available so far. Infrared data are still under discussion, but the Raman spectrum has been interpreted (*29f*) in terms of localization. It does seem clear that the rate of valence interchange according to Eq. (1) is rapid compared with the NMR time scale (*29b*); the possibility remains that the rate may be comparable with the frequencies of certain bond vibrations.

Complex **VII** (*137*) seems quite clearly to be of the average valency type (Fig. 1a, curves 3,3). Again, there is a near infrared electronic absorption band, but it is narrower than that expected for an intervalence band and is not subject to solvent shifts. The conproportionation constant is large ($K_{\text{con}} \geq 10^{13}$) and the valences are delocalized at least on the infrared time scale ($k_{\text{ex}} > 10^{13}$ sec^{-1}).

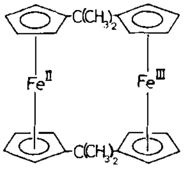
The difficulties of interpretation presented by some of these complexes are well illustrated by the sequence of ferrocene derivatives (**VIII** to **X**). The spectrum of **VIII** shows a near-infrared absorption as expected for a mixed valence complex, but the band has a shoulder, and at low temperatures is resolved into two bands. Complex **IX** has a well-defined band almost certainly ascribable to intervalence transfer, but complex **X** with a similar molecular structure has no such



(VIII)



(IX)



(X)

band. The review paper by Morrison and Hendrickson (*102*) should be consulted for further details and comments on the electronic states of these and related compounds.

Studies have also been made of the effect of nonbridging ligands attached unsymmetrically, i.e., to only one ruthenium atom. Regardless of the nature of the ligand, the charge-transfer absorption is shifted to higher energy (*2e,f,29d*). This is because if ligand L stabilizes ruthenium(III) (e.g., $L = Cl^-$) the ground state of the complex becomes LRu(III)·X·Ru(II)(env), whereas if it stabilizes ruthenium(II) (e.g., L = pyridine), we get Ru(III)·X·Ru(II)L(env). In either case, the charge-transfer energy now includes a contribution due to the difference in stability, ΔG_{PS}, between precursor and successor states, e.g.,

$$\begin{tikzcd} \mathrm{LRu(III)\cdot X\cdot Ru(II)(env)} \arrow[r, "\Delta G_{CT}"] \arrow[dr, "\Delta G_{PS}"'] & \mathrm{LRu(II)\cdot X\cdot Ru(III)(env)^*} \\ & \mathrm{LRu(II)\cdot X\cdot Ru(III)(env)} \arrow[u, "\Delta G_{FC}"'] \end{tikzcd} \qquad (50)$$

Values of ΔG_{PS} have not been obtained experimentally, but free-energy data for analogous systems such as the redox couple $\mathrm{LRu(III)X} + e^- \rightleftharpoons \mathrm{LRu(II)X}$ are known and a plot of ΔG_{CT} against ΔG_E[LRu(III)X] has been found to be linear with unit slope, as expected (*29d*).

F. Directly Bonded Complexes

Systems in which the donor and acceptor atoms are directly linked are extremely common and were among the first electron transfer systems to be spectroscopically characterized (*48*, *69*). The transition may be between localized states as in the aqueous ion $FeCl^{2+}$ or delocalized states as in $OsCl_6$. In the former case, the ground state can be written $(H_2O)_5Fe^{3+}\cdot Cl^-$, with excitation to $(H_2O)_5Fe^{2+}Cl$; in the latter case, whether one writes an ionic or a covalent formula, the transferring electron may be said to leave a "hole" which is symmetrically distributed over the 6 chlorine atoms (*69a*). No case is known in which donor and acceptor atoms are of the same element. There are several binuclear complexes with metal–metal bonds that could be formulated as mixed valence species, e.g., $\mathrm{Re(III)Re(IV)Cl_8}^-$, Ru(II) $\mathrm{Ru(III)(OAc)_4Cl}$(*25*), $\mathrm{Rh(II)Rh(III)(OAc)_4}^+$(*148*), but in each case there is evidence that the valence states are equivalent on the infrared time scale. With suitable distortions of bond lengths, some localization would occur, for example, by compressing the bonds at one end of the molecules, and lengthening the bonds at the other end, and these would represent modes of vibration. Such modes would be expected, therefore, to show electronic coupling and this might be revealed by a study of the infrared spectrum, but no such studies have been reported as yet.

1. *Octahedral Metal Complexes: Ligand-to-Metal Charge Transfer*

We shall discuss the energetics of these processes by referring first to a specific example, the complex $Ru(NH_3)_5I^{2+}$. This has an intense absorption in the visible region and a recent MCD study confirms its assignment as iodide → ruthenium charge transfer (*47*). From known equilibrium data, we may obtain the free energy of the state $Ru(NH_3)_5OH_2^{2+}(aq) + I(aq)$, and the question is whether or not we can link this to the excited charge-transfer complex in a meaningful way. It is suggested that we may do so as follows. In the convention already established, we write the excited complex as $[Rh(II)NH_3)_5{\cdot}I(env^*)]^{2+}$, indicating a species with the electronic configuration as shown but with all atoms and solvent molecules in the positions appropriate to the ground state $Ru(NH_3)_5I^{2+}$. Let this be dissociated into I(env)* and $Ru(NH_3)_5^{2+}(env^*)$, where the former is the same species as previously defined, i.e., an iodine atom with a solvation environment characteristic of the iodide ion, and the latter is a ruthenium(II) ion with one vacant position in the inner sphere, with five inner-sphere ammonia ligands attached at positions characteristic of ruthenium (III), and with an outer-sphere solvent shell likewise characteristic of ruthenium(III). On relaxing the solvent and ammonia molecules, but not filling the sixth ligand position, we arrive at $Ru(NH_3)_5^{2+}(env)$, a five-coordinate ruthenium(II) complex with outer sphere solvation. This, in turn, closely parallels the definition of the activated complex involved in ligand exchange reactions by the dissociative or SN_1 mechanism. For example, in the aquation of $Co(III)(NH_3)_5X$ complexes, there is evidence that in the transition state the CoN_5 framework remains intact, the Co—X group is fully broken, and that incoming groups have little specific interaction with the Co atom, while at the same time there is an appreciable stabilization of the five-coordinate system by solvation (*9*). We may, therefore, estimate the energy of this species by using the free energy of activation for the water-exchange process:

$$Ru(NH_3)_5OH_2^{2+} + H_2O^{18} \xrightarrow{k} Ru(NH_3)_5O^{18}H_2^{2+} + H_2O \tag{51}$$

$$Ru(NH_3)_5OH_2^{2+} \xrightleftharpoons{\Delta G^\ddagger} [Ru(NH_3)_5^{2+}]^\ddagger + H_2O \tag{52}$$

where $\Delta G^\ddagger$ is related to the second-order rate constant k by

$$k = Z\exp(-\Delta G^\ddagger/RT) \tag{53}$$

and Z is the specific rate for the diffusion-controlled reaction (*92a*). The completed cycle (Scheme 1) contains three unknowns that may

$$\begin{tikzcd}
\mathrm{Ru(NH_3)_5{}^{*2+}(env)} + & \mathrm{I(env^*)} \arrow[r, "\Delta Y_W{}^*"] & \mathrm{[Ru(II)(NH_3)_5 \cdot I(env^*)]^{2+}} \\
\mathrm{Ru(NH_3)_5{}^{2+}(env)} + \arrow[u, "\Delta Y_{FC}(A)"] & \mathrm{I(env)} \arrow[u, "\Delta Y_{FC}(B^+)"] \arrow[ur, "\Delta Y^*"] & \\
\mathrm{Ru(NH_3)_5OH_2{}^{2+}(env) + I(env)} \arrow[u, "\Delta Y^\ddagger"] & & \\
\mathrm{Ru(NH_3)_5OH_2{}^{3+}(env) + I^-(env)} \arrow[u, "\Delta Y_E(A^+)\quad \Delta Y_E(B^+)"] \arrow[rr, "\Delta Y_W"] & & \mathrm{[Ru(III)(NH_3)_5 \cdot I\ (env)]^{2+}} \arrow[uuu, "\Delta Y_{CT}"']
\end{tikzcd}$$

SCHEME 1

be grouped together as

$$\Delta Y^* = \Delta Y_{FC}(A) + \Delta Y_{FC}(B^+) + \Delta Y_W^* \tag{54}$$

giving

$$\Delta Y^* = \Delta Y_{CT} + \Delta Y_W - \Delta Y^\ddagger - \Delta Y_E(A^+) + \Delta Y_E(B^+) \tag{55}$$

where, in this case, $A = Ru(NH_3)_5OH_2{}^{2+}$ and $B = I^-$.

Calculations of ΔG^* based on this cycle are shown in Table VII. We can only comment qualitatively on the trends observed in these results, and it must be remembered that $\Delta G_W{}^*$, and, therefore, also ΔG^*, may contain substantial attrative or repulsive contributions from the bond term [see Eq. (13)].

It does, however, seem significant that the highest ΔG^* are associated with the most ionic complexes, $Fe(H_2O)_5X^{2+}$, and that there is little difference between the complexes with the two halogens, X = Cl, Br (as with the outer-sphere complexes shown in Table III). If, in these cases, $\Delta G_W{}^*$ were close to zero, the values $\Delta G^* \sim 43$ kcal mole^{-1} would represent the sum of the two reorganization energies, and again, the values are not very different from those observed in the outer-sphere case. The very much smaller values of ΔG^* for $Ru(NH_3)_5X^{2+}$ complexes (X = Cl, Br, I) might suggest that the reorganization energy of Ru $(NH_3)_5{}^{2+}$ is correspondingly smaller, but the appreciable difference

TABLE VII

DIRECTLY BONDED COMPLEXES: ENERGY PARAMETERS FOR THE CHARGE-TRANSFER PROCESS $(A^+—B) \rightarrow (A—B^+)$

Complex $A^+—B$	ΔG_{CT}	$-\Delta G_E(A^+)$	$\Delta G_E(B^+)$[a]	ΔG_W	$-\Delta G^{\ddagger}$[b]	ΔG^*
$(NH_3)_5Ru(III)I^{2+}$	52.6[c]	+3.7[d]	−31.5	−2.3[d]	−15.2[e]	7.7
$(NH_3)_5Ru(III)Br^{2+}$	72.1[c]	+3.7[d]	−45.0	−1.9[d]	−15.2[e]	13.7
$(NH_3)_5Ru(III)Cl^{2+}$	87.2[c]	+3.7[d]	−57.4	−3.0[d]	−15.2[e]	15.7
$(H_2O)_5Ru(III)Cl^{2+}$	91.0[f]	+5.0[g]	−57.4	−2.0[h]	—	—
$(H_2O)_5Fe(III)Br^{2+}$	75.3[i]	+17.6[j]	−45.0	+0.4[k]	−8.5[l]	39.8
$(H_2O)_5Fe(III)Cl^{2+}$	89.5[i]	+17.6[j]	−57.4	−0.8[k]	−8.5[l]	40.4
$(NC)_5Co(III)I^{3-}$	86.7[m]	−27.1[n]	−31.5	−2.2[o]	0.0[p]	25.9
$(NC)_5Co(III)Br^{3}$	97.0[m]	−27.1[n]	−45.0	0.0[o]	0.0[p]	24.9
$(NC)_5Co(III)Cl^{3-}$	108.0[m]	−27.1[n]	−57.4	+1.5[q]	0.0[p]	~25
$(H_3N)_5Co(III)I^{2+}$	74.7[m]	−8.6[r]	−31.5	+0.8[s]	—	—
$(H_3N)_5Co(III)Br^{2+}$	91.0[m]	−8.6[r]	−45.0	+0.6[s]	—	—
$(H_3N)_5Co(III)Cl^{2+}$	103.1[m]	−8.6[r]	−57.4	−0.1[s]	—	—
$I_2{\cdot}I^-$	81.3[t]	3.0[u]	−31.5	−4.0[v]	0.0[w]	49.8
$I_2{\cdot}Br^-$	106.0[t]	3.0[u]	−45.0	−1.6[x]	0.0[w]	62.4
$I_2{\cdot}Cl^-$	115.4[t]	3.0[u]	−57.4	−1.0[t]	0.0[w]	60.4
$Br_2{\cdot}Br^-$	108.0[t]	—	−45.0	−1.9[y]	—	—
$Br_2{\cdot}Cl^-$	117.7[t]	—	−57.4	−0.3[z]	—	—
$Cl_2{\cdot}Cl^-$	122.8[t]	—	−57.4	+1.9[aa]	—	—

[a] Berdinikov and Bazhin (*14*).

[b] Calculated using Eq. (53), with $k = k'[H_2O]^{-1}$, where k' is the first-order specific rate of water exchange. We have used 2.303 RT = 1.36 kcal mole^{-1}, $[H_2O] = 55.5\ M$, $Z = 10^{10.5} M^{-1}$ sec^{-1}.

[c] Hartmann and Buschbeck (*60*).

[d] Endicott and Taube (*46*).

[e] J. A. Stritar (*129*).

[f] Cady and Connick (*17*).

[g] Mercer and Buckley (*97*).

[h] Estimated from $Ru(NH_3)_5Cl^{2+}$, by analogy with $Rh(H_2O)_5Cl^{2+}$ and $Rh(NH_3)_5Cl^{2+}$ (*94*).

[i] Rabinowitch (*117*).

[j] Zielen and Sullivan (*154*).

[k] Rabinowitch and Stockmayer (*118*).

[l] Swift and Connick (*131*).

[m] Miskowski and Gray (*100*).

[n] Taking the polarographic half-wave potential ($E_{1/2}$ = −1.45 volts, versus standard caloriel electrode hence $E^{O}_{1/2}$ = −1.18 volts) in 1.0M CN^- as the measure of the reversible electrode potential (*64*).

[o] At 40°C (*57*).

[p] Assumed. The $Co(CN)_5{}^{3-}$ ion has a tetragonal pyramidal structure equivalent to a regular octahedral structure with one ligand removed. There is, however, a change in color in going from the solid state to the aqueous solution, which suggests weak hydration to give $[Co(CN)_5{}^{3-}{\cdot}H_2O](aq)$ (*15a*).

[q] Assumed.

[r] Yalman (*150*).

[s] Langford (*80*).

[t] Meyerstein and Treinin (*99*).

[u] Baxendale and Bevan (*9a*).

[v] Katzin and Gebert (*72*).

[w] Assumed. The bimolecular decay constant k for $I_2{}^- + I_2{}^- \rightarrow I_2 + 2I^-$ is close to the diffusion-controlled limit, viz. $k = 10^9\ M^{-1}$ sec^{-1} (*9a*).

[x] Daniele (*31*).

[y] Daniele (*32*).

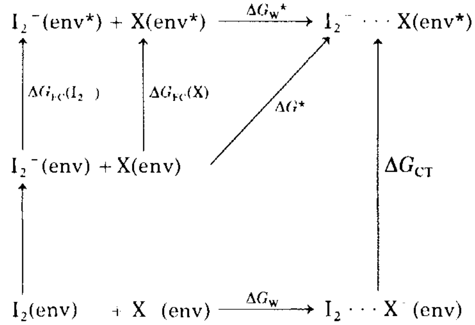
[z] Daniele (*33*).

[aa] Zimmerman and Strong (*155*).

between the iodo and bromo complexes, and the much higher value $\Delta G_{FC} = 42 \pm 2$ kcal mole^{-1} already obtained for the ion pair Ru $(NH_3)_6{}^{2+}\cdot I$, suggest that the metal–halogen bond is responsible for the difference. Possibly the Ru^{2+} ion and I atom should be considered as "soft" acid and base, respectively, so that $\Delta G_W{}^*$ would become more negative along the sequence X = Cl, Br, I. A similar comment could apply to complexes $Co(CN)_5X^{3-}$, but here there is the difference that the pentacoordinate cobalt(II) fragment $Co(CN)_5{}^{3-}$ is a known chemical species (*15a*), weakly hydrated in the sixth-ligand position, but showing very little tendency to add another ligand (*15b*). Thus, $\Delta G_W{}^*$ is more likely to be small or positive than to be substantially negative, and we may conclude that, for a given halogen, the difference in ΔG^* between $Co(CN)_5X^{3-}$ and $Fe(H_2O)_5X^{2+}$ is largely a difference in the reorganization energy. The fact that ΔG_{FC} is lower for $Co(CN)_5{}^{3-}$ than for $Fe(H_2O)_5{}^{2+}$, in spite of higher ionic charge, suggests that the inner-sphere bond adjustment contributes less in the pentacyano than in the pentaaquo cases. It would be interesting to have data for $Fe(III)(CN)_5X^{3-}$ complexes for comparison with the cobalt systems and with $Fe(CN)_6{}^{3-}$.

2. *Interhalogen Complexes*

A cycle analogous to Scheme 1 is shown in Scheme 2 for systems with iodine as oxidant and halide ion X^- as reductant. Formulas $(I_2 \cdots X^-)$(env), $I_2{}^-$(env), and I_2(env) denote the species I_2X^-, $I_2{}^-$, and I_2 with atomic configurations (i.e., bond distances and solvation) at equilibrium, whereas $(I_2{}^- \cdots X)$(env*), $I_2{}^-$(env*), and I(env*) denote I_2X^-, $I_2{}^-$, and I with the atomic configurations of $(I_2 \cdots X^-)$, I_2, and I^-, respectively.



SCHEME 2

Calculations of ΔG^* are shown in Table VII. Because $\Delta G_W{}^*$ is probably similar to ΔG_W, the high value of ΔG^*, as compared with those for octahedral complexes, is to be attributed to inner-sphere reorganization of I_2^- i.e., to differences between the equilibrium bond distances in I_2^- and I_2. The magnitude of this effect can be roughly estimated as follows. First, from thermodynamic data on the reaction $I + I^- \rightleftharpoons I_2^-$ in aqueous solution, and with the aid of an assumed radius for the ion I_2^-, Baxendale (*9a*) has deduced the gas-phase electron affinity of the I_2 molecule, namely, $\Delta H \cong -56$ kcal mole^{-1} for

$$I_2(g) + e^-(g) \rightarrow I_2^-(g) \tag{56}$$

where the molecule ion $I_2^-(g)$ has the same bond length as I_2^- at equilibrium in solution. Second, from a correlation of charge-transfer spectra of complexes of benzene with various electron acceptors, Jortner and Sokolov (*71*) have estimated the *vertical* electron affinity of the iodine molecule, namely $\Delta H = -36$ kcal mole^{-1} for the reaction

$$I_2(g) + e^-(g) \rightarrow I_2^-(g)^* \tag{57}$$

where $I_2^-(g)^*$ has the same bond distance as I_2. Strictly speaking, the latter value refers to solvated species in benzene, not in the gas phase, but, if this difference can be neglected, we obtain the enthalpy of compression of the bond in I_2^- in the gas phase, namely $\Delta H \simeq 20$ kcal mole^{-1} for

$$I_2^-(g) \rightarrow I_2^-(g)^* \tag{58}$$

If we accept this as an estimate of the inner-sphere contribution to the term $\Delta G_{FC}(I_2^-)$ in Scheme 2, it suggests that not more than half of the observed Franck–Condon barrier can be attributed to solvent reorganization effects.

G. FURTHER SINGLE-ION PROCESSES

1. *Electron Transfer to Solvent*

Various strongly reducing ions such as I^-, $Fe(CN)_6^{4-}$, and Cr^{2+} exhibit absorption bands in solution whose energies correlate with the oxidation potentials, and it is well-established that these arise from a process in which one electron is lost. Earlier workers (*120*) described the process in different ways, postulating, for example, the generation of a "free electron," or of a reduced water molecule, H_2O^-; but Platzman and Franck (*116*) argued convincingly that the excited state is one in which the electron, although effectively detached from the central ion, remains localized in the potential field of the orientated solvent molecules. This description, which has been retained in all subsequent analyses (*49*, *127*), is close to that of the solvated electron;

and, indeed, the hydrated electron was first introduced (*49*) as a hypothetical entity in the discussion of these spectra, shortly before it was discovered experimentally.* In the cycle,

$$\begin{tikzcd}
A^+(aq^*) + e^-(aq) \arrow[r, "\Delta G_W^*"] & (A^+\cdot e^-)(aq^*) \\
A^+(aq) + e^-(aq) \arrow[u, "\Delta G_{FC}"'] \arrow[ur, "\Delta G^*"] & A(aq) \arrow[u, "\Delta G_{CT}"'] \arrow[l, "\Delta G_E^e - \Delta G_E(A^+)"']
\end{tikzcd} \tag{59}$$

the term $(A^+\cdot e^-)(aq^*)$ denotes the ion-to-solvent charge-transfer excited state, $e^-(aq)$ is the solvated electron, and $A^+(aq^*)$ is the hypothetical state of the A^+ ion with solvent molecules reorganized (or, rather, disorganized) into the positions characteristic of the reduced ion A(aq). Term ΔG_W^* is analogous to the work terms introduced in previous cycles in that it represents the work done in bringing the solvated electron from infinity and superimposing it on the configuration of A^+ (aq^*). Platzman and Franck (*116*) took $\Delta G_W^* = 0$, assuming that in the excited state the electron is so far from the nucleus that there is no coulombic interaction. Later studies of the spectra have confirmed that the excited electron has a large effective radius. The process labeled ΔG_W^* could, in turn, be subdivided into two stages—first desolvating the electron and placing it in the continuum level and, then, relocalizing the electron at the position of $A^+(aq^*)$. On the contrary, however, we shall consider the Franck–Condon and work terms together, introducing the quantity ΔG^*, defined by

$$\Delta G^* = \Delta G_W^* + \Delta G_{FC} \tag{60}$$

which is directly related to the experimentally measurable quantities

$$\Delta G^* = \Delta G_{CT} - \Delta G_E^e + \Delta G_E(A^+) \tag{61}$$

where ΔG_E^e is the standard free energy of the process

$$\tfrac{1}{2}H_2(g) \rightarrow e^-(aq) + H^+(aq) \tag{62}$$

and $\Delta G_E(A^+)$ is defined by Eq. (18) (Section II,A).

The available data are listed in Table VIII. The best-studied systems are the halide ions, and there is a considerable literature (*127*) on the

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* Friedman wrote "$e^-(aq)$ is defined as the electron in equilibrium with respect to solvation by the water, it being assumed that such an equilibrium is possible because the reaction $e^- + H_2O = H + OH^-$ is slow compared with the rate of orientation of water molecules about an ion (*49*)."

TABLE VIII

SINGLE-ION CHARGE-TRANSFER PROCESSES

Complex	Radii (10^{-10} m)[a]		Free-energy terms (kcal mole^{-1})				
(reduced form)				Ion-to-solvent[b]		Solvent-to-ion[b]	
A	Complex A	Complex A^+	$\Delta G_E(A^+)$	ΔG_{CT}	ΔG^*	$\Delta G_{CT}'$	$\Delta G^{*\prime}$
Cl^-	1.81	0.99	−57.4[h]	158.2[s]	34.6	91.1[y]	215
Br^-	1.95	1.14	−45.0[h]	143.2[s]	30.2	103.8[y]	215
I^-	2.16	1.33	−31.5[h]	126.7[s]	29.0	111.8[y]	210
OH^-	1.40[c]	0.74[g]	−42.8[h]	153.2[s]	44.1	124.5[y]	234
CN^-	1.82[c]	—	−42.8[h]	>150[s]	>41	—	—
NO_2^-	1.55[c]	1.55[e]	−22.5[h]	135.7[s]	47.0	—	—
ClO_2^-	1.95[d]	1.95[e]	−21.6[i]	>150[s]	>62	—	—
NCS^-	1.95[c]	1.95[e]	−39.6[aa]	132.6[bb]	26.7	—	—
$Fe(CN)_6^{4-}$	4.3[c]	4.3[e]	−8.2[j]	106[t]	31.7	—	—
$Ru(CN)_6^{4-}$	4.5[e]	4.5[e]	−19.7[k]	115 ± 10[u]	~30	—	—
Cr^{3+}	0.69	0.56	−50 ± 10[l]	~150[v]	~35	—	—
Ce^{3+}	1.11	1.01	−40[m]	—	—	92[z]	198
Mn^{2+}	0.80	0.66	−34[n]	~155[v]	~60	—	—
Fe^{2+}	0.76	0.64	−18[o]	~150[v]	~70	122[z]	206
$Ru(NH_3)_6^{2+}$	0.74[f]	0.7[e]	−2[p]	104[p,w]	36	—	—
Ti^{3+}	0.76	0.68	+1[q]	~135[v]	~60	—	—
Cr^{2+}	0.84	0.69	+9[r]	106[x]	49	—	—

[a] Pauling radii. Unless otherwise stated, these are taken from Phillips and Williams(*114*, pp. 109, 152).

[b] The ΔG^* and $\Delta G^{*\prime}$ are calculated using Eqs. (59) and (63) of the text, and taking $\Delta G_E(e) = 66.3$ kcal mole^{-1} (*70a*).

[c] "Thermochemical radii" (*151*).

[d] Estimated from radius of NO_2^- by comparison of Cl—O distance in NH_4ClO_2 with N—O distance in $NaNO_2$ (*130*).

[e] Estimated.

[f] Assumed same as for Co^{2+}.

[g] Taken as half the O—O bond distance in H_2O_2.

[h] Berdnikov and Bazhin (*14*).

[i] Troitskaya *et al.* (*140*).

[j] Hanania *et al.* (*59*).

[k] DeFord and Davidson (*34*).

[l] Haight (*56*).

[m] Conley (*24*).

[n] Vetter and Manecke (*141*).

[o] Zielen and Sullivan (*154*).

[p] Meyer and Taube (*98a*).

[q] Calculated using E° ($TiOH^{3+} + H^+ + e^- \rightleftharpoons Ti^{3+}$) = −0.055 volt (*139*) and assuming K($Ti^{4+} \rightleftharpoons TiOH^{3+} + H^+$) = 1$M$.

[r] Latimer (*82*).

[s] Friedman (*49*).

[t] Shirom and Stein (*123*).

[u] Guttel and Shirom (*55*).

[v] Schläfer (*121*). (Values of ν_{CT} estimated from a rather small-scale diagram printed in the text.)

[w] Hintze and Ford (*62*).

[x] Dainton and James (*30c*).

[y] Treinin and Hayon (*138*).

[z] Rabinowitch (*117*).

[aa] Wilmarth *et al.* (*147*).

[bb] Gusarsky and Treinin (*54*).

nature of the excited state, and the dependence of ΔG_{CT} on temperature (*127b*) and solvent composition (*127e, f, g*). The more highly reducing complex ions, such as $Fe(CN)_6^{4}$ and $Ru(CN)_6^{4-}$, also have charge transfer to solvent states as evidenced by their photochemical behavior (*1, 30d*), but in some cases, such as $IrCl_6^{3-}$, it is difficult to distinguish these states from the alternative possibility of metal-to-ligand charge transfer (*1e*).

There has also been some discussion of the spectra of cations. As early as 1951 it was shown that for a series of transition metal ions, the low-energy threshold of the ultraviolet absorption correlates with the thermodynamic redox potential in the sequence $V^{2+} < Cr^{2+} < Fe^{2+} < Co^{2+} < Mn^{2+} < Ni^{2+}$ (*30*), and photoelectron detachment processes have been detected on irradiation in the near ultraviolet region (*30d, 23*); but with the exception of $Cr^{2+}\cdot aq$, which in perchlorate media has a well-defined shoulder at ca. 37.0 kK, the actual charge-transfer bands are not easy to locate. Prior to this, the spectra of B-group ions had been discussed. For example, $Tl^{+}\cdot aq$ ion shows a well-defined peak at 46.7 kK, which was originally assumed to be due to charge transfer (*48b*); but it is now assigned to an internal $6s^2 \rightarrow 6s6p$ transition (*69b*). Similar bands are seen in spectra of the other s^2 ions, Sn^{2+}, Pb^{2+}, Bi^{3+}, etc. (*69b*). Ion Ag^+ has peaks in the range 44.7, 47.9, and 51.9 kK (*69c*), but these seem too low in energy to be due to metal-to-solvent charge transfer and should, perhaps, be assigned to the reverse transition, that is, solvent-to-metal. Several ruthenium(II) complexes (*98*), however, show absorption peaks at around 37.0 kK which have been described as "formally ligand field in assignment but having significant charge-transfer character" (*98b*). The case of the $Ru(bip)_3^{2+}$ complex is more difficult to assess: the luminescent excited state was assigned as metal-to-ligand charge transfer because the absorption band shows no solvent shifts (*86*); but there is also no change in frequency when the ligand is deuterated, and, on this basis, some charge transfer to solvent character is proposed (*98c*). However, the lifetime of the excited state is such that the solvent molecules will be equilibrated in the excited state, so these data are not directly relevant to the present study.

2. *Electron Transfer from Solvent*

The reverse process, photochemical transfer of an electron from the solvent molecule to the central metal ion, has been postulated in the case of several of the more strongly oxidizing metal ions, and, more recently, on the basis of an extensive study of the spectra of free radicals such as halogen atoms and OH. By analogy with Eq.

(59), we may construct the cycle

$$\begin{tikzcd}
\mathrm{A}(\mathrm{aq}^{+}\cdot{}^{*}) + \mathrm{e}^{-}(\mathrm{aq}) & \mathrm{A}(\mathrm{aq}^{*}) \arrow[l, "\Delta G_{\mathrm{W}}{}^{*\prime}"'] \\
\mathrm{A}^{+}(\mathrm{aq}) + \mathrm{e}^{-}(\mathrm{aq}) \arrow[u, "\Delta G_{\mathrm{CT}}'"'] \arrow[r, "\Delta G_{\mathrm{L}}(\mathrm{A}^{+}) - \Delta G_{\mathrm{L}}{}^{\mathrm{S}}"] & \mathrm{A}(\mathrm{aq}) \arrow[u, "\Delta G_{\mathrm{FC}}'"'] \arrow[ul, "\Delta G^{*\prime}"']
\end{tikzcd} \tag{63}$$

Here $\mathrm{A}(\mathrm{aq}^{+}\cdot{}^{*})$ denotes the solvent-to-ion charge-transfer excited state, and $\mathrm{A}(\mathrm{aq}^{*})$ is the hypothetical state of the A ion with the solvent molecules reorganized in the configuration appropriate for $\mathrm{A}^{+}\cdot(\mathrm{aq})$. Term $\Delta G^{*\prime}$ is a work term analogous to ΔG^{*}. Values of $\Delta G^{*\prime}$ calculated from the cycle are shown in Table VIII.

In the case where both processes can be studied for the same atom or ion (e.g., transfer from iodide ion to solvent and from solvent to iodine atom), the two cycles may be combined to give

$$(\Delta G_{\mathrm{CT}} + \Delta G_{\mathrm{CT}}') = (\Delta G_{\mathrm{FC}} + \Delta G_{\mathrm{FC}}') + (\Delta G_{\mathrm{W}}{}^{*} + \Delta G_{\mathrm{W}}{}^{*\prime}) \tag{64}$$

and

$$(\Delta G^{*} - \Delta G^{*\prime}) = (\Delta G_{\mathrm{FC}} - \Delta G_{\mathrm{FC}}') + (\Delta G_{\mathrm{W}}{}^{*} - \Delta G_{\mathrm{W}}{}^{*\prime}) \tag{65}$$

From the discussion that follows in Section *III*, it may be expected that the terms ΔG_{FC} and $\Delta G_{\mathrm{FC}}'$ in Eq. (65) will roughly cancel. It is apparent, however, that terms $\Delta G_{\mathrm{W}}{}^{*}$ and $\Delta G_{\mathrm{W}}{}^{*\prime}$ do not cancel even approximately. The difference $(\Delta G^{*} - \Delta G^{*\prime})$ remains roughly constant for the four negative ions A listed in Table VIII (i.e., -180 ± 5 kcal mole^{-1} for A = halide or hydroxide ion) and changes substantially on going to the cation (-135 kcal mole^{-1} for A = $\mathrm{Fe}^{2+}\cdot\mathrm{aq}$).

III. Theory

A. Ionic Solvation

In Section II, A we defined the processes of electron ionization in the gas phase and of electron transfer to the continuum in the solution phase:

$$\mathrm{A(g)} \rightarrow \mathrm{A^{+}(g)} + \mathrm{e^{-}(g)} \tag{15}$$

$$\mathrm{A(aq)} \rightarrow \mathrm{A^{+}(aq)} + \{\mathrm{e}^{-}\}_{\mathrm{aq}} \tag{16a}$$

In the electrostatic theory (*16*) of solvation, these processes are compared with the classical process of charging. Starting with a body A′ having the same boundary as the desired ion A^{+}, electric charge is removed by infinitesimal stages to yield the charge distribution characteristic of A^+. This may be written as

$$A'(g) \rightarrow A^+(g) + \{-\}_0 \tag{66}$$

where the state symbols (g) have the same meaning as before, and $\{-\}_0$ denotes 1 mole of "electricity," infinitely dispersed *in vacuo* and at zero potential (*53*). For the analogous process in solution, the solvent is considered as a uniform dielectric medium, the body A′ is replaced by a cavity of the same shape, and an electric field is slowly applied to give the field characteristic of A^+(aq). This may be written as

$$A'(aq) \rightarrow A^+(aq) + \{-\}_{aq} \tag{67}$$

where A′ and A^+ denote cavities as described, (aq) denotes the dielectric medium with the equilibrium polarization where appropriate; and $\{-\}_{aq}$ denotes 1 mole of electricity infinitely dispersed in the medium.

It will be noted that, if the charged species in equations (15) and (66) are deemed to be at zero potential, then it may be supposed that those in equations (16a) and (67) are at some other potential, namely, the "inner potential" or the average potential over the bulk solvent phase. However, there is no way of unambiguously defining this potential, and it does not enter into the calculations (*53*).

All of the preceding can be restated, with appropriate verbal changes, for the formation of a negative species A^-(aq).

The work done in process (66) is given by

$$W^0 = (\epsilon_0/2)\int_V \mathbf{E}_C \cdot \mathbf{E}_C \, dV \tag{68}$$

where the vector $\mathbf{E}_C$ is the field set up in the vacuum by the ion A^+, and ϵ_0 is the permittivity of free space. The integration is carried over all space.* Similarly (*85*) for process (67) the work, subject to certain conditions,† is

$$W = (\epsilon_0/2D_s)\int_V \mathbf{E}_C \cdot \mathbf{E}_C \, dV \tag{69}$$

---

* This statement needs qualification when the charge distribution of A^+ involves point charges, but the conclusions are not affected (see Ref. *98b*).

† The principal assumptions involved in the derivation of Eq. (69) are (i) that dielectric image effects are negligible; (ii) that the charges, dipoles, etc., are the same in the solvated ion A^+(env) as in the gaseous ion A^+(g), i.e., the ion A^+ is nonpolarizable; and (iii) that the dielectric is isotropic and unsaturated. Condition (i) is always fulfilled if the surface of the ion is an equipotential surface. In some more detailed treatments, image effects are accounted for by assigning a dielectric constant D_i to the interior of the ion. If however $D_i \ll D_s$, the more detailed equation reduces again to Eq. (69); e.g., see Ref. *76*.

where D_s is the static dielectric constant. It is then assumed that the difference in work between processes (15) and (16a) is the same as the difference in work between processes (66) and (67) so that for the chemical process

$$\mathrm{A^+(g) + e^-(g) \rightarrow A^+(aq) + \{e^-\}_{aq}} \tag{70}$$

we have[‡]

$$\Delta G_{\mathrm{env}} = \frac{L\epsilon_{\mathrm{o}}}{2}\left[1 - \frac{1}{D_{\mathrm{s}}}\right]\int \mathbf{E}_{\mathrm{C}}\cdot\mathbf{E}_{\mathrm{C}}\,dV \tag{71}$$

where L is Avogadro's constant.

For a spherical ion of radius a with a centrally distributed charge ze, Eq. (71) yields the well-known expression (*16a*):

$$\Delta G_{\mathrm{env}} = \frac{L}{4\pi\epsilon_0}\left[1 - \frac{1}{D_{\mathrm{s}}}\right]\frac{z^2e^2}{2\mathrm{a}} \tag{72}$$

B. Continuum Theory for Electron Transfer Processes

Marcus (*92*) elaborated the continuum theory by separating the polarization of the dielectric into two superimposed polarizations: the "nonequilibrium polarization," and the "equilibrium polarization." In the precursor complex p there is a characteristic charge distribution giving a field $\mathbf{E}_{\mathrm{C}}{}^{p}$, and both polarizations are at equilibrium. When the photon is absorbed the charge distribution rapidly changes to a new value with an associated field $\mathbf{E}_{\mathrm{C}}{}^{s}$. The nonequilibrium polarization remains at its old value, but the equilibrium polarization changes to a new value, jointly determined by the charges and the nonequilibrium polarization.

The reorganization energy for the successor state ΔG_{FC}, is given by the difference in environmental energy between the excited state s^* and the ground state s [Eq. (3)]. Thus (*65*), subject to the same conditions as govern Eq. (69),

$$\Delta G_{\mathrm{FC}} = \frac{L\epsilon_0}{2}\left[\frac{1}{D_0} - \frac{1}{D_{\mathrm{s}}}\right]\oint [\mathbf{E}_{\mathrm{C}}{}^{p} - \mathbf{E}_{\mathrm{C}}{}^{s}]^2\,dV \tag{73}$$

[‡] The energy change for process (70) is identified as a free-energy change on the grounds that both processes (66) and (67) are reversible. The question remains as to whether it is the Gibbs or the Helmholtz free energy. For rigid dielectrics, there is no differenc. For liquids at constant pressure, it is commonly assumed (see, e.g., Refs. *47* and *114*) to be the Gibbs free energy, but this is not strictly correct since it fails to take account of the compression of the dielectric under the influence of the applied field. For a rigorous discussion, see Ref. *47a*.

Vector $(\mathbf{E}_C{}^p - \mathbf{E}_C{}^s)$ is itself a field and it defines a charge distribution, namely the distribution which *in vacuo* would exert that field. Expression (73) may, therefore, be read as the free energy of transfer of a body bearing the appropriate charge distribution, from a medium of dielectric constant D_s to another medium of dielectric constant D_0. For the case of charge transfer to or from the continuum, $(\mathbf{E}_C{}^s - \mathbf{E}_C{}^p)$ is centrally distributed with a net charge of 1 unit; for transfer to or from the solvent, it is centrally distributed but uncharged, with a "core" of charge of one sign, surrounded by a region of opposite sign. For transfer between two localized centers, it approximates to a finite dipole of charges $\pm e$. It is important to note that, although the shapes and sizes of the molecules affect the result, the overall ionic charges do not. It also follows directly from Eq. (73) that, in the spherically symmetrical cases, or in dipolar cases provided only that the boundary is symmetrical about the mid-point of the line joining the two charges and regardless of the actual shape, the reorganization energy is the same for transfer in either direction:

$$\Delta G_{\mathrm{FC}} = \Delta G_{\mathrm{FC}}{}' \tag{74}$$

This would apply, for example, to two metal ions of equal radius, either separate from each other or joined by a symmetrical bridging group, provided that the oxidized and reduced forms of the ions had the same radii.

We conclude this section by mentioning some important integrated forms of Eq. (73).

Case a. Isolated Spherical Ion

In the photoemission process (Section II,A), the "electron acceptor" is the supposed completely delocalized state of the electron. For a spherical ion of radius a, Eq. (73) then reduces to

$$\Delta G_{\mathrm{FC}} = \frac{Le^2}{4\pi\epsilon_0}\left(\frac{1}{D_0} - \frac{1}{D_s}\right)\cdot\frac{1}{2a} \tag{75}$$

Case b. Spherical Ions at Long Distance

The approximation used by Marcus (*92a*) and Hush (*66*) in the discussion of outer-sphere electron transfer between spherical ions assumes that the ions are far enough apart so that the fields around each one can be considered spherically symmetrical, but not so far apart that the coulombic force between them can be neglected. This leads to

$$\Delta G_{\text{FC}} = \frac{Le^2}{4\pi\epsilon_0}\left(\frac{1}{D_0} - \frac{1}{D_s}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right) \tag{76}$$

where a_1 and a_2 are the ionic radii, and R is the interionic distance.

Case c. Spherical Ions at Short Distance

When the distance R is not large compared with the radius sum $(a_1 + a_2)$, the problem of evaluating ΔG_{FC} becomes very complicated; there is, in fact, no possible solution in closed form (*95*). Kharkats (*74a*) has recently proposed the equation

$$\Delta G_{\text{FC}} = \frac{Le^2}{4\pi\epsilon_0}\left(\frac{1}{D_0} - \frac{1}{D_s}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} - f(R,a_1) - f(R,a_2)\right) \tag{77}$$

where functions $f(R,a_1)$, $f(R,a_2)$ are defined by

$$f(R,r) = \frac{1}{4} \cdot \frac{R}{R^2 - r^2}\left[\frac{r}{R} - \frac{1}{2}\left(1 - \frac{r^2}{R^2}\right) \ln \frac{(R + r)}{(R - r)}\right] \tag{78}$$

For the case of a "contact ion pair" ($R = a_1 + a_2$), the additional terms account for ca. 6% of ΔG_{FC} when $a_1 = a_2$, or 11% when $a_1 = a_2/3$. Nevertheless, Eq. (77) is only an approximation; it is obtained by allowing for the volumes of the ions, but it still depends on taking the field around each ion as spherically symmetrical and neglecting the effect of the other ion; that is to say, the boundary conditions are not obeyed.

In a more sophisticated treatment (*74b*), Kharkats has attempted to allow for the mutual influence of the fields of the two ions by assuming the ions to be completely polarizable (i.e., analogous to metallic spheres) and by calculating as a first approximation the dipole induced on each ion by the point charge of the other. The resulting equation is extremely complex, but from the authors' graphs it can be seen that the modification has a significant effect. For the contact case, $R = a_1 + a_2$, the additional terms contribute a 27% increase in ΔG_{FC} when $a_1 = a_2$, and a larger increase when $a_1 \neq a_2$. But this is still only a first approximation—a complete calculation would consider not only the dipole, quadrupole, etc., induced on sphere 1 by the charge of sphere 2; but also the new dipole, etc., induced on sphere 1 by the induced dipole, etc., of sphere 2; and so on *ad infinitum*. And for a completely polarizable ion the net effect would be that as the ions approached toward contact, the effective centers of the two point charges that constitute the dipole would move to the point of contact, and the expression for ΔG_{FC} would diverge to infinity (*19*).

Case d. Ellipsoidal Model

A more realistic model for complexes of the bridged or directly bonded types (see Sections II, E and F) is suggested in Fig. 2. The boundary surface is a prolate ellipsoid of revolution, and the field ($E_C^p - E_C^s$) is taken to be that of a finite dipole due to equal and opposite charges placed at the foci. If the distance between oxidizing and reducing centers is R, the dipole moment change (assuming complete localization of valencies) is $p = eR$. The problem of integrating equations such as Eq. (73) for an ellipsoidal boundary was thoroughly treated by Westheimer and Kirkwood (*145*) in connection with their studies of the activity coefficients of dipolar solutes.

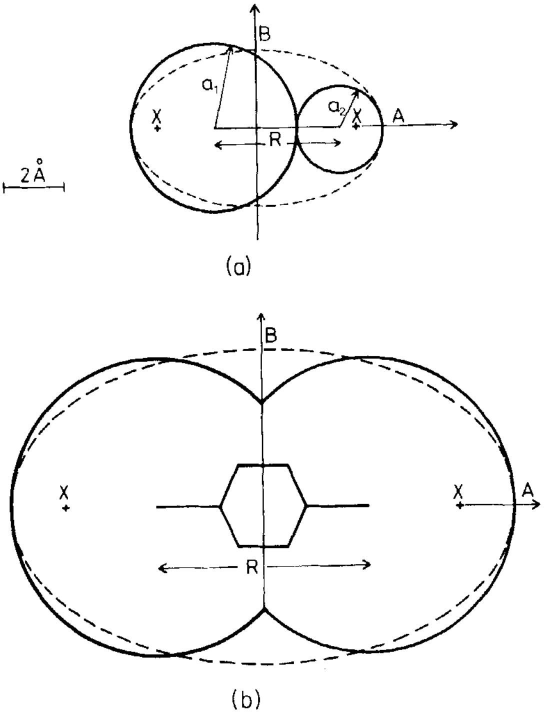

FIG. 2. Scale drawings of (a) the outer-sphere successor complex $Ru(NH_3)_6^{2+}\cdot I$ and (b) the bridged mixed-valence complex $Cl(bip)_2Ru(pyz)Ru(bip)_2Cl^{3+}$, with assumed dimensions as shown in Tables IX and X. The dotted lines are boundaries of ellipsoids (raddi A, B) having the same volumes as the complexes. Points X, X are foci of the ellipsoids.

Adapting their result to the present case, the present writer (*19a*) obtained:

$$\Delta G_{\mathrm{FC}} = \frac{Lp^2}{8\pi\epsilon_0 A^2 B}\left(\frac{1}{D_0} - \frac{1}{D_s}\right) S(\lambda_0) \tag{79}$$

$$S(\lambda_0) = \sum_{n=0}^{\infty} \tfrac{1}{2}(1 - (-1)^n)(2n + 1)\lambda_0(\lambda_0{}^2 - 1)Q_n(\lambda_0)/P_n(\lambda_0) \tag{80}$$

where A and B are the semimajor and semiminor axes of the ellipsoid, $\lambda_0{}^2 = A^2/(A^2 - B^2)$, and $P_n(\lambda_0)$ and $Q_n(\lambda_0)$ are Legendre polynomials of the first and second kinds, of degree n. Expression $S(\lambda_0)$ depends only on the eccentricity of the ellipsoid: it varies from $S \cong 0.65$ when $\lambda_0 = 1$ to $\mathrm{S} = 1$ in the limit $\lambda_0 \to \infty$.

Case e. Spherical Ion, Point Dipole

Proceeding to the limit $\lambda_0 \to \infty$, as the radii A and B become equal, the foci of the ellipsoid converge at the center. The result is a spherical ion, with a point dipole located at the center. Equation (73) then reduces to

$$\Delta G_{\mathrm{FC}} = \frac{Lp^2}{8\pi\epsilon_0 a^3}\left(\frac{1}{D_0} - \frac{1}{D_s}\right) \tag{81}$$

where $a = A = B$. The same expression can also be deduced from an earlier calculation by Kirkwood (*76a*).

IV. Conclusions

A. Single-Ion Processes

The processes discussed in Sections II, A and G are formally similar in that the electron donor has approximately spherical symmetry. In the photoemission process, the electron acceptor is the supposedly completely delocalized state of the electron, whereas in the charge-transfer to solvent process, properly so called, the acceptor is the spherically symmetrical polarization field set up by the donor ion in the solvent.

For the former process, Eq. (75) may be applied, and, on comparing this with the Born equation (72), we see that the Franck–Condon energy is expected to be proportional to the solvation energy

$$\Delta G_{\mathrm{FC}} = \left(\frac{1}{D_0} - \frac{1}{D_s}\right)\left(1 - \frac{1}{D_s}\right)^{-1} \Delta G_{\mathrm{env}} \tag{82}$$

TABLE IX

COMPARISON OF CALCULATED AND OBSERVED REORGANIZATION ENERGIES, USING THE SEPARATE-SPHERES MODEL

Successor complex[a] ($A \cdots B^+$)	Assumed ionic and atomic radii[b,c]		Assumed internuclear distance[c]	ΔG_{FC}(kcal mole^{-1})		
	a_1	a_2	R	calc.[d]	obs.	χ[e]
$Ru(NH_3)_6^{2+} \cdot Cl$	0.74[f]	0.99	3.55[j]	164	41[o]	0.14
$Ru(NH_3)_6^{2+} \cdot Br$	0.74[f]	1.14	3.70[j]	154	45[o]	0.16
$Ru(NH_3)_6^{2+} \cdot I$	0.74[f]	1.33	3.89[j]	145	41[o]	0.15
$Ru(en)_3^{2+} \cdot I$	0.74[f]	1.33	4.23[k]	149	36[o]	0.13
$MnO_4^{2-} \cdot Ag^{2+}$	0.52[g]	0.97[h]	3.63[l]	219	40[p]	0.10
$Cl(bip)_2Ru(II)(pyz)Ru(III)(bip)_2Cl^{3+}$	0.74[f]	0.63[i]	6.99[m]	243	23[q]	0.06
$(NH_3)_5Ru(II)(py{-}py)Ru(III)(NH_3)_5^{5+}$	0.74[f]	0.63[i]	11.3[m]	330	27.5[q]	0.03
$(C_5H_5)Fe(II)(C_5H_4{-}C_5H_4)Fe(III)(C_5H_5)^+$	0.76	0.64	6.4[n]	233	18.5[q]	0.03

[a] Abbreviations: bip = 2:2′-bipyridyl; pyz = 1:4-pyrazine; py—py = 4:4′-bipyridyl.

[b] Pauling radii (*114*, pp. 109, 152).

[c] Units are 10^{-10} m.

[d] Equation (76).

[e] Equation (84).

[f] Assumed same as for Co^{2+}.

[g] Assumed same as for Cr^{6+}.

[h] Assumed same as for Ag^{2+}.

[i] Assumed same as for Co^{3+}.

[j] Using outer-sphere radius of $Ru(NH_3)_6^{2+}$, assumed same as that of $Co(NH_3)_6^{2+}$, i.e., 2.56 Å, estimated from the Co—I distance in solid $Co(NH_3)_6I_2$ (4.72 Å) by subtracting the radius of I^- (*149*).

[k] Using outer-sphere radius of $Ru(en)_3^{2+}$, assumed same as that of $Co(en)_3^{3+}$, i.e., 2.90 Å, estimated from the mean Co—Br distance in solid $Co(en)_3Br_3 \cdot H_2O$ (4.85 Å), by substracting the radius of Br^- (*149*).

[l] Sum of Mn—O distance in $KMnO_4$ (1.55 Å) and Ag—O distance in AgO (2.08 Å) (*130*).

[m] Bond lengths in pyrazine and bipyridyl estimated from suitable molecules; Ru—N distance assumed same as R—NO in $Ru(NH_3)_4(NO)(OH)Cl_2$ (*130*).

[n] Calculated as $R = (x^2 + y^2)^{1/2}$, where x is Fe—Fe distance and y is inter-ring distance in $Fe(C_5H_4{-}C_5H_4)_2Fe$ (*89*).

[o] Table III.

[p] Table V.

[q] Table VI.

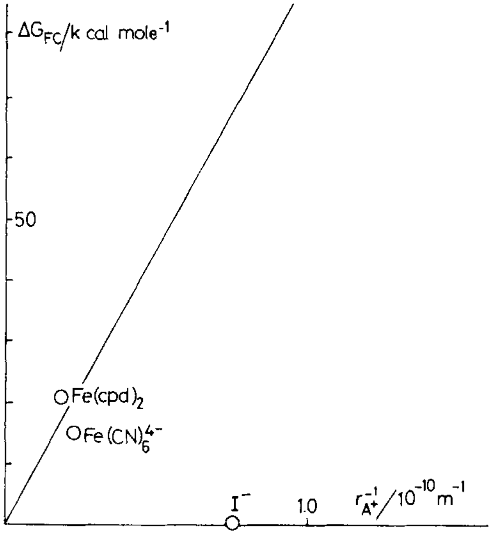

FIG. 3. Single-ion reorganization energies ΔG_{FC} (Table II) compared with the predictions of Eq. (75). Radii $r(A^+)$ are those of the oxidized forms of the complexes, i.e., of I, $Fe(CN)_6{}^{3-}$ and $Fe(cpd)_2{}^+$.

The values of ΔG_{FC} calculated above are listed in Table IX and plotted against $(1/r_{A^+})$ in Fig. 3. The straight line is drawn with slope calculated from Eq. (75), using $D_s = 78.5$, $D_0 = 1.78$, for water at 25°C. The points for iodide ion is clearly unacceptable, as already discussed, but it seems unlikely that any revision will bring $\Delta G_{FC}(I)$ up from zero to the predicted value of ca. 70 kcal mole^{-1}. Clearly more data are needed before the continuum theory can be subjected to even an approximate quantitative test, but already we may forecast that the dependence of ΔG_{FC} on ionic radius will be less sensitive than Eq. (75) implies.

A similar conclusion follows from the more extensive data on charge transfer to solvent and vice versa. Quantities ΔG^* and $\Delta G^{*\prime}$ calculated for these systems in Section II,G are not the Franck–Condon energies because they include the unknown interaction energies $\Delta G_W{}^*$ and $\Delta G_W{}^{*\prime}$ which may vary from system to system; nevertheless, the main sources of variation are likely to be ΔG_{FC} and $\Delta G_{FC}'$.

The data for charge transfer to solvent are shown in Fig. 4 as a plot of ΔG^* against $1/a$. It appears that there is a general correlation, with the following notable exceptions. First, the bent polyatomic ions $NO_2{}^-$ and $ClO_2{}^-$, but not the linear NCS^-, have reorganization energies significantly higher than predicted. Friedman showed (*49*) that this could be accounted for by bond strain in the excited state,

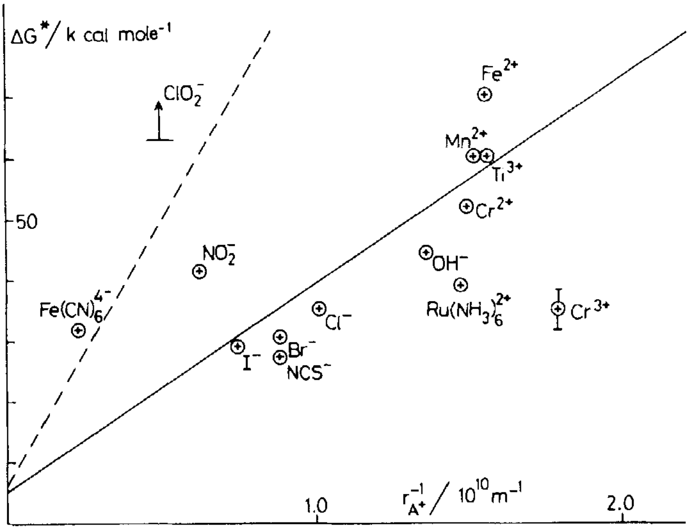

FIG. 4. Single-ion charge-transfer to solvent data. Correlation of ΔG^* (Table VIII) with $1/r(\mathrm{A}^+)$, where $r(\mathrm{A}^+)$ is the crystal radius of the oxidized form of the ion. The dashed line is drawn with slope predicted from Eq. (75).

and this is supported by later structural studies. The bond angles in the gaseous molecules NO_2, ClO_2 are, respectively, 18° and 7° smaller than those of the corresponding anions in ionic crystals, and there are measurable differences in the bond lengths (*130*). Second, for $Fe(CN)_6{}^{4-}$ (and for $Ru(CN)_6{}^{4-}$ not shown in Fig. 4), ΔG^* is again more positive than might have been expected in view of the very large ionic radius; and this may reflect a positive work term $\Delta G_W{}^*$ due to the high overall negative charge. Lastly, the Cr^{3+} ion is significantly out of line even when full allowance is made for the uncertainty in the Cr^{4+}/Cr^{3+} reduction potential.

The remaining data can be fitted to a straight line, and, for comparison with other data and with theory, we may write

$$\Delta G^* \simeq \frac{Le^2}{4\pi\epsilon_0} \cdot \chi \cdot \frac{1}{2a} + \text{constant} \tag{83}$$

with $\chi = 0.21$ to be compared with $(D_0{}^{-1} - D_s{}^{-1}) = 0.55$. The uncertainty as to the size and variability of $\Delta G_W{}^*$ inhibits further discussion. What is required here is a more extended study including donor ions of diverse charge types so that the $\Delta G_W{}^*$ and ΔG_{FC} can be estimated separately.

The less extensive data for charge transfer in the reverse direction are similarly plotted in Fig. 5. Within the series of four equally charged

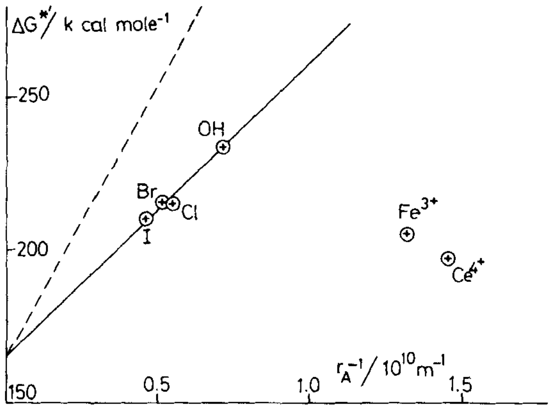

FIG. 5. Single-ion charge-transfer from solvent data. Correlation of $\Delta G^{*\prime}$ (Table VIII) with $1/r(\mathrm{A})$, where $r(\mathrm{A})$ is the crystal radius of the reduced form of the ion. The dashed line is drawn with the slope predicted from Eq. (75).

species there is a good correlation of $\Delta G^{*\prime}$ with $(1/a)$; but more data on cationic complexes are needed before any further comments can be made.

B. DONOR–ACCEPTOR PROCESSES

Here we consider together all systems in which the donor and acceptor sites are both separate and localized, i.e., those discussed in Sections II, B to F. A representative selection is shown in Table IX. The complexes are written as successor complexes $(\mathrm{A} \cdots \mathrm{B}^+)(\mathrm{env})$. The internuclear distances have been estimated from bond distances in analogous known complexes, there being no crystal structure data for any of the actual species listed in Table IX.

To compare the experimental values of ΔG_{CF} with the predictions of the Marcus–Hush theory, there would seem to be two worthwile approaches.

1. *Separate Sphere Model*

We consider the central atoms of the complexes as spheres, using the Pauling radii, and treat the solvent, the inner-sphere ligands, and the bridging ligands where present, as the medium within which electron transfer takes place. This is a very gross approximation, since, apart from the lack of homogeneity of the medium as thus defined, there are important electronic interactions. Such interactions will be largely of two sorts: the charges on the oxidant and reductant ions will be partially delocalized onto the neighboring ligands; and the wave functions of the two centers will sometimes be mixed, either directly or via bridging ligand orbitals, so that the effective charge transferred is less than 1 electron. We subsume all these effects under the general headings of polarity and polarizability of the ligands.

The equation appropriate to this approximation is Eq. (76), and for each system we have, therefore, calculated an empirical coefficient χ, defined by

$$\Delta G_{\mathrm{FC}} = \frac{Le^2}{4\pi\epsilon_0} \cdot \chi \cdot \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right] \tag{84}$$

Values of χ are listed in Table IX. As with the single-ion values, they are all less than 0.55, and this is evidently a measure, although a rather crude measure, of the electronic effect just mentioned. The inner-sphere ligands can be arranged in order of decreasing χ, in the series $NH_3 \approx$ en $>$ O $>$ pyrazine $\approx$ biscyclopentadienyl $\approx$ 4,4′-bipyridyl and this coincides roughly with increasing polarizability or covalent bonding. A more refined treatment might seek to relate χ to the polarizabilities of the ligands as measured from the refractive indexes of suitable compounds.

2. *Ellipsoid Model*

In this case we consider the whole complex, including inner-sphere ligands and bridging ligands if any, as an ellipsoidal body (Fig. 2) and use Eqs. (79) and (80). In deriving these equations, it has been assumed that the average dielectric constant over the interior of the molecule is small compared with that of the solvent [see footnote in Section III, A regarding derivation of Eq. (69)]. This is a considerable oversimplification, because the polarizabilities of inner-sphere ligands such as I^- and pyrazine are considerably greater than that of water, as estimated from the refractive indices of suitable compounds; but, on the other hand, if the inner-sphere ligands are dielectrically saturated the error in our assumption is less.

The radii used, and the resulting values of $\Delta G_{\mathrm{FC}}^{\mathrm{out}}$, are shown in Table X. The semimajor axes A have been estimated from crystallographic data, and the semiminor axes B have been calculated so that the volume of the ellipsoid is equal to the estimated volume of the complex. The dipole moments have been taken as $p = eR$.

For the four outer-sphere complexes listed in Table X the calculated $\Delta G_{\mathrm{F}}^{\mathrm{out}}$ are similar to, although slightly larger than, the experimental total ΔG_{FC}. This can be considered satisfactory agreement, and it

TABLE X

COMPARISON OF CALCULATED AND OBSERVED REORGANIZATION ENERGIES, USING THE ELLIPSOID MODEL

Successor complex[a]	Assumed radii of ellipsoids[b,c]			Reorganization energies[e]			
				Calcd.[f]	Observed		
$A \cdots B^+$	A	B	$S(\lambda_0)$[d]	$\Delta G_{\mathrm{FC}}^{\mathrm{out}}$	ΔG_{FC}	$\Delta G_{\mathrm{FC}}^{\mathrm{in}}$	$\Delta G_{\mathrm{FC}}^{\mathrm{out}}$
$Ru(NH_3)_6{}^{2+} \cdot Cl$	3.55[g]	2.24[k]	0.77	50	41[m]	—	—
$Ru(NH_3)_6{}^{2+} \cdot Br$	3.70[g]	2.22[k]	0.75	51	45[m]	—	—
$Ru(NH_3)_6{}^{2+} \cdot I$	3.89[g]	2.22[k]	0.73	53	41[m]	—	—
$Ru(en_3)_3{}^{2+} \cdot I$	4.23[g]	2.51[k]	0.75	46	36[m]	—	—
$Cl(bip)_2Ru(pyz)Ru(bip)_2Cl^{3+}$	8.4[h]	5.1[l]	0.76	15	22.6[n]	15.6[o]	7.0[o]
$(NH_3)_5Ru(py{-}py)Ru(NH_3)_5{}^{5+}$	8.2[i]	2.7[l]	0.70	137	27.5[n]	10.0[p]	17.5[p]
$(C_5H_5)Fe(C_5H_4{-}C_5H_4)Fe(C_5H_5)^+$	6.5[j]	3.4[l]	0.70	35	18.5[n]	—	—

[a] Abbreviations: bip = 2:2′-bipyridyl; pyz = 1:4 pyrazine; py—py = 4:4′-bipyridyl.

[b] Units are 10^{-10} m.

[c] Equation (79).

[d] Equation (80).

[e] Aqueous medium 25°C. Units are kcal mole^{-1}.

[f] Calculated from Eqs. (79) and (80), using $p = eR$, where R is the internuclear distance as shown in Table IX.

[g] $A = R$.

[h] $A = \frac{1}{2}R + r$, where r is the radius of the $Ru(bip)_2Cl$ moieties, assumed to be same as that of $V(bip)_3$, i.e., half the nearest-neighbor V—V distance in $V(bip)_3$ (*3*).

[i] $A = \frac{1}{2}R + r$, where r is the outer-sphere radius of $Ru(NH_3)_6{}^{2+}$ (see Table IX, footnote *j*).

[j] $A = \frac{1}{2}R + r$, where r is the radius of the $Fe(C_5H_5)$ moiety, assumed to be same as that of $Fe(C_5H_5)_2$, i.e., half the mean nearest-neighbor Fe—Fe distance in solid $Fe(C_5H_5)_2$ (*42*).

[k] $B = (a_1{}^2 - a_1a_2 + a_2{}^2)^{1/2}$, where a_1 and a_2 are outer-sphere radii of component ions.

[l] Calculated so that $(4/3)\pi AB^2$ is the volume of the complex.

[m] Table III.

[n] Table VI.

[o] Callahan and Meyer (*18*).

[p] Tom *et al.* (*137*).

confirms that in these cases at least the model is a reasonable one and that the outer-sphere part of the reorganization energy is a substantial contribution to the whole. The lack of dependence of ΔG_{FC} on the nature of the halide ion is particularly noteworthy.

The three bridged complexes show rather diverse behavior. For $Cl(bip)_2Ru(pyz)Ru(bip)_2Cl^{3+}$, the calculated $\Delta G_{\mathrm{F}}^{\mathrm{out}}$ is quite small and is less than the experimental ΔG_{FC}; for $(NH_3)_5Ru(py{-}py)Ru(NH_3)_5{}^{5+}$, the calculated $\Delta G_{\mathrm{F}}^{\mathrm{out}}$ is much greater, and this is due about equally to the greater internuclear distance and to the smaller thickness of the inner coordination sphere surrounding each ruthenium atom. Such a large discrepancy between theory and experiment does not seem explicable wholly by deficiencies in the model, and it may be suggested that here there is some delocalization of valencies in the ground state. It will be noted that $\Delta G_{\mathrm{FC}}^{\mathrm{out}}$ depends on the square of the effective dipole moment change; hence a reduction of p by a factor of about 2 would be sufficient to bring this complex into line with the pyrazine-bridged complex. For the diiron complex $(C_5H_5)Fe(C_5H_4 \cdot C_5H_4)Fe(C_5H_5)^+$, a reduction of p by about 1.7 is implied.

Several authors have pointed out that it is possible to distinguish the inner- and outer-sphere parts of ΔG_{FC} by studying solvent effects. It is assumed that $\Delta G_{\mathrm{FC}}^{\mathrm{in}}$ [Eq. (14)] is independent of the nature of the solvent, whereas $\Delta G_{\mathrm{FC}}^{\mathrm{out}}$ is proportional to $(D_0^{-1} - D_s^{-1})$ as shown in Section III,B. Thus, when ΔG_{FC} is plotted against $(D_0^{-1} - D_s^{-1})$, a straight-line dependence is expected, and extrapolation to $(D_0^{-1} - D_s^{-1}) = 0$ gives $\Delta G_{\mathrm{FC}}^{\mathrm{in}}$. In this way it was shown that $\Delta G_{\mathrm{FC}}^{\mathrm{out}}$ is negligible for complexes $(NH_3)_5Ru(pyz)Ru(NH_3)^{5+}$ (*29d*) and $(NH_3)_5RuNC{\cdot}CN\,Ru(NH_3)_5{}^{5+}$ (*136*) consistent with complete delocalization of valencies. Values of $\Delta G_{\mathrm{FC}}^{\mathrm{out}}$ for two other ruthenium(II)–ruthenium(III) complexes are shown in Table X. The closest agreement between theory and experiment occurs with complex $Cl(bip)_2Ru(pyz)Ru(bip)_2Cl^{3+}$.

Variations in transition energy $h\nu_{\mathrm{CT}}$ with solvent are, of course, well established in charge-transfer spectroscopy of organic systems, and have been used many times to establish scales of solvent polarity (*10*). However, all this work has been based on unsymmetrical charge-transfer systems: typical examples being the ion pair $CH_3NC_5H_5{}^+{\cdot}I^-$ yielding the radical pair $CH_3NC_5H_5{\cdot}I$ on excitation. The charge-transfer energy is then the sum of two contributions, as shown in Eq. (3), and it seems likely that the main contribution to the solvent shift lies in the thermal free-energy difference ΔG_{PS} rather than in the Franck–Condon energy ΔG_{FC}. Callaghan *et al.* have synthesized the unsymmetrical bridged complex $(H_3N)_5Ru(III)(pyrazine)Ru(II)(bip)_2Cl^{4+}$ and found an appreciable dependence of $h\nu_{\mathrm{CT}}$ on solvent (*2e*); and the same comment would apply.

In summary, it appears from this discussion that Franck–Condon energies can now be calculated for a diverse group of inorganic charge-transfer systems and that, although the accuracy of individual values is uncertain, it is possible qualitatively to rationalize the differences between analogous systems. Absolute predictions are much less satisfactory at the present time, and the electrostatic theory based on a dielectric continuum has only very limited applicability to the systems that have so far been studied. When inner-sphere reorganization effects are dominant, as is frequently the case, a treatment based on the distortion of individual bonds, using force constants from vibrational spectroscopy, would seem to be more promising. In the calculation of equilibrium solvation energies ΔG_{env}, significant improvements have been achieved by considering ion–dipole interactions in the inner-sphere region, and using continuum theory only for the outer region [*9*, *114* (Chapter 5)]. The application of this method to thermal activation energies of electron transfer has been considered in some detail, although not yet exhaustively, by Hush (*65*). An alternative approach would be to retain the continuum model but to introduce the concept of dielectric saturation. Sophisticated treatments of this kind, again for the equilibrium situation, have been reviewed by Padova (*113*).

The outstanding need, however, is for more experimental data, especially on systems simple enough to be treated theoretically. Photoemission data are of particular interest, but their interpretation will call for more thermodynamic data on oxidation–reduction systems in nonaqueous solvents. Theoretical treatments of single-ion solvation energies for solvents other than water, and at temperatures other than room temperature, are also necessary if the arguments outlined in the foregoing are to be developed. More data are needed on mixed-valence binuclear metal complexes with known structures, and with negligible or small interaction between oxidizing and reducing centers in the ground state. A point of particular interest here is the effect of changing internuclear distance: long-range electron transfer occurs in the gas phase (*104*), and as semiconduction in the solid state (*28*), but it has never been unambiguously demonstrated for metal complex ions in solution. Yet, long-range transfer is frequently discussed in connection with biological systems; and the decisive experiments may yet come from the study of appropriately synthesized inorganic models.

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