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ELECTROCHEMICAL STUDIES OF SOME TRANSITION METAL CRYPTATES
AND AN INVESTIGATION OF THE REACTION ENTROPIES
OF TRANSITION METAL REDOX COUPLES

By

Edmund L. Yee

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ABSTRACT

ELECTROCHEMICAL STUDIES OF SOME TRANSITION METAL CRYPTATES AND AN INVESTIGATION OF THE REACTION ENTROPIES OF TRANSITION METAL REDOX COUPLES

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Electrochemical methods were used to monitor the aqueous complexation and redox chemistry of the trivalent and divalent europium and ytterbium (2.2.1) and (2.2.2) cryptates. All of these complexes were electrochemically reversible and substitutionally inert on the cyclic-voltammetric time scale. The substantially lower thermodynamic stabilities of the trivalent cryptates (compared to the corresponding divalent complexes) arise from large enthalpic destabilizations which outweigh smaller entropic stabilizations. These differences can be explained in terms of the relative hydration of the uncomplexed trivalent and divalent ions and comply with the trends observed for alkali metal and alkaline earth cryptates having comparable ionic radii. The strong associations of the trivalent Eu and Yb cryptates with hydroxide and fluoride were found to be comparable to those reported for the aquated cations and these anions.

For cations of approximately constant size, striking decreases in the cryptate formation and dissociation rates are observed as the cation charge increases from one to three. These rate variations and their enthalpic and entropic components reflect the

increased changes in cation hydration which accompany cryptate formation when the cation charge increases. The dissociation of the lanthanide cryptates is substantially catalyzed by acid, and this can be attributed to the need to alter the ligand conformation before or during the removal of the cation from the cryptate cavity.

The homogeneous self-exchange rate constants of $\text{Eu}(2.2.1)^{3+/2+}$ and $\text{Eu}(2.2.2)^{3+/2+}$ were calculated by using the Marcus cross-relation and rate data from cross reactions involving these cryptates. The greatly enhanced self-exchange rates of the cryptates relative to that for $\text{Eu}_{\text{aq}}^{3+/2+}$ were ascribed to smaller solvent- and ligand-reorganization components in the activation barriers of the cryptate systems.

The half-cell reaction entropies $\Delta S_{\text{rc}}^\circ$, for some $\text{M}(\text{III})/(\text{II})$ redox couples in aqueous solution were determined with a non-isothermal cell arrangement. Reaction entropies in the 36-49 e.u. range were found for aquo couples. Several substitutionally inert ruthenium $(\text{III})/(\text{II})$ complexes were employed to scrutinize ligand effects on $\Delta S_{\text{rc}}^\circ$. The sizable decreases in $\Delta S_{\text{rc}}^\circ$ which accompany the replacement of aquo ligands by amines were attributed to less extensive solvent-ligand hydrogen bonding by the latter ligands. Large reductions in $\Delta S_{\text{rc}}^\circ$ resulted when aquo and ammine ligands were replaced by anionic ligands. Examinations of couples containing chelating ligands disclosed substantial differences in $\Delta S_{\text{rc}}^\circ$ between $\text{Co}(\text{III})/(\text{II})$ couples and the corresponding $\text{Ru}(\text{III})/(\text{II})$ and $\text{Fe}(\text{III})/(\text{II})$ systems. These could be attributed to ligand-conformation and electron-delocalization factors.

A correlation between the self-exchange rate of a redox couple and its reaction entropy was found. This relation arises since both ΔS_{rc}° and outer- and inner-shell reorganization energies are related to solvent-structuring effects.

Reaction entropies and formal potentials were employed to calculate the free-energy, enthalpic, and entropic driving forces necessary for a thorough comparison of the predictions of the conventional Marcus model of outer-sphere electron transfer with the experimental rate constants and activation parameters for cross reactions involving cationic transition metal complexes. The considerable disagreements between the experimental and predicted values found at very large driving forces were compatible with the presence of sizable, unfavorable work terms in the formation of the binuclear collision complex. An analysis of the activation parameters indicated that these work terms may be due to the reorganization of solvating water molecules that is needed in order to form the highly charged collision complex.

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INTRODUCTION

Electron-transfer reactions that involve transition metal ions form the basis of many scientifically and technologically important processes, so it is crucial that attempts be made to reach a better understanding of the factors which govern the redox thermodynamics and kinetics of these cations. One effective method to scrutinize the behavior of a metal ion redox couple is to vary its ligand environment in some appropriate fashion. This variation is often accompanied by changes in the standard potential of the couple and in the lability of the respective oxidation states, by modifications in the degree and type of solvent structure around the metal complex, and by alterations in the mechanism by which electron transfer occurs.

Among the numerous ligands and complexes which have been or could be employed for such studies are cryptands, a class of polyoxadiazamacrobicycles, and cryptates, the complexes which these cryptands form with metal ions. In these complexes, the cation is encapsulated within a molecular cavity defined by the ligand, and this uncommon structure is expected to modify the redox properties of the enclosed metal ion couple in an interesting and unusual fashion. The elucidation of these ligand effects will require the investigations of the cryptate ligation processes and redox thermodynamics that are recounted in Chapter III along with the studies of the redox kinetics

of these complexes which are described in Chapter VI. While little work has been done on electroactive cryptates, some of the previous findings regarding cryptate complexation thermodynamics and kinetics do have a bearing on the results detailed in Chapter III. Therefore, this earlier material is summarized in Section A of Chapter I.

While some useful trends concerning ligand effects may be gleaned from the transition metal cryptates, their unusual structure may restrict the conclusions of this study to a number of specific points. One way to achieve a broader view of ligand influences is to determine the ionic entropies of transition metal ions and the factors which affect these quantities. Such measurements can be utilized to obtain information on the degree of hydration around an ion and on the extent and type of interactions between the ligands and the solvent. In Chapter IV, entropy data for a series of related transition metal couples are used to ascertain the ligand effects on the redox thermodynamics of these complexes.

Since solvent reorganization is a major component of the activation barrier in electron transfer reactions, one would expect that the solvent structure around an ionic reactant would have a strong influence on the redox kinetics of this species. Ionic entropies should provide insights into this structure and thus will be helpful in explaining trends in redox reactivity. In fact, a correlation between entropies and redox rate parameters is found and discussed in Chapter IV.

The entropies of some transition metal ions have been determined,

but very little has been done in a systematic manner, especially with respect to the ligand dependences of these entropies. Section B of Chapter I attempts to introduce some unity to the field of ionic entropies. It is especially important to make some sense of the various scales of entropy that are employed since no standard convention has been agreed upon.

The combination of the appropriate ionic entropies will yield the entropy of reaction for complexation and redox processes. The former application will prove useful in Chapter III when cryptate stabilities are discussed in entropic and enthalpic terms. The latter employment of entropies will be essential in Chapter V when the limitations of the contemporary theories of homogeneous electron-transfer kinetics are examined. As a preparation for this analysis, Section C of Chapter I briefly summarizes these theories. An overview of some of the principal electron-transfer mechanisms is also given since these concepts and the theories mentioned above will be needed to analyze and to understand the kinetic data for cryptate redox reactions presented in Chapter VI.

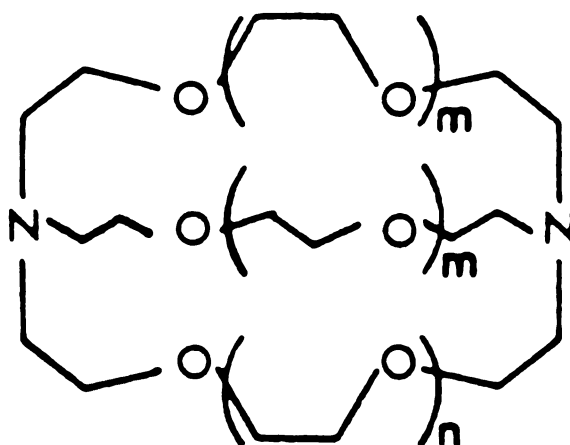
CHAPTER I
HISTORICAL BACKGROUND

A. Historical Background - Cryptates

Cryptands were first synthesized by Lehn and co-workers in 1969 (1,2). (The macrobicyclic ligands used in this study are more precisely designated [2]-cryptands to distinguish them from the tricyclic [3]-cryptands and the tetracyclic [4]-cryptands.) All of these cryptands contain three polyether strands attached to two bridgehead nitrogens. The common names of the cryptands consist simply of the number of ether oxygens in each of these strands. Figure 1 gives the structure and the common names of the cryptands used in this work.

The polyether strands of a cryptand define a three-dimensional molecular cavity. Thus, the cryptands (2.2.2), (2.2.1), and (2.1.1) have a cavity radii of 1.4, 1.1, and 0.8 Å, respectively (3). A metal ion of the proper size can be encapsulated within this cavity to yield an inclusion complex (3). In actual practice, these cryptate complexes are frequently made simply by mixing the ligand and a suitable salt of the metal ion in an appropriate solvent.

The crystal structures of a number of these cryptates have been determined, principally by Weiss and co-workers (4,5). The inclusion complexes have several structural features in common. The metal ion lies within the molecular cavity of the ligand. The cryptand has an *endo-endo* conformation; i.e., the lone pairs on the nitrogen atoms point into the cavity. It is also possible for the ligand to adopt configurations where both electron pairs are directed away from the cavity (*exo-exo*) or where one pair points into the cavity while the



$m = 1, n = 1$ (2.2.2)

$m = 1, n = 0$ (2.2.1)

$m = 0, n = 1$ (2.1.1)

Figure 1. Structures of some common cryptands.

other points away (*endo-exo*) (3). When the size of the metal ion closely matches that of the cryptand cavity, the heteroatoms of the ligand tend to be symmetrically distributed around the ion. On the other hand, some distortion of the ligand occurs when the metal ion is too large or too small for the cryptand cavity (5).

A good deal of the interest in and the work on cryptands has stemmed from the discovery that these ligands are capable of forming stable complexes with alkali metal cations in aqueous and nonaqueous solutions (3,6). Along with the crown cyclic polyethers first synthesized by Pederson (7-10), the cryptands gave rise to the new field of the study of alkali metal complexation. Investigations of the influences on the stability of the alkali metal cryptates have found that each cryptand has its own size selectivity. Simply stated, for a given cryptand, the most stable alkali metal cryptate has the closest match between the radius of the cation and that of the ligand's molecular cavity. The other alkali metal complexes of this particular cryptand would be less stable and would contain a cation which was unsuitably large or small with respect to the ligand cavity. Thus Na^+ with a radius of 1.02 Å (11) forms the most stable alkali metal complex with the (2.2.1) cryptand (cavity radius = 1.1 Å (3)), while K^+ (radius = 1.38 Å) plays the corresponding role for (2.2.2), which has a cavity radius of 1.4 Å (3). However, it has been noted (12) that one cannot think of this selectivity as a simple consequence of one cation having a better steric fit into the ligand cavity. The observed selectivity is the product of a combination of several factors, including the change in enthalpy which results when the solvent molecules in the metal ion's first coordination sphere are replaced by the ligand and

the entropic effects arising from the desolvation of the cation and cryptand which accompanies the formation of the complex (12).

Alkaline earth cations also form stable cryptates and several studies of the formation thermodynamics of these complexes have been published (3,6,12). For alkali metal and alkaline earth ions of comparable radius, the divalent ion has generally been found to form more stable cryptates (6,13). The greater stability of the divalent cryptates is not merely due to greater ion-dipole interactions between the cation and the bonding sites of the ligand. An examination of the complexation thermodynamics for alkali metal and alkaline earth cryptates (12) revealed that the enthalpies of complexation for the divalent ions were comparable to or less favorable than those for monovalent ions of similar size. Thus, the increased stabilities of the alkaline earth complexes arise from entropic factors. The hydration around one of these divalent ions is more extensive than that for the corresponding monovalent ion, so one expects a more favorable entropy of complexation when the divalent hydration shell is removed upon the encapsulation of the metal ion within the cavity of the cryptand.

Studies of cryptate thermodynamics have not been limited to alkali metal and alkaline earth complexes. The formation constants for a number of transition metal cryptates have been determined (14-17) with the same potentiometric methods which were used for most of the alkali metal and alkaline earth systems. While Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^+ , and Tl^+ form a number of stable cryptates, the d-block transition metal ions, Ni^{2+} , Zn^{2+} , and Co^{2+} , do not show much tendency to follow suit. Of the d-block ions, only Cu^{2+} forms cryptates with appreciable

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stability constants. The relative instability of the cryptates of the d-block ions has been explained as a combination of size incompatibility and hard-soft acid-base considerations (15). The d-block cations studied all have radii of about 0.70 to 0.75 Å (18) which would be too small for the (2.2.1) and (2.2.2) cavities. The (2.2.1) cryptand has a cavity radius of 0.8 Å which would be a good match for the cation radii given above. However, the (2.2.1) complexes are still not very stable. The majority of the donor groups of this ligand are oxygen atoms, but the d-block ions have a greater affinity for nitrogen donors. Therefore, the instability of these (2.1.1) complexes is at least partly the result of relatively unfavorable interactions between the cations and the donor atoms of the ligand. To verify this, Lehn and Montavon synthesized a ligand which was analogous to (2.1.1) except that the two oxygen atoms in the diether strand were replaced by two N-CH₃ groups. This tetraaza ligand formed complexes with d-block ions which were at least five orders of magnitude more stable than the corresponding (2.1.1) cryptates (15).

While cryptate thermodynamics has received a good deal of attention, the kinetics of cryptate formation and dissociation has not been neglected either. Studies have been performed in aqueous and non-aqueous solution, and several kinetic techniques have been employed, including proton and alkali metal NMR (nuclear magnetic resonance) (19-23), temperature jump (24), and stopped-flow (25-28). Investigations of cryptate ligation kinetics have concentrated almost exclusively on the alkali metal and alkaline earth complexes. (The only exceptions to this pattern are Tl(2.2.2)⁺ (19) and Ag(2.2.1)⁺ (27).) However, much useful information may be gleaned from these studies.

What follows will be concerned with aqueous solutions since these are the media employed in the kinetic studies of the present work.

Within a given charge and ligand type, cryptate stability is more clearly reflected in the dissociation rate constant k_d rather than the formation rate constant k_f . The most stable cryptate will generally have the smallest k_d (26) although a number of anomalies (e.g. $\text{Sr}(2.2.1)^{2+}$) are present. A comparison between the k_f and k_d values of alkali metal and alkaline earth cryptates reveals that greater differences tend to be found between charge types than within a given charge type. The k_f and k_d for alkaline earth cryptates are consistently much smaller than those for the alkali metal complexes.

Some insight into the factors which determine these relative values has been gained by examining the activation entropies of the formation and dissociation reactions. In particular, the activation entropies for the dissociation process usually are negative quantities having appreciable magnitudes. This has led a number of workers (13,26) to conclude that the activated complex for the formation and dissociation reactions bears a greater resemblance to the separated reactants (i.e., metal ion and ligand) than it does to the cryptate product. One can think of the dissociation reaction as proceeding via a transition state in which some water molecules coordinate to the metal ion. While the metal ion is still bound to the cryptand, there is a good possibility that the cation is no longer inside the molecular cavity (26). The alkaline earth ions, as a consequence of their greater charge, will tend to structure the solvent to a greater extent in this transition state than alkali metal ions would. This is supported by a study of the activation entropies for the dissociation of the (2.2.2)

cryptates. The Na^+ and K^+ complexes have positive activation entropies while the corresponding quantities for the Ca^{2+} , Sr^{2+} , and Ba^{2+} cryptates are considerably more negative. Similar trends may be seen for the (2.2.1) complexes, although the data for the K^+ complex are not available.

It has also been noted (13,26) that the k_f values for the alkali metal and alkaline earth cryptates follow the same pattern as the rates of water exchange in the hydration shells of the cations although the actual formation rates are several orders of magnitude slower than those for the water exchange. The correspondence between k_f and the water exchange rates has led to the conclusion that partial or complete desolvation of the cation occurs prior to or during the rate-determining step of cryptate formation (26). Of course, the extent of desolvation which is thought to occur here must be in harmony with the general description of the activated complex given in the preceding paragraph. The much smaller k_f values relative to the water exchange rates have been explained in terms of two alternative or possibly coexistent effects (26). To begin with, the concentration of the reactive conformation of the cryptand may be quite low. This would imply an unfavorable pre-equilibrium before the rate-determining step. In addition, a large steric barrier to cryptate formation may exist as a consequence of the possibility that first bond formation may be difficult with the relatively rigid cryptands.

Under a given set of conditions, cryptate formation and dissociation follow simple second-order and first-order rate laws, respectively (26). However, kinetic studies of these processes are not completely free from complications. Cox and Schneider have found that the

dissociation rates of many cryptates are acid catalyzed (27). The experimental dissociation rate constants k'_d had acid dependencies of the form

$$k'_d = k_d + k_H [H^+] \quad (1)$$

The presence of the acid catalyses furnishes one with information on the mechanism of the dissociation reaction. Cryptates can be considered to exist in solution as an equilibrium mixture of three conformations: the *endo-endo*, *exo-endo*, and *exo-exo*. The *endo-endo* is the most stable thermodynamic form and is the conformation found in the solid state, as mentioned previously. However, dissociation can occur when the cryptate is any of these three forms (19). Because at least one nitrogen in the *exo-endo* and *exo-exo* forms is directed away from the interior of the cavity, one can conceive of a mechanism in which protonation at this site occurs prior to the rate-determining removal of the metal ion from the cryptate cavity (27). Such a preceding step could give rise to the $k_H [H^+]$ term in eqn (1). The k_d term can then be seen to stem from a mechanistic pathway in which the metal ion exits the cryptate cavity while the ligand remains in an *endo-endo* conformation. Because the lone pairs on the nitrogens remain directed into the cryptate cavity, there is little chance for protonation to occur prior to the rate-determining removal of the cation. The combination of the two pathways described here results in the two terms of eqn (1). The observed acid catalyses originate in the stabilization of an intermediate (the *exo-endo* or *exo-exo* conformation) via the protonation of one of the nitrogens on the ligand. It is also enlightening to note that the dissociation rates of several

cryptates (e.g. $\text{Sr}(2.2.1)^{2+}$) show little, if any, acid dependence. This has been interpreted as an indication that the conversion of the *endo-endo* to *exo-endo* and *exo-exo* forms is the rate-determining step in the aquation of these cryptates (27). Thus no protonation preceding the rate-controlling step is found for either the *endo-endo* or the *exo-endo/exo-exo* dissociation pathways.

Several electrochemical studies of cryptates have been performed. The great majority of these have been carried out by Peter and Gross with propylene carbonate as the solvent (29-36). Britz and Knittel have produced the only electrochemical study conducted in aqueous solution (37). This work dealt with an investigation of the adsorption of $\text{K}(2.2.2)^+$ at a dropping mercury electrode. A combination of drop-time measurements and a.c. polarography was employed to determine the maximum surface coverage and the diffusion coefficient of the $\text{K}(2.2.2)^+$ ion.

Most of the work of Peter and Gross has been devoted to the electrochemistry of alkaline metal and alkaline earth cryptates in propylene carbonate (29-33,35). Several points have emerged. The electroreductions of the cryptates occur at considerably more negative potentials than those for the corresponding solvated metal ions. This result is not unexpected. The oxidized form of the alkali metal or alkaline earth is stabilized by complexation with the cryptand. An electrode of greater reducing power (i.e., more negative potential) is required to reduce such a species to the metallic state. Prolonged electrolysis of solutions of $\text{K}(2.2.2)^+$ has shown that the products of the electroreduction of this complex are the amalgam $\text{K}^\circ(\text{Hg})$ and the free ligand (35). Gisselbrecht, Peter, and Gross have also studied the electrochemistry

of other cryptates. In cyclic voltammograms of the $\text{Tl}(2.2.2)^+$ complex, one could observe peaks corresponding to the electroreduction and electrooxidation of the cryptate (34). In contrast, the voltammograms of the alkali metal and alkaline earth cryptates have no anodic peaks which can be attributed to an oxidation which involves the complex (32,35).

The complexes of (2.2.1) and (2.2.2) with Fe^{2+} , Co^{2+} , and Ni^{2+} have been investigated as well (36). The electrochemical reductions of these cryptates in propylene carbonate were found to be irreversible deposition reactions and to occur at more negative potentials than the reductions of the corresponding solvated metal ions. (The $\text{Ni}(2.2.1)^{2+}$ complex is the sole exception to this second trend.) While these alkali metal, alkaline earth, and transition metal cryptates which undergo deposition reactions are interesting electrochemical systems for several reasons, they are far from ideal for studies of the fundamental parameters which affect redox reactivity. For these complexes, the analysis of electron-transfer kinetics is complicated by the ligation reactions which are involved in the deposition process.

Given the above considerations, one comes to the conclusion that a more suitable cryptate would be one in which both halves of a metal ion redox couple would remain in complexed form and in solution. These properties would yield mechanistically simpler systems which are free from the preceding or following chemical steps that accompany a deposition. These simple, straightforward systems would be a crucial component in a fundamental and unambiguous investigation of the factors which control redox thermodynamics and kinetics.

One may examine the preceding information and trends and speculate

that a europium or ytterbium cryptate couple might have the desirable features which were described above. The radii of Eu^{2+} (1.17 Å (11)) and Yb^{2+} (0.93 Å (18)) are such that one would expect these ions to have stable (2.2.1) and (2.2.2) complexes, if the size criteria formulated from the alkali metal and alkaline earth systems are valid for these lanthanide ions. It has been stated the chemical properties of divalent lanthanide ions are similar to those of the alkaline earth ions having comparable radii (38). Thus, there is no reason to suspect that the factors which govern the thermodynamic and kinetic stabilities of the alkaline earth cryptates will be qualitatively different to those for the Eu^{2+} and Yb^{2+} cryptates.

In aqueous solution, both of these divalent lanthanide ions can be converted to the trivalent ion in a simple one-electron oxidation. Whether a similar one-electron interconversion in aqueous solution can be found for the cryptates of Eu and Yb is one of the objectives of this investigation. In addition, the kinetic stabilities of the trivalent and divalent forms of these complexes will be determined. This information would be useful in determining the suitability of the lanthanide systems for redox studies since complexes with slow dissociation kinetics are required in order to minimize the mechanistic complications arising from ligation reactions which coincide with the electron-transfer process.

Furthermore, a study of the thermodynamic stabilities of the Eu and Yb cryptates will be necessary. This will be needed for determining the thermodynamic contributions to the redox reactivity of the Eu and Yb complexes. As usual, an analysis in terms of enthalpies and entropies will provide more detailed information than could be acquired

solely from free energies. One effective method for obtaining such entropic and enthalpic data is through the employment of ionic entropies and particularly reaction entropies as is now discussed.

B. Reaction Entropies

Partial molal entropies can be exceedingly useful when one investigates the thermodynamic properties of a species in solution. The partial molal entropy of the i th component of a system $\bar{S}_i$ can be defined as the temperature dependence (under constant solution composition and pressure) of μ_i , the chemical potential of component i

$$(\partial\mu_i/\partial T)_P = \bar{S}_i \quad (2)$$

In solution studies one frequently focuses attention on one ion. Under these circumstances, it would seem appropriate to think in terms of partial molal entropies for single ions. Strictly speaking, only the partial molal entropy of a neutral salt (i.e., the sum of the ionic entropies for the cation and anion) is experimentally accessible (39). However, methods are available for estimating single ion entropies. One may arbitrarily assign an entropy value to some ion and thus obtain a relative scale of single ion partial molal entropies. It is conventional to use the scale based on the assumption that $\bar{S}_{H^+}^\circ = 0$ (39). An alternative approach is to estimate the absolute entropy of an ion in solution by means of an extrathermodynamic assumption. Several different assumptions have yielded similar values of $\bar{S}_{H^+}^\circ$ (40). An approximate value of $\bar{S}_{H^+}^\circ = -5$ e.u. (e.u. $\equiv$ cal deg⁻¹ mol⁻¹) was obtained by each of these methods (40). Once one absolute ionic entropy is set, the relative scale of entropies mentioned above can be easily converted into an absolute scale. While the scope for interpretation is somewhat

smaller with the relative scale, an ionic entropy from either scale contains valuable information on the interactions between an ion and the solvent molecules surrounding it.

Because transition metal ions are used extensively in studies of redox thermodynamics and kinetics, the entropies of such ions are of especial interest to the present work. Some investigations of these systems have already been conducted. The entropies of these ions have been found to depend markedly on the ionic charge and on the types of ligands coordinated to the metal ion (41-44). In examining the various possible reasons for this wide variation in entropies, one can see how electrostatic effects (45,46) contribute to the first dependence. The "structure-making" and "structure-breaking" ability of the ion in solution will also have a decided influence on the ionic entropy (47-49).

While individual ionic entropies have a great deal of utility, a variation of this concept is particularly appropriate when dealing with redox systems. One can consider ΔS_{rc}° , the difference in partial molal entropies of the reduced and oxidized forms of a redox couple. Under this definition ΔS_{rc}° is the reaction entropy for a half-cell reaction and can be regarded as the entropic analog to the half-cell electrode potential. One can employ ΔS_{rc}° in a variety of circumstances for a substantial number of purposes. A relative measure of the degree of solvent ordering around the oxidized and reduced forms of a metal ion complex is available through the use of ΔS_{rc}° . The entropy of reaction for a homogeneous redox reaction can be calculated by taking the difference between the ΔS_{rc}° values of the two redox couples involved. Large ΔS_{rc}° values are frequently found, so that this term can be the

predominant constituent of the free-energy driving force for an electrode reaction (50). By combining the appropriate values of ΔS_{rc}° one can obtain the difference in the entropies of formation between the oxidized and reduced forms of a metal ion complex. This will definitely be applicable when comparing the complexation thermodynamics of the trivalent and divalent lanthanide cryptates.

As evidenced by the above discussion, a knowledge of ΔS_{rc}° values can be very useful. Unfortunately, a comparative shortage of data exists in the literature. Moreover, some of these data are contradictory, possibly as a consequence of the different entropy scales which are in use. Nonetheless, it has been determined that the ΔS_{rc}° values of transition metal couples are considerably influenced by the ligands which are coordinated to the metal ion. For one-electron aquo cation redox couples, ΔS_{rc}° values in the 40 to 50 e.u. range are found, provided that one employs the normal convention and writes the half-cell reaction as a reduction (41,45,49). In contrast, metal ion complexes containing large organic ligands have been found to have much smaller ΔS_{rc}° values (51). This effect has been ascribed to the efficacy of the organic ligands in shielding the cation from the surrounding water molecules (51).

While some helpful points have emerged from the results described above, it is clear that a study of wider scope and greater depth is needed. In particular, ΔS_{rc}° values are required for transition metal couples containing other ligands besides aquo or large organics. This could enable ligand influences on ΔS_{rc}° to be discerned. The dearth of data on other ligand systems can be traced to a lack of suitable redox couples. In aqueous solution, most transition metal ion complexes

which contain common unidentate ligands are not stable in both oxidation states. In at least one of these states, the complex will be unstable with regard to dissociation, chemical oxidation, or other reactions. These circumstances preclude the measurement of the equilibrium cell potentials of these couples. Furthermore, the determination of ionic entropies is prevented since these quantities are frequently obtained from the temperature dependences of cell potentials (40).

This situation has recently been significantly improved when it was determined that several ruthenium(III)/(II) complexes were substitutionally inert in both oxidation states, at least on the time scale of cyclic voltammetry and other electrochemical perturbation techniques (52-56). Some osmium(III)/(II) ammine couples have been found to have similar properties (57,58). The Ru and the Os couples are electrochemically reversible (i.e., have fast heterogeneous charge-transfer kinetics), and as a consequence, cyclic voltammetry can be used to obtain accurate values of the equilibrium cell potentials.

Thus, the ΔS_{rc}° values for these Ru(III)/(II) and Os(III)/(II) couples should be experimentally accessible. Aside from their intrinsic value these data could also find application as a means of estimating ΔS_{rc}° values for other systems. The reaction entropies for Cr(III)/(II) and Co(III)/(II) complexes (which cannot be determined directly) might be roughly approximated by the ΔS_{rc}° for the analogous Ru or Os system. This procedure is not without some justification. Empirical correlations (41-44) suggest that ΔS_{rc}° values for simple transition metal couples are chiefly functions of the type of ligand involved and of the charge on the cation. The actual identity of the central metal ion appears to be of less significance. Given the paucity of data at

present, it is obvious that a generalization such as this cannot be either verified or refuted until further investigations are carried out.

C. Homogeneous Electron-Transfer Kinetics of Transition Metal Complexes

The great practical and theoretical importance of homogeneous redox reactions has encouraged extensive research in this area. In particular, much attention has been devoted to the kinetics and mechanisms of these reactions. Significant progress has been made for those reactions where oxidation-reduction is actually brought about by electron transfer (as opposed to reactions which occur via atom transfer or some other complex mechanism). The mechanistic simplicity of such electron-transfer reactions has been one of the primary reasons behind the progress in this field (59,60).

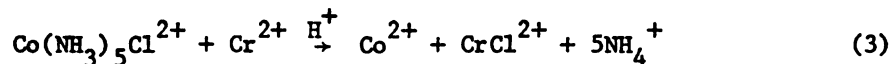
Probably the most significant and useful advancement in the area of electron-transfer mechanisms is the concept of outer-sphere and inner-sphere processes (59). The basic notion here is that an electron-transfer reaction can be placed in one of two broad classifications on the basis of the geometry of the transition state. In an outer-sphere mechanism, the coordination shells of the oxidant and reductant remain intact while electron transfer occurs. Although some perturbation of the coordination shell is allowed (and usually necessary as will be seen later), no bond rupture takes place in an outer-sphere process. In contrast, an inner-sphere mechanism involves definite changes in the coordination shells of the reactants. For transition metal complexes, these changes often yield a species in which one ligand is common to the coordination spheres of both reactants. In this arrangement, the ligand serves to connect the two metal centers. Consequently,

the mechanisms of reactions which proceed via such transition states or intermediates are frequently termed "ligand-bridged mechanisms", and one commonly finds that "inner-sphere" and "ligand-bridged" are used synonymously.

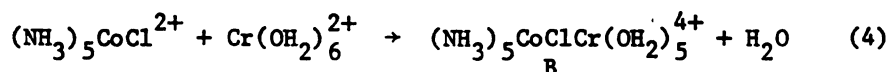
Because the understanding of a redox reaction can be greatly improved by a knowledge of its mechanism, one finds that the characterization of a reaction as inner sphere or outer sphere is one of the main concerns of the redox kineticist. The assignment of a mechanism can be straightforward, difficult, or impossible, depending on the chemical properties of the reactants (59). When both reactants are substitutionally inert on the timescale of the redox reaction, an outer-sphere mechanism is the only one possible (60). The same restriction applies to a reaction containing one inert and one labile reactant as long as the inert species has no unoccupied binding sites which could coordinate with its labile reaction partner (60). Thus a cognizance of the ligation kinetics of a transition metal complex is a crucial requirement for an investigation of its electron-transfer reactions. In the case of the present study of the redox kinetics of the Eu cryptates, one sees that a knowledge of the dissociation kinetics of these complexes will have both intrinsic worth and a direct bearing on the characterization of the electron-transfer mechanism.

A consideration of the substitutional inertness of the reactants is not the only means by which one may distinguish outer-sphere and inner-sphere reactions. One of the first methods employed was the examination of the products of the redox reaction. Taube's pioneering efforts in this field (61-63) and also in the general area of redox kinetics and reaction mechanisms must be acknowledged at this point.

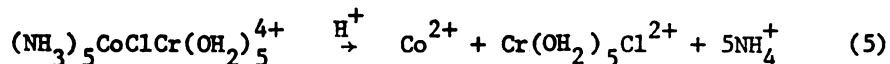
The product analysis method takes advantage of the substitutional inertness or lability of the reactants and products of certain redox reactions. This can be best illustrated by examining one of these reactions; e.g. the reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ with Cr^{2+} :



This is a rapid reaction. The $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and CrCl^{2+} complexes are substitutionally inert and only aquate slowly. On the other hand, Co^{2+} and Cr^{2+} are labile species. The preceding points lead one to conclude that this is an inner-sphere reaction which involves the formation of a chloride-bridged intermediate or transition state B:



The lability of the Cr^{2+} ion allows the bridged species B to be produced. An intramolecular electron transfer occurs within B to yield Co(II) and Cr(III) . This followed by the cleavage of B to yield the reaction products:

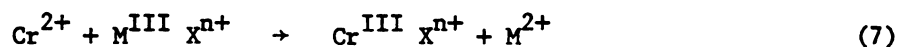


The lability of the Co(II) ion combined with the substitutional inertness of Cr(III) leads to the rupture of the Co-Cl bond and to the chloride being frozen into the coordination sphere of the Cr(III) ion. For the sake of argument, one can imagine that reaction (3) could proceed via an outer-sphere electron transfer to yield Co^{2+} , Cr^{3+} and free Cl^- . A subsequent ligand-substitution reaction yields the CrCl^{2+} complex which is found in the product analysis:



Such an outer-sphere route can be ruled out because of the substitutional inertness of Cr^{3+} and rapidity of the redox reaction. The electron-transfer reaction would occur and the analysis of the products would be carried out well before reaction (6) could occur to any significant extent. Thus an inner-sphere mechanism is the only one which is consistent with the properties of the reactants and products. Additional confirmation was obtained when the reaction was carried out in the presence of $^{36}\text{Cl}^-$. None of this isotope was found coordinated to the Cr^{3+} ion (59,61-63) which reaffirms the assertion that equation (6) and hence the outer-sphere pathway do not contribute significantly to the production of CrCl^{2+} .

Because many redox reactions involving Cr^{2+} are rapid and since Cr^{3+} is substitutionally labile, several other mechanistic studies have employed Cr^{2+} as a reducing agent for Co(III) , Cr(III) , and Fe(III) complexes (59,64). These reactions can be written as



where X is the potential bridging ligand. In each case the detection of $\text{CrX}^{\text{n}+}$ has served to verify the presence of an inner-sphere pathway.

Reducing agents other than Cr^{2+} have also been used. Co(CN)_5^{3-} and $\text{Ru(NH}_3)_5\text{OH}_2^{2+}$ are similar to Cr^{2+} in that they aquate very slowly after oxidation. Thus the technique of separation by ion exchange followed by spectral identification which was used on the products of the Cr^{2+} reactions, can be applied equally well to the products of the Co(CN)_5^{3-} and $\text{Ru(NH}_3)_5\text{OH}_2^{2+}$ reactions (59,65,66).

Other mechanistic studies have employed Fe^{2+} or V^{2+} as reductants. While the product species (Fe^{3+} or V^{3+}) hydrolyze rapidly, the

appropriate remnants of the ligand-bridged intermediates can be observed using flow techniques (59).

Another method for identifying an inner-sphere mechanism is to detect the bridged species itself. This is unambiguous evidence only when both of the products are substitutionally inert (59). Thus the reactions of Cr^{2+} with Ru(III) chloride complexes have yielded $\text{Cr}^{\text{III}} - \text{Cl} - \text{Ru}^{\text{II}}$ species (67,68). Other reactions have been characterized as inner-sphere by this method (59).

One may sometimes diagnose reaction mechanisms from a careful inspection of rate constants or activation parameters. For example, the activation parameters for ligand substitution on the V^{2+} ion are comparable to those found for the reactions between V^{2+} and certain oxidizing agents. It is strongly suspected that an inner-sphere electron-transfer mechanism is operative and that the rate-determining step is the displacement of an aquo ligand on V^{2+} by the bridging ligand (69,70).

Second-order rate laws of the form:

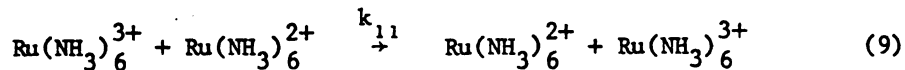
$$\text{Rate} = k [\text{reductant}][\text{oxidant}] \quad (8)$$

are usually found for both inner-sphere and outer-sphere reactions. Thus no mechanistic assignments can be made when such experimental behavior is observed. However, when dealing with reactions where at least one of the reactants has an aquo ligand, one frequently finds that the rate constant k shows an inverse dependence on $[\text{H}^+]$. Often the rate constant is found to be the sum of two contributions. One of these is an acid-independent term while the other is the $[\text{H}^+]^{-1}$ term. This inverse term can be a very significant fraction of the experimentally observed rate constant, and in some reactions, the

contribution of the $[\text{H}^+]^{-1}$ term is so large that the $[\text{H}^+]$ -independent term cannot be reliably determined. The inverse-acid term is generally attributed to the presence of an inner-sphere mechanism which proceeds via a hydroxide bridge (71-73). In more explicit terms, the reaction involves the deprotonation of one of the aquo ligands (this pre-equilibrium step is the source of the $[\text{H}^+]^{-1}$ term), followed by the formation of the hydroxide-bridged intermediate or transition state, and finally concludes with the electron-transfer step and any other following chemical process. Therefore, the $[\text{H}^+]$ -dependence of the rate constant may provide a clue to the mechanism as long as an aquo ligand is present on one of the reactants.

While determinations of mechanism are very important to the study of redox reactions, one is still left with the problem of formulating quantitative explanations for the experimentally observed rate constants. Considerable theoretical work has addressed this question and significant progress has been made, especially in the case of outer-sphere reactions (59,60,74). The calculation of the energy barrier to electron transfer is simplified for outer-sphere processes because of the absence of bond formation and breakage (59,60). Several theories dealing with this area have emerged (74) including those of Hush (75) and Levich and Dogonadze (76), but the treatment of Marcus has been the most successful and widely used (77-79). The Marcus theory may be approached on two levels. It can be used in an absolute sense to calculate outer-sphere electron-transfer rate constants without the use of other rate data, or it can serve as a relative theory which begins with some existing rate parameters and employs these to calculate the corresponding values for other reactions (60).

A summary of the Marcus theory can be started by considering a self-exchange reaction, i.e., one in which the oxidant and reductant are from a single redox couple.



is an example of such a reaction. Obviously no net chemical reaction occurs, and consequently $\Delta G^\circ = 0$ for self-exchange reactions. The absolute Marcus theory attempts to obtain the self-exchange rate constant k_{11} by calculating the associated free energy of activation. In order to do this, the reaction is assumed to be weakly adiabatic. This implies two conditions. First, the interaction between the two reactants is sufficiently small so that neither is directly perturbed by the presence of the other. Thus the activation of the two reaction centers occurs independently. The second condition requires that the interaction between the reactants is strong enough to allow κ , the probability for electron transfer in the activated complex, to approach unity. The requirement of weak adiabaticity may seem overly restrictive, but fortunately most redox reactions which have been studied do indeed satisfy this condition (80).

Before continuing on, it should be pointed out that this section is only considering thermal electron-transfer reactions, i.e., those which occur without the absorption of light. Only thermal energy is used in surmounting the activation barrier. Furthermore, the Franck-Condon principle applies in these systems. In more specific terms, because electronic motion occurs much more rapidly than nuclear vibration, the reactants have no time to change their nuclear geometry while

the electron-transfer act takes place. Consequently, there are actually two activated complexes, one for the reactants and the other for the products. These are isoenergetic states which differ only in the location of the transferred electron. In the reactants' activated complex, this electron is located on the reducing agent, while in the products' activated complex, the electron is found on the reduction product. The laws of thermodynamics require electron transfer between isoenergetic states. In principle, a nonisoenergetic transfer could be employed to circumvent the First Law (74).

Having dealt with these preliminaries, one can now consider the free energy of activation. It is helpful to think of this quantity as a sum of contributions which stem from the individual events which make up the activation process. The sequence begins with the diffusion of the reactants toward each other to form the so-called precursor complex. The energy involved here is the electrostatic work (and other forms of work) which must be done when bringing the reactants together from an infinite separation to one which corresponds to the internuclear distance in the activated complex. This term can be quite appreciable, particularly in those cases when like-charged species are being brought together.

Once the reactants are in the precursor state, the remainder of the activation process occurs. Changes in the nuclear coordinates must occur in order to reach the activated complex. The isoenergetic constraints which were described above dictate the nature and the degree of these changes. Both the inner coordination sphere of the reactants and the surrounding solvent must be modified appropriately. The energies associated with these processes are respectively designated

the inner-shell and the outer-shell terms. The inner-shell term has its origins in the distortions in the metal-ligand bond distances and the changes in ligand conformation which are necessary to attain the activated complex. For example, in the reduction of a trivalent ion to its divalent form, the M(III)-L bond would be required to stretch to a length which was intermediate to those for M(III)-L and M(II)-L. The same considerations apply to the other reactant. The outer-shell term may be regarded along similar lines. The solvent orientation in the activated complex will be intermediate to those surrounding the reactants in the precursor complex and the products in the analogous successor state.

One can summarize the preceding discussion by beginning with the relationship between the self-exchange rate constant k_{11} and the free energy of activation ΔG^* :

$$k_{11} = Z \exp(-\Delta G^*/RT) \quad (10)$$

where Z is the bimolecular collision frequency, R is the gas constant, and T is the absolute temperature. As discussed previously, the free energy of activation can be expressed as the sum of contributions from each of the steps in the activation process

$$\Delta G^* = w_r + \Delta G_{in}^* + \Delta G_{out}^* \quad (11)$$

where w_r is the work required to form the precursor state from the separated reactants, and ΔG_{in}^* and ΔG_{out}^* are the inner-shell and outer-shell terms described above.

It is important to note that the Marcus formulations are associated with a kinetic model in which each collision between reactants of the

proper energy and orientation leads to reaction. This differs from the transition-state or ion-pair pre-equilibrium model which is widely applied to solution reactions. The Marcus model is concerned with the non-equilibrium energy fluctuations of the system rather than a formal equilibrium between the transition state and the reactants. A recent paper by Brown and Sutin (81) has addressed these two models with regard to the self-exchange rate parameters for some Ru(III)/(II) complexes. The Marcus effective-collision model was found to agree more closely with the experimental results.

Analytical expressions for each of the terms in equation (11) have been derived. If the work in forming the precursor state is considered to be purely electrostatic in nature, the appropriate expression for w_r can be obtained from Debye-Hückel theory (81):

$$w_r = \frac{z_1 z_2 e^2 N}{\epsilon_s a (1 + Ba\mu)^{1/2}} \quad (12)$$

where z_1 and z_2 are the charges on the reactants, e is the electronic charge, N is Avogadro's number, ϵ_s is the (static) dielectric constant of the solvent, a is the distance between the centers of the reactants in the precursor state, B is the Debye-Hückel parameter (82) and μ is ionic strength. The inner-shell term is given by (74,79,81):

$$\Delta G_{in}^* = \frac{6 f_1 f_2 (\Delta a)^2}{2(f_1 + f_2)} \quad (13)$$

where f_1 and f_2 are the force constants for the metal-ligand bonds in the reactants and Δa is the difference between the equilibrium M-L bond distances in these two species. The metal-ligand bonds are assumed to behave harmonically. The expression for the outer-shell

term is (74,79,81):

$$\Delta G_{\text{out}}^* = \frac{e^2}{4} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{a} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \quad (14)$$

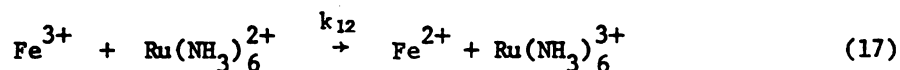
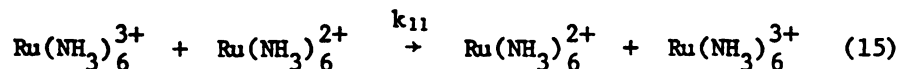
where a_1 and a_2 are the radii of the reactants, ϵ_{op} is the optical dielectric constant (equal to the square of the refractive index of the solvent) and the other terms have already been defined above.

In this case, the solvent is assumed to be a dielectric continuum.

As formulated here, the absolute Marcus theory is a remarkable achievement since it allows the calculation of a rate constant from non-kinetic quantities. The theory has performed well in qualitative comparisons between related complexes and has proved useful as a conceptual structure within which activation barriers may be treated in terms of separate components (60). As a tool for making quantitative predictions, the Marcus theory has met with partial success (60). Reasonable agreements between calculated and experimental self-exchange rate constants have been observed for some systems (81) but this is not always the case (60). One point which is of particular interest to the present work involves the entropy of activation. Many outer-sphere self-exchange reactions have been found to have considerable entropies of activation ($\Delta S^\ddagger \approx -30$ e.u.) (83). A $\Delta S^\ddagger$ value of about -20 e.u. is expected at zero ionic strength but theory predicts an essentially negligible value at the ionic strengths employed for most experimental studies (60). This question will be discussed in Chapter V and a possible explanation will be advanced.

While the Marcus theory has encountered problems when used in absolute terms, it has been quite successful when employed in a relative

sense. For the purpose of illustrating the relative theory the following reactions will be considered.



Reactions (15) and (16) are examples of the previously described self-exchange reaction. Reaction (17) differs from the other two in that its reactants are from two different redox couples. Such reactions are designated "cross reactions" (59). The self-exchange rate constants can be considered to reflect the intrinsic reactivity of the single couple which is involved. Rate constants for cross reactions are a less clear-cut measure of reactivity since they are composites of the intrinsic reactivities of the oxidant and reductant combined with the effect of the non-zero ΔG° on the activation barrier. The achievement of the relative Marcus theory has been its ability to relate the cross-reaction rate constants to those for the constituent self-exchange reactions. The activation free energy of the cross reaction, ΔG_{12}^* , can be considered to consist of contributions from the intrinsic (self-exchange) barriers, $0.5\Delta G_{11}^*$ and $0.5\Delta G_{22}^*$, combined with $0.5\Delta G_{12}^\circ$, the lowering of the activation barrier due to the favorable free energy of reaction, ΔG_{12}° . The assumption of weak adiabaticity removes the need for any coupled activation of the redox centers. Thus, one finds independent additive contributions from each redox couple involved. In summary, the activation barrier of a cross

reaction can be given by (60):

$$\Delta G_{12}^* = 0.5(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12}^\circ) \quad (18)$$

This equation can also be expressed in terms of rate constants (59,60,74,79), which yields the Marcus cross-relation:

$$k_{12} = (k_{11} k_{22} K_{12} f)^{1/2} \quad (19)$$

where K_{12} is the equilibrium constant for the cross reaction and f is given by

$$\log f = (\log K_{12})^2 / 4 \log (k_{11}k_{22}/Z^2) \quad (20)$$

The f term is a correction factor which accounts for the parabolic shape of the activation barrier. (Equation (18) is a simplified form which does not include this term.)

The cross-reaction rate constants calculated using equation (19) have generally agreed quite well with experimental results (59,60). While this is a substantial accomplishment, some difficulties remain. The cross-relation does not work well for reactions involving $\text{Co}(\text{OH}_2)_6^{3+}$ (60). Detailed studies have isolated the thermodynamic (ΔG_{12}°) and intrinsic (ΔG_{11}^* and ΔG_{22}^*) factors which make up ΔG_{12}^* . While the thermodynamic term tends to comply with equation (18), some exceptions have been found for the intrinsic contributions (60). A possible explanation is that nonelectrostatic work terms resulting from the formation of precursor state may not always cancel each other completely (77). The limitations of the relative Marcus theory will be examined in greater detail in Chapter V and some possible sources of these problems will be discussed.

CHAPTER II
EXPERIMENTAL ASPECTS

A. Apparatus

Electrochemical measurements were carried out in conventional glass cells having working and reference compartments separated by a "very fine" or "ultrafine" grade frit obtained from Corning Inc. These frits had an average porosity of 1-3 μm and prevented significant mixing of the solutions in the two compartments in the 2-3 hours required for most experiments. The capacity of the working compartment was in the 5-10 ml range. The working compartment, the liquid junction formed in the frit, and part of the salt bridge between the working compartment and the reference electrode were surrounded by a jacket through which water from a Braun Melsungen circulating thermostat could be circulated. This enabled the temperature within this region to be controlled to within $\pm 0.05^\circ\text{C}$. A separate jacket around the reference compartment enabled the temperature of this part of the cell to be controlled independently when necessary.

Bulk electrolyses were performed in cells in which the counter electrode was given its own compartment adjacent to the working compartment but separated from the latter by means of a frit. For applications which required substantial current densities, a similar cell with more porous frits was employed to minimize resistance problems.

B. Electrochemical Techniques

1. Common Features

All solutions were deoxygenated by bubbling with prepurified nitrogen or argon which had been passed through a series of wash bottles containing V(II) solution. The final bottle in the series

contained water and served to humidify the gas so that prolonged bubbling would not result in extensive evaporation of the solution in the working compartment.

Saturated aqueous calomel reference electrodes (SCE) were used throughout this work, although the choice of the fill solution was dictated by the experimental conditions. In most cases, a SCE filled with saturated KCl (KSCE) was used. In concentrated perchlorate media, a KSCE suffers from problems arising from the limited solubility of KClO_4 . Precipitation of this salt in the liquid junction of the electrode can lead to spurious potentials. Therefore a SCE filled with saturated NaCl (NaSCE) was employed when working with perchlorate solutions. The potentials in this work are quoted versus the KSCE although in a good many cases they were actually measured versus a NaSCE.

A platinum wire served as the counter electrode for most experiments. When larger currents were passed, a platinum gauze was used.

2. Cyclic Voltammetry

Cyclic voltammograms were obtained by means of a PAR 174A polarographic analyzer (Princeton Applied Research Corp.) coupled with a Hewlett-Packard HP 7045A X-Y recorder. Sweep rates in the 50-1000 mV/sec range were used in this work. Under these conditions and with the above instrumentation, peak potentials could be measured with a precision of $\pm 1-2$ mV.

Several working electrodes were used in the cyclic voltammetric studies. For redox couples with relatively negative standard potentials, a commercial (Metrohm Model E410, Brinkmann Instruments)

hanging mercury drop electrode (HMDE) was used. An electrode area of about 0.03 cm^2 was employed for most studies. Mercury has a limited anodic range, so for work at positive potentials ($E > +200$ to 300 mV vs. KSCE), a glassy carbon or platinum "flag" electrode was employed. The latter consisted of a 2 mm^2 sheet of platinum foil spot-welded to a fine platinum wire. The Pt flag electrode was pretreated by immersion in warm 1:1 HNO_3 followed by activation by passage over a Bunsen burner flame. The literature procedure for the pretreatment of glassy carbon electrodes (84) was found to do very little to improve their performance as measured by the residual current and the anodic limit. Therefore, these electrodes were not chemically pretreated before use.

3. Polarography

The instrumentation used for cyclic voltammetry was also employed to obtain dc polarograms. Sweep rates between 0.5 and 5 mV/s were utilized. The working electrode was a DME (dropping mercury electrode). Mercury flow rates of $1\text{--}2 \text{ mg/s}$ and column heights of $\sim 50 \text{ cm}$ were used. The drop time could be mechanically controlled to be 1, 2, or 5 sec. by means of a PAR 174/70 drop timer.

4. Preparative Electrolyses

Constant-potential electrolyses were performed with a PAR 174A or a PAR 173 potentiostat. The latter was used when currents greater than 10 mA were required. A stirred Hg pool served as the working electrode while a Pt gauze electrode was used as the counter electrode. The electrolyzed solution was kept under a blanket of deoxygenated nitrogen or argon to prevent any reactions with atmospheric O_2 .

5. Potentiometric Methods

A Corning Digital 109 pH meter combined with a regular glass electrode or a miniature combination pH electrode was used for pH measurements and potentiometric titrations. The study of fluoride ion association employed an Orion Model 94-09A fluoride ion-selective electrode.

C. Materials

1. Cryptates

Solid cryptate samples were obtained from Dr. O. A. Gansow's group. The syntheses of $\text{Eu}(2.2.1)\text{Cl}_3$, $\text{Eu}(2.2.2)\text{Cl}_3$, $\text{Eu}(2.2.1)(\text{NO}_3)_3$, $\text{Eu}(2.2.2)(\text{NO}_3)_3$, $\text{Yb}(2.2.1)\text{Cl}_3$, and $\text{Eu}(2.2.1)\text{Cl}_3$ involved mixing the appropriate Eu or Yb salt with the cryptand in a nonaqueous solvent such as acetonitrile. After this mixture is refluxed for a few hours, the complex is precipitated from solution by the addition of ethyl ether (85).

The $\text{Eu}(2.2.1)$, $\text{Eu}(2.2.2)$, and $\text{Yb}(2.2.1)$ complexes can also be synthesized in aqueous solution. One can prepare aqueous Eu^{2+} and Yb^{2+} by electrolyzing solutions of Eu^{3+} and Yb^{3+} in 0.1 M Et_4NClO_4 (tetraethylammonium perchlorate) at -1.1 and -1.4 V, respectively. A slight excess of the appropriate cryptand is then added to yield the cryptate complex. This divalent form of the cryptate can then be oxidized to the trivalent state by an electrolysis at the appropriate potential (about 100-200 mV anodic of the formal potential of the cryptate given in Chapter III). The complexes made in this fashion display the same electrochemical behavior as that found for the solid cryptate samples. The yield of $\text{Yb}(2.2.1)^{2+}$ was somewhat low due to the hydrolysis of Yb^{2+}

which occurs in the basic solution produced by the addition of the cryptand. The (2.2.2), (2.2.1), and (2.1.1) cryptands were obtained from PCR, Inc.

2. Reagents and Solvents

Except where otherwise noted, the reagents employed in this work were analytical grade and used without further purification. Samples of Et_4NClO_4 (from Eastman or G. F. Smith) used in making supporting electrolytes were recrystallized from water. This resulted in substantial reductions in the background polarographic current. Water was purified by the use of a Milli-Q purification system (Millipore Corp.). Spectral-grade nonaqueous solvents dried over molecular sieves were used in the nonaqueous studies. Mercury which had been triply distilled under vacuum (Bethlehem Apparatus Co.) was employed in the HMDE and DME and as the pool electrode in electrolyses.

3. Transition Metal Complexes and Compounds

Solutions of $\text{V}_{\text{aq}}^{2+}$ were synthesized as follows: a solution of VO_2^+ is made by dissolving V_2O_5 in an appropriate acid (usually HClO_4). At least a five-fold excess of acid must be used if the dissolution of the V_2O_5 is to occur in a reasonable length of time (i.e., less than 1-2 days). Electrolysis of the VO_2^+ at -1100 mV under a nitrogen atmosphere at a mercury pool yields $\text{V}_{\text{aq}}^{2+}$. The reduction consumes H^+ , and this must be remembered when a knowledge of the H^+ concentration is necessary. The $\text{V}_{\text{aq}}^{2+}$ solution produced using this method can be converted to $\text{V}_{\text{aq}}^{3+}$ by electrolyzing at -300 mV.

The preparation of solutions of $\text{U}_{\text{aq}}^{3+}$ involved electrolysis of uranyl perchlorate (obtained from G. F. Smith Co.) in 0.5 M HClO_4 at a stirred mercury pool at -1000 mV. A subsequent electrolysis

at -650 mV yielded U_{aq}^{4+} . A nitrogen atmosphere was maintained over the solutions throughout the electrolyses.

Solutions of Eu_{aq}^{3+} were obtained by dissolving Eu_2O_3 in an appropriate acid. In order to dissolve the oxide within a reasonably short period of time, a stoichiometric excess of acid must be used.

The $Fe(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$, $Co(bpy)_3^{2+}$, and $Co(phen)_3^{2+}$ complexes (where bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) were prepared by mixing the metal ion with at least a five-fold excess of the ligand. These complexes were generally studied in a KCl supporting electrolyte since they were only slightly soluble in perchlorate media.

$Ru(NH_3)_6 \cdot Cl_3$ (obtained from Matthey Bishop) served as the starting material for the syntheses of several other ruthenium ammine complexes. $Ru(NH_3)_5Cl \cdot Cl_2$ was made by refluxing $Ru(NH_3)_6 \cdot Cl_3$ in 1:1 HCl for 4-5 hours. $Ru(NH_3)_5NCS \cdot (ClO_4)_2$ was synthesized using the procedure of Lim et al. (52). A 10-15 mM solution of $Ru(NH_3)_5Cl \cdot Cl_2$ in 0.1 M $NaCF_3COO$, 1mM CF_3COOH was made. An electrolysis at -700 mV under an argon atmosphere yielded the $Ru(NH_3)_5OH_2^{2+}$ complex. (Substitution of Cl^- by H_2O occurs at an appreciable rate with divalent Ru. The tendency of Ru(II) to form dinitrogen complexes necessitates the use of the argon atmosphere.) A ten-fold excess of NaSCN was added, and the color of the solution changed from faint yellow to red-orange, indicating the formation of $Ru(NH_3)_5NCS^+$. An electrolysis at -80 mV converted this divalent complex to $Ru(NH_3)_5NCS^{2+}$. The solution was then removed from the electrolysis cell and $Ru(NH_3)_5NCS \cdot (ClO_4)_2$ was precipitated out by the dropwise addition of a slight excess of 5 M $NaClO_4$.

The $Ru(NH_3)_5OH_2^{3+}$ complex was prepared by two methods. The procedure

of Lim et al. (52) begins by electrolyzing a solution of 2-3 mM $\text{Ru}(\text{NH}_3)_5\text{Cl}\cdot\text{Cl}_2$ in 0.2 M NaCF_3COO , 1 mM CF_3COOH under argon at -700 mV to yield $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$. This solution was removed from the electrolysis cell and added to a solution of AgCF_3COO which had been made by dissolving Ag_2O in CF_3COOH . The silver solution had sufficient Ag^+ to precipitate out all Cl^- and to oxidize the divalent Ru complex to $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$. The resulting solution was filtered to remove AgCl and Ag . The electrolysis cell was cleaned in order to remove any residual Cl^- , and the filtrate was returned to the cell. An electrolysis at 0.0 V reduced any excess Ag^+ in solution. Thus, one should obtain a solution of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$ in NaCF_3COO at the end of this procedure. A modification of this method served as the second means for synthesizing the $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$ complex. After the initial electrolysis of the $\text{Ru}(\text{NH}_3)_5\text{Cl}\cdot\text{Cl}_2$, the solution was kept in the cell. A second electrolysis was then carried out at -50 mV. This oxidized the $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ produced in the first electrolysis to $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$. Neither method was ideal since both yielded solutions containing a slight $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ contamination. Fortunately, the standard potentials of the $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+/+}$ and $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$ couples are sufficiently well separated so that the latter complex can be studied without significant interference from the former. Solutions of the $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ complex were made by adding base (NaOH) to solutions of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$.

The $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ complex (where py = pyridine) was synthesized as follows: a 1 mM solution of $\text{Ru}(\text{NH}_3)_5\text{Cl}\cdot\text{Cl}_2$ in 0.1 M NaCF_3COO , 1 mM CF_3COOH was electrolyzed at -700 mV under an argon atmosphere for about 3½ hours. The resulting light yellow solution of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ turned a bright yellow-green upon the addition of

2.5 mM pyridine. The color change indicated the formation of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$.

The *cis*- and *trans*- $\text{Ru}(\text{OH}_2)_2(\text{bpy})_2^{2+}$ complexes were made by starting with $\text{Ru}(\text{bpy})_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ (obtained from Dr. G. M. Brown). The carbonate complex was dissolved in 1 M HpTS (pTS^- = p-toulenesulfonate) to yield *cis*- $\text{Ru}(\text{OH}_2)_2(\text{bpy})_2^{2+}$. The high acid concentration is necessitated by the large pKa value of the trivalent form of the *cis* complex [pKa $\sim$ 1 based on pKa = 0.85 for the closely similar $\text{Ru}(\text{bpy})_2(\text{py})\text{OH}_2^{3+}$ complex (86,87)]. Because it is photosensitive, the *cis*- $\text{Ru}(\text{OH}_2)_2(\text{bpy})_2^{2+}$ complex must be shielded from light. The *trans* isomer was obtained by exposing the *cis* form to sunlight.

Solutions of the $\text{Ru}(\text{NH}_3)_4\text{bpy}^{2+}$ complex were made as follows: a 1.5 mM solution of *cis*- $\text{Ru}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{Cl}$ (obtained from Dr. F. B. Anson) in 0.1 M NaCF_3COO , 5 mM CF_3COOH was electrolyzed under argon at -550 mV for about two hours to yield $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{2+}$. The solution was then made 14 mM in bpy. About 30 minutes are required for the $\text{Ru}(\text{NH}_3)_4\text{bpy}^{2+}$ complex to form quantitatively.

Several complexes were obtained from outside sources. $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2 \cdot (\text{ClO}_4)_2$, *cis*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2 \cdot (\text{CF}_3\text{SO}_3)_2$, $\text{Ru}(\text{en})_3 \cdot \text{Br}_3$, and $\text{Ru}(\text{bpy})_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ were kindly provided by Dr. Gilbert Brown. Professor Larry Bennett's group supplied a sample of $\text{Ru}(\text{NH}_3)_4\text{phen} \cdot (\text{CF}_3\text{SO}_3)_2 \cdot 3\text{H}_2\text{O}$. $\text{Co}(\text{sep})\text{Cl}_3$ (where sep = sepulchrates, see reference 88 for further details) was obtained from Professor John Endicott. $\text{Ru}(\text{bpy})_3 \cdot \text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was purchased from G. F. Smith.

The procedure of Bottomley and Tong (89) was used to synthesize $\text{Os}(\text{NH}_3)_6 \cdot \text{I}_3$. A solution of 0.5 g of Na_2OsCl_6 (from Matthey Bishop Inc.) in 15 ml of concentrated ammonia was made and 0.12 g of NH_4Cl was added

to duplicate the solution conditions of the Bottomley preparation. After the addition of 0.5 g of Zn dust, the solution was refluxed for five hours under an argon atmosphere. (The reaction is $2\text{OsCl}_6^{2-} + 12\text{NH}_3 + \text{Zn} \rightarrow 2\text{Os}(\text{NH}_3)_6^{3+} + \text{Zn}^{2+} + 12\text{Cl}^-$). The solution was allowed to cool to room temperature and 3 ml of ammonia were then added. The solid Zn and Os which had been produced were filtered off. The filtrate was cooled in an ice bath, and 2 g of KI were added. The yellow precipitate of $\text{Os}(\text{NH}_3)_6 \cdot \text{I}_3$ was isolated by filtration. The solution cannot be cooled excessively since KI will precipitate along with the Os complex.

The synthesis of TlClO_4 involved combining stoichiometric quantities of Tl_2CO_3 (Alfa Ventron) and HClO_4 . A solid brown impurity remained after the Tl_2CO_3 had dissolved. This solid was removed by filtration, and the filtrate was concentrated to about a quarter of its original volume. The solution was cooled and TlClO_4 was allowed to crystallize from solution. The yield is about 80% of the theoretical value.

D. Kinetic Methods

1. Cryptate Aquation Studies

Aquation rate constants for the Eu and Yb cryptates were obtained by recording polarographic limiting currents or cyclic voltammetric peak currents as a function of time. This yields concentration vs. time data since these two currents (after correction for background) are proportional to cryptate concentration. The timescale of these electrochemical techniques is sufficiently short relative to those of the aquation reactions so that each recorded current is essentially a measure of the instantaneous concentration. The

polarographic method has slightly better precision since reproducible electrode areas are more easily attained with a DME than with a HDME.

2. Homogeneous Redox Reactions - Principles

Polarography was used in a similar fashion to follow the homogeneous redox reactions of the cryptates. In this case, the measurement is complicated by the presence of the coreactant, which is also an electroactive species. In fact the limiting current cannot serve as a practical measure of the cryptate concentration when both the cryptate and its coreactant are electrochemically reversible. Under these conditions, the current recorded at a given potential would contain contributions from both of the redox couples present. For example, difficulties would be encountered if one wanted to follow the progress of a reaction between $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Eu}(2.2.1)^{2+}$ by monitoring the polarographic oxidation current of $\text{Eu}(2.2.1)^{2+}$. Depending on the potential region employed for the measurement, the observed current will be either the difference between the $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction current and the $\text{Eu}(2.2.1)^{2+}$ oxidation current or the sum of the oxidative currents of $\text{Eu}(2.2.1)^{2+}$ and the reaction product, $\text{Ru}(\text{NH}_3)_6^{2+}$. Similar considerations would apply if one attempted to watch the formation of the $\text{Eu}(2.2.1)^{3+}$ reaction product. In any case, one cannot obtain unambiguous determinations of the concentrations of the reactants or products.

Fortunately, a number of well-characterized inorganic redox couples are electrochemically irreversible since they have, or can be made to have, slow heterogeneous charge-transfer kinetics. If the

degree of irreversibility is sufficiently large, one will find a potential region within which neither the oxidized form of the couple is reduced nor the reduced form is oxidized. The appropriate form of this couple can then serve as a reductant or oxidant for a cryptate since the concentration of this last species can be monitored in the potential region described above without any interference from the other couple.

Polarography appears to be the best method available for the study of the homogeneous redox reactions in this work. The cryptates and a number of the other coreactants do not have any absorption bands in the visible or near ultraviolet regions of the spectrum which would be suitable for spectrophotometric use. The nature of cyclic voltammetry is incompatible to the present situation where both forms of a redox couple are found in solution during the course of the redox reaction. In cyclic voltammetry, one can calculate a concentration from the appropriate peak current; i.e., a potential sweep is required to obtain the desired information. Obviously, a potential scan for this purpose will require the selection of an initial potential which is well anodic or cathodic of the standard potential of the redox couple under study. If, for example, an anodic initial potential is imposed on the system, all of the reduced form of the couple in the vicinity of the working electrode will be converted to the oxidized form. The ensuing sweep will reflect this concentration distribution and not the one existing in bulk solution. Analogous considerations hold if a cathodic initial potential is chosen. The superiority of polarography stems from the fact that each current measurement is made

under essentially constant-potential conditions. The perturbation applied to the system is the growth of the drop on the DME. In contrast, cyclic voltammetry perturbs a system by applying a linear ramp of potential.

3. Homogeneous Redox Reactions - Experimental Specifics

Five homogeneous electron-transfer reactions involving Eu cryptates were studied: $\text{Eu(2.2.1)}^{3+} + \text{Eu}_{\text{aq}}^{2+}$, $\text{Eu(2.2.1)}^{3+} + \text{V}_{\text{aq}}^{2+}$, $\text{Eu(2.2.1)}^{2+} + \text{Co(NH}_3)_6^{3+}$, $\text{Eu(2.2.2)}^{3+} + \text{Eu}_{\text{aq}}^{2+}$, and $\text{Eu(2.2.2)}^{3+} + \text{V}_{\text{aq}}^{2+}$. All kinetic runs were made at $25.0 \pm 0.1^\circ\text{C}$. Efforts were made to minimize the amount of cryptate sample used in each run in order to conserve the rather limited supply. In order to facilitate data analysis, pseudo first-order conditions were employed with the non-cryptate reactant present in at least a ten-fold excess.

Experiments involving $\text{Eu}_{\text{aq}}^{2+}$ began with an electrolysis of 1-5 mM $\text{Eu}_{\text{aq}}^{3+}$ in 20 mM Et_4NClO_4 ($\mu = .1$ or $.2$) at -1.2 V to yield a solution of the divalent cation. The adsorption of the Et_4N^+ cation gives rise to kinetic double-layer effects which slow the charge-transfer rates of $\text{Eu}_{\text{aq}}^{3+}$ and $\text{Eu}_{\text{aq}}^{2+}$. Polarograms of the $\text{Eu}_{\text{aq}}^{3+}$ and $\text{Eu}_{\text{aq}}^{2+}$ solutions show no faradaic current between -200 and -800 mV. The concentration of the cryptates can be monitored by recording the polarographic current at some potential in this region. After the electrolysis, the homogeneous reaction was initiated by adding a known quantity of solid $\text{Eu(2.2.1)(NO}_3)_3$ or Eu(2.2.2)Cl_3 to the $\text{Eu}_{\text{aq}}^{2+}$ solution. The latter was stirred during this process and kept under a N_2 or Ar blanket. The solid cryptate dissolved in at most 1-2 seconds. This mixing time is not significant relative to the half lives of the

redox reactions. The reduction of Eu(2.2.1)^{3+} and Eu(2.2.2)^{3+} was followed by recording the polarographic current at -700 mV as a function of time. A correction for the background (charging) current was applied to the recorded data. The potentials used for these measurements were in the diffusion-limited regions of the polarographic waves of Eu(2.2.1)^{3+} and Eu(2.2.2)^{3+} . From the Ilkovic equation (see Chapter III), the corrected current is directly proportional to the cryptate concentration. The acid dependence of the rate constant was studied for both the $\text{Eu(2.2.1)}^{3+/2+}$ and the $\text{Eu(2.2.2)}^{3+/2+}$ reactions.

A similar procedure was employed in the $\text{V}_{\text{aq}}^{2+}$ reactions. A solution of 2-5 mM VO_2^+ was electrolyzed at -1.2 V to yield $\text{V}_{\text{aq}}^{2+}$. The solution was then made 20 mM in Et_4NClO_4 . The Et_4N^+ ion could not be present initially because the resultant double-layer effects would slow the electroreduction rates of VO_2^+ excessively. Ionic strengths of 0.1 were used in the $\text{Eu(2.2.1)}^{3+} - \text{V}_{\text{aq}}^{2+}$ and $\text{Eu(2.2.2)}^{3+} - \text{V}_{\text{aq}}^{2+}$ reactions, although the former was carried out in a $\text{KPF}_6/\text{HCl}/\text{Et}_4\text{NClO}_4$ electrolyte and the latter reaction used a $\text{LiClO}_4/\text{HClO}_4/\text{Et}_4\text{NClO}_4$ electrolyte. It was not possible to obtain reliable kinetic data for the $\text{Eu(2.2.1)}^{3+} - \text{V}_{\text{aq}}^{2+}$ reaction in concentrated perchlorate media. The homogeneous redox reaction was initiated by adding a known quantity of $\text{Eu(2.2.1)(NO}_3)_3$ or Eu(2.2.2)Cl_3 (with stirring) to the solution of $\text{V}_{\text{aq}}^{2+}$. The loss of the trivalent cryptate was monitored by recording the polarographic limiting current at about -600 mV. Significantly more cathodic potentials could not be used since appreciable currents due to $\text{V}_{\text{aq}}^{3+}$ reduction were observed in this region.

The preparation for the $\text{Co}(\text{NH}_3)_6^{3+} - \text{Eu}(2.2.1)^{2+}$ reaction began with the electrolysis of a $\sim 1 \text{ mM}$ solution of $\text{Eu}(2.2.1)(\text{NO}_3)_3$ at -900 mV to obtain $\text{Eu}(2.2.1)^{2+}$. A $(\text{C}_3\text{H}_7)_4\text{NClO}_4/\text{LiClO}_4/\text{HClO}_4$ electrolyte ($\mu = 0.05$) was used because the double-layer effects arising from the strong adsorption of the $(\text{C}_3\text{H}_7)_4\text{N}^+$ ion slowed the electroreduction of $\text{Co}(\text{NH}_3)_6^{3+}$ to a point where it would not interfere with the observations of $\text{Eu}(2.2.1)^{2+}$. The double-layer effects resulting from Et_4N^+ adsorption were not sufficient for this purpose. The electrolysis of the cryptate had to be carried out quickly in order to minimize the loss of $\text{Eu}(2.2.1)^{2+}$ which occurs through the dissociation reaction: $\text{Eu}(2.2.1)^{2+} \rightarrow \text{Eu}_{\text{aq}}^{2+} + (2.2.1)$. Fortunately, the reduction could be completed in 20-30 minutes. While the electrolysis was being carried out, a 20 mM solution of $\text{Co}(\text{NH}_3)_6^{3+}(\text{ClO}_4)_3$ was deoxygenated by bubbling with nitrogen. A known volume of this solution was transferred to the $\text{Eu}(2.2.1)^{2+}$ solution by means of a gas-tight syringe. The ensuing reaction was followed by recording the $\text{Eu}(2.2.1)^{2+}$ polarographic limiting current at -300 mV as a function of time. More anodic potentials could not be used because the $\text{Eu}_{\text{aq}}^{2+}$ which was produced from the $\text{Eu}(2.2.1)^{2+}$ dissociation would also yield an oxidation current in this region. The low solubility of $\text{Co}(\text{NH}_3)_6^{3+}$ in perchlorate media coupled with the need to maintain pseudo first-order conditions limited the $\text{Co}(\text{NH}_3)_6^{3+}$ concentration to the $5\text{--}10 \text{ mM}$ range.

The cryptate redox rate constants and those for cryptate aquation were generally found to have relative precisions of 5-10% as determined from the average deviation of 3-10 kinetic runs.

CHAPTER III

ELECTROCHEMICAL STUDIES OF EUROPIUM AND YTTERBIUM

CRYPTATE FORMATION IN AQUEOUS SOLUTION

A. Introduction

The study of the europium and ytterbium cryptates has several interesting features. The trivalent Eu and Yb complexes are the first trivalent cryptates to be scrutinized in aqueous solution (with the exception of a La^{3+} - macrotricyclic cryptate (90)). The comparison of the complexation thermodynamics and kinetics of these trivalent cryptates with the corresponding quantities for monovalent and divalent cryptates should provide useful insights into the factors (such as ionic charge and size) which influence cryptate formation. If the electrochemistry of the Eu and Yb cryptates is anything like that for the aquo ions, these complexes will be the first electroactive cryptates to be studied in aqueous solution, and electrochemical techniques should prove to be quite effective for the investigation of their properties. These methods can be employed to determine the relative stabilities of the trivalent and divalent forms of the Eu and Yb cryptates and to analyze these stabilities in terms of enthalpic and entropic components. In addition, the electrochemical behavior of these complexes will yield some general information on the effect of cryptate formation on the electrochemical reactivity of europium and ytterbium.

B. Results

1. Complexation Thermodynamics

Cathodic-anodic cyclic voltammograms were obtained for each of the trivalent cryptates. Substantial changes in the electrochemical behavior of the $\text{Eu}^{3+/2+}$ and $\text{Yb}^{3+/2+}$ couples are found when these

ions are encapsulated within cryptate cavities. The cyclic voltammograms shown in Figure 2 are typical. Figure 2a contains the voltammetric waves observed for the reduction and subsequent oxidative regeneration of $\text{Eu}_{\text{aq}}^{3+}$ in acidified 0.5 M NaClO_4 . The results are independent of acid concentration for pH 1-4. The separation between the cathodic and anodic peak potentials is large and sweep-rate dependent, reflecting the electrochemical irreversibility (i.e., the slow heterogeneous charge-transfer kinetics) of the $\text{Eu}_{\text{aq}}^{3+/2+}$ couple (91). On the other hand, the corresponding voltammograms for $\text{Eu}(2.2.1)^{3+}$ in 0.5 M NaClO_4 shown in Figure 2b have a much smaller, sweep-rate independent peak separation of 65 mV, which is quite close to the 57-mV value expected for electrochemically reversible, one-electron couples at room temperature (92). Similar peak separations are found for the other cryptate couples studied.

The observed peak separations demonstrate that the heterogeneous electron-transfer rate constants of the Eu cryptates are at least two orders of magnitude larger than those for $\text{Eu}_{\text{aq}}^{3+/2+}$. In order to yield reversible cyclic voltammograms with the sweep rates used in these studies, the Eu cryptates must have k_s values of at least $\sim .01 \text{ cm s}^{-1}$, where k_s is the electrochemical charge-transfer rate constant at the standard potential of the couple of interest (92,93). In contrast, $\text{Eu}_{\text{aq}}^{3+/2+}$ has been found to have a k_s value of $\sim 8 \times 10^{-5} \text{ cm s}^{-1}$ (94). Thus a considerable alteration in the electrochemical reactivity of the europium couple occurs when it is encapsulated within a cryptate cavity.

The formal potentials E_f for $\text{Eu}(2.2.1)^{3+/2+}$ and $\text{Eu}(2.2.2)^{3+/2+}$

Figure 2. Cathodic-anodic cyclic voltammograms
of $\text{Eu}_{\text{aq}}^{3+}$ and $\text{Eu}(2.2.1)^{3+}$.

Key: (a) $0.4 \text{ mM } \text{Eu}^{3+}$ in $0.5 \text{ M } \text{NaClO}_4$ at pH 2.

(b) $0.35 \text{ mM } \text{Eu}(2.2.1)^{3+}$ in $0.5 \text{ M } \text{NaClO}_4$ at pH 7.

Electrode area = 0.032 cm^2 .

Sweep rates: (1) 200 mV s^{-1} ; (2) 50 mV s^{-1} .

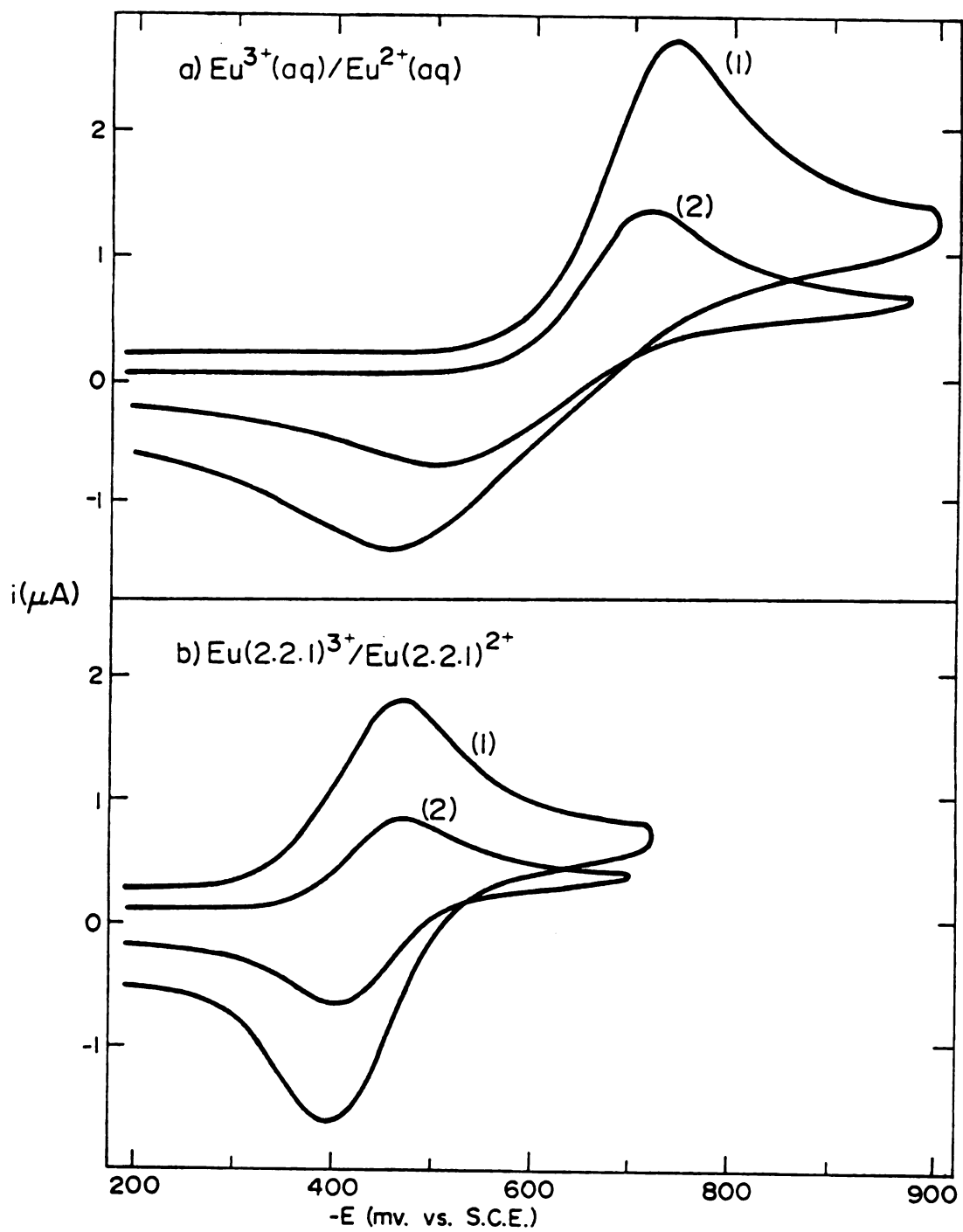


Figure 2.

obtained from the mean of the cathodic and anodic peak potentials (95) were found to be markedly more positive than for $\text{Eu}_{\text{aq}}^{3+/2+}$. Analogous behavior was also observed for $\text{Eu}(2_{\text{B}}.2.1)^{3+/2+}$ (96) and $\text{Yb}(2.2.1)^{3+/2+}$ redox couples. These results are summarized in Table 1, along with data for the Eu and Yb aquo couples. Identical cyclic voltammograms with peak separations of about 60 mV were obtained for the cryptate couples in the absence and presence of added cryptand over the range of sweep rates $50\text{--}500 \text{ mV s}^{-1}$, for solutions in the pH 1-9 range, and for supporting electrolytes containing sodium, barium, or tetraethylammonium cations which have widely differing abilities to compete for the cryptand (6). These results indicate that both the trivalent and divalent cryptates are substitutionally inert on the cyclic voltammetric timescale. Since the difference in formal potentials E_f between the complexed and uncomplexed one-electron redox couples can be related directly to the difference in the free energy driving force for these processes, we can write

$$\Delta E_f = (2.303 RT/F) \log(K_{\text{III}}/K_{\text{II}}) = (\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ})/F \quad (1)$$

where $\Delta G_{\text{III}}^{\circ}$ and $\Delta G_{\text{II}}^{\circ}$ are the free energies of complexation for the trivalent and divalent species, respectively, and K_{III} and K_{II} are the corresponding stability constants. The resulting values of $(\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ})$ are listed in Table 1.

It is seen that the stabilities of the trivalent cryptates are consistently and substantially smaller than those of the corresponding divalent cryptates; i.e., the values of $(\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ})$ are

Table 1. Thermodynamics of some Europium and Ytterbium Cryptate Redox Couples in Noncomplexing Media at 25°C.

Redox Couple	Electrolyte	$-E_f^a$ mV	ΔS_{rc}^b e.u.	$\Delta G_{III}^c - \Delta G_{II}^c$ kcal.mol ⁻¹	$\Delta H_{III}^d - \Delta H_{II}^d$ kcal.mol ⁻¹	$\Delta S_{III}^e - \Delta S_{II}^e$ e.u.
$Eu^{3+/2+}_{aq}$	0.1M $\overline{NaPTS}$ (pH 3)	626	48			
$Eu(2.2.1)^{3+/2+}$	0.1M $\overline{Et_4NC10_4}$	425		4.6	10.7	20.5
	0.1M $\overline{NaClO_4}$	425				
$Eu(2.2.2)^{3+/2+}$	0.5M $\overline{NaClO_4}$ (pH 2-7)	435	27.5			
	0.1M $\overline{Et_4NC10_4}$	205		9.7	17.7	27
	0.5M $\overline{NaClO_4}$	215	21			
$Eu(2_B.2.1)^{3+/2+}$	0.5M $\overline{NaClO_4}$	370		5.9		
$Yb^{3+/2+}_{aq}$	0.1M $\overline{KPF_6}$ (pH 5)	1423	48			
	0.1M $\overline{Et_4NC10_4}$	1105		7.4	11.9	15
$Yb(2.2.1)^{3+/2+}$	0.5M $\overline{NaClO_4}$	1110	33			

Notes to Table 1.

^a Formal potential of redox couple vs. KSCE, obtained from average of cathodic and anodic peak potentials of reversible cyclic voltammogram.

^b Reaction entropy of redox couple; determined using nonisothermal cell arrangement. (See Chapter IV.)

^c Difference between free energies of complexation of corresponding trivalent and divalent cryptates, obtained from E_f values using eqn(1).

^d Obtained from $(\Delta H_{III}^{\circ} - \Delta H_{II}^{\circ}) = (\Delta G_{III}^{\circ} - \Delta G_{II}^{\circ}) + T(\Delta S_{III}^{\circ} - \Delta S_{II}^{\circ})$.

^e Obtained from ΔS_{rc}° using eqn(2).

large and positive. In order to ascertain the factors responsible for this behavior, it is desirable to evaluate the enthalpic and entropic contributions to $(\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ})$. This can be achieved by determining the reaction entropies $\Delta S_{\text{rc}}^{\circ}$ for the various redox couples. This quantity is discussed in great detail in Chapter IV. For the present, it is only necessary to note that $\Delta S_{\text{rc}}^{\circ}$ is essentially equal to the difference $(\bar{S}_{\text{red}}^{\circ} - \bar{S}_{\text{ox}}^{\circ})$ between the partial molal entropies of the reduced and oxidized halves of the redox couple. The values of $\Delta S_{\text{rc}}^{\circ}$ are also given in Table 1. These values can be used to determine the difference in the entropies of complexation between the trivalent and divalent species $(\Delta S_{\text{III}}^{\circ} - \Delta S_{\text{II}}^{\circ})$ from

$$\Delta S_{\text{III}}^{\circ} - \Delta S_{\text{II}}^{\circ} = (\Delta S_{\text{rc}}^{\circ})_{\text{aq}} - (\Delta S_{\text{rc}}^{\circ})_{\text{crypt}} \quad (2)$$

where $(\Delta S_{\text{rc}}^{\circ})_{\text{aq}}$ and $(\Delta S_{\text{rc}}^{\circ})_{\text{crypt}}$ are the reaction entropies for the corresponding aquo and cryptate redox couples, respectively (97). Inspection of Table 1 reveals that the values of $(\Delta S_{\text{III}}^{\circ} - \Delta S_{\text{II}}^{\circ})$ are also positive, so that the large positive values of $(\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ})$ are associated with still larger values of the corresponding enthalpic terms $(\Delta H_{\text{III}}^{\circ} - \Delta H_{\text{II}}^{\circ})$.

It is clearly desirable to obtain absolute values of these thermodynamic complexation parameters for either the trivalent or divalent cryptates. Since both the nitrogens on the (2.2.1) and (2.2.2) cryptands have a strong tendency to be protonated, the required stability constants could in principle be determined by the pH-titration method used by Lehn and Sauvage (6). For the present systems, a slightly more direct method can be employed since the

concentration ratios of lanthanide cryptate to free lanthanide $[\text{LnC}]/[\text{Ln}]$ in equilibrated solutions containing a stoichiometric excess of the cryptand can be directly determined from the magnitude of the reversible voltammetric peaks for the $\text{LnC}^{3+/2+}$ couple combined with the known total lanthanide concentration. These ratios $[\text{LnC}]/[\text{Ln}]$ determined as a function of pH yield the required cryptate stability constants when coupled with the known pK_a values for the free cryptands (6).

Attempts to determine K_{III} for either $\text{Eu}(2.2.1)^{3+}$ or $\text{Eu}(2.2.2)^{3+}$ in this manner failed for two reasons. First, the rate constant for ligand exchange with $\text{Eu}(2.2.1)^{3+}$ is extremely small (*vide infra*) so that times of the order of a few months would be required to attain equilibrium (98). Second, neither trivalent complex is sufficiently stable to form significantly at pH values below those where precipitation of Eu(III) as Eu(OH)_3 occurs (pH=7). Nonetheless, approximate values of K_{II} for the divalent cryptates $\text{Eu}(2.2.1)^{2+}$ and $\text{Eu}(2.2.2)^{2+}$ could be obtained using the above procedure since Eu^{2+} is stable over the pH range (ca. 5-9) required for the pH titration. The ligand exchange rate for $\text{Eu}(2.2.2)^{2+}$ is rather small (half-life for aquation $\tau_{1/2} \sim 6$ hours at 25°C) which necessitated long equilibration times (~ 1 day). Coupled with the sensitivity of Eu^{2+} to air oxidation, this difficulty limited somewhat the accuracy of the resulting stability constants and precluded determination of K_{II} for $\text{Yb}(2.2.1)^{2+}$. The values of K_{II} obtained in $0.1 \text{ M Et}_4\text{NClO}_4$ at 25°C are $2 \pm 1 \times 10^9 \text{ M}^{-1}$ for $\text{Eu}(2.2.1)^{2+}$ and $3 \pm 2 \times 10^{10} \text{ M}^{-1}$ for $\text{Eu}(2.2.2)^{2+}$. Unfortunately, the reproducibility of these values was not sufficient

to allow useful estimates of ΔH_{II}° and ΔS_{II}° to be obtained from the temperature dependence of K_{II} .

The trivalent cryptates exhibit a surprisingly strong tendency to associate with fluoride and hydroxide ions. The addition of F^{-} or OH^{-} ions to $NaClO_4$ at a constant ionic strength results in shifts in the formal potentials of the lanthanide cryptate couples to markedly more negative potentials. Significant potential shifts to more negative values were also observed upon the addition of oxalate, phthalate, and phosphate anions, although small or negligible effects were observed with sulfate, chloride, azide, and nitrate anions up to concentrations around 0.1 M. The magnitude of these potential shifts ΔE_f^x were found to be linearly dependent upon $\log[X]$, where $[X]$ is the concentration of fluoride or hydroxide anions. Some typical results are shown in Figure 3, which is a plot of $-E_f^F$ versus $\log_{10}[F^{-}]$ at $\mu = 0.5$ for the $Eu(2.2.1)^{3+/2+}$ couple. Two linear regions are obtained, with slopes of 57 mV and 116 mV. (Virtually identical slopes were observed if the logarithm of the fluoride activity, obtained using a fluoride ion-selective electrode, was plotted instead of $\log_{10}[F^{-}]$.) This behavior is expected if $Eu(2.2.1)^{3+}$ and possibly also $Eu(2.2.1)^{2+}$ associate with fluoride anions to form substitutionally labile complexes. Then we can write (99)

$$-\Delta E_f^x = (2.303RT/F) \{ \log \beta_{MX_p} - \log \beta_{MX_q} + (p-q) \log[X] \} \quad (3)$$

or

$$-\Delta E_f^x = (2.303RT/F) \{ \log \beta_{MX_p} + p \log[X] \} \quad (4)$$

Figure 3. Plot of E_f^F , the formal potential for the $\text{Eu(2.2.1)}^{3+/2+}$ couple in the presence of fluoride anions, vs. the logarithm of the fluoride concentration. Ionic strength held constant at 0.5 with sodium perchlorate.

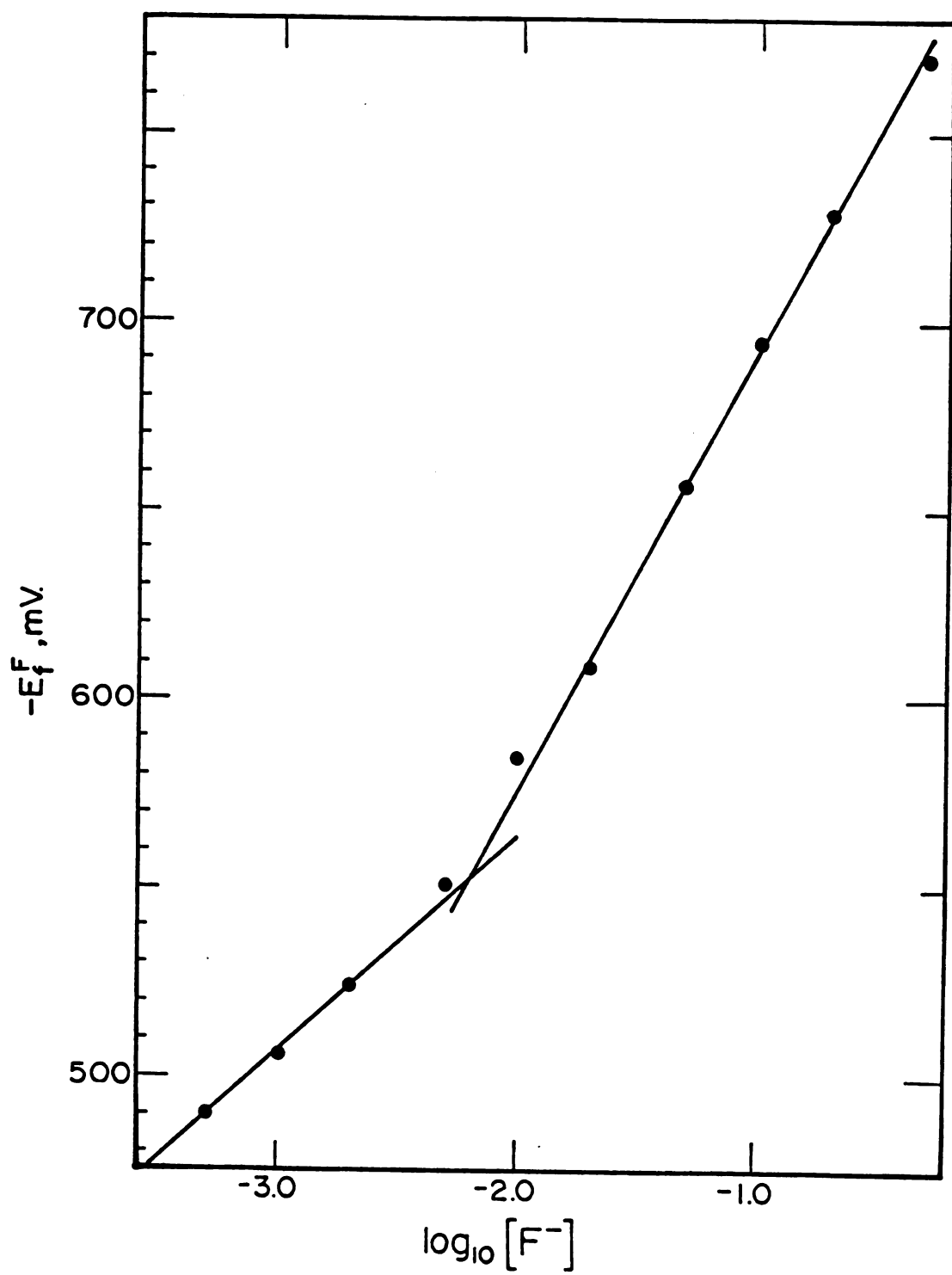


Figure 3.

where β_{MX_p} and β_{MX_q} are the (cumulative) stability constants of the oxidized and reduced complexes having the stoichiometry p and q , respectively. Equation (3) will apply when both the oxidized and reduced species form stable complexes with X , and equation (4) when only the oxidized species undergoes complexation under the conditions of the experiment (100). To decide between these two possibilities for the present systems, absolute values of β_{MX_p} were determined for the association of trivalent cryptates with F^- and OH^- by means of potentiometric titrations using a fluoride ion-selective electrode and a pH electrode, respectively. The values of β_{MX_p} were found to agree consistently with the values determined using equation (4). It was therefore deduced that only the trivalent cryptates significantly associate with F^- and OH^- under the experimental conditions employed ($[F^-], [OH^-] \sim 10^{-3}$ to 0.5 M). Consequently, from equation (4) the two linear regions in Figure 3 with slopes of 57 and 116 mV correspond to $\text{Eu}(2.2.1)^{3+}$ - F^- stoichiometries of 1:1 and 1:2, respectively, with cumulative stability constants β_1 and β_2 equal to $2 \times 10^4 \text{ M}^{-1}$ and $3 \times 10^6 \text{ M}^{-2}$. Large values of β_1 and β_2 were also deduced for the association between $\text{Eu}(2.2.1)^{3+}$ and OH^- . Although $\text{Eu}(2.2.2)^{3+}$ was also found to associate strongly with OH^- , quantitative studies were precluded by a very rapid base-catalyzed cryptate dissociation observed for this system. A summary of β_1 and β_2 values determined for the trivalent cryptates with F^- and OH^- is given in Table 2, along with the corresponding data for Eu_{aq}^{3+} and Yb_{aq}^{3+} taken from the literature.

Table 2. Cumulative Formation Constants for Association between Europium and Ytterbium Cryptates and Fluoride and Hydroxide Ions.

Cation-Anion pair	Medium	$\beta_{1,\underline{M}}^{-1^a}$	$\beta_{2,\underline{M}}^{-2^b}$
Eu(2.2.1) $^{3+}$ -F $^{-}$	0.5M NaClO $_4$ -NaF	$2 \times 10^4{}^c$	$3 \times 10^6{}^c$
Eu(2.2.1) $^{3+}$ -OH $^{-}$	0.5M NaClO $_4$ -NaOH	$3 \times 10^5{}^c$	$7 \times 10^6{}^c$
Eu(2.2.2) $^{3+}$ -F $^{-}$	0.5M NaClO $_4$ -NaF	$3 \times 10^4{}^c$	$7 \times 10^6{}^c$
Yb(2.2.1) $^{3+}$ -F $^{-}$	0.5M NaClO $_4$ -NaF	-	$3 \times 10^6{}^c$
Eu $^{3+}$ _{aq} -F $^{-}$	0.5M NaClO $_4$ -NaF	$2.5 \times 10^3{}^d$	$3 \times 10^6{}^d$
Eu $^{3+}$ _{aq} -OH $^{-}$	0.3M NaClO $_4$ -NaOH	$\sim 5 \times 10^5{}^e$	-
Yb $^{3+}$ _{aq} -F $^{-}$	0.5M NaClO $_4$ -NaF	$4 \times 10^3{}^f$	-

^aFormation constant for 1:1 complex.

^bFormation constant for 1:2 complex.

^cDetermined from shift in formal potential ΔE_f^x upon addition of complexing anion X using eqn(4), and by potentiometric titration (see text).

^dFrom A. Aziz, S. J. Lyle, Anal. Chim. Acta., 47, 49 (1969).

^eCalculated from $pK_a = 8.3$, given in U.K. Frolova, V.N. Kumok, V. V. Serebrennikov, Izvest. V.U.Z. Khim., 9, 176 (1966).

^fFrom B.N. Ivanov-Emin, V.A. Zaitseva, A.M. Egorov, Russ. J. Inorg. Chem., 13, 1368 (1968).

The β_1 and β_2 values have relative precisions of 5% as obtained from the average deviation of five determinations.

2. Complexation and Dissociation Kinetics

Since both the trivalent and divalent lanthanide cryptates are substitutionally inert on the timescale of cyclic voltammetry, this technique can be used to monitor the kinetics of ligand exchange. In principle the kinetics of either complexation or dissociation could be monitored. However, in practice it is only feasible to monitor the latter processes in this manner because the rates of complexation are typically rapid, and in any case the trivalent cryptates cannot be produced in aqueous media from the cryptand and the metal cation due to hydrolysis of the latter species at the pH values (>8) where the cryptand is significantly deprotonated.

Table 3 summarizes rate constants and activation parameters for the dissociation of five europium and ytterbium cryptates. The progress of the dissociation reactions was followed by periodically monitoring the cathodic or anodic voltammetric peak heights for the trivalent and divalent cryptates, respectively. Concentration-time data for the dissociation reactions were obtained from these cyclic voltammetric peak currents by using (92b):

$$i_p = .4463 (nF)^{3/2} A (D\nu/RT)^{1/2} c \quad (5)$$

where i_p is the peak current (corrected for background) in μA , A is the electrode area in cm^2 , D is the diffusion coefficient of the reacting species in $cm^2 s^{-1}$, c is the bulk concentration in mM , ν is the scan rate in $V \cdot s^{-1}$ and the other terms have their usual meaning. Concentrations were also calculated from polarographic

Table 3. Rate Constants and Activation Parameters for Dissociation of Europium and Ytterbium Cryptates at 25°C.

Cryptate	Medium	k_d^a sec. ⁻¹	$\Delta H_d^\ddagger b$ kcal.mol. ⁻¹	$\Delta S_d^\ddagger c$ e.u.
Eu(2.2.1) ³⁺	0.5M NaClO ₄ (pH ~7)	4.1×10^{-7}	-	-
	0.5M NaClO ₄ (pH 2.5)	3.0×10^{-7}	18.9 ^d	-25.5 ^d
	0.1M Et ₄ NC10 ₄ (pH 2.5)	4.0×10^{-7}	19.2 ^d	-23.5 ^d
Eu(2.2.1) ²⁺	0.1M Et ₄ NC10 ₄ (pH 2.5)	2.0×10^{-4}	15.1 ^e	-25.0 ^e
Eu(2.2.2) ³⁺	0.1M Et ₄ NC10 ₄ (pH ~7)	1.1×10^{-3}	13.8 ^e	-26.0 ^e
Eu(2.2.2) ²⁺	0.05M Et ₄ NC10 ₄	3.0×10^{-5}	18.8 ^d	-16.0 ^d
	+ 0.033M Ba(NO ₃) ₂			
Yb(2.2.1) ³⁺	0.5M NaClO ₄	1.3×10^{-6}	22.3 ^d	-10.5 ^d

^aFirst-order rate constant for cryptate dissociation at 25°C, obtained at pH values where the acid-independent pathway dominates, i.e., where $k'_d \approx k_d$ (eqn(9)).

^bEnthalpy of activation for cryptate dissociation, determined from eqn(7).

^cEntropy of activation for cryptate dissociation, determined from eqn(8).

^dDetermined over the temperature range 25-60°C.

^eDetermined over the temperature range 5-35°C.

limiting currents by using the Ilkovic equation (92b):

$$i_d = 706 n D^{1/2} m^{2/3} t_d^{1/6} c \quad (6)$$

where i_d is the (baseline-corrected) limiting current in μA , m is the mercury flow rate through the DME in $mg\ s^{-1}$, t_d is the drop time in seconds, and the other terms have the same meaning and units as in equation (5).

The dissociation reactions of the trivalent and divalent cryptates adhere to first-order kinetics. Plots of $\ln c$ (or $\ln i_p$ or $\ln i_d$) vs. time are linear over several half lives. The enthalpy and entropy of activation ($\Delta H^\ddagger$ and $\Delta S^\ddagger$ respectively) were calculated from the temperature dependence of the dissociation rate constant k_d (101):

$$\Delta H^\ddagger = -R \frac{d \ln k_d}{d(1/T)} - RT \quad (7)$$

$$\Delta S^\ddagger = \Delta H^\ddagger / T + R \ln(k_B T/h) - R \ln k_d \quad (8)$$

where k_B is the Boltzmann constant, and h is Planck's constant.

(Strictly speaking, k_d is the acid-independent rate constant defined in equation (9)).

Experimental conditions were arranged so that the dissociation reactions went essentially to completion. Initially, strongly acidic solutions were employed to achieve this end. However, for some reactions it was found that the apparent first-order rate constants for dissociation k'_d increased significantly as the pH was lowered. This pH dependence was determined to be in accordance with the rate law:

$$k'_d = k_d + k_H [H^+] \quad (9)$$

Similar behavior has been noted previously for the dissociation kinetics of univalent and divalent cryptates in aqueous media (27). The derived values of k_d and k_H for the dissociation kinetics of four europium cryptates are given in Table 4. The values of k_d given in Table 3 were obtained under conditions where the acid-dependent term in equation (9) is unimportant, i.e., where $k_d \approx k'_d$. For some reactions, this condition could only be achieved by working in neutral media where the cryptand released by the dissociation reaction could prevent aquation of the remaining cryptate. In such cases the occurrence of such back-(complexation) reactions was prevented by adding a small stoichiometric excess of a metal cation such as Ba^{2+} that will strongly complex the released cryptand (6). Unlike protons, these complexing agents were not found to have any significant effect upon k'_d .

Table 4. Acid Acceleration of Europium Cryptate Dissociation at 25°C.

Cryptate	Medium	k_d^a sec ⁻¹	k_H^b M^{-1} sec ⁻¹	k_{H^+}/k_d M^{-1}
Eu(2.2.1) ³⁺	1M LiClO ₄ /HClO ₄	3×10^{-7}	$\sim 1.0 \times 10^{-6}$	~ 3
Eu(2.2.1) ²⁺	1M LiClO ₄ /HClO ₄	1×10^{-4}	2.5×10^{-3}	40
Eu(2.2.2) ³⁺	0.1M LiClO ₄ /HClO ₄	1×10^{-3}	0.2	200
Eu(2.2.2) ²⁺	0.1M LiClO ₄ /HClO ₄	$\sim 5 \times 10^{-5}$	7.5×10^{-3}	~ 150

^aFirst-order rate constant for acid-independent aquation pathway, obtained from intercept of plot of k'_d versus $[H^+]$ (eqn (9)).

^bSecond-order rate constant, determined from slope of plot of k'_d versus $[H^+]$ (eqn (9)).

The presence of significant concentrations of OH^- and F^- were also found to have a marked accelerating effect upon the dissociation rates of the trivalent lanthanide cryptates. For example, the addition of 50 mM OH^- or F^- to 0.5 M NaClO_4 reduced $\tau_{1/2}$ for the aquation of Eu(2.2.1)^{3+} at 25°C from 27 days to 22 minutes and 2.8 days, respectively. Table 5 summarizes these effects.

Table 5. Anion Effects on Eu(2.2.1)^{3+} Dissociation.

Anion	Anion Concentration (M)	k_d^a (sec^{-1})
OH^-	.02	1.6×10^{-4}
	.046	5.2×10^{-4}
	.10	1.3×10^{-3}
F^-	.01	1.0×10^{-6}
	.05	2.9×10^{-6}
	.50	1.4×10^{-5}

^aDissociation rate constant for Eu(2.2.1)^{3+} , determined at 25 C. Ionic strength = 0.5.

C. Discussion

1. The Effects of Varying the Cation Charge upon Cryptate Thermodynamics

In view of the substantial differences in the complexation thermodynamics between corresponding divalent and trivalent lanthanide cryptates (Table 2), it is of interest to compare these results with the thermodynamic parameters for other divalent cations of comparable size, as well as for univalent cations.

Table 6 summarizes values of the free energies (ΔG_C°), enthalpies (ΔH_C°), and entropies (ΔS_C°) of complexation for alkali and alkaline earth cations with (2.2.1) and (2.2.2) cryptands as well as for the lanthanides considered here and the post-transition metal cation Pb^{2+} . The values ΔG_C° given for Eu^{2+} and Eu^{3+} cryptates were obtained from the measured values of K_{II} for the divalent complexes together with the corresponding values of ($\Delta G_{III}^\circ - \Delta G_{II}^\circ$) given in Table 1. Also listed in Table 6 are estimates of the ionic radius of each cation. These values were obtained using the method of Goldschmidt but are from the more recent compilation of Shannon and Prewitt (11) and are estimated for a coordination number of six. Although there are a number of scales of ionic radii which differ to a greater or lesser degree (102a), there is reason to believe that the scale used here provides a reasonable approximation ($\pm 0.1 \text{ \AA}$) to at least the relative radii of the bare ions in aqueous solution (102b) as well as the effective cation radii within the cryptate cavities. The use of larger coordination numbers such as eight, which may be appropriate for the larger cations considered here, increases the absolute values of the ionic radii by ca. $0.1\text{--}0.15 \text{ \AA}$, but the differences between the values remain relatively unchanged provided that the coordination numbers do not greatly depend upon the cation size (11).

The large variations in ΔG_C° and particularly in the enthalpic and entropic components ΔH_C° and ΔS_C° seen between different cations of Group I and II have been discussed by Lehn and co-workers (6,12). The markedly increasing values of $-\Delta G_C^\circ$ seen as the ionic radii of the

Table 6. Free Energies, Enthalpies, and Entropies of Complexation of Various Metal Cations with (2.2.1) and (2.2.2) Cryptands at 25°C.

Cation	r_c^a Å	(2.2.1) Cryptand			(2.2.2) Cryptand		
		$-\Delta G_c^\circ$ kcal.mol. ⁻¹	$-\Delta H_c^\circ$ kcal.mol. ⁻¹	ΔS_c° e.u.	$-\Delta G_c^\circ$ kcal.mol. ⁻¹	$-\Delta H_c^\circ$ kcal.mol. ⁻¹	ΔS_c° e.u.
Li ⁺	0.59	3.4 ^{b,c}	0.0 ^c	11.4 ^c	1.7 ⁱ	1.4 ⁱ	1 ⁱ
Na ⁺	1.02	7.2 ^c	5.4 ^c	6.2 ^c	5.3 ^{b,c}	7.4 ^c	-7 ^c
K ⁺	1.38	5.4 ^{b,c}	6.8 ^c	-4.7 ^c	7.2 ^c	11.4 ^c	-14 ^c
Rb ⁺	1.49	3.5 ^{b,c}	5.4 ^c	-6.5 ^c	5.9 ^{b,c}	11.8 ^c	-19.8 ^c
Cs ⁺	1.70				2.0 ⁱ	5.2 ⁱ	-11 ⁱ
Ca ²⁺	1.00	9.5 ^{b,c}	2.9 ^c	22 ^c	6.0 ^{b,c}	0.2 ^c	19.5 ^c
Sr ²⁺	1.16	10.0 ^{b,c}	6.1 ^c	13.1 ^c	10.9 ^{b,c}	10.3 ^c	2 ^c
Ba ²⁺	1.36	8.6 ^{b,c}	6.3 ^c	7.7 ^c	12.9 ^{b,c}	14.1 ^c	-4.0 ^c
Pb ²⁺	1.18				16.9 ^j	13.8 ^j	10.1 ^j
Eu ²⁺	1.17	12.7 ^d	(8.8) ^h	(13) ^f	14.3 ^d	(13.7) ^h	(2) ^f
Eu ³⁺	0.95	8.1 ^e	(-1.9) ^h	(33.5) ^g	4.6 ^e	(-4.0) ^h	(29) ^g

Notes to Table 6.

^a Ionic radius for metal cation, taken from the compilation in ref. 11 for coordination number six.

^b From ref. 6; determined at ionic strength $\mu = 0.5$.

^c From ref. 12; $\mu \sim 0.05$.

^d Determined from experimental value of K_{II} (see text).

^e Calculated from ΔG_c° for the corresponding Eu(II) cryptate combined with the value of $(\Delta G_{III}^\circ - \Delta G_{II}^\circ)$ given in Table 1; $\mu = 0.1$.

^f Estimated value; obtained by assuming ΔS_c° to be equal to ΔS_c° for the corresponding Sr cryptate (see text).

^g Calculated by combining ΔS_c° for the corresponding Eu(II) cryptate with the value of $(\Delta S_{III}^\circ - \Delta S_{II}^\circ)$ given in Table 1; $\mu \sim 0.5$.

^h Calculated from the corresponding ΔG_c° and ΔS_c° values.

ⁱ From M. H. Abraham, A. F. Danil de Namor, and W. H. Lee, extended abstracts, 29th Meeting, I.S.E., Budapest, Hungary, 1978.

^j From ref. 17.

cations approach the radius of the cryptate cavity (ca. 1.1 and 1.4 Å for (2.2.1) and (2.2.2) cryptates, respectively) could be due in part to steric factors associated with the fit of the cation into the relatively inflexible cryptate cavity (6). However, these variations in ΔG_c° consist of marked alterations in ΔS_c° as well as ΔH_c° . This indicates that an important factor determining the sensitivity of cryptate stability to cation size is the partial desolvation of the cation that is required in order for cryptate formation to be accomplished (12). Thus the large increases in $-\Delta H_c^\circ$ and $-\Delta S_c^\circ$ that generally occur as the cation radius increases for a given cationic charge (Table 6) undoubtedly stem in part from the decreasingly negative hydration enthalpy and the decreasingly negative hydration entropy of the aquated cations under these circumstances (12). Such influences also appear to be paramount in determining the dependence of cryptate thermodynamics upon the cation charge. Thus cations such as Na^+ and Ca^{2+} , or K^+ and Ba^{2+} have similar ionic radii, and yet the divalent cations exhibit markedly less favorable values of $-\Delta H_c^\circ$ for formation of either (2.2.1) or (2.2.2) cryptates. These differences are nevertheless counteracted by markedly more favorable values of ΔS_c° so that $-\Delta G_c^\circ$ is typically larger for the divalent compared with the univalent cations. The variations in ΔH_c° are in harmony with the markedly more negative hydration enthalpies for divalent cations compared with those for univalent cations of similar size (12,103). Although increasing the cationic charge will result in increasingly favorable ion-dipole interactions with the cryptate ether moieties,

these interactions are expected to be relatively less favorable compared with those involving the solvent molecules on account of the smaller dipole moment of dimethyl ether versus water (12). These factors therefore result in a net increase in ΔH_C° as the cationic charge increases. The more positive values of ΔS_C° for the divalent cryptates undoubtedly result from the more negative hydration entropies of the divalent versus univalent cations. These stem from a greater degree of "solvent ordering" (or less "solvent disordering") in the vicinity of the former cations (103) which is markedly diminished or removed upon cryptate formation (12).

The differences in both cation size and charge between Eu^{3+} and Eu^{2+} are therefore both expected to play important roles in determining the relative stabilities of their (2.2.1) and (2.2.2) cryptates. Thus Eu^{3+} has a noticeably smaller ionic radius (0.95 Å) than Eu^{2+} (1.17 Å) which, along with the increase in the cationic charge, contributes towards a markedly more negative hydration enthalpy for the former cation (103). These two factors taken together appear to account nicely for the relatively more positive values of ΔH_C° and ΔS_C° seen for Eu(III) versus Eu(II) cryptate formation (Table 1). The larger value of $(\Delta H_{\text{III}}^\circ - \Delta H_{\text{II}}^\circ)$ seen for $\text{Eu(2.2.2)}^{3+/2+}$ (17.7 kcal. mol⁻¹) compared with $\text{Eu(2.2.1)}^{3+/2+}$ (10.7 kcal. mol⁻¹) could be anticipated since the ΔH_C° values of (2.2.2) cryptates appear to be more sensitive to cation size than those of (2.2.1) cryptates, at least for cations of comparable size to Eu^{3+} and Eu^{2+} (Table 6). For example, ΔH_C° for Ca(2.2.2)^{2+} is 10.2 kcal. mol⁻¹ less negative

than for $\text{Sr}(2.2.2)^{2+}$, whereas ΔH_c° for $\text{Ca}(2.2.1)^{2+}$ is ca. 4 kcal mol⁻¹ less negative than for $\text{Sr}(2.2.1)^{2+}$. One reason for the behavioral difference between (2.2.2) and (2.2.1) cryptates may be the greater size mismatch between these cations and the cavity of the former ligand.

The similar effects seen for the complexation thermodynamics of the other lanthanide couples $\text{Eu}(2_{\text{B}}.2.1)^{3+/2+}$ and $\text{Yb}(2.2.1)^{3+/2+}$ (Table 1) also support these arguments. The relative instability of $\text{Yb}(2.2.1)^{3+}$ versus $\text{Yb}(2.2.1)^{2+}$, arising again from a marked enthalpic destabilization outweighing a smaller entropic stabilization, is expected in view of the smaller ionic radius of Yb^{3+} (0.86 Å (11,18)) compared to Yb^{2+} (0.93 Å (18)).

Table 6 also lists the absolute values of ΔG_c° for $\text{Eu}(2.2.1)^{2+}$ and $\text{Eu}(2.2.2)^{2+}$ obtained from the experimental values of K_{II} , along with ΔG_c° for the corresponding Eu(III) cryptates calculated by combining the divalent results with the data in Table 1. Although the ionic radii of Sr^{2+} and Eu^{2+} are very similar, it is seen that the values of $-\Delta G_c^\circ$ for the latter cation are significantly larger with both (2.2.1) and (2.2.2) cryptands (by 2.7 and 3.4 kcal mol⁻¹, respectively). These differences may arise from weak covalent bonding between the oxygen and nitrogen atoms of the cryptand with the unfilled 4f-orbitals on Eu^{2+} . Although the chemistry of divalent lanthanide ions closely resembles that for the corresponding alkaline earth cations having similar ionic radii (38), the stability constant of the Eu^{2+} -EDTA complex is also somewhat larger than for the Sr^{2+} -EDTA complex (104).

It is interesting to note that Pb^{2+} , which has an ionic radius close to those for Sr^{2+} and Eu^{2+} (Table 6), exhibits a value of $-\Delta G_c^\circ$ for (2.2.2) cryptate formation which is markedly larger than for Sr^{2+} (Table 6). This difference can also be attributed to the influence of covalent bonding.

Although absolute values of ΔH_c° and ΔS_c° were not determined for the lanthanide cryptates, rough estimates are included in Table 6 for comparison purposes. The entropy values were obtained by assuming that ΔS_c° for $\text{Eu}(2.2.1)^{2+}$ and $\text{Eu}(2.2.2)^{2+}$ are approximately equal to those for $\text{Sr}(2.2.1)^{2+}$ and $\text{Sr}(2.2.2)^{2+}$. Values of ΔH_c° were then computed by combining these estimates of ΔS_c° with the experimental values of ΔG_c° . Although this procedure may be questionable, it is supported by the similar activation entropies observed for the dissociation of corresponding Sr^{2+} and Eu^{2+} cryptates (*vide infra*).

2. Association of Lanthanide Cryptates with Small Anions

It has been asserted that cryptates provide an unusually effective way of shielding the encapsulated ions from their environment. However, the strong ion association found between the tri-positive cryptates and F^- and OH^- is a striking example of the limitations of this argument. Particularly unexpected is the finding that both the first and second cumulative association constants β_1 and β_2 are comparable to or even larger than the values for the corresponding aquo lanthanide cations (Table 2). Therefore it is possible that one or two anions are able to approach closely or even contact Eu^{3+} or Yb^{3+} despite the encapsulation of the cations within

the cryptate cavity. Inspection of molecular models reveals that such small anions could indeed fit between the polyether strands of the cryptate, although a significant distortion of the symmetrical *endo-endo* form is required in order to bring two anions into contact with the encapsulated cation. Bearing in mind that the measured association constants reflect the ability of the anion to compete with water molecules for sites adjacent to the metal cation, it is plausible that the surprising stability of the cryptate-anion complexes arises simply from the markedly weaker solvation of the cryptate cation compared with the aquated metal cation. An alternative way of rationalizing the experimental results is to regard the cryptand which surrounds the cation as a region of saturated dielectric and therefore of low dielectric constant which will enhance the coulombic attraction between the encapsulated cation and the incoming anions. It is not clear if the cation-anion associates involve direct cation-anion contact or solvent-separated ion pairs. It therefore may not be necessary for the complexing anions to be buried between the cryptate polyether strands in order to achieve strongly favorable interactions with the metal ion.

3. The Effects of Varying the Cation Charge upon Cryptate Substitution Kinetics

The kinetic parameters for the dissociation of lanthanide cryptates summarized in Table 3 exhibit some surprising features. Most prominently, the rate constant k_d for dissociation of $\text{Eu}(2.2.1)^{3+}$ is almost three orders of magnitude smaller than for the corresponding

divalent cryptate $\text{Eu}(2.2.1)^{2+}$ despite the substantially lower thermodynamic stability of the former complex (Table 1). Even the enormously larger driving force for the dissociation of $\text{Eu}(2.2.2)^{3+}$ compared with $\text{Eu}(2.2.1)^{2+}$ [$(\Delta G_{\text{III}}^{\circ} - \Delta G_{\text{II}}^{\circ}) = 9.7 \text{ kcal. mol.}^{-1}$, Table 1] results in values of k_d that are only ca. 30-fold larger for the former cryptate. As in the case of the corresponding thermodynamic parameters, some insight into the factors responsible for this behavior can be obtained by comparing the rate constants and activation parameters for $\text{Eu}(\text{III})$ and $\text{Eu}(\text{II})$ cryptate dissociation and formation with corresponding data for cryptates of alkali and alkaline earth cations having similar ionic radii. Tables 7 and 8 contain such data for (2.2.1) and (2.2.2) cryptates, respectively. The values of k_c for the europium cryptates were obtained by combining the values of k_d given in Table 3 with the values of ΔG_c° listed in Table 1. Approximate estimates of the corresponding activation parameters $\Delta H_c^{\ddagger}$ and $\Delta S_c^{\ddagger}$ are listed in Tables 7 and 8; these were similarly obtained using the estimates of ΔH_c° and ΔS_c° given in Table 6.

Inspection of Tables 7 and 8 reveals the importance of the charge as well as the size of the cation in determining the kinetics of cryptate substitution. Thus for the series of cations Na^+ , Ca^{2+} , Eu^{3+} which have comparable radii, both k_d and k_c fall dramatically as the cation charge increases. For example, $\text{Eu}(2.2.1)^{3+}$ exhibits values of k_c and k_d that are ca. 10^7 -fold smaller than for $\text{Na}(2.2.1)^+$ and ca. 10^4 -fold smaller than for $\text{Ca}(2.2.1)^{2+}$ (Table 7). Since Eu^{2+} and Sr^{2+} have very similar ionic radii and also exhibit comparable kinetic parameters with both (2.2.1) and (2.2.2) cryptands (Tables 7 and 8), it

Table 7. Rate Constants and Activation Parameters for Formation and Dissociation of some (2.2.1) Cryptates at 25°C.

Cation	a r_c Å	b k_d sec. ⁻¹	$\Delta H_d^\ddagger$ kcal.mol. ⁻¹	$\Delta S_d^\ddagger$ e.u.	e k_c M ⁻¹ sec. ⁻¹	$\Delta H_c^\ddagger$ kcal.mol. ⁻¹	$\Delta S_c^\ddagger$ e.u.
Na ⁺	1.02	15.5 ^{h,i}	12.3	-11.7	4×10 ⁶ ^{h,i}	6.9	-5.5
K ⁺	1.38	2×10 ^{3j}			3×10 ^{7j}		
Ca ²⁺	1.00	6.5×10 ⁻⁴ ^{h,i}	13.4	-28.2	5.8×10 ³ ^{h,i}	10.5	-6.2
		2.2×10 ⁻³ ^k	15.1	-20	1.6×10 ⁴ ^k	13.8	7
Sr ²⁺	1.16	1.45×10 ⁻³ ^{h,i}	14.6	-22.5	3.2×10 ⁴ ^{h,i}	8.5	-9.4
Ba ²⁺	1.36	6.4×10 ⁻² ^{h,i}	15.0	-13.8	1.3×10 ⁵ ^{h,i}	8.7	-6.1
Eu ²⁺	1.17	2.0×10 ⁻⁴ ^l	15.1	-25	4×10 ⁵ ^m	(6.3)	(-12)
Eu ³⁺	0.95	4.1×10 ⁻⁷ ^l	19.2	-23.5	0.35 ^m	(21.1)	(10)
Yb ³⁺	0.85	1.3×10 ⁻⁶ ^l	22.3	-10.7			

Notes to Table 7.

^aCrystallographic ionic radius, from Table 6.

^bRate constant for cryptate dissociation, acid-independent pathway.

^cActivation enthalpy for dissociation.

^dActivation entropy for dissociation.

^eRate constant for cryptate formation.

^fActivation enthalpy for cryptate formation.

^gActivation entropy for cryptate formation.

Data Sources:

^hB. G. Cox and H. Schneider, to be published; determined at
 $\mu \sim 10^{-3} - 10^{-2}$.

ⁱRef. 27.

^jRef. 24.

^kRef. 26.

^lFrom Table 3.

^mCalculated from the kinetic parameters for cryptate dissociation combined with the thermodynamic data in Table 6.

Table 8. Rate Constants and Activation Parameters for Formation and Dissociation of some (2.2.2) Cryptates at 25°C.

Cation	a r_c Å	b k_d sec. ⁻¹	c $\Delta H_d^\ddagger$ kcal.mol. ⁻¹	d $\Delta S_d^\ddagger$ e.u.	e k_c M. ⁻¹ sec. ⁻¹	f $\Delta H_c^\ddagger$ kcal.mol. ⁻¹	g $\Delta S_c^\ddagger$ e.u.
Na ⁺	1.02	147 ⁿ	14.5	16.1	1.9×10 ^{6ⁿ}	8.7	-0.5
K ⁺	1.38	7.8 ^{h,i} 9 ^j	20.3	13.9	3.0×10 ^{6^{h,i}} 2×10 ^{6^j}	9.3	2.4
Ca ²⁺	1.00	0.185 ^h 0.26 ^k	10.8 8.4	-25.8 -33	6.9×10 ^{3^h} 7.3×10 ^{3^k}	10.6 7.9	-5.6 -14
Sr ²⁺	1.16	7.1×10 ^{-5^h} 1.0×10 ^{-4^k} 1×10 ^{-4^o}	18.9 17.7	-14.1 -17	1.3×10 ^{4^h} 1.0×10 ^{4^k} 6×10 ^{3^o}	8.3 7.4	-11.9 -15
Ba ²⁺	1.36	1.8×10 ^{-5^{h,i}} 2.2×10 ^{-5^k}	21.0 20.9	-9.8 -9	9×10 ^{4^{h,i}} 7×10 ^{4^k}	6.7 6.8	-13.5 -13
Eu ²⁺	1.17	3.0×10 ^{-5^l}	18.8	-16	9.5×10 ^{5^m}	(5.1)	(-14)
Eu ³⁺	0.95	1.1×10 ^{-3^l}	13.8	-26	2.5 ^m	(17.8)	(3)

Notes to Table 8.

^aCrystallographic ionic radius, from Table 6.

^bRate constant for cryptate dissociation, acid-independent pathway.

^cActivation enthalpy for dissociation.

^dActivation entropy for dissociation.

^eRate constant for cryptate formation.

^fActivation enthalpy for cryptate formation.

^gActivation entropy for cryptate formation.

Date Sources

^hB. G. Cox and H. Schneider, to be published; determined at $\mu \sim 10^{-3} - 10^{-2}$.

ⁱRef. 27.

^jRef. 24.

^kRef. 26.

^lFrom Table 3.

^mCalculated by combining the kinetic parameters for cryptate dissociation with the thermodynamic data in Table 6.

ⁿRef. 22.

^oRef. 3.

is likely that these behavioral differences between Eu^{3+} and the lower charged cations result chiefly from the influences of ionic rather than covalent bonding.

The first possibility to be considered in interpreting such variations in the complexation kinetics is that they may be connected with the rates of substitution of water molecules in the coordination sphere of the cations. However, the "characteristic rates" of water substitution (105) for tripositive lanthanides, heavier alkaline earth, and alkali metal cations are all extremely fast (10^7 - 10^8 , 10^8 - 10^9 , and ca. 10^9 sec^{-1} , respectively (105). It has been suggested (25) that the rate constants k_c for complexation of cryptands with alkali metal and alkaline earth cations that are markedly below these water substitution rates may be due partly to the need for the complexing cation to bind with the *endo-endo* form of the cryptand, whereas the *exo-exo* conformation could be the predominant form in solution. However, since the 10^6 - to 10^7 -fold difference in k_c between Na^+ and Eu^{3+} , for example, is much greater than the corresponding variation in water substitution rates, it is likely that an additional factor is chiefly responsible at least for the large energy barriers observed in the complexation of multicharge cations. It is plausible that an important component of these energy barriers arises from the inability of the relatively rigid ligand to achieve a smooth stepwise replacement of water molecules in the metal coordination sphere by the cryptand coordinating groups, so that the loss of solvating water molecules may not be immediately compensated by the formation of cation-cryptand bonds (3,26).

As noted previously (3,25,26), the large changes in cryptate thermodynamic stability induced by variations in the radii of univalent or divalent cations (Table 6) are chiefly reflected in k_d rather than k_c (Tables 7 and 8), suggesting that the transition states more closely resemble the separated cation and cryptand rather than the cryptate (3,25,26,28). This latter result can be reconciled with the larger sensitivity of k_c to cation charge by noting that the hydration energies of simple cations are much more sensitive to ionic charge than to size (103). Therefore any partial desolvation of the cation required to reach the transition state from the separated reactants is expected to result in a greater dependence of the activation barrier on the charge rather than the size of the cation.

Further insight into the factors influencing these reactivity patterns can be obtained by inspecting the corresponding activation parameters (Tables 7 and 8). By and large, the marked variations in ΔS_c° seen for the univalent and divalent cryptates as the cation size and charge varies (Table 6) are primarily reflected in the activation entropies for the dissociation reactions $\Delta S_d^\ddagger$. The majority of the activation entropies for complexation $\Delta S_c^\ddagger$ are small and negative (ca. -5 to -10 e.u.). Since an activation entropy of ca. -10 to -15 e.u. is predicted on statistical grounds from the loss of translational entropy ΔS_t attending such association reactions (106), the values of $\Delta S_c^\ddagger$ support the above contention that no drastic changes in the solvent structure surrounding the cation are required in order to form the transition state from the separated reactants.

In contrast, however, the large differences in ΔS_c° between $\text{Eu}(2.2.1)^{3+}$ and $\text{Eu}(2.2.1)^{2+}$, and between $\text{Eu}(2.2.2)^{3+}$ and $\text{Eu}(2.2.2)^{2+}$ are chiefly reflected in $\Delta S_c^\ddagger$ rather than $\Delta S_d^\ddagger$ (Tables 7 and 8). Consequently, the markedly smaller values of k_c for the $\text{Eu}(\text{III})$ cryptates compared to $\text{Eu}(\text{II})$ and other divalent cryptates arise from substantially larger enthalpic barriers $\Delta H_c^\ddagger$ (Tables 7 and 8). The differences in activation entropy suggest that the solvent surrounding the Eu^{3+} cation in the transition state is substantially less "ordered" than around the uncomplexed cation. Indeed, the ionic entropy $\bar{S}^\circ$ of Eu^{3+} is large and negative (107), reflecting its large solvent "structure-making" ability (108). A good deal of this extensive hydration shell may be required to be removed in order to form the transition state, resulting in the observed large positive values of $\Delta H_c^\ddagger$ as well as $\Delta S_c^\ddagger$.

It has been pointed out that the significant acid catalyses observed for the dissociation of a number of metal cryptates suggest that it is often necessary to alter the cryptate conformation from the stable *endo-endo* form to one where at least one of the two bridgehead nitrogens has its lone pair pointing outwards (*exo-endo* or *exo-exo* conformation) prior to or within the transition state (27). The significant acid catalyses of the dissociation of the $\text{Eu}(\text{III})$ and $\text{Eu}(\text{II})$ cryptates (Table 4) indicate that such a mechanism is also applicable to these systems. Inasmuch as any clear trends can be discerned in the ratios k_H/k_d of the rate constants for the acid-catalyzed and uncatalyzed pathways, it appears from the data in Table 4 and reference 27 that k_H/k_d increases as the charge/radius

ratio of the cation increases and as the thermodynamic (or kinetic) stability of the cryptate decreases. The ratio k_H/k_d also is generally larger for (2.2.2) compared with (2.2.1) cryptates. The role of the proton in accelerating the dissociation reaction may be to aid the *endo-endo* to *exo-endo* conformational change by forming an incipient nitrogen-proton bond as the nitrogen-metal bond is broken, or it may simply provide a more favorable dissociation pathway once this conformational change has occurred (27). The smaller or undetectable acid catalysis in the more stable cryptates may arise from the greater difficulty of accomplishing this conformation change due to their tendency to be less flexible than cryptates having cavities that are markedly larger than the encapsulated cations.

The very marked acceleration of the dissociation rates of trivalent lanthanide cryptates by OH^- or F^- is not surprising in view of the strong binding of these anions to the cryptates. These anions could lower the energy barrier to dissociation by distorting the cryptate conformation and enlarging the space between the polyether strands so that the encapsulated cation can exit the cavity more easily. Additionally, the bound anions will act to lower the effective charge of the assembly, thus reducing the extent of the solvation changes which must occur in order for the cation to be removed from the cryptate cavity. It is interesting to note that these substantial accelerations of the cryptate dissociation rates occur in spite of the considerable thermodynamic *stabilization* of the cryptates by both fluoride and hydroxide (Table 2).

CHAPTER IV

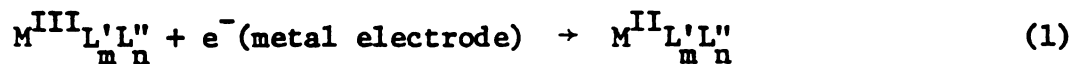
REACTION ENTROPIES OF TRANSITION METAL REDOX COUPLES

A. Introduction

While the ionic entropies of a number of transition metal complexes have been determined (see Historical Background), no systematic study has been conducted on the dependence of the entropies on the nature of the metal ion or on the ligands coordinated to the cation. Ru(III)/(II) couples can be used to explore the ligand effects since Ru(III) and Ru(II) complexes containing a variety of ligands are known. As stated previously, the substitutional inertness of Ru(III) and Ru(II) allows electrochemical determinations of the reaction entropies of these systems. The influence of the central metal ion on the ionic entropy of its complexes can be investigated by obtaining the reaction entropies for a series of redox couples having the same ligand structure and charge type. A large number of M(III)/M(II) couples is available so that complexes of this charge type will be used to investigate the metal dependence. A wide variation in metal ions is not possible with most unidentate ligands due to the instability of many of these complexes with regard to aquation. Fortunately, many complexes containing chelating ligands should be sufficiently stable to maintain their structural integrity in both the oxidized and the reduced forms. Therefore the employment of chelating systems will allow one to achieve the desired diversity in the nature of the complexed metal ion.

B. Determination of Reaction Entropies

The reaction entropy has already been defined in Chapter I but it is useful to present this definition more formally. One can consider the reaction



in which M is a metal which has trivalent and divalent oxidation states, L' and L'' are neutral or anionic ligands, and the number of L' and L'' coordinated to M is given by m and n, respectively. The reaction entropy ΔS°_{rc} of the $M^{III}_{L'L''_{m n}}/M^{II}_{L'L''_{m n}}$ redox couple can then be defined as the standard entropy change for reaction (1). This definition can also be stated as

$$\Delta S^{\circ}_{rc} = \bar{S}^{\circ}_{II} - \bar{S}^{\circ}_{III} \quad (2)$$

where $\bar{S}^{\circ}_{II}$ and $\bar{S}^{\circ}_{III}$ are the absolute ionic entropies of $M^{II}_{L'L''_{m n}}$ and $M^{III}_{L'L''_{m n}}$, respectively. The ΔS°_{rc} definition can be expanded to include other classes of redox couples but this work will only deal with those of the M(III)/M(II) type.

Reaction (1) is only a half of a complete electrochemical cell reaction. Consequently, any determination of the ΔS° for this reaction must involve some sort of extrathermodynamic assumption. Several of these have been proposed, and some reliable methods for the quantitative estimation of ionic entropies and ΔS°_{rc} values have been developed from these assumptions. Criss and Solomon have assembled a helpful summary of the various procedures (40).

Of the several methods of determining ΔS_{rc} which are available, the most convenient from the viewpoint of the present study is the one which utilizes a nonisothermal cell (109,110). This is basically an electrochemical cell in which the reference and working compartments are maintained at different temperatures. One nonisothermal arrangement which was frequently employed in the present work can be written as:



The temperature in regions AB and CD was maintained at the ambient value, while that of region BC (i.e., the working compartment) was varied, usually between 3° and 60°C. The formal potential E_f^{ni} across this nonisothermal cell was determined as a function of temperature. The temperature coefficient of this potential $\frac{dE_f^{ni}}{dT}$ can be divided into three components

$$\frac{dE_f^{ni}}{dT} = \frac{d\phi_{tlj}}{dT} + \frac{d\phi_{tc}}{dT} + \frac{d\phi_f^m}{dT} \quad (3)$$

where ϕ_{tlj} is the Galvani potential difference across the thermal liquid junction within the KCl salt bridge (point B in the cell diagram), ϕ_{tc} is the "thermocouple" potential difference between the hot and cold sections of the mercury working electrode, and ϕ_f^m is the Galvani metal-solution potential at the working electrode. The important quantity in the present content is $d\phi_f^m/dT$ since

$$\Delta S_{rc}^\circ = F(d\phi_f^m/dT) \quad (4)$$

Therefore one can obtain ΔS_{rc}° values from measurements of the formal potential if the temperature coefficients of ϕ_{tlc} and ϕ_{tc} are known or can be estimated.

Absolute values of the Thomsen coefficient, $d\phi_{tc}/dT$, are known for several metals and are usually found to be on the order of a few microvolts per degree. Mercury and platinum, which served as the working electrode materials in this study, have Thomsen coefficients of about 14 and 6 $\mu V/deg$, respectively, over the 0° - $100^{\circ}C$ temperature range (111). The experimental dE_f^{ni}/dT values are usually 1-2 mV/deg so it is clear that the contribution of the Thomsen coefficient to the temperature coefficient of E_f^{ni} is essentially negligible.

Relative rather than absolute values of $d\phi_{tlj}/dT$ are thermodynamically accessible but there is good evidence to indicate that this quantity is not greater than 50 $\mu V/deg$ for most aqueous electrolytes (109,110). Much larger values are found with strongly acidic or basic media (110b), in analogy to the considerable isothermal liquid junction potentials which can arise in such media. The use of concentrated aqueous KCl in the region of the thermal gradient (in effect, the employment of a "nonisothermal salt bridge") has been suggested by de Bethune et al. (110b) as a way to minimize $d\phi_{tlc}/dT$. Although reservations have been expressed concerning the exact soundness of this assumption (110c), there is little question that $d\phi_{tlj}/dT$ is at most 20 $\mu V/deg$ and is quite likely to be considerably smaller. Extremely accurate measurements of ΔS_{rc}° will definitely be hampered by the uncertainty in $d\phi_{tlj}/dT$, but this uncertainty will be essentially negligible within the context of the present study, in

which the precision of the dE_f^{ni}/dT determinations was only $\pm 50 \mu V/\text{deg}$. An uncertainty in ΔS_{rc}° of $\pm 0.5-1$ e.u. arises from this thermal liquid junction problem but this is quite small compared to the measured ΔS_{rc}° values, which can range up to 50 e.u. Furthermore, comparisons of the ΔS_{rc}° values of various systems will be unaffected by the $d\phi_{t1j}/dT$ effect since the value of this last quantity will depend on the composition of the salt bridge and not on the individual redox couple under study. The ΔS° values for homogeneous redox reactions, which can be obtained from the difference in ΔS_{rc}° values of the redox couples involved, will be free of the above effects since the uncertainties in ΔS_{rc}° will cancel when this difference is taken. On the basis of the preceding discussion it can be concluded that, for the purposes of the present study:

$$\Delta S_{rc}^\circ = F(dE_f^{ni}/dT) \quad (5)$$

The formal potentials which are needed for determinations of ΔS_{rc}° can be conveniently obtained from measurements of $E_{1/2}$, the (polarographic) half-wave potential. For a reversible cyclic voltammogram, $E_{1/2}$ is the average of the cathodic and anodic peak potentials (92b). A simple relationship exists between E_f and $E_{1/2}$ (93,112):

$$E_{1/2} = E_f + (RT/nF) \ln (D_{II}/D_{III})^{1/2} \quad (6)$$

where D_{II} and D_{III} are the diffusion coefficients of the reduced and oxidized species, respectively. The D_{II}/D_{III} ratio is usually close to unity so that $E_{1/2}$ differs from E_f by only 2-3 mV. In the context of the present work, the temperature coefficient of the

$(RT/nF)\ln(D_{II}/D_{III})^{1/2}$ term must be negligible so that $dE_{1/2}^{n1}/dT$ can be equated to dE_f^{n1}/dT . The validity of this assumption was confirmed by using the limiting polarographic and cyclic voltammetric peak currents of the oxidized and reduced forms of the representative couples, $\text{Eu}^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, to obtain values of D_{II} and D_{III} as a function of temperature (113). These determinations allow one to estimate that an error of less than 0.5-1 e.u. in ΔS_{rc}° stems from the equation of the temperature dependences of E_f^{n1} and $E_{1/2}^{n1}$. Therefore, one is justified in writing

$$\Delta S_{rc}^\circ = F(dE_{1/2}^{n1}/dT) \quad (7)$$

The procedure described here yields ΔS_{rc}° values which are absolute entropy differences for redox couples. Other reaction entropy measurements and scales are found in the literature. Unfortunately, little has been done to reconcile the conflicting conventions which exist. One popular scale stems from the determination of reaction entropies from the temperature dependence of the cell potential of an isothermal cell (114); i.e., one in which no temperature gradient exists between the working and reference electrode and in which the temperature of the entire cell is varied. Reaction entropies for single redox couples are then obtained by assuming $\Delta S_{rc}^\circ = 0$ for the reaction $\text{H}^+ + e \rightleftharpoons 1/2 \text{H}_2$. In effect, a relative scale is established for ΔS_{rc}° . Reaction entropies on the absolute scale can be obtained by adding 21 e.u. to the relative values (40,114). (This conversion is derived by recalling the estimated entropy of 5 e.u. for H^+ in aqueous solution (40), and by combining this with an entropy value of

31.2 e.u. for hydrogen gas at 25°C (115) to compute a value of $\Delta S_{rc}^{\circ} = 21$ e.u. (on the absolute scale) for the H^{+}/H_2 couple.)

As noted in Chapter I, a relative scale of ionic entropies can be set up by arbitrarily assigning a value of zero to the ionic entropy of hydrogen ion. Such assumptions will not affect the value of the reaction entropy since they will cancel when the difference between ionic entropies is calculated. However, care must be taken to avoid mixing values from the relative and absolute scales when taking such a difference. Both scales are used in the literature, and in some papers it is not obvious which scale is being employed. Furthermore, ΔS_{rc}° values from older papers often refer to oxidation processes. Such values will have the opposite sign to those in this work where the reaction entropy is defined in equations (1) and (2) in terms of reduction reactions.

C. Practical Aspects of Nonisothermal Cells

As shown in the preceding section, the nonisothermal salt bridge is a crucial component of the nonisothermal cell. In the present experiments, 3.5 M KCl was employed in the salt bridge for most experiments. The solution in the bridge must contain cations and anions of similar, if not identical, mobilities (116). This requirement is met by K^{+} and Cl^{-} (116,117). The solubility of KCl is slightly greater than 3.5 M even at 2°C, the lowest temperature used in this study, so no problems with precipitation of KCl are encountered.

The composition of the salt bridge can be important under some

conditions. With experiments performed in neutral supporting electrolytes, a negligible change in dE_f^{ni}/dT was found when the supporting electrolyte was used in the salt bridge in place of the 3.5 M KCl. An appreciable alteration in the value of dE_f^{ni}/dT was observed when the analogous comparison was made with acidic supporting electrolytes (i.e. where $[H^+] > 5\%$ of the total ionic strength). In these particular cases, 3.5 M KCl was employed to minimize the isothermal junction potential between the salt bridge and the acidic supporting electrolyte.

For experiments conducted in concentrated perchlorate electrolytes, one cannot use 3.5 M KCl in the salt bridge since the precipitation of the sparingly soluble salt, $KClO_4$, in the liquid junction will give rise to spurious potentials. This problem can be avoided by employing 3 M NH_4Cl in the salt bridge. The mobilities of NH_4^+ and Cl^- are quite similar (117), so NH_4Cl is a good replacement for KCl.

Some attention must also be devoted to the actual physical dimensions of the salt bridge. The electrochemical cell was constructed so that the temperature drop within the nonisothermal salt bridge was confined to a short distance (< 1 cm) within a glass tube having an internal diameter of about 0.8 cm. These features prevented the development of any significant concentration gradients due to thermal diffusion (the Soret effect). Considerably larger values of $d\phi_{t1j}/dT$ would result from the presence of a Soret effect (109,110b) but the lack of any significant thermal-diffusion effect was demonstrated by the fact that cell potentials were found to be stable to within 1 mV even after several hours under nonisothermal conditions.

D. Results

An orderly presentation of the results is facilitated by dividing them into three categories on the basis of the ligand structure and type of central metal ion. This arrangement will also allow one to make comparisons within and between classifications to determine the factors which influence the reaction entropy.

1. Aquo Couples

The reaction entropy ΔS_{rc}° of six aquo couples of the type $M(OH_2)_n^{3+/2+}$ were studied: $Cr(OH_2)_6^{3+/2+}$, $V(OH_2)_6^{3+/2+}$, $Fe(OH_2)_6^{3+/2+}$, $Ru(OH_2)_6^{3+/2+}$, $Eu(OH_2)_n^{3+/2+}$, and $Yb(OH_2)_n^{3+/2+}$. These systems were chosen because their formal potentials allow them to be conveniently studied at mercury or platinum electrodes, and they exhibit substantial variations in the electronic structure of the central metal ions. Previous determinations of ΔS_{rc}° for these couples are sparse. The absolute ionic entropies of Fe^{3+} and Fe^{2+} have been determined (41), and an estimate of ΔS_{rc}° for $Ru(OH_2)_6^{3+/2+}$ has been reported from electrochemical measurements (118).

Most data for the $Cr^{3+/2+}$ and $Eu^{3+/2+}$ couples in perchlorate media were obtained using potentiometry because the small heterogeneous electron-transfer rates for these systems resulted in distinctly irreversible cyclic voltammograms. However, in sodium *p*-toluenesulfonate (NapTS) media, the strong specific adsorption of *p*-toluenesulfonate anions resulted in almost reversible cyclic voltammograms for the $Eu^{3+/2+}$ couple. Accurate values of $E_{1/2}$ could still be obtained from such "quasi-reversible" voltammograms in the usual way provided that the cathodic-anodic peak separation lies in

the range 57 to ca. 90 mV (93). For the remaining aquo couples, essentially reversible or quasi-reversible cyclic voltammograms were obtained, at least after the addition of small quantities of NapTS. The resulting values of ΔS_{rc}° are listed in Table 9, together with other pertinent information. It is seen that some limited dependence of ΔS_{rc}° upon the nature of the metal ion is observed. The dependence of ΔS_{rc}° upon ionic strength was investigated for $\text{Eu}^{3+/2+}$ and was found to be small (Table 9). Good agreement between the earlier and present determinations are found for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ (Table 9), but a large qualitative discrepancy is seen for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$. A possible reason for this disparity is that the isothermal cell measurements of ref. 118 were complicated by an unknown temperature dependence of the electrode potential of the glass reference electrode used in that study.

2. Ruthenium(III)/(II) and Osmium(III)/(II) Couples Containing Monodentate Ligands

The reaction entropies of twelve Ru(III)/(II) couples containing ammine, aquo, and simple anionic ligands were evaluated. These systems were selected in order to scrutinize the effects of replacing ammine by aquo ligands and of changing the charge type of the couple resulting from substitution of the ammine and aquo ligands by simple anions. The results are summarized in Table 10. For all of these systems, the heterogeneous electron-transfer rates were sufficiently rapid so that the cyclic voltammograms were essentially reversible even at the highest sweep rates (100 V s^{-1}). However, the relative lability of the Ru^{II} state for the $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+/+}$ and

Table 9. Reaction Entropies for Various $M(OH_2)_n^{3+/2+}$ Redox Couples.

Couple	Electrolyte	$E_{1/2}^a$ mV	Temp. Range °C.	ΔS_{rc}^b e.u.
$Cr(OH_2)_6^{3+/2+}$ ^f	1M $\underline{NaClO_4}$ (pH 2)	-660	3-60	49 ^c
$Fe(OH_2)_6^{3+/2+}$ ^g	0.2M $\underline{LiClO_4}$ (pH 1-1.8)	500	3-60	43 ^d (48 ^h)
$V(OH_2)_6^{3+/2+}$ ^f	0.2M $\underline{LiClO_4}$ (pH 1-1.8)	-475	3-60	37 ^d
$Eu(OH_2)_6^{3+/2+}$ ^f	0.02M $\underline{NapTS}^j$ (pH 3) ^e	-628	3-60	48.5 ^d
	0.1M $\underline{NapTS}^j$ (pH 3) ^e	-626	3-60	48 ^d
	1M $\underline{NaClO_4}$ (pH 3) ^e	-620	3-60	45.5 ^{c,d}
$Yb(OH_2)_6^{3+/2+}$ ^f	0.1M $\underline{KPF_6}$ (pH ~5) ^e	-1423	3-60	48 ^d
$Ru(OH_2)_6^{3+/2+}$ ^f	0.3M $\underline{HpTS}^j$	-16	3-50	36 ^{d,k} (-33 ^f)

Notes to Table 9.

^aReversible half-wave potential in mV, determined at 25°C against a KSCE held at ambient temperature ($23 \pm 0.3^\circ\text{C}$); related to E_f by equation (7).

^bReaction entropy of redox couple in e.u. ($\text{cal K}^{-1} \text{mole}^{-1}$) at 25°C; determined by using equation (6). Experimental precision estimated to be ± 1 e.u., accuracy within 1-2 e.u. (see text). Values in parentheses are from literature sources.

^cDetermined using a combination of potentiometry and dc polarography.

^dDetermined using cyclic voltammetry (sweep rates: $50 - 500 \text{ mV s}^{-1}$).

^e $E_{1/2}$ found to be unaffected by pH variations of at least one unit around the pH value given.

^fDetermined using HMDE.

^gDetermined using Pt electrode.

^hCalculated by taking the difference in the relative ionic entropies given in ref. 41.

ⁱCalculated from isothermal cell data given in ref. 118 by noting that $\Delta S_{rc}^\circ = 21 \text{ e.u.}$ for the reaction $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2$ (40,114).

^j $p\text{TS} = p\text{-toulene sulfonate.}$

^kDetermined by P. D. Tyma.

Table 10. Reaction Entropies for Various Ru(III/II) and Os(III/II) Redox Couples Containing Unidentate Ligands.

Couple	Electrolyte	$-E_{1/2}^a$ (mV)	Temp. Range, °C	ΔS_{rc}^b (e.u.)
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	0.02M KPF_6	175	3-60	19 ± 0.5^c
	0.25M KPF_6	183(193 ^g , 187 ^h)	15-60	17 ± 0.5^c
	0.1M NaClO_4	178	15-60	$19 \pm 0.5^{c,d}(7^j)$
	0.2M CF_3COONa	180	3-60	16.5 ± 0.5^c
	0.8M CF_3COONa	188	3-60	14 ± 0.5^c
$\text{Os}(\text{NH}_3)_6^{3+/2+}$	0.05M CF_3COONa	990(1010 ⁱ)	3-65	18 ± 0.5^c
$\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$	0.2M CF_3COOH	162(178 ^g , 174 ^h)	3-60	$25 \pm 2^c(17.5^j)$
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$	0.1M HPTS	135(144 ^g , 140 ^h)	3-60	26 ± 2^c
$\text{Ru}(\text{NH}_3)_5\text{OH}^{2+/+}$	0.2M NaOH	653(664 ^g)	5-50	0 ± 3^c
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ f	0.1M CF_3COONa	-73	3-60	17 ± 1^c
$\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+/+}$	0.02M KPF_6	130	3-60	15 ± 0.5^c
	0.4M KPF_6	140(111 ^g)	3-60	15 ± 0.5^c
$\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+/+}$	0.5M NaClO_4	295(286 ^g)	2-45	$10 \pm 2^{d,l}$
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4\text{Cl}_2^{+/0}$	1M NaClO_4	350(344 ^g , 326 ^h)	2-28	$10 \pm 4^{d,l}$

Table 10. (cont.)

Couple	Electrolyte	$-E_{1/2}^a$ (mV)	Temp. Range, °C	ΔS_{rc}^b (e.u.)
$\text{Ru}(\text{OH}_2)_6^{3+/2+}$	0.3M <u>HpTS</u>	16(30 ^k)	3-50	$36 \pm 3^{c,m}(-33^k)$
$\text{Ru}(\text{OH}_2)_5\text{Cl}^{2+/+}$	1M <u>HpTS</u>	165	3-40	28 ± 3^c
<i>cis</i> - $\text{Ru}(\text{OH}_2)_4\text{Cl}_2^{+/0}$	0.1M <u>HpTS</u>	268	4-35	$25 \pm 2^{c,m}$

Notes to Table 10.

^aReversible half-wave potential in mV vs. ambient KSCE; determined at 25°C by cyclic voltammetry at a HMDE (except for $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ in which a Pt electrode was used). See notes to Table 9 for further details. Values in parentheses are from the indicated literature sources and correspond to comparable experimental conditions.

^bReaction entropy of redox couple in e.u. at 25°C (see notes to Table 9). Stated precision was estimated from the scatter of experimental points in the vicinity of 25°C. Values in parentheses are from the indicated literature sources.

^cDetermined using cyclic voltammetry sweep rates in the range 50–500 mV s⁻¹.

^dDetermined using sweep rates in the range 1–100 V s⁻¹.

^e_pTS = *p*-toluenesulfonate.

^f_{py} = pyridine.

^gReference 52.

^hReference 54.

ⁱReference 56.

^jReference 119.

^kReference 118.

^lDetermined by K. L. Guyer.

^mDetermined by P. D. Tyma.

$\text{Ru}(\text{NH}_3)_4\text{Cl}_2^{+/0}$ couples necessitated the use of large sweep rates ($1\text{--}100 \text{ V sec}^{-1}$) in order to avoid significant aquation of Ru^{II} during the potential scan. Estimates of $\Delta S_{\text{rc}}^\circ$ have previously been obtained for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$ and $\text{Ru}(\text{en})_3^{3+/2+}$ from the temperature dependence of the equilibrium constants for reduction of the Ru(III) complexes by $\text{Np}_{\text{aq}}^{3+}$ coupled with an estimate of $\Delta S_{\text{rc}}^\circ$ for the $\text{Np}_{\text{aq}}^{4+/3+}$ couple (119). While reasonable agreement between the present and earlier determinations is found for $\text{Ru}(\text{en})_3^{3+/2+}$, substantial differences are seen for the other two systems (Table 10). These discrepancies may arise from systematic errors in the kinetic analysis employed to determine the equilibrium constants in ref. 119 when these quantities are much larger than unity. Significant differences are also seen between present and earlier determinations of $E_{1/2}$ for some Ru(III)/(II) couples (Table 10). In view of the care taken to minimize liquid junction potentials in the present work, these differences probably arise chiefly from the presence of such potentials in the earlier work combined with the slightly different thermal conditions employed here.

Two main trends are seen upon inspecting the data given in Table 10. Firstly, the stepwise replacement of ammonia by aquo ligands results in large increases in $\Delta S_{\text{rc}}^\circ$. Secondly, the substitution by anionic ligands results in significant decreases in $\Delta S_{\text{rc}}^\circ$. A value of $\Delta S_{\text{rc}}^\circ$ for $\text{Os}(\text{NH}_3)_6^{3+/2+}$ is also given in Table 10 for comparison with $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. The reaction entropies for these two systems containing the same ligands are in close agreement.

3. Redox Couples Containing Chelating Ligands

In contrast to redox couples containing only simple unidentate ligands as considered above, a significant quantity of information has been gathered previously on the reaction entropies of couples containing chelating ligands. One reason is that such complexes are often sufficiently stable so that even labile oxidation states can remain in the complexed form in the presence of small stoichiometric excesses of the chelating ligands. Consequently it becomes feasible to determine values of ΔS_{rc}° for redox pairs such as Co(III)/(II) when bound to some chelating ligands. The lability coupled with the weak complexing ability of the Co(II) state precludes such studies of Co(III)/(II) couples containing only unidentate ligands. The simplest example is $\text{Co(en)}_3^{3+/2+}$, which provides an interesting comparison with $\text{Ru(en)}_3^{3+/2+}$. The relevant data for these couples are given in Table 11. It is seen that the values of ΔS_{rc}° for these two redox couples are strikingly different. The large value of ΔS_{rc}° for $\text{Co(en)}_3^{3+/2+}$ (37 e.u.) is surprising in view of the markedly smaller values seen for other amine complexes (Table 11), but is in accord with an earlier determination (120).

Consequently, we decided to evaluate ΔS_{rc}° for some other related Co(III)/(II) couples. The tris-1,10-phenanthroline and tris-2,2'-pipyridine Fe(III)/(II) and Ru(III)/(II) couples have previously been found to exhibit values of ΔS_{rc}° that are close to zero (51,121). The present determinations of ΔS_{rc}° for $\text{Fe(phen)}_3^{3+/2+}$ and $\text{Fe(bpy)}_3^{3+/2+}$ are in close agreement with these earlier values.

Table 11. Reaction Entropies for Various M(III)/(II) Couples Containing Chelating Ligands.

Couple	Electrolyte	Temp.		ΔS°_{rc} (e.u.)	b
		$E_{1/2}$ (mV)	Range, °C.		
$Ru(en)_3^{3+/2+}$ ^{c,e}	0.1M KPF_6	-60	3-60	13 ± 0.5 (11^1)	
$Co(en)_3^{3+/2+}$ ^{c,e}	1M $NaClO_4$ + 50mM en	-460($-448, \mu=0^j$)	3-60	37 ± 2 ($40^j, \mu=0$)	
$Fe(phen)_3^{3+/2+}$ ^{d,f}	0.05M KCl + 25mM phen	870(865, $\mu=0.05^k$)	4-45	3 ± 2 ($0, \mu=0^k, l$)	
$Fe(bpy)_3^{3+/2+}$ ^{d,g}	0.05M KCl + 25mM bpy	845(865, $\mu=0.05^k$)	4-45	2 ± 2 ($2, \mu=0^k, l$)	
$Ru(bpy)_3^{3+/2+}$ ^{d,g}	0.1M CF_3COOH	1048(1100, $\mu=0^k$)	3-60	1 ± 2 ($0, \mu=0^k$)	
<i>cis</i> - $Ru(NH_3)_2(bpy)_2$ ^{3+/2+ d,g}	0.1M CF_3COONa , 10mM CF_3COOH	642	3-60	6.5 ± 1	
<i>cis</i> - $Ru(NH_3)_2(bpy)_2$ ^{3+/2+ d,g}	1M HPTS	641	3-60	9 ± 1	
$Ru(NH_3)_4bpy$ ^{3+/2+ d,g}	0.1M CF_3COONa	284	3-60	12.5 ± 1	
$Ru(NH_3)_4phen$ ^{3+/2+ d,g}	0.095M CF_3COONa + 5mM CF_3COOH	289	3-60	14.5 ± 1	

Table 11. (cont.)

Couple	Electrolyte	$E_{1/2}^a$ (mV)	Temp. Range, °C.	ΔS_{rc}^b (e.u.)
<i>cis</i> -Ru(OH ₂) ₂ (bpy) ₂ ^{3+/2+} d, g	1M <u>HpTS</u>	640	3-60	8.5 ± 1
<i>trans</i> -Ru(OH ₂) ₂ (bpy) ₂ ^{3+/2+} d, g	1M <u>HpTS</u>	457	3-60	8.5 ± 1
Co(phen) ₃ ^{3+/2+} d, f	0.05M <u>KCl</u> + 25mM <u>phen</u>	145	3-45	22 ± 3 (18 ^m)
Co(bpy) ₃ ^{3+/2+} d, g	0.05M <u>KCl</u> + 25mM <u>bpy</u>	70	3-40	22 ± 3 (21 ^m)
Co(sep) ^{3+/2+} c, h	0.1M <u>NaClO₄</u>	-540 (-540 ⁿ)	3-50	19 ± 2
Fe(C ₅ H ₅) ₂ ^{+ / 0} d	0.1M <u>LiClO₄</u>	127	3-40	-5 ± 2

Notes to Table 11.

^aReversible half-wave potential in mV vs. ambient KSCE; determined at 25°C by cyclic voltammetry using sweep rates of 50–500 mV s⁻¹ (see notes to Table 9 for more details). Values in parentheses are from literature sources and determined at the indicated ionic strength μ .

^bReaction entropy of redox couple at 25°C in e.u. (see notes to Table 9 for further details). Quantities in parentheses are literature values determined at the indicated ionic strength. No μ value is given when the literature study and the present study employed the same ionic strength.

^cDetermined using HMDE.

^dDetermined using platinum and glassy carbon electrodes.

^e_{en} = ethylenediamine.

^f_{phen} = 1,10-phenanthroline.

^g_{bpy} = 2,2'-bipyridine.

^h_{sep} = 1,3,6,8,10,13,16,19-octaazabicyclo(6.6.6)eicosane. The trivial name for this ligand is sepulchrates (see reference 88).

ⁱReference 119.

^jReference 120.

^kReference 121.

^lReference 51.

^mCalculated from isothermal cell data (A. Ciana and V. Crescenzi, quoted Table V of M. Chou, C. Creutz, and N. Sutin, J. Am. Chem. Soc., 99, 5615 (1977)).

ⁿReference 88.

Relatively small values of ΔS_{rc}° are also maintained for *cis*- and *trans*- $\text{Ru}(\text{OH}_2)_2(\text{bpy})_2^{3+/2+}$ (Table 11). However, the measured values of ΔS_{rc}° for $\text{Co}(\text{phen})_3^{3+/2+}$ and $\text{Co}(\text{bpy})_3^{3+/2+}$ are both substantially different from zero (ca. +25 e.u., Table 11). It therefore again appears that such Co(III)/(II) amine couples exhibit "anomalously" large ΔS_{rc}° values. On the other hand, ΔS_{rc}° for the "capped ethylenediamine" $\text{Co}(\text{sep})^{3+/2+}$ couple (88) is much smaller than for $\text{Co}(\text{en})_3^{3+/2+}$ (Table 11).

E. Discussion

1. Ligand Effects on Reaction Entropies

It has been known for some time that the entropies of simple aquo cations can be correlated with surprising success using empirical relations involving the ionic charges and radii (41,45). Using the Latimer-Powell relation (41) and known crystallographic radii (18), ΔS_{rc}° for the first-row transition metal couples in Table 9 are calculated to be ca. 45 e.u., in good agreement with the experimental results. However, the smaller values observed for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ and $\text{V}(\text{OH}_2)_6^{3+/2+}$ (36 and 37 e.u.) and the larger values for $\text{Eu}(\text{OH}_2)_n^{3+/2+}$ and $\text{Yb}(\text{OH}_2)_n^{3+/2+}$ (48 e.u.) are not predicted by this relation. The classical Born equation can only yield predicted values of ΔS_{rc}° in reasonable agreement with these results by inserting the radii of the bare cations (45), rather than the radii including the coordinated water molecules which intuitively seem more appropriate, especially for transition metal cations. These large experimental values of ΔS_{rc}° are probably a consequence of the release of water molecules

surrounding the primary coordination sphere that are strongly orientated ("frozen") in the tripositive oxidation state (47,48). Indeed, such solvent structuring effects provide the most widely accepted and intuitively reasonable explanation for the wide variations found in ΔS_{rc}° (47-49,51).

In this connection, it is interesting to note that simple M(III)/(II) ammine couples exhibit values of ΔS_{rc}° which are substantially less than for the corresponding aquo couples (Tables 9 and 10). Thus, for both $Ru(NH_3)_6^{3+/2+}$ and $Os(NH_3)_6^{3+/2+}$, $\Delta S_{rc}^\circ \approx 18$ e.u., whereas for $Ru(OH_2)_6^{3+/2+}$ and other hexaaquo couples, $\Delta S_{rc}^\circ \gtrsim 36$ e.u. Since the size, shape, and electrostatic properties of ammonia and water ligands are comparable (122), these differences suggest that rather specific interactions between the coordinated and surrounding water molecules are responsible for the large values of ΔS_{rc}° observed for the aquo systems. It seems reasonable that the large degree of solvent ordering around tripositive, compared to dipositive, aquo cations arises partly from the ability of the relatively acidic aquo protons to form hydrogen bonds with surrounding water molecules (47,48). The weakly acidic ammine protons presumably have a much lower tendency to aid the central cationic charge in orienting solvating water molecules in this manner. These results are not unexpected on the basis of the empirical entropy correlation of George et al., which also indicates that the entropies of ammine complexes decrease less with increasing cationic charge compared with aquo systems (43,44). The much lower "structure-making" ability of tripositive ammine, compared with aquo, complexes is also borne out by the much smaller effective hydrated

radii for ion transport that are observed for the former complexes (123). The differing magnitudes in the electrostatic double-layer effects observed for the electroreduction of Cr(III) aquo and ammine complexes suggest that such differences in the extent of hydration also survive within the electrode-solution interfacial region (124). Since the Born relation predicts for +3/+2 couples that $\Delta S_{rc}^{\circ} = \frac{47.1}{r_e} \text{ e.u.}$ where r_e is the effective radius of the ion (45), and the radius of $M(\text{NH}_3)_6^{3+/2+}$ is ca. 3 Å (122), then this relation predicts for the couples $\Delta S_{rc}^{\circ} \approx 16 \text{ e.u.}$ The close agreement between the Born prediction and the experimental results for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Os}(\text{NH}_3)_6^{3+/2+}$ (Table 10) indicates that there is no extensive solvent ordering around these species even in the tripositive state, although dielectric saturation effects (46) may complicate the application of this simple model even to such substitutionally inert complexes. The substitution of ammine by aquo ligands in the series of couples $\text{Ru}(\text{NH}_3)_{6-x}(\text{OH}_2)_x^{3+/2+}$ is accompanied by sizable increases in ΔS_{rc}° , especially for $x = 1$ (Table 10), indicating that substantial solvent structuring can occur even around an isolated aquo ligand. The experimental values of ΔS_{rc}° for both $\text{Eu}(\text{OH}_2)_n^{3+/2+}$ (Table 9) and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ (Table 10) depend only slightly upon the total ionic strength, confirming that this quantity is chiefly a consequence of ion-solvent, rather than ion-ion interactions. The small decreases in ΔS_{rc}° at ionic strengths approaching unity are probably due in part to ion-pairing in the tripositive oxidation state, so that the effective ionic charge of this state is less than +3.

The substitution of ammine or aquo ligands by simple anions in Ru(III)/(II) couples consistently results in substantial decreases in ΔS_{rc}° (Table 10). This effect could arise for at least two reasons. Firstly, the reduction in the net ionic charges is always expected to lower ΔS_{rc}° on the basis of the classical Born model since ΔS_{rc}° is predicted to depend on the difference of the squares of the ionic charges on the two ions forming the redox couple. Secondly, the replacement of hydrogen-bonding ligands by electronegative ligands should decrease the extent of solvent structuring around these cations. To varying degrees, these two factors are probably responsible for the observed behavior of the chloro and isothiocyanato complexes in Table 10. The more dramatic decrease in ΔS_{rc}° for $\text{Ru}(\text{NH}_3)_5\text{OH}^{2+/+}$ compared with $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$ (Table 10) can reasonably be attributed to the different hydrogen bonding characteristics of OH^- and OH_2 . Thus OH^- can hydrogen bond to surrounding water molecules via the oxygen atom, which should be favored on electrostatic grounds by coordination to Ru(II) rather than Ru(III). In contrast, hydrogen bonding involving aquo ligands will be electrostatically favored by coordination to Ru(III) rather than Ru(II) since the hydrogen atoms on the ligands will participate in the bonding.

Although the data for the aquo couples in Table 9 indicate that some dependence of ΔS_{rc}° upon the electronic structure of the central metal cation is to be expected, part of the variations could arise from differences in the number of aquo ligands that are bound to the central metal ion. Thus n is undoubtedly greater than six for

$\text{Eu}(\text{OH}_2)_n^{3+/2+}$ and $\text{Yb}(\text{OH}_2)_n^{3+/2+}$ which can result in a greater number of hydrogen bonds with the surrounding solvent and may account for the especially large values of $\Delta S_{\text{rc}}^\circ$ that are observed for these couples. The reduction of V(III) to V(II) could be accompanied by an increase in the number of bound water molecules (including those held by hydrogen bonding). Such a change is sterically reasonable in view of the large ionic radius of V^{2+} ($r \approx 0.8 \text{ \AA}$ (11)) and would result in a smaller value of $\Delta S_{\text{rc}}^\circ$, as is observed. Similarly, Cr(II) is highly Jahn-Teller distorted (125), and the axial ligands in $\text{Cr}(\text{OH}_2)_6^{2+}$ are very weakly held. As a consequence, the conversion of Cr(III) to Cr(II) is accompanied by a decrease in the number of bound water molecules. This could be responsible in part for the relatively large value of $\Delta S_{\text{rc}}^\circ$. Differences in the polarizing power of the various cations may also be a factor. The $\Delta S_{\text{rc}}^\circ$ values for Ru(III)/(II) couples containing simple unidentate ligands given in Table 10 could provide workable estimates of $\Delta S_{\text{rc}}^\circ$ for other couples with the same ligand constitution and charge type. However, it is apparent from the data given in Table 11 that this assumption may not be reasonable for complexes that contain chelating ligands. Thus the values of $\Delta S_{\text{rc}}^\circ$ for Co(III)/(II) complexes containing ethylenediamine, *o*-phenanthroline, and bipyridine ligands are about 25 e.u. larger than for corresponding complexes involving other metal cations. These results are both surprising and somewhat puzzling. The behavioral difference between $\text{Ru}(\text{en})_3^{3+/2+}$ and $\text{Co}(\text{en})_3^{3+/2+}$ might be explained by differences in ligand conformation that are known for the trivalent complexes (126) giving rise to differences in the surrounding water structure.

However, this explanation seems less plausible for the much larger and structurally more open phenanthroline and bipyridine complexes. The values of ΔS_{rc}° close to zero that were previously found for other phenanthroline and bipyridine couples have been explained by the supposed ability of these aromatic ligands to "shield" the central metal ion from the surrounding solvent (51,121). The contrasting behavior of the corresponding Co(III)/(II) couples clouds this explanation somewhat. Certainly a common feature of these Co(III)/(II) couples is that the change in electronic structure $(t_{2g})^6 \rightarrow (t_{2g})^5(e_g)^2$ that occurs upon reduction must result in a greater degree of bond stretching and possibly stereochemical change compared with Fe(III)/(II) and Ru(III)/(II) couples which involve the conversion $(t_{2g})^5 \rightarrow (t_{2g})^6$. One of the consequences is presumably the release of "bound" water molecules in going from Co(III) to Co(II). The relatively small ΔS_{rc}° (19 e.u.) found for the Co(sep)^{3+/2+} couple (Table 11) could be a consequence of the "tighter" structure of the macrobicyclic ligand effectively excluding specifically bound water in the higher oxidation state. Furthermore, the much smaller ΔS_{rc}° values for the Ru(III)/(II) and Fe(III)/(II) phenanthroline and bipyridine complexes may arise partly from significant delocalization of the added t_{2g} electron around the aromatic rings. This delocalization can result in additional solvent ordering around these ligands in the divalent state which will counteract the decrease in charge density at the metal center. In the Ru and Fe systems these effects apparently negate each other, yielding ΔS_{rc}° values close to zero.

It would be enlightening to ascertain the functional form of the ligand effect on ΔS_{rc}° , assuming, of course, that such a relation exists. In other words, with respect to the reaction $M^{III}L'_mL''_n + e^- \rightarrow M^{II}L'_mL''_n$, it is useful to determine how ΔS_{rc}° is affected by changes in m and n . Such information will yield further insight into the various ligand influences on solvent polarization and will allow interpolation and extrapolation of ΔS_{rc}° values between related redox couples.

The simplest approach to the present question is to consider that the observed value of ΔS_{rc}° for a redox couple arises from independent, additive contributions from each ligand in the complex. This particular model also forms the basis of the empirical entropy correlations of George et al. (43,44). The dielectric-continuum Born model could also be used to calculate ΔS_{rc}° values, although one can expect some problems since this model treats the nonsymmetrical complexes in this study as uniformly charged spheres. Some of the results of this investigation will be employed to judge the suitability of these simple treatments for predicting the reaction entropies of mixed-ligand complexes (i.e., those containing two different types of ligands).

Table 12 summarizes the experimental values of ΔS_{rc}° for octahedral mixed ligand redox couples of the type $ML'_mL''_n(III)/(II)$ for which values are also available for the corresponding "pure ligand" couples $ML'_x(III)/(II)$ and $ML''_y(III)/(II)$. Listed for each couple is the reaction entropy $(\Delta S_{rc}^\circ)^{Born}$ that is calculated with the Born model

Table 12. Reaction Entropies for Various Redox Couples of the Type $M L_n^{m+}$ (III)/(II)

Redox Couple	ΔS_{rc}^a , e.u.	$(\Delta S_{rc}^e)^{std}$, e.u.	b	$(\Delta S_{rc}^e)^{Born}$, e.u.	c
$Ru(bpy)_3^{3+/2+}$	1			7.0	
<i>cis</i> - $Ru(NH_3)_2(bpy)_2^{3+/2+}$	6.5	7		8.6	
$Ru(NH_3)_4bpy^{3+/2+}$	12.5	12.5		10.9	
$Ru(NH_3)_4phen^{3+/2+}$	14.5			10.5	
$Ru(NH_3)_5py^{3+/2+}$	17	15.5		12.6	
$Ru(NH_3)_6^{3+/2+}$	18.5			14.6	
$Ru(NH_3)_5OH_2^{3+/2+}$	25	21.5		14.5	
<i>cis</i> - $Ru(NH_3)_4(OH_2)_2^{3+/2+}$	26	24.5		14.5	
$Ru(OH_2)_6^{3+/2+}$	36			14.5	
<i>cis</i> - $Ru(OH_2)_2(bpy)_2^{3+/2+}$	6 ^d	12.5		8.5	
<i>trans</i> - $Ru(OH_2)_2(bpy)_2^{3+/2+}$	6 ^d	12.5		8.5	
$Fe(bpy)_3^{3+/2+}$	2			7	
$Fe(CN)_4bpy^{-/2-}$	-29 ^e	-28		-5.5	
$Fe(CN)_6^{3-/4-}$	-41.5 ^e			-15	

Notes to Table 12.

^aExperimental value of ΔS°_{rc} taken from Tables 9-11 unless otherwise noted.

^bReaction entropy for mixed-ligand couples estimated from the experimental values of the two appropriate pure-ligand couples by linear interpolation (see text).

^cReaction entropy calculated from the Born model by using equation (8).

^dThese are estimated values for $\mu = 0.1$. Direct determinations at this ionic strength are precluded by hydrolysis (see experimental section). The tabulated values are estimated from those determined in 1M HpTS (Table 11) by assuming an ionic-strength dependence similar to that of *cis*- $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$ (Table 11).

^eReferences 51, 114, and 121.

by using the relation (46):

$$(\Delta S_{rc}^{\circ})^{\text{Born}} = 9.65 (z_{\text{ox}}^2 / \bar{a}_{\text{ox}} - z_{\text{red}}^2 / \bar{a}_{\text{red}}) \quad (8)$$

where z_{ox} and z_{red} are the net charges and $\bar{a}_{\text{ox}}$ and $\bar{a}_{\text{red}}$ are the equivalent radii (81) of the oxidized and reduced species, respectively. (The $\bar{a}$ value for a complex was taken to be equal to half of the cube root of the product of the diameters along the three L-M-L axes (81). Values of the equivalent radii were taken from reference 81 or estimated from ionic radii (11,18).) Also given for the mixed-ligand couples are reaction entropies $(\Delta S_{rc}^{\circ})^{\text{est}}$ that were estimated by linear interpolation from the experimental values of ΔS_{rc}° for the corresponding two pure ligand couples, i.e., by assuming that the two types of ligands provide additive contributions to ΔS_{rc}° that are proportional to the number of each ligand type present in the mixed-ligand couples.

For the Ru(III)/(II) couples containing ammine and bipyridine ligands, excellent agreement is seen between ΔS_{rc}° and $(\Delta S_{rc}^{\circ})^{\text{est}}$, whereas the Born model fails to predict the marked decreases in ΔS_{rc}° that are observed as the number of bipyridine groups increases, particularly in going from $c\text{-Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$ to $\text{Ru}(\text{bpy})_3^{3+/2+}$. These results suggest that differences in local solvation of the individual ligands rather than changes in the average distance of closest approach of the solvent to the metal charge center are largely responsible for the observed large variations in ΔS_{rc}° . This finding is perhaps not surprising for complexes containing large ligands such as bipyridine where a number of the solvating water molecules

will lie in the vicinity of the aromatic rings away from the metal charge center and the other ligands. As mentioned previously, the addition of an electron to such Ru(III) complexes to form Ru(II) could well give rise to two competing effects upon the surrounding solvent structure. The water molecules close to the ruthenium center, including those surrounding any ammine ligands, will be less polarized and therefore less "ordered" in the lower oxidation state, giving rise to a positive contribution to ΔS_{rc}° . However, the water molecules adjacent to the bipyridine rings could well experience an increase in polarization in going to the Ru(II) state since the added t_{2g} electron will be significantly delocalized around the aromatic rings, acting to increase their net charge density. This latter effect would yield a negative contribution to ΔS_{rc}° which will be roughly proportional to the number of pyridine rings. Therefore the stepwise replacement of ammine by bipyridine or pyridine ligands would result in an approximately linear decrease in ΔS_{rc}° , as observed. For $\text{Ru}(\text{bpy})_3^{3+/2+}$, these two effects presumably cancel, yielding $\Delta S_{rc}^\circ \approx 0$. The small (or slightly negative) values of ΔS_{rc}° observed for Ru(III)/(II), Fe(III)/(II), and Os(III)/(II) polypyridine couples have been previously ascribed to the efficient shielding of the metal center from the solvent by these ligands (51). This last explanation seems less reasonable since the polypyridine ligands will allow some solvent molecules to approach close to the metal center along the open channels formed by the planar aromatic rings. Also, the markedly larger values of ΔS_{rc}° (22 e.u.) observed for both $\text{Co}(\text{bpy})_3^{3+/2+}$ and $\text{Co}(\text{phen})_3^{3+/2+}$ (Table 11) can be more easily understood on the basis

of the present model. These $\text{Co(III)} \rightarrow \text{(II)}$ reactions involve the electronic conversion $t_{2g}^6 \rightarrow t_{2g}^5 e_g^2$ which should minimize the extent of electron delocalization in the reduced state, therefore discouraging any increase in solvent polarization in the vicinity of the pyridine rings. This change in electronic configuration will also yield a marked expansion of the cobalt center (127) and hence an especially large decrease in the polarization of nearby water molecules.

We have obtained further evidence that favors the present interpretation from the observation that the ferrocinium/ferrocene couple has a distinctly *negative* value of ΔS_{rc}° in aqueous media (-5 e.u., Table 11). Since this couple is of the charge type +1/0, the simple dielectric-polarization model predicts a small positive value of ΔS_{rc}° . The negative ΔS_{rc}° can be explained by noting that the electron added in the reduction will be substantially delocalized around the cyclopentadienyl rings in a manner similar to the polypyridine couples. Furthermore, the "sandwich" structure of the ferrocinium/ferrocene couple should largely prevent the close approach of solvent molecules to the metal center. Consequently in this case the predominant contribution to ΔS_{rc}° is anticipated to be the increased polarization of water molecules adjacent to the aromatic rings in the lower oxidation state, in accordance with the observed negative value of ΔS_{rc}° . Negative values of ΔS_{rc}° have also been observed for some blue copper protein couples having the charge type +1/0 and have been interpreted in terms of hydrophobic effects in the vicinity of the copper redox center (128).

As noted previously, the large values of ΔS_{rc}° typically observed for aquo couples have been attributed to field-assisted hydrogen bonding between the aquo ligands and the surrounding water molecules. This effect is apparent when it is noted that the substitution of a single aquo ligand into $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ yields a proportionately larger increase in ΔS_{rc} than those which result from subsequent aquo substitutions (Tables 10 and 12). However, there is reasonable agreement between ΔS_{rc}° and $(\Delta S_{rc}^\circ)^{\text{estd}}$ for $\sigma\text{-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$. On the other hand, substitution of one bipyridine in $\text{Ru}(\text{bpy})_3^{3+/2+}$ by two aquo ligands yields somewhat smaller values of ΔS_{rc}° compared to $(\Delta S_{rc}^\circ)^{\text{estd}}$ (Table 12). It is possible that the extent of hydrogen bonding involving aquo ligands is very sensitive to the electrostatic and steric environment. Therefore, it may be generally difficult to achieve accurate predictions of ΔS_{rc}° values for mixed-ligand couples containing aquo ligands.

Since a large number of complexes employed in redox kinetics contain anionic ligands, it is of interest to examine the stepwise changes in ΔS_{rc}° that occur as anions are substituted into the coordination sphere. Substantial and even qualitative changes in ΔS_{rc}° are generally expected from the Born model as well as from local solvation effects due to the variations in the overall charges of the complexes. Unfortunately, suitable data are extremely sparse. Table 12 contains data for three Fe(III)/(II) couples containing bipyridine and/or cyanide ligands. Again it is seen that the estimated value for the mixed-ligand couple $\text{Fe}(\text{CN})_4\text{bpy}^{-/2-}$ is in reasonable agreement

with the experimental value of ΔS_{rc}° , while the Born model fails to provide adequate estimates of ΔS_{rc}° for all three couples.

The assumption that the reaction entropies for mixed-ligand couples arise from simple linear additive contributions from each ligand would appear to provide a useful, though approximate, means of estimating ΔS_{rc}° under some circumstances. However, often one or both ΔS_{rc}° values for the corresponding pure ligand couples are unavailable. If it is assumed that values of ΔS_{rc}° depend chiefly on the ligands and the charge type of the redox couple, the required reaction entropies could be inferred from those for other couples containing the same ligands. George et al. (43,44) have used ionic entropy data to obtain empirical parameters for various ligands which allow estimates of ΔS_{rc}° to be made for couples containing these ligands. As was discussed earlier, this approach has serious limitations since in some cases ΔS_{rc}° can be significantly dependent on the nature as well as the charges of the central metal ions. Nevertheless, the method could be employed, albeit with caution, to estimate the *changes* in ΔS_{rc}° resulting from minor alterations in ligand composition.

2. Correlations between Outer-Sphere Self-Exchange Rates and Reaction Entropies

Aside from yielding information on the thermodynamics of ion solvation, reaction entropies also provide insight into some factors that influence redox reactivity. In order to recognize the origin and the utility of the relationship between ΔS_{rc}° and homogeneous electron-transfer rates, one must recall that the free energy of activation

ΔG_{11}^* for an outer-sphere self-exchange reaction consists of inner-shell (ΔG_{in}^*) and outer-shell (ΔG_{out}^*) contributions arising from the structural reorganization of the reactants and the surrounding solvent, respectively, that are required to yield the activated complex for electron transfer. A correlation is expected between ΔG_{out}^* and ΔS_{rc}° since both reflect changes in the solvent structure which take place in the course of a redox reaction. The outer-shell term stems from the alterations in solvent polarization that transpire when the activated complex is formed from the reactants (or more precisely, from the precursor complex). The reaction entropy is a measure of the solvent reorganization which occurs around one of the reactants when it is converted to a product. The Franck-Condon restrictions on electron transfer tend to yield an activated complex having properties intermediate to those of the reactants and products. Thus, in this simple analysis, the entropy change associated with solvent reorganization in the activation process is related to some fraction of ΔS_{rc}° .

It must be emphasized that one cannot expect some sort of direct correspondence (such as an equation) between ΔS_{rc}° and ΔG_{out}^* . After all, the overall ΔS° for a self-exchange reaction is zero since no net reaction occurs. Therefore, ΔS_{rc}° is not linked to the electron-transfer rates via an entropic driving-force effect. Furthermore, ΔG_{out}^* refers to the activation of two reactants, while ΔS_{rc}° is concerned with just one redox center. Fortunately, the outer-sphere reactions considered here are weakly adiabatic, and the absence of strong coupling between the reactants in such processes allows each redox center to be treated independently from a conceptual viewpoint.

(It remains to be seen whether the process of bringing two highly charged species together will lead to effects that neither would produce by itself, even if it is assumed that a weak mutual interaction occurs between these species. This point is discussed in Chapter V.)

In addition to the possible correlation between ΔS_{rc}° and ΔG_{out}^* , one could expect some relation between reaction entropies and ΔG_{in}^* . As noted previously (e.g., in the discussion of the ΔS_{rc}° values for Co(III)/(II) couples), ΔS_{rc}° becomes larger as the difference in the effective radii $\Delta \bar{a}$ of the reduced and oxidized species increases. Since large values of $\Delta \bar{a}$ are also associated with large inner-shell contributions to ΔG_{11}^* , some factors that tend to increase ΔG_{in}^* are expected to increase ΔS_{rc}° as well. Thus, one generally cannot use ΔS_{rc}° to separate the inner-shell and outer-shell components of ΔG_{11}^* , but some correlation between ΔS_{rc}° and ΔG_{11}^* should be found.

The interpretation of ΔG_{11}^* is simplest for redox couples which undergo weakly adiabatic electron transfer and for which the change in metal-ligand bond distances is not large. For such systems the inner-shell contribution ΔG_{in}^* is small and calculable, and the outer-sphere contribution ΔG_{out}^* can be obtained from ΔG_{11}^* (81). Although suitable systems are not abundant, Ru(III)/(II) couples containing ammine and/or polypyridine ligands provide such a class (81). Estimates of ΔG_{out}^* for various $\text{Ru}(\text{NH}_3)_x(\text{bpy})_{3-x}^{3+/2+}$ couples where $x = 0-3$ have recently been made (81). These are listed in Table 13 along with the corresponding values of ΔG_{out}^* (calcd). The latter

Table 13. Comparison between Activation Free Energies for Some Ruthenium (III)/(II) Self-Exchange Reactions and the Reaction Entropies for the Corresponding Redox Couples at 25°C.

Exchange Reaction/ Redox Couple	$\bar{a},$ Å	$\Delta G_{\text{out}}^*,$ kcal.mol. ⁻¹	$\Delta G_{\text{out}}^* (\text{calcd}),$ kcal.mol. ⁻¹	$\Delta S_{\text{rc}}^{\circ},$ e.u.	$\Delta S_{\text{rc}}^{\circ} (\text{calcd})^e$ e.u.
$\text{Ru}(\text{bpy})_3^{3+/2+}$	6.8	3.4	3.3	1	7.0
$\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$	5.6	4.0	4.0	6.5	8.6
$\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$	4.4	5.1	5.1	12.5	10.9
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$	3.8	5.8	5.9	17	12.6
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	3.3	7.3	6.8	18.5	14.6

^aEquivalent radius of reacting cation, taken from reference 81.

^bOuter-shell (solvent) contribution to the activation free energy for the self-exchange reaction.

Obtained from $\Delta G_{\text{out}}^* = RT(\ln Z - \ln k_{11}) - \Delta G_{\text{in}}^* - w_r$, where Z is the collision frequency for the particular pair of reactants, k_{11} is the observed rate constant, ΔG_{in}^* is the inner-shell contribution, and w_r is the electrostatic work required to form the collision complex from the separated reactants.

Data taken from Table IV of reference 81.

^cOuter-shell contribution calculated from Marcus theory (79); taken from Table IV of reference 81.

^dReaction entropy of redox couple, taken from Tables 10 and 11 (obtained at ionic strength $\mu = 0.1 \text{ M}$).

^eReaction entropy of redox couple calculated from the Born model, taken from Table 12.

quantities were calculated by using the Marcus model which treats the surrounding solvent as a dielectric continuum (81). The values of ΔS_{rc}° for these ruthenium couples are given in Table 13 along with the corresponding values of $\Delta S_{rc}^\circ(\text{calcd})$ calculated using the dielectric-continuum Born model (see reference 81 and equation (8) from the previous section). Table 13 also includes values of $\bar{a}$, the equivalent radius of the reacting cation. Because of the very similar $\bar{a}$ values found for the trivalent and divalent Ru complexes considered here (81), one can list a single value for both halves of the redox couple.

It is seen that the increasing values of ΔG_{out}^* that are observed as the smaller ammonia ligands replace bipyridine in the ruthenium coordination sphere are also associated with markedly increasing values of ΔS_{rc}° . This is not surprising since greater changes in solvent polarization are required for electron transfer as the effective radii of the reactants decrease (79,81). The dielectric-continuum estimates of $\Delta G_{out}^*(\text{calcd})$ and $\Delta S_{rc}^\circ(\text{calcd})$ are seen to be in broad agreement with the corresponding experimental parameters. However, it is interesting to note that there is substantially better agreement between ΔG_{out}^* and $\Delta G_{out}^*(\text{calcd})$ than between ΔS_{rc}° and $\Delta S_{rc}^\circ(\text{calcd})$. This behavior may be related to the fact that $\Delta G_{out}^*(\text{calcd})$ is mainly determined by the optical dielectric constant ϵ_{op} (see reference 79 and equation (12) from Chapter I), rather than by the static dielectric constant ϵ_s . The latter determines the value of $\Delta S_{rc}^\circ(\text{calcd})$ (46). It is known that ϵ_{op} is much less sensitive to

solvent structure than is ϵ_g , so that any breakdown in the validity of the dielectric-continuum model of ion-solvent interactions caused by an alteration in the solvent structure in the vicinity of the solute is likely to affect ΔG_{out}^* to a much smaller extent than $\Delta S_{\text{rc}}^\circ$.

Most other outer-sphere exchange reactions involve significant changes in metal-ligand bond distances so that the inner-shell reorganization energy ΔG_{in}^* forms a sizable component of ΔG_{11}^* . This is particularly true of $\text{M}(\text{OH}_2)_6^{3+/2+}$ reactions, and some reactions of this type are listed in Table 14. This table also includes values of the self-exchange rate constant k_{11} , ΔG_{11}^* , and $\Delta S_{\text{rc}}^\circ$ for the aquo couples and a number of other 3+/2+ redox couples containing ammine, ethylenediamine, or bipyridine ligands. (The tabulated values of the activation free energy were corrected for the electrostatic work w_r required to form the collision complex by using the equation $\Delta G_{11}^* = RT(\ln Z - \ln k_{11}) - w_r$ where Z is the bimolecular collision frequency (81)). The ammine and ethylenediamine complexes, in particular, form an interesting comparison with the aquo complexes since all three ligands are of comparable size so that the outer-shell terms ΔG_{out}^* should be similar, at least on the basis of the dielectric-continuum treatment of Marcus (79). The data from Tables 13 and 14 are also presented in Figure 4 as a plot of $\Delta S_{\text{rc}}^\circ$ versus ΔG_{11}^* .

Inspection of Table 14 and Figure 4 reveals that there is a general tendency of $\Delta S_{\text{rc}}^\circ$ to increase along with ΔG_{11}^* , although not surprisingly there is a considerable scatter in the individual points. For the aquo couples, the increasing values of $\Delta S_{\text{rc}}^\circ$ as well as of ΔG_{11}^* are

Table 14. Comparison between Kinetic Parameters for Selected Outer-Sphere Self-Exchange Reactions and Reaction Entropies for Corresponding Redox Couples at 25°C.

Exchange Reaction/ Redox Couple	k_{ex}^a $\text{M}^{-1}\text{s}^{-1}$	ΔG_{11}^{*b} kcal.mol^{-1}	ΔS_{rc}^c e.u.
$\text{Cr}(\text{OH}_2)_6^{3+/2+}$	$\sim 2 \times 10^{-7} (1.0)^{133}$	~ 24	50
$\text{V}(\text{OH}_2)_6^{3+/2+}$	$1.5 \times 10^{-2} (2.0)^{135}$	17.4	37
$\text{Fe}(\text{OH}_2)_6^{3+/2+}$	$4(0.55)^{136}$	13.8	43
$\text{Ru}(\text{OH}_2)_6^{3+/2+}$	$\sim 60 (1.0)^{132}$	~ 12	36
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	$3 \times 10^3 (0.1)^{81}$	8.2	18.5
$\text{Ru}(\text{en})_3^{3+/2+}$	$3 \times 10^3 (0.1)^{81}$	8.9	13
$\text{Ru}(\text{bpy})_3^{3+/2+}$	$4 \times 10^8 (0.1)^{137}$	3.4	1
$\text{Co}(\text{en})_3^{3+/2+}$	$8 \times 10^{-5} (1.0)^{138}$	20.4	38
$\text{Co}(\text{sep})^{3+/2+}$	$5(0.2)^{88}$	14.4	19
$\text{Co}(\text{bpy})_3^{3+/2+}$	$\sim 20 (0.1)^{139}$	13.4	22

^aRate constant for acid-independent self-exchange pathway; obtained from indicated reference numbers. Ionic strengths are given in parentheses.

^bFree energy of activation for the self-exchange reaction, corrected for the electrostatic work required to form the collision complex.

^cReaction entropy of redox couple, obtained at (or extrapolated to) ionic strength $\mu = 0.1$ M. Data from Tables 9-11.

Figure 4. Plot of the activation energy for some outer-sphere self-exchange reactions vs. the reaction entropy for the redox couples.

Key to symbols: (1) $\text{Ru}(\text{bpy})_3^{3+/2+}$, (2) $\text{Ru}(\text{en})_3^{3+/2+}$,
 (3) $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, (4) $\text{Co}(\text{bpy})_3^{3+/2+}$, (5) $\text{Co}(\text{en})_3^{3+/2+}$,
 (6) $\text{Co}(\text{sep})_3^{3+/2+}$, (7) $\text{Ru}(\text{OH}_2)_6^{3+/2+}$, (8) $\text{Fe}(\text{OH}_2)_6^{3+/2+}$,
 (9) $\text{V}(\text{OH}_2)_6^{3+/2+}$, (10) $\text{Cr}(\text{OH}_2)_6^{3+/2+}$, (11) $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$,
 (12) $\text{Ru}(\text{NH}_3)_4(\text{bpy})_2^{3+/2+}$, (13) $\text{Ru}(\text{NH}_3)_5(\text{py})_2^{3+/2+}$.

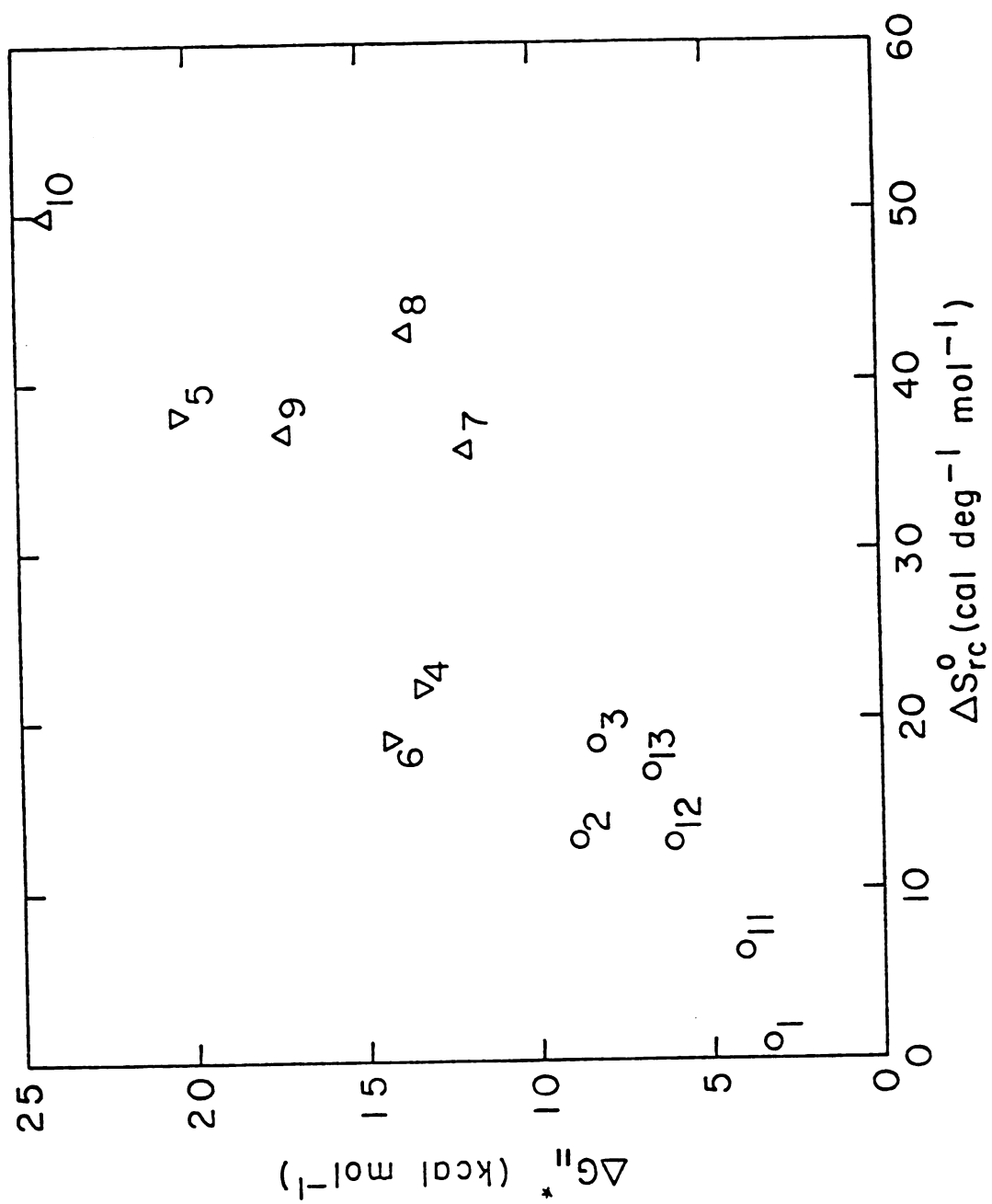


Figure 4.

broadly compatible with the conventional explanation which ascribes the latter changes to increasing values of the inner-shell contribution ΔG_{in}^* . Thus the $\text{Cr}(\text{OH}_2)_6^{3+/2+}$ exchange reaction involves transfer of an antibonding e_g electron which is expected to yield substantially larger values of $\Delta \bar{a}$ than the $\text{Ru}(\text{OH}_2)_6^{3+/2+}$, $\text{Fe}(\text{OH}_2)_6^{3+/2+}$, and $\text{V}(\text{OH}_2)_6^{3+/2+}$ exchange reactions which involve transfer of a nonbonding t_{2g} electron. Indeed, the $\text{Cr}(\text{OH}_2)_6^{3+/2+}$ reaction exhibits the largest values of both ΔG_{11}^* and ΔS_{rc}° . However, substantial differences in ΔG_{11}^* , which do not correlate in any simple way with ΔS_{rc}° , are observed between the $\text{Ru}(\text{OH}_2)_6^{3+/2+}$, $\text{Fe}(\text{OH}_2)_6^{3+/2+}$, and $\text{V}(\text{OH}_2)_6^{3+/2+}$ reactions. Of these aquo couples, $\Delta \bar{a}$ has been directly determined using crystallographic data only for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$; a value of 0.14 Å was obtained (129). This value of $\Delta \bar{a}$ leads to a calculated value of k_{11} that is in good agreement with the measured value for the $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ system (130). The approximation of $\Delta \bar{a}$ for $\text{V}(\text{OH}_2)_6^{3+/2+}$ can be obtained by noting that the difference in ionic radii for six-coordinate $\text{V}^{3+/2+}$ is 0.15 Å (11). The corresponding difference for $\text{Fe}^{3+/2+}$ is 0.14 Å (11) which agrees well with $\Delta \bar{a}$ for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$. Thus, $\Delta \bar{a}$ for $\text{V}(\text{OH}_2)_6^{3+/2+}$ is expected to be slightly larger than that for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$, but this does not completely account for the substantially slower exchange rate of the vanadium couple. Furthermore, the $\Delta \bar{a}$ values for these two couples would lead one to predict that $\text{V}(\text{OH}_2)_6^{3+/2+}$ have a larger ΔS_{rc}° than $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ which is the opposite of what is actually found.

One factor which complicates the interpretation of the results

for the aquo redox couples is the lack of information concerning the coordination numbers of many of the ions of interest. Thus, as noted previously, the vanadium results can be explained by an increase in the number of bound water molecules which could well accompany the reduction of V(III) to V(II). This increase in the solvent structuring around the V(II) ion will result in a smaller value of ΔS_{rc}° , as is observed, and will yield an additional contribution to ΔG_{11}^* which will act to decrease the self-exchange rate. Similar considerations can be applied to Cr(II). The aquo ligands in the axial positions of the hydrated ion are weakly held as a consequence of Jahn-Teller distortion (as mentioned in the previous section). Thus, the reduction of Cr(III) to Cr(II) will result in an effective decrease in the number of bound water molecules. This change in the coordination shell could be responsible in part for the large ΔS_{rc}° and ΔG_{11}^* for $\text{Cr}(\text{OH}_2)_6^{3+/2+}$.

The data in Table 14 and Figure 4 reveal that a dependence of ΔG_{11}^* upon ΔS_{rc}° is also obtained for non-aquo redox couples. Thus both ΔG_{11}^* and ΔS_{rc}° are markedly larger for $\text{Co}(\text{en})_3^{3+/2+}$ than for $\text{Ru}(\text{en})_3^{3+/2+}$; similar differences are also seen between $\text{Co}(\text{bpy})_3^{3+/2+}$ and $\text{Ru}(\text{bpy})_3^{3+/2+}$. It is likely that the larger values of ΔS_{rc}° for the cobalt couples are related to their larger $\Delta \bar{a}$ values. (As an example of the size of the values which are involved, $\Delta \bar{a} = 0.18 \text{ \AA}$ for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ while the corresponding quantity for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is $0.04 \text{ \AA}$ (127).) The larger values of ΔG_{in}^* and hence of ΔG_{11}^* for the Co systems are at least partly a result of these larger $\Delta \bar{a}$ values (131).

The observed differences can also be discussed in terms of electronic structure. The cobalt(III) complexes are low t_{2g}^6 spin while the cobalt(II) complexes are high spin $t_{2g}^5 e_g^2$, so a spin multiplicity change accompanies the electron transfer. The ruthenium(III) and ruthenium(II) complexes are all low spin, and as a result no spin multiplicity change accompanies the electron transfer. A consequence of the spin multiplicity change in the cobalt system is nonadiabaticity (that is, κ , the probability of electron transfer within the activated complex, is $\ll 1$; nonadiabaticity increases the apparent value of ΔG_{11}^* since ΔG_{11}^* can be considered to include the term $-RT \ln \kappa$). It has been estimated (131) that κ for the $\text{Co}(\text{NH}_3)_6^{3+/2+}$ exchange reaction is $\sim 10^{-4}$. If a similar factor applies to the $\text{Co}(\text{en})_3^{3+/2+}$ exchange reaction, ΔG_{11}^* for the ethylenediamine couple should be decreased by about 5 kcal mol^{-1} . Although this correction is appreciable (and reduces the scatter in Figure 4) substantial differences between the cobalt and ruthenium systems remain even after corrections for spin multiplicity.

Obviously other factors are also operant. The different ligand conformations in $\text{Co}(\text{en})_3^{3+}$ and $\text{Ru}(\text{en})_3^{3+}$ (126) would have an effect on the inner-shell reorganization of these complexes and hence on ΔG_{11}^* . This difference could also be partly responsible for the observed ΔS_{rc}° values since the availability of the metal ion to the solvent will be affected by the conformations of the ligands around the cation. Some of the variations between $\text{Ru}(\text{bpy})_3^{3+/2+}$ and $\text{Co}(\text{bpy})_3^{3+/2+}$ can be explained in terms of the delocalization of the added electron in $\text{Ru}(\text{bpy})_3^{2+}$ around the aromatic rings. As discussed previously, the

electronic structure of $\text{Co}(\text{bpy})_3^{2+}$ precludes a similar effect within this complex. In $\text{Ru}(\text{bpy})_3^{2+}$, the increased charge density of the ligands induces an increase in the degree of structuring in the solvent immediately adjacent to the aromatic rings. Thus the reduction of $\text{Ru}(\text{bpy})_3^{3+/2+}$ to $\text{Ru}(\text{bpy})_3^{2+}$ is accompanied by a small change in solvent ordering, and this provides some explanation for the small $\Delta S_{\text{rc}}^\circ$ and $\Delta G_{11}^\ddagger$ values of this couple. One can conclude that effects other than $\Delta \bar{a}$ and nonadiabaticity give rise to many of the differences between the $\text{Co}(\text{III})/(\text{II})$ and $\text{Ru}(\text{III})/(\text{II})$ systems. Unfortunately, it is more difficult to treat the ligand-conformation and electron-delocalization factors in a quantitative manner.

The differences in $\Delta S_{\text{rc}}^\circ$ for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$, $\text{Ru}(\text{OH}_2)_6^{3+/2+}$, and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ have recently been used to provide an estimate of $\Delta \bar{a} \sim 0.1 \text{ \AA}$ for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ (132). The accuracy of this estimate depends upon the extent to which $\Delta S_{\text{rc}}^\circ$ for the aquo couples differs from similar ammine couples due to the hydrogen-bonding ability of the aquo ligands. Taking $\Delta \bar{a}$ for the $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ couple as $0.14 \text{ \AA}$, the empirical entropy correlation of Powell and Latimer (41) predicts that $\Delta S_{\text{rc}}^\circ$ should only be about 10 e.u. lower for an analogous aquo couple for which $\Delta \bar{a} = 0$. However, $\Delta S_{\text{rc}}^\circ$ for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple ($\Delta \bar{a} = 0.04 \text{ \AA}$ (127)) is 25 e.u. smaller than for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ (Table 14). Most likely, therefore, hydrogen-bonding effects do contribute to $\Delta S_{\text{rc}}^\circ$ for the aquo couples.

Despite the complexities, there appears to be a consistent correlation between $\Delta G_{11}^\ddagger$ and $\Delta S_{\text{rc}}^\circ$ for the outer-sphere exchange reactions

considered here. The apparent simplicity of this correlation is somewhat deceiving since some of the factors which contribute to ΔS_{rc}° may not always affect ΔG_{11}^* in a similar way. Nevertheless, the correlation could be used in carefully selected systems as a means of estimating $\Delta \bar{a}$ and hence ΔG_{in}^* . More importantly, the relationship supplies further clues to the nature of the solvent-rearrangement process required for electron transfer.

CHAPTER V

ACTIVATION PARAMETERS FOR HOMOGENEOUS OUTER-SPHERE ELECTRON-TRANSFER REACTIONS: COMPARISONS BETWEEN SELF-EXCHANGE AND CROSS REACTIONS USING THE MARCUS THEORY

A. Introduction

As noted in Chapter I, the adiabatic model of outer-sphere electron transfer developed by Marcus and others predicts that there should be a simple relationship between the kinetics of homogeneous cross reactions and the corresponding self-exchange processes. This relationship (the "Marcus cross-relation") has commonly been formulated as equation (1):

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (1)$$

$$\log f_{12} = (\log K_{12})^2 / 4 \log (k_{11}k_{22}/Z^2) \quad (1a)$$

where k_{11} and k_{22} are the rate constants for the two constituent self-exchange (homonuclear) reactions, k_{12} and K_{12} are the rate and equilibrium constants, respectively, for the corresponding cross (heteronuclear) reaction, and Z is the bimolecular collision frequency in solution. Numerous tests of the applicability of eqn (1) to experimental kinetic data have been made. It has frequently been observed that the predictions of eqn (1) agree reasonably well with experimental results (60,140). The observed values of k_{12} , k_{12}^{obs} , are often within an order of magnitude or so of the values, k_{12}^{calc} , that are calculated from k_{11} and k_{22} using eqn (1). However, it has recently become clear that there are a disturbingly large number of reactions for which k_{12}^{obs} and k_{12}^{calc} are in substantial disagreement (132,134,141-145). For most of these systems, it is found that $k_{12}^{\text{obs}} < k_{12}^{\text{calc}}$ and that the difference between k_{12}^{obs} and k_{12}^{calc} increases as the equilibrium constant K_{12} increases (134,142-144).

Another puzzling feature of homogeneous outer-sphere redox processes between like-charged ions is that the entropies of activation $\Delta S^\ddagger$ for self-exchange as well as cross reactions are typically large and negative (ca. -20 to -35 e.u.) and insensitive to variations in ionic strength (81,144b). Such values of $\Delta S^\ddagger$ are predicted by simple electrostatic theory at low ionic strengths, but $\Delta S^\ddagger$ for self-exchange reactions is theoretically predicted to increase markedly with increasing ionic strengths to a value close to -10 e.u. (60,81,146).

In view of these striking discrepancies between theory and experiment, it seems worthwhile to examine the capability of the Marcus model to predict the relative values of the free energies, enthalpies, and entropies of activation for corresponding self-exchange and cross reactions. Such an investigation should help to pinpoint the factors that are responsible for the observed breakdown of eqn (1). Few tests have been made of the ability of the Marcus model to correlate activation parameters for corresponding self-exchange and cross reactions (134,145) because many of the required enthalpies and entropies of the cross reactions, ΔH_{12}° and ΔS_{12}° , have been unavailable. However, the standard (formal) potentials and reaction entropies tabulated in Chapter IV can be used to obtain accurate ΔH_{12}° and ΔS_{12}° values at the ionic strengths that are typically employed for kinetic measurements. In the present work, these thermodynamic quantities are utilized to compare the experimental activation parameters for a range of outer-sphere cross reactions with those that are predicted by the Marcus

treatment from the kinetic parameters of the corresponding self-exchange reactions.

This analysis will provide an additional insight into the limitations of the Marcus and related models in describing the energetics of homogeneous outer-sphere electron-transfer processes.

B. Kinetic Formulations and Results

1. Free Energies of Activation

For the present purposes, eqn (1) can be usefully rewritten in terms of free energies of activation (134,147):

$$\Delta G_{12}^* = 0.5(\Delta G_{11}^* + \Delta G_{22}^*) + 0.5(1 + \alpha) \Delta G_{12}^\circ \quad (2)$$

$$\alpha = \Delta G_{12}^\circ / 4(\Delta G_{11}^* + \Delta G_{22}^*) \quad (2a)$$

where ΔG_{12}° and ΔG_{12}^* are the "standard" free energy driving force and the activation free energy, respectively, for the cross reaction (determined at the appropriate ionic strength), and ΔG_{11}^* and ΔG_{22}^* are the free energies of activation for the self-exchange reactions. The activation free energies appearing in eqn (2) should be corrected for the work of forming the collision (precursor) complex from the separated reactants since they are actually reorganization energies within such a binuclear assembly (79). Eqn (2) should therefore be written for the experimentally accessible ("apparent") free energies of activation $(\Delta G^*)_{app}$ in the form (79):

$$\begin{aligned} (\Delta G_{12}^*)_{app} = & 0.5[(\Delta G_{11}^*)_{app} + (\Delta G_{22}^*)_{app}] + 0.5(\Delta G_{12}^W + \Delta G_{21}^W - \Delta G_{11}^W - \Delta G_{22}^W) \\ & + 0.5\Delta G_{12}^\circ + \frac{(\Delta G_{12}^\circ + \Delta G_{21}^W - \Delta G_{12}^W)^2}{8[(\Delta G_{11}^*)_{app} + (\Delta G_{22}^*)_{app} - \Delta G_{11}^W - \Delta G_{22}^W]} \quad (3) \end{aligned}$$

The apparent free energies of activation are related to the experimental second-order rate constants k^{obs} by (74,79)

$$k^{\text{obs}} = Z \exp[-(\Delta G^*)_{\text{app}}/RT] \quad (4)$$

where Z is the bimolecular collision frequency. In eqn (3), ΔG_{12}^W and ΔG_{21}^W are the free energies required to form the precursor and successor ("collision") complexes from the separated reactants and products, respectively, and ΔG_{11}^W and ΔG_{22}^W are the corresponding work terms for the constituent self-exchange reactions. For cross reactions between like-charged ions of similar structure, it is expected that $\Delta G_{12}^W \approx \Delta G_{21}^W \approx \Delta G_{11}^W \approx \Delta G_{22}^W = \Delta G^W$, so that eqn (3) can be simplified to

$$(\Delta G_{12}^*)_{\text{app}} = 0.5[(\Delta G_{11}^*)_{\text{app}} + (\Delta G_{22}^*)_{\text{app}}] + 0.5(1+\alpha)\Delta G_{12}^{\circ} \quad (5)$$

$$\alpha = \Delta G_{12}^{\circ}/4[(\Delta G_{11}^*)_{\text{app}} + (\Delta G_{22}^*)_{\text{app}} - 2\Delta G^W] \quad (5a)$$

In principle, the presence of positive values of ΔG^W in eqn (5) can explain the common observation that cation-cation reactions with large driving forces have observed cross-reaction rate constants k_{12}^{obs} are substantially smaller than the values k_{12}^{calc} that are calculated using eqn (1). For small values of ΔG_{12}° , the influence of α on the driving-force term in eqn (5) will generally be small since $\alpha\Delta G_{12}^{\circ}$ is proportional to the square of ΔG_{12}° (eqn (5a)), so that eqn (5) will approximately reduce to eqn (2) under these conditions, irrespective of the value of ΔG^W . However, as the magnitude ΔG_{12}° increases, the effect of α upon the driving-force term will increase so that the presence of positive values of ΔG^W will act to enlarge progressively the values

of $(\Delta G_{12}^*)_{app}$ calculated from eqn (5). This yields $k_{12}^{obs} < k_{12}^{calc}$ since eqn (1) and its free energy analogue, eqn (2), do not include work terms. The above argument is qualitatively reasonable, but the usual procedure of calculating work terms from the Debye-Hückel model is inadequate in a quantitative sense because the values obtained, $(\Delta G^W)_{DH}$, are not large enough to explain the extent of the observed discrepancies (134). Nevertheless, it seems quite plausible that another, larger component of ΔG^W , ΔG_s^W , could arise from the mutual solvent ordering which accompanies convergence of the two cationic reactants. Consequently eqns (5) and (5a) can conveniently be rewritten in terms of "Debye-Hückel corrected" free energies of activation $(\Delta G^*)_{corr}$:

$$(\Delta G_{12}^*)_{corr} = 0.5[(\Delta G_{11}^*)_{corr} + (\Delta G_{22}^*)_{corr}] + 0.5(1+\alpha)\Delta G_{12}^\circ \quad (6)$$

$$\alpha = \Delta G_{12}^\circ / 4[(\Delta G_{11}^*)_{corr} + (\Delta G_{22}^*)_{corr} - 2\Delta G_s^W] \quad (6a)$$

$$\text{where } (\Delta G^*)_{corr} = (\Delta G^*)_{app} - (\Delta G^W)_{DH} = \Delta G^* + \Delta G_s^W \quad (7)$$

$$\text{and (81) } (\Delta G^W)_{DH} = \frac{Z_1 Z_2 e^2 N}{\epsilon_s \bar{a} (1 + B \bar{a} \mu^{1/2})} \quad (8)$$

where Z_1 and Z_2 are the charges of the two reactants, e is the electronic charge, N is Avogadro's number, ϵ_s is the (static) dielectric constant, B is the Debye-Hückel parameter (82), μ is the ionic strength, and $\bar{a}$ is the distance between the centers of the reacting ions in the collision complex.

Eqns (6) and (6a) will be employed as a convenient means of examining the relationship between the experimental activation free energies

of corresponding self-exchange and cross reactions in terms of the Marcus model. These equations also provide the basis for exploring the behavior of the individual enthalpic and entropic components. Although the hypothesis embodied in the use of the term ΔG_s^W in eqn (6a) cannot be proven, it will be shown that the algebraic forms of eqns (6) and (6a) are nicely consistent with most of the available experimental data.

Tables 15 and 16 summarize the rate parameters for the acid-independent pathways of a number of homogeneous self-exchange reactions between various cationic complexes. Table 15 also includes E_f and ΔS_{rc}° values for the redox couples involved in these reactions. The listed values of $(\Delta G_{11}^*)_{corr}$ (or $\Delta G_{22}^*)_{corr}$) were obtained in the following ways. For reactions for which the self-exchange rate constants k_{11}^{obs} have been determined, values of $(\Delta G_{11}^*)_{corr}$ were obtained by using eqns (4), (7), and (8), assuming that $Z = 6 \times 10^{10} M^{-1} sec^{-1}$ (152,153). The listed values of k_{11}^{obs} for $Ru_{aq}^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Ru(NH_3)_5py^{3+/2+}$ self-exchange are quoted from the literature (81, 132, 145) and were obtained from cross-reaction rate constants by using eqn (1). These cross reactions had small driving forces and involved the Ru complex of interest and a structurally similar coreactant. The justification for this method of calculation is that eqn (1) has been found to be consistently successful under these conditions (134). Values of the "Debye-Hückel corrected" rate constants k_{11}^{corr} are also given in Table 15. These were obtained from k_{11}^{obs} using the relation $\ln k_{11}^{corr} = \ln k_{11}^{obs} + (\Delta G_{DH}^W)/RT$. No quantitative values of k_{11}^{obs} are

Table 15. Kinetic and Thermodynamic Parameters of Some Self-Exchange Reactions at 25°C.

Redox Couple	a	b	c	d
	E_f mV. vs. s.c.e.	ΔS_{rc}° e.u.	k_{11}^{obs} M. ⁻¹ sec. ⁻¹	k_{11}^{corr} M. ⁻¹ sec. ⁻¹
Co ^{3+/2+} _{aq}	1680 ¹⁴⁸	~45 ^e	3.3(3) ¹⁵¹	8
Fe ^{3+/2+} _{aq}	500(0.2)	43	4(0.5) ¹³⁶	15
Ru ^{3+/2+} _{aq}	-15(0.3)	36	~60(1) ¹³²	200
V ^{3+/2+} _{aq}	-475(0.2)	37	0.015(2) ¹³⁵	0.03
Eu ^{3+/2+} _{aq}	-625(0.1)	48		(4 × 10 ⁻⁴)
Cr ^{3+/2+} _{aq}	-660(1)	49		(2 × 10 ⁻⁶)
Yb ^{3+/2+} _{aq}	-1425(0.1)	48		(~0.1)
U ^{4+/3+} _{aq}	-880(0.5)	48		(0.5)
Np ^{4+/3+} _{aq}	-80(1) ¹⁴⁹	52 ¹⁵⁰		(~0.02)
Ru(NH ₃) ₆ ^{3+/2+}	-180(0.2)	18	~3 × 10 ³ (0.1) ⁸¹	~5 × 10 ⁴
Ru(en) ₃ ^{3+/2+}	-60(0.1)	13	~3 × 10 ³ (0.1) ⁸¹	~5 × 10 ⁴
Co(en) ₃ ^{3+/2+}	-460(1)	37	8 × 10 ⁻⁵ (1) ¹³⁸	2.5 × 10 ⁻⁴
Co(phen) ₃ ^{3+/2+}	145(0.05)	22	~40(0.1) ¹³⁹	~150
Co(bpy) ₃ ^{3+/2+}	70(0.05)	22	~20(0.1) ¹³⁹	~80
Ru(bpy) ₃ ^{3+/2+}	1045(0.1)	1	2 × 10 ⁹ (1) ¹³⁷	~1 × 10 ¹⁰
Ru(NH ₃) ₅ py ^{3+/2+}	75(0.1)	17	4.7 × 10 ⁵ (1) ¹⁴⁵	1.5 × 10 ⁶

Notes to Table 15.

- ^a Formal potential of redox couple in mV vs. KSCE. Ionic strength μ given in parentheses. Data from Tables 9-11 except where otherwise noted. For most systems, E_f becomes only $\sim 5 - 10$ mV more negative with increasing μ over the range $\mu \sim 0.1$ to 1.0. Superscripts are the reference numbers of the data sources.
- ^b Reaction entropy of redox couple. Data from Tables 9-11 except where otherwise noted. Quoted values were obtained at the same ionic strengths as E_f . Superscripts are the reference numbers of the data sources.
- ^c Observed second-order rate constant for the acid-independent pathway. Corresponding ionic strength given in parentheses. Superscripts are the reference numbers of the data sources.
- ^d Rate constant corrected for the Debye-Hückel work $(\Delta G^W)_{DH}$ of forming the collision complex from the separated reactants (eqn (8)). Quoted values are obtained from $\ln k_{11}^{corr} = \ln k_{11}^{obs} + (\Delta G^W)_{DH}/RT$. The $\bar{a}$ values used in eqn (8) were estimated from the sum of the radii of the reactants. Estimated rate constants are given in parentheses (see text).
- ^e Estimated value.

Table 16. Kinetic Parameters of Some Self-Exchange Reactions at 25°C.

Redox Couple	k_{11}^{corr} ^a M. ⁻¹ sec. ⁻¹	$(\Delta G_{11}^*)_{\text{corr}}$ ^b kcal.mol. ⁻¹	$(\Delta H_{11}^*)_{\text{corr}}$ ^c kcal.mol. ⁻¹	$-(\Delta S_{11}^*)_{\text{corr}}$ ^d e.u.
Co ^{3+/2+} _{aq}	8	13.5	10.2	11
Fe ^{3+/2+} _{aq}	15	13.1	8.6	15
Ru ^{3+/2+} _{aq}	200	11.6	~7.0 ^g	~15 ^g
V ^{3+/2+} _{aq}	0.03	16.8	~12.5	15
Eu ^{3+/2+} _{aq}	(4 × 10 ⁻⁴)	19.3 ^e	~15.0 ^g	~15 ^g
Cr ^{3+/2+} _{aq}	(2 × 10 ⁻⁶)	22.5 ^e	~18.0 ^g	~15 ^g
Yb ^{3+/2+} _{aq}	(~0.1)	~15.5 ^e	~11 ^g	~15 ^g
U ^{4+/3+} _{aq}	(0.5)	15.1 ^e	~9.0 ^h	~20 ^h
Np ^{4+/3+} _{aq}	(~0.02)	~17.0 ^f	~11 ^h	~20 ^h
Ru(NH ₃) ₆ ^{3+/2+}	~5 × 10 ⁴	8.3	3.2	17
Ru(en) ₃ ^{3+/2+}	~5 × 10 ⁴	8.3	3.2	17
Co(en) ₃ ^{3+/2+}	2.5 × 10 ⁻⁴	19.6	13.4	22
Co(phen) ₃ ^{3+/2+}	~150	11.7	4.5	24
Co(bpy) ₃ ^{3+/2+}	~80	12.1	7.0	17
Ru(bpy) ₃ ^{3+/2+}	~1 × 10 ¹⁰	~1	~1 ⁱ	~0 ⁱ
Ru(NH ₃) ₅ py ^{3+/2+}	1.5 × 10 ⁶	6.3	2.4	13

Notes to Table 16.

^aRate constant corrected for $(\Delta G^W)_{DH}$. Values taken from Table 15.
For further details see notes to Table 15.

^bFree energy of activation corrected for Debye-Hückel work term.
Values calculated from k_{11}^{corr} by using eqn (4) with
 $Z \approx 6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (152). (Eqn (4) expresses a relationship
between k^{obs} and $(\Delta G^*)_{app}$, but the equation can be used with equal
validity for k^{corr} and $(\Delta G^*)_{corr}$.)

^cEnthalpy of activation corrected for Debye-Hückel work term. Values
obtained from experimental activation enthalpies by using eqn (13)
and $(\Delta H^*)_{11,corr} = (\Delta H^*)_{11,app} - (\Delta G^W)_{DH}$ (see text). Except where
otherwise noted, the experimental enthalpies were obtained from
the same data source as used for the corresponding k_{11}^{obs} in
Table 15.

^dEntropy of activation, obtained from experimental activation
entropies $\Delta S^\ddagger$ by adding 10 e.u. (eqn (12)). Experimental values
are from the same data sources as the corresponding k_{11}^{obs} values
listed in Table 15 (unless otherwise noted).

^eEstimated from electrochemical exchange rate data (see text).

^fEstimated from the kinetics of the $\text{Ru(en)}_3^{3+} - \text{Np}_{aq}^{3+}$ reaction
(Table 19) by using eqn (7) (see text).

^g $(\Delta S^*)_{11,corr}$ assumed to be -15 e.u. $(\Delta H^*)_{11,corr}$ was calculated from
 $(\Delta G^*)_{11,corr}$ on the basis of this assumption (see text).

^h $(\Delta S^*)_{11,corr}$ assumed to be -20 e.u. $(\Delta H^*)_{11,corr}$ was calculated from
 $(\Delta G^*)_{11,corr}$ on the basis of this assumption (see text).

ⁱEstimated value (134).

apparently available for the aquo couples, $\text{Eu}_{\text{aq}}^{3+/2+}$, $\text{Cr}_{\text{aq}}^{3+/2+}$, $\text{Yb}_{\text{aq}}^{3+/2+}$, $\text{U}_{\text{aq}}^{4+/3+}$, and $\text{Np}_{\text{aq}}^{4+/3+}$. However, self-consistent estimates of $(\Delta G^*)_{11}^{\text{corr}}$ for these reactions were obtained as follows. The electrochemical exchange rates for these and other aquo redox couples have been determined at the mercury-aqueous interface and have been found to yield a consistent correlation with the rates of corresponding homogeneous self-exchange and cross reactions (94,154). This can be expressed as $(\Delta G^*)_{\text{corr}}^{\text{e}} = 0.47(\Delta G^*)_{\text{corr}}^{\text{h}} - 0.5 \text{ kcal (94)}$, where $(\Delta G^*)_{\text{corr}}^{\text{e}}$ and $(\Delta G^*)_{\text{corr}}^{\text{h}}$ are the corresponding electrochemical and homogeneous free energies of activation, respectively, that have been corrected for the appropriate electrostatic work terms. The listed values of $(\Delta G^*)_{11}^{\text{corr}}$ for $\text{Eu}_{\text{aq}}^{3+/2+}$, $\text{Cr}_{\text{aq}}^{3+/2+}$, $\text{Yb}_{\text{aq}}^{3+/2+}$, and $\text{U}_{\text{aq}}^{4+/3+}$ were obtained in this manner. A justification for employing this method is that the resulting estimates of $(\Delta G^*)_{11}^{\text{corr}}$ are consistently within ca. 0.5 kcal of the values estimated (by use of eqn (6)) from the kinetics of cross reactions having small driving forces (see below). The listed value of $(\Delta G^*)_{11}^{\text{corr}}$ for $\text{Np}_{\text{aq}}^{4+/3+}$ was determined from the kinetics of the $\text{Ru}(\text{en})_3^{3+} - \text{Np}_{\text{aq}}^{3+}$ reaction (Tables 19 and 20) by using the latter method, since the electrochemical exchange rate for this couple is not available. Discussion of the activation enthalpies and entropies will be reserved for a more appropriate time (i.e., in section 2).

Tables 17 and 18 list the available kinetic parameters for the acid-independent pathways of a number of cross reactions between the various aquo couples listed in Tables 15 and 16. Values of the "Debye-Hückel corrected" free energies of activation $(\Delta G^*)_{12}^{\text{corr}}$ were

Table 17. Driving Forces and Rate Constants for Cross Reactions Between Aquo Cations at 25°C.

Oxidant	Reductant	$-\Delta G_{12}^{\circ}$ ^a	k_{12}^{obs} ^c	k_{12}^{corr} ^c
		kcal mol ⁻¹	M ⁻¹ sec ⁻¹	M ⁻¹ sec ⁻¹
Co ³⁺	Fe ²⁺	27.2	50(1) ¹⁵⁵	150
Co ³⁺	V ²⁺	49.5	$9 \times 10^5(3)$ ¹⁵⁶	2×10^6
Co ³⁺	Cr ²⁺	53.9	$1.3 \times 10^4(3)$ ¹⁵⁶	2×10^4
Co ³⁺	U ³⁺	58.9	$1.1 \times 10^6(2)$ ^{144a}	3×10^6
Fe ³⁺	Ru ²⁺	11.9	$2.3 \times 10^3(1)$ ¹³²	7×10^3
Fe ³⁺	V ²⁺	22.5	$1.8 \times 10^4(1)$ ^{144b}	6×10^4
Fe ³⁺	Eu ²⁺	25.9	$7 \times 10^3(1)$ ¹⁵⁷	2×10^4
Fe ³⁺	Cr ²⁺	26.7	$2.3 \times 10^3(1)$ ¹⁵⁸	7×10^3
Fe ³⁺	U ³⁺	31.7	$4 \times 10^5(2)$ ^{144a}	8×10^5
Ru ³⁺	V ²⁺	10.6	$2.8 \times 10^2(1)$ ¹³²	9×10^2
Np ⁴⁺	V ²⁺	9.1	$1.3(1)$ ¹⁵⁹	4
V ³⁺	Eu ²⁺	3.5	$9 \times 10^{-3}(2)$ ¹⁶⁰	2×10^{-2}
V ³⁺	U ³⁺	9.2	$85(2)$ ¹⁶¹	250
Eu ³⁺	Cr ²⁺	0.8	$\sim 2 \times 10^{-5}(0.5)$ ¹⁶⁰	8×10^{-5}
Cr ³⁺	U ³⁺	5.0	$6.2 \times 10^{-2}(2)$ ^{144c}	0.15

Notes to Table 17.

^aFree energy driving force for cross reaction, determined from the formal potentials listed in Table 15 by using $\Delta G_{12}^{\circ} = F(E_f^{\text{ox}} - E_f^{\text{red}})$ where E_f^{ox} and E_f^{red} are the formal potentials of the couples undergoing oxidation and reduction, respectively.

^bObserved second-order rate constants for acid-independent pathway. Corresponding ionic strength given in parentheses. Reference numbers of the data sources appear as superscripts.

^cRate constant corrected for the Debye-Hückel work of forming the collision complex from the separated reactants. See note (d) to Table 15.

Table 18. Free Energies of Activation and Driving Forces for Cross Reactions Between Aquo Cations at 25°C.

Oxidant	Reductant	$-\Delta G_{12}^{\circ}$ kcal mol ⁻¹	$(\Delta G_{12}^{\circ})_{\text{corr}}$ kcal mol ⁻¹	$0.5\alpha\Delta G_{12}^{\circ}$ kcal mol ⁻¹	$0.5\alpha\Delta G_{12}^{\circ}$ kcal mol ⁻¹	ΔG_s^W kcal mol ⁻¹
Co ³⁺	Fe ²⁺	27.2	11.7	3.3	12.0	10.2
Co ³⁺	V ²⁺	49.5	6.1	10.1	19.6	7.3
Co ³⁺	Cr ²⁺	53.9	8.6	10.1	17.6	7.6
Co ³⁺	U ³⁺	58.9	5.9	15.2	21.1	4.1
Fe ³⁺	Ru ²⁺	11.9	9.5	0.7	3.1	
Fe ³⁺	V ²⁺	22.5	8.2	2.1	4.5	8.2
Fe ³⁺	Eu ²⁺	25.9	8.8	2.6	5.6	8.8
Fe ³⁺	Cr ²⁺	26.7	9.5	2.5	5.1	8.9
Fe ³⁺	U ³⁺	31.7	6.7	4.5	8.5	6.3
Ru ³⁺	V ²⁺	10.6	10.7	0.5	1.8	
Np ²⁺	V ²⁺	9.1	13.9	0.3	1.7	
V ³⁺	Eu ²⁺	3.5	17.0	0	0.7	
V ³⁺	U ³⁺	9.2	11.4	0.3	0	
Eu ³⁺	Cr ²⁺	0.8	~20.3	0	-0.2	
Cr ³⁺	U ³⁺	5.0	15.8	0.1	-0.5	

Notes to Table 18.

^a Free energy driving force for cross reaction, taken from Table 17.

^b Free energy of activation, calculated from k_{12}^{corr} (Table 17) by using eqn (4). See note (b) to Table 16.

^c α_o determined from eqn (6a) by using the $(\Delta G_{11}^*)_{\text{corr}}$ values for the appropriate self-exchange reactions (Table 16) and $\Delta G_s^W = 0$. (Table 16 contains $(\Delta G_{11}^*)_{\text{corr}}$ values but these can be used as $(\Delta G_{11}^*)_{\text{corr}}$ or $(\Delta G_{22}^*)_{\text{corr}}$ in eqn (6a) since the "11" and "22" subscripts only serve to distinguish one of the constituent self-exchange reactions from the other.)

^d Calculated from eqn (6) by inserting the appropriate values of $(\Delta G_{11}^*)_{\text{corr}}$ and $(\Delta G_{22}^*)_{\text{corr}}$ (Table 16), and $(\Delta G_{12}^*)_{\text{corr}}$, and ΔG_{12}° (this table).

^e Apparent work required to form the collision complex from the separated reactants; determined from the listed α_o and α values by using eqn (9) (see text).

were again obtained from the experimental rate constant k_{12}^{obs} by using eqns (4), (7), and (8). Tables 19 and 20 summarize the corresponding data for cross reactions involving the non-aquo redox couples that are listed in Tables 15 and 16. Also included in Tables 17-20 are the free energies of reaction ΔG_{12}° for the cross reactions. These latter quantities were determined from the difference in the formal potentials E_f at 25°C that are given in Table 15 for the appropriate pairs of redox couples. These values of E_f were obtained by means of cyclic voltammetry (see Chapter IV) using suitably non-complexing media at ionic strengths that are comparable to those employed for the corresponding kinetic measurements. [Although some values of E_f were determined at ionic strengths different from those employed for the kinetic studies, this is of little consequence since the variation of E_f with μ is typically small (≤ 10 mV) in the range of ionic strengths ($\mu \approx 0.1-1$) used for the kinetic measurements. Furthermore, these differences will tend to cancel when the pair of E_f values used to calculate ΔG_{12}° are determined at similar ionic strengths.]

The experimental values of $(\Delta G_{12}^*)_{\text{corr}}$ for each cross reaction given in Tables 18 and 20 were then compared with the predictions of eqns (6) and (6a) using the following approach. The quantity $0.5\alpha\Delta G_{12}^{\circ}$ was calculated for each cross reaction by inserting into eqn (6) the appropriate values of $(\Delta G_{12}^*)_{\text{corr}}$, $(\Delta G_{11}^*)_{\text{corr}}$, $(\Delta G_{22}^*)_{\text{corr}}$, and ΔG_{12}° that are listed in Tables 16, 18, and 20. An analogous quantity, which will be designated $0.5\alpha_o\Delta G_{12}^{\circ}$, was determined from $(\Delta G_{11}^*)_{\text{corr}}$, $(\Delta G_{22}^*)_{\text{corr}}$, and ΔG_{12}° by using eqn (6a) with the assumption that

Table 19. Driving Forces and Rate Constants for Cross Reactions Involving Non-Aquo Cations at 25°C.

Oxidant	Reductant	^a $-\Delta G_{12}^\circ$	^b k_{12}^{obs}	^c k_{12}^{corr}
		kcal mol ⁻¹	M ⁻¹ sec ⁻¹	M ⁻¹ sec ⁻¹
Ru(NH ₃) ₆ ³⁺	V _{aq} ²⁺	6.8	$1.5 \times 10^3 (0.48)^{162}$	$\sim 2 \times 10^4$
Ru(NH ₃) ₆ ³⁺	Eu _{aq} ²⁺	10.3	$2.3 \times 10^3 (1)^{163}$	7×10^3
Ru(NH ₃) ₆ ³⁺	Cr _{aq} ²⁺	11.1	$2 \times 10^2 (0.2)^{164}$	2×10^3
Ru(NH ₃) ₆ ³⁺	Yb _{aq} ²⁺	28.7	$4.5 \times 10^7 (1)^{163}$	1.5×10^8
Ru(NH ₃) ₆ ³⁺	Np _{aq} ³⁺	-2.3	$0.3 (1)^{119}$	~ 2
Ru(NH ₃) ₆ ³⁺	U _{aq} ³⁺	16.0	$1.5 \times 10^5 (1)^{165}$	9×10^5
Ru(en) ₃ ³⁺	Np _{aq} ³⁺	0.5	$8.5 (1)^{119}$	40
Ru(en) ₃ ³⁺	U _{aq} ³⁺	18.8	$8.4 \times 10^5 (1)^{165}$	4×10^6
Ru(NH ₃) ₅ py ³⁺	V _{aq} ²⁺	12.7	$3 \times 10^5 (1)^{134}$	1×10^6
Ru(NH ₃) ₅ py ³⁺	Eu _{aq} ²⁺	16.1	$5.4 \times 10^4 (1)^{134}$	1.5×10^5
Ru(NH ₃) ₅ py ³⁺	Ru(NH ₃) ₆ ²⁺	5.9	$1.4 \times 10^6 (1)^{134}$	4×10^6
Fe _{aq} ³⁺	Ru(NH ₃) ₆ ²⁺	15.7	$3.5 \times 10^5 (0.1)^{166}$	$\sim 6 \times 10^6$
Ru _{aq} ³⁺	Ru(NH ₃) ₆ ²⁺	3.8	$1.4 \times 10^4 (1)^{132}$	4×10^4
Fe _{aq} ³⁺	Ru(en) ₃ ²⁺	12.9	$1.4 \times 10^5 (0.1)^{166}$	$\sim 3 \times 10^6$
Fe _{aq} ³⁺	Ru(NH ₃) ₅ py ²⁺	9.8	$5.8 \times 10^4 (1)^{145}$	1.7×10^5
Co(phen) ₃ ³⁺	Ru(NH ₃) ₆ ²⁺	7.5	$1.5 \times 10^4 (0.1)^{134}$	$\sim 1 \times 10^5$
Co(bpy) ₃ ³⁺	Ru(NH ₃) ₆ ²⁺	5.8	$1.1 \times 10^4 (0.1)^{134}$	$\sim 1 \times 10^5$
Co(phen) ₃ ³⁺	Ru(NH ₃) ₅ py ²⁺	1.6	$2 \times 10^3 (1)^{134}$	6×10^3
Co(en) ₃ ³⁺	V _{aq} ²⁺	0.3	$7 \times 10^{-4} (1)^{167}$	2.5×10^{-3}
Co(en) ₃ ³⁺	Eu _{aq} ²⁺	3.8	$\sim 5 \times 10^{-3} (1)^{168}$	2×10^{-2}

Table 19. (cont.)

Oxidant	Reductant	^a $-\Delta G_{12}^{\circ}$	^b k_{12}^{obs}	^c k_{12}^{corr}
		kcal mol ⁻¹	M ⁻¹ sec ⁻¹	M ⁻¹ sec ⁻¹
Co(en) ₃ ³⁺	Cr _{aq} ²⁺	4.6	3×10^{-4} (1) ¹⁶⁷	1×10^{-3}
Co(en) ₃ ³⁺	U _{aq} ³⁺	9.6	0.13 (0.2) ¹⁶⁹	2.5
Co(en) ₃ ³⁺	Yb _{aq} ²⁺	22.2	4.5×10^2 (0.18) ¹⁷⁰	$\sim 1 \times 10^4$
Co(phen) ₃ ³⁺	V _{aq} ²⁺	14.3	4×10^3 (1) ¹³⁴	$\sim 1 \times 10^4$
Co(bpy) ₃ ³⁺	V _{aq} ²⁺	12.6	1.1×10^3 (2) ¹⁷¹	2×10^3
Ru(bpy) ₃ ³⁺	Fe _{aq} ²⁺	12.4	7.2×10^5 (1) ¹⁷²	2×10^6

^aFree energy driving force for cross reaction, determined from the E_f values listed in Table 15 by using $\Delta G_{12}^{\circ} = F(E_f^{\text{ox}} - E_f^{\text{red}})$. See note (a) to Table 17.

^bObserved second-order rate constants for acid-independent pathway. Corresponding ionic strength given in parentheses. Superscripts denote the reference numbers of the data sources.

^cRate constant corrected for the Debye-Hückel work of forming the collision complex from the separated reactants. See note (d) to Table 15.

Table 20. Free Energies of Activation and Driving Forces for Cross Reactions Involving Non-Aquo Cations at 25°C.

Oxidant	Reductant	$-\Delta G_{12}^\circ$ ^a kcal mol ⁻¹	$(\Delta G_{12}^\ddagger)$ ^b corr kcal mol ⁻¹	$0.5\alpha_o\Delta G_{12}^\circ$ ^c kcal mol ⁻¹	$0.5\alpha\Delta G_{12}^\circ$ ^d kcal mol ⁻¹	ΔG_s^W ^e kcal mol ⁻¹
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{V}_{\text{aq}}^{2+}$	6.8	8.8	0.23	-0.4	
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{Eu}_{\text{aq}}^{2+}$	10.3	9.5	0.5	0.8	
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{Cr}_{\text{aq}}^{2+}$	11.1	10.2	0.5	0.3	
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{Yb}_{\text{aq}}^{2+}$	28.7	3.5	4.3	6.0	3.4
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{Np}_{\text{aq}}^{3+}$	-2.3	14.3	0	0	
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{U}_{\text{aq}}^{3+}$	16.0	6.6	1.4	2.9	5.9
$\text{Ru}(\text{en})_3^{3+}$	$\text{Np}_{\text{aq}}^{3+}$	0.5	12.5	0	0.1	
$\text{Ru}(\text{en})_3^{3+}$	$\text{U}_{\text{aq}}^{3+}$	18.8	5.7	1.9	3.4	5.3
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$	$\text{V}_{\text{aq}}^{2+}$	12.7	6.5	0.9	1.3	
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$	$\text{Eu}_{\text{aq}}^{2+}$	16.1	7.6	1.3	2.8	6.6
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	5.9	5.7	0.3	1.4	
$\text{Fe}_{\text{aq}}^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	15.7	5.5	1.4	2.7	5.3
$\text{Ru}_{\text{aq}}^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	3.8	8.4	0.1	0.3	

Table 20. (cont.)

Oxidant	Reductant	$-\Delta G_{12}^{\circ a}$ kcal mol ⁻¹	$(\Delta G_{12}^{\circ})_{\text{corr}}^b$ kcal mol ⁻¹	$0.5\alpha_0 \Delta G_{12}^{\circ c}$ kcal mol ⁻¹	$0.5\alpha \Delta G_{12}^{\circ d}$ kcal mol ⁻¹	$G_s^W e$ kcal mol ⁻¹
$\text{Fe}_{\text{aq}}^{3+}$	$\text{Ru}(\text{en})_3^{2+}$	12.9	6.0	1.0	1.8	4.6
$\text{Fe}_{\text{aq}}^{3+}$	$\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$	9.8	7.6	0.6	2.8	
$\text{Co}(\text{phen})_3^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	7.5	7.9	0.4	1.7	
$\text{Co}(\text{bpy})_3^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	5.8	7.9	0.2	0.6	
$\text{Co}(\text{phen})_3^{3+}$	$\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$	1.6	9.5	0	1.3	
$\text{Co}(\text{en})_3^{3+}$	$\text{V}_{\text{aq}}^{2+}$	0.3	18.3	0	0.2	
$\text{Co}(\text{en})_3^{3+}$	$\text{Eu}_{\text{aq}}^{2+}$	3.8	17.4	0	-0.2	
$\text{Co}(\text{en})_3^{3+}$	$\text{Cr}_{\text{aq}}^{2+}$	4.6	18.8	0.1	0.1	
$\text{Co}(\text{en})_3^{3+}$	$\text{U}_{\text{aq}}^{3+}$	9.6	14.2	0.3	1.6	
$\text{Co}(\text{en})_3^{3+}$	$\text{Yb}_{\text{aq}}^{2+}$	22.2	9.2	1.8	2.7	5.7
$\text{Co}(\text{phen})_3^{3+}$	$\text{V}_{\text{aq}}^{2+}$	14.3	9.2	0.9	2.1	~8
$\text{Co}(\text{bpy})_3^{3+}$	$\text{V}_{\text{aq}}^{2+}$	12.6	10.2	0.7	2.0	
$\text{Ru}(\text{bpy})_3^{3+}$	$\text{Fe}_{\text{aq}}^{2+}$	12.4	6.1	1.4	5.2	5.0

Notes to Table 20.

- ^a Free energy driving force for cross reaction, taken from Table 19.
- ^b Free energy of activation, calculated from k_{12}^{corr} (Table 19) by using eqn (4). See note (b) to Table 16.
- ^c α_o calculated by using eqn (6a) with the $(\Delta G_{11}^*)_{\text{corr}}$ values for the appropriate self-exchange reactions (Table 16) and by assuming that $\Delta G_s^W = 0$. See note (b) to Table 18.
- ^d Calculated from eqn (6) by inserting the appropriate values of $(\Delta G_{11}^*)_{\text{corr}}$ and $(\Delta G_{22}^*)_{\text{corr}}$ (from Table 16), and $(\Delta G_{12}^*)_{\text{corr}}$, and ΔG_{12}° (from this table).
- ^e Apparent work required to form the collision complex from the separated reactants; determined from the listed α_o and α values by using eqn (9) (see text).

$\Delta G_s^W = 0$. Regarded in terms of the constituent activation free energies, $0.5\alpha\Delta G_{12}^\circ$ contains contributions from self-exchange and cross reactions while $0.5\alpha_o\Delta G_{12}^\circ$ contains only kinetic parameters from self-exchange reactions. The resulting values of $0.5\alpha\Delta G_{12}^\circ$ and $0.5\alpha_o\Delta G_{12}^\circ$ are listed in adjacent columns in Tables 18 and 20. From eqns (6) and (6a), it is seen that the difference between these two quantities, $0.5\Delta G_{12}^\circ(\alpha-\alpha_o)$, equals the difference between the experimental values of $(\Delta G_{12}^*)_{\text{corr}}$ and the values of $(\Delta G_{12}^*)_{\text{corr}}^{\text{calc}}$ that are calculated from the self-exchange and driving force parameters with eqns (6) and (6a) and by assuming that $\Delta G_s^W = 0$. For most cross reactions with small enough driving forces so that the "quadratic term" $0.5\alpha_o\Delta G_{12}^\circ$ is small ($\lesssim 0.5 \text{ kcal mol}^{-1}$), inspection of Tables 18 and 20 reveals that $0.5\alpha\Delta G_{12}^\circ \approx 0.5\alpha_o\Delta G_{12}^\circ$, at least within the expected accuracy of the activation free energies used (probably $\pm 0.5\text{--}1 \text{ kcal mol}^{-1}$). In other words, $(\Delta G_{12}^*)_{\text{corr}} \approx (\Delta G_{12}^*)_{\text{corr}}^{\text{calc}}$ so that eqn (1) will be approximately obeyed, in accordance with earlier conclusions (60,134,140). (Admittedly, for a few of these reactions, eqn (1) was employed to obtain one or both of the self-exchange parameters used in Tables 15 and 16.) This agreement is expected since the relative values of $0.5\alpha\Delta G_{12}^\circ$ and $0.5\alpha_o\Delta G_{12}^\circ$ will be very insensitive to the magnitude of ΔG_s^W when the magnitude of ΔG_{12}° is small. However, for cross reactions with larger absolute values of ΔG_{12}° , it is seen that $0.5\alpha_o\Delta G_{12}^\circ < 0.5\alpha\Delta G_{12}^\circ$ [i.e., $(\Delta G_{12}^*)_{\text{corr}}^{\text{calc}} < (\Delta G_{12}^*)_{\text{corr}}$], as expected if $\Delta G_s^W > 0$ in eqn (6a) since

$$\Delta G_s^W = \frac{\Delta G_{12}^\circ}{8} \left(\frac{1}{\alpha_o} - \frac{1}{\alpha} \right) \quad (9)$$

Estimates of ΔG_s^W obtained from eqn (9) for reactions with suitably large values of the quadratic driving force term $0.5\alpha_o \Delta G_{12}^\circ$ (>1 kcal mol⁻¹) are also given in Tables 18 and 20. For most reactions involving two aquo reactants $\Delta G_s^W \sim 6-9$ kcal mol⁻¹ (Table 18). For reactions involving only one aquo reactant, $\Delta G_s^W \sim 4-6$ kcal mol⁻¹ (Table 20).

2. Entropies and Enthalpies of Activation

In view of the marked differences between the experimental free energies of activation and those calculated from the conventional form of the Marcus cross-relation as expressed in eqns (1) or (2), it is of particular interest to compare the behavior of the constituent enthalpies and entropies of activation with the predictions of the Marcus model.

Expressions similar to eqn (2) can be written for the corresponding entropies and enthalpies of activation (134,147):

$$\Delta S_{12}^* = 0.5(\Delta S_{11}^* + \Delta S_{22}^*)(1-4\alpha^2) + 0.5(1+2\alpha)\Delta S_{12}^\circ \quad (10)$$

$$\Delta H_{12}^* = 0.5(\Delta H_{11}^* + \Delta H_{22}^*)(1-4\alpha^2) + 0.5(1+2\alpha)\Delta H_{12}^\circ \quad (11)$$

where α is defined by eqn (2a), ΔS_{12}^* and ΔH_{12}^* are the activation entropy and enthalpy for the cross reaction, ΔS_{11}^* and ΔS_{22}^* are the activation entropies for the constituent self-exchange reactions, ΔH_{11}^* and ΔH_{22}^* are the activation enthalpies for these self-exchange reactions, and ΔS_{12}° and ΔH_{12}° are the entropic and enthalpic driving forces for the cross reaction. Since it is conventional to compute

entropies and enthalpies of activation from rate data by using the pre-exponential factor $k_B T/h$ rather than Z , the quantities ΔS^* and ΔH^* which appear in eqns (10) and (11) are related to the former quantities, $\Delta S^\ddagger$ and $\Delta H^\ddagger$, by (134,147)

$$\Delta S^* = \Delta S^\ddagger - R \ln(hZ/k_B T) + 0.5R \quad (12)$$

$$\Delta H^* = \Delta H^\ddagger + 0.5RT \quad (13)$$

Eqns (10) and (11) can be written in a form compatible with eqn (6) by noting that ΔS^* and ΔH^* are reorganizational parameters that may differ from the "Debye-Hückel corrected" entropies and enthalpies of activation, $(\Delta S^*)_{\text{corr}}$ and $(\Delta H^*)_{\text{corr}}$, by the work terms ΔS_s^W and ΔH_s^W , respectively, such that $(\Delta S^*)_{\text{corr}} = \Delta S^* + \Delta S_s^W$ and $(\Delta H^*)_{\text{corr}} = \Delta H^* + \Delta H_s^W$. (Thus S_s^W and H_s^W are the entropic and enthalpic components of G_s^W , the solvent-related work term described in the previous section.) From the preceding expressions, one can write

$$\begin{aligned} (\Delta S_{12}^*)_{\text{corr}} - \Delta S_s^W &= 0.5[(\Delta S_{11}^*)_{\text{corr}} + (\Delta S_{22}^*)_{\text{corr}} - 2\Delta S_s^W](1-4\alpha^2) \\ &\quad + 0.5(1+2\alpha)\Delta S_{12}^\circ \end{aligned} \quad (14)$$

$$\begin{aligned} (\Delta H_{12}^*)_{\text{corr}} - \Delta H_s^W &= 0.5 [(\Delta H_{11}^*)_{\text{corr}} + (\Delta H_{22}^*)_{\text{corr}} - 2\Delta H_s^W](1-4\alpha^2) \\ &\quad + 0.5(1+2\alpha)\Delta H_{12}^\circ \end{aligned} \quad (15)$$

where α is given by eqn (6a) and $-\Delta G_s^W = -\Delta H_s^W + T\Delta S_s^W$. Since relatively large values of ΔG_s^W were required in order to fit the experimental

free energies of activation with eqn (6), it is of interest to compare the predictions of eqns (14) and (15) with the experimental entropies and enthalpies of activation, respectively, in order to ascertain if the major contribution to ΔG_s^W arises from ΔS_s^W or ΔH_s^W .

Tables 21 and 22 list the cross reactions considered in Tables 17-20 for which activation parameters have been determined. The listed values of $(\Delta H_{12}^*)_{\text{corr}}$ were obtained from the experimental quantities $\Delta H^\ddagger$ by using eqn (13) to yield $(\Delta H_{12}^*)_{\text{app}}$ and then by assuming that $(\Delta H_{12}^*)_{\text{corr}} = (\Delta H_{12}^*)_{\text{app}} - (\Delta G_{\text{DH}}^W)$. This presumes that the coulombic work of forming the collision complexes from the separated reactants is entirely of enthalpic origin at the high ionic strengths encountered. The support for this assertion is that the dependence of the rate constant upon ionic strength for a number of outer-sphere redox reactions has been found to be due almost entirely to the enthalpic term (81,144b). The listed values of $(\Delta S^*)_{\text{corr}}$ were therefore obtained directly from the conventional experimental quantities $\Delta S^\ddagger$ by using eqn (12) (which simply involved the addition of 10 e.u. to $\Delta S^\ddagger$).

Activation parameters $(\Delta H_{11}^*)_{\text{corr}}$ and $(\Delta S_{11}^*)_{\text{corr}}$ for the self-exchange reactions of interest were given in Table 16. Since some of these quantities have not been directly determined, it was necessary to estimate them from the listed values of $(\Delta G_{11}^*)_{\text{corr}}$. It was assumed that $(\Delta S_{11}^*)_{\text{corr}} = -15$ e.u. for $\text{Ru}_{\text{aq}}^{3+/2+}$, $\text{Eu}_{\text{aq}}^{3+/2+}$, $\text{Cr}_{\text{aq}}^{3+/2+}$, and $\text{Yb}_{\text{aq}}^{3+/2+}$, since this value has been observed for both $\text{Fe}_{\text{aq}}^{3+/2+}$ and $\text{V}_{\text{aq}}^{3+/2+}$ self-exchange. For $\text{U}_{\text{aq}}^{4+/3+}$ and $\text{Np}_{\text{aq}}^{4+/3+}$ exchange, $(\Delta S_{11}^*)_{\text{corr}}$ was taken as

Table 21. Thermodynamic Parameters for Some Cross Reactions at 25°C.

Oxidant	Reductant	$-\Delta G_{12}^{\circ a}$ kcal mol ⁻¹	$-\Delta H_{12}^{\circ b}$ kcal mol ⁻¹	$\Delta S_{12}^{\circ c}$ e.u.
Co ³⁺ _{aq}	Fe ²⁺ _{aq}	27.2	27	0
Co ³⁺ _{aq}	Cr ²⁺ _{aq}	53.9	55.5	-5
Co ³⁺ _{aq}	U ³⁺ _{aq}	58.9	60	-3
Fe ³⁺ _{aq}	Ru ²⁺ _{aq}	11.9	9.8	7
Fe ³⁺ _{aq}	V ²⁺ _{aq}	22.5	20.7	6
Fe ³⁺ _{aq}	Eu ²⁺ _{aq}	25.9	27.4	-5
Fe ³⁺ _{aq}	U ³⁺ _{aq}	31.7	33.2	-5
Np ⁴⁺ _{aq}	V ²⁺ _{aq}	9.1	4.6	15
V ³⁺ _{aq}	Eu ²⁺ _{aq}	3.5	6.8	-11
V ³⁺ _{aq}	U ³⁺ _{aq}	9.2	12.5	-11
Ru(NH ₃) ₆ ³⁺	V ²⁺ _{aq}	6.8	12.5	-19
Ru(NH ₃) ₆ ³⁺	Np ³⁺ _{aq}	-2.3	7.9	-34
Ru(NH ₃) ₆ ³⁺	U ³⁺ _{aq}	16.0	25.0	-30
Ru(en) ₃ ³⁺ _{aq}	Np ³⁺ _{aq}	0.5	12.2	-39
Ru(en) ₃ ³⁺	U ³⁺ _{aq}	18.8	29.3	-35
Ru(NH ₃) ₅ py ³⁺	V ²⁺ _{aq}	12.7	19.0	-21
Ru(NH ₃) ₅ py ³⁺	Eu ²⁺ _{aq}	16.1	25.7	-32

Table 21. (cont.)

Oxidant	Reductant	$-\Delta G_{12}^{\circ}$ ^a kcal mol ⁻¹	$-\Delta H_{12}^{\circ}$ ^b kcal mol ⁻¹	ΔS_{12}° ^c e.u.
Fe ³⁺ _{aq}	Ru(NH ₃) ₆ ²⁺	15.7	8.2	25
Fe ³⁺ _{aq}	Ru(en) ₃ ²⁺	12.9	3.9	30
Fe ³⁺ _{aq}	Ru(NH ₃) ₅ py ²⁺	9.8	1.7	27
Co(phen) ₃ ³⁺	Ru(NH ₃) ₆ ²⁺	7.5	6.3	4
Co(phen) ₃ ³⁺	Ru(NH ₃) ₅ py ²⁺	1.6	-0.2	6
Co(en) ₃ ³⁺	Yb ²⁺ _{aq}	22.2	25.5	-11
Co(phen) ₃ ³⁺	V ²⁺ _{aq}	14.3	18.8	-15
Co(bpy) ₃ ³⁺	V ²⁺ _{aq}	12.6	17.1	-15
Ru(bpy) ₃ ³⁺	Fe ²⁺ _{aq}	12.4	25.3	-43

^aFree energy driving force for the indicated cross reaction. Values taken from Tables 17-20.

^bEntropy driving force for cross reaction, determined from the listed ΔG_{12}° and ΔS_{12}° values by using $\Delta H_{12}^{\circ} = \Delta G_{12}^{\circ} + T\Delta S_{12}^{\circ}$.

^cEntropy driving force for cross reaction, determined from the reaction entropies for the appropriate redox couples (Table 15) by using $\Delta S_{12}^{\circ} = (\Delta S_{rc}^{\circ})^{\text{red}} - (\Delta S_{rc}^{\circ})^{\text{ox}}$, where $(\Delta S_{rc}^{\circ})^{\text{red}}$ and $(\Delta S_{rc}^{\circ})^{\text{ox}}$ are the reaction entropies for the couples undergoing reduction and oxidation, respectively.

Table 22. Comparison of Activation Parameters for Cross Reactions Determined at 25°C with Those Calculated from Marcus Theory.

Oxidant	Reductant	$(\Delta G^*)_{12}$ corr kcal mol ⁻¹	^a $(\Delta H^*)_{12}$ corr kcal mol ⁻¹	^b $(\Delta H^*)_{12}$ corr kcal mol ⁻¹	^c $(\Delta S^*)_{12}$ corr e.u.	^d $(\Delta G^*)_{12}$ calc kcal mol ⁻¹	^e $(\Delta H^*)_{12}$ calc kcal mol ⁻¹	^f $(\Delta S^*)_{12}$ calc e.u.
Co ³⁺ _{aq}	Fe ²⁺ _{aq}	11.7	8.0		-13	3.2	0.3	-9
Co ³⁺ _{aq}	Cr ²⁺ _{aq}	8.6	9.2		+2	1.1	-0.7	-6
Co ³⁺ _{aq}	U ³⁺ _{aq}	5.9	1.2		-16	0	0.3	+1
Fe ³⁺ _{aq}	Ru ²⁺ _{aq}	9.5	6.4		-10	7.1	3.6	-12
Fe ³⁺ _{aq}	V ²⁺ _{aq}	8.2	3.4		-16	5.8	2.6	-11
Fe ³⁺ _{aq}	Eu ²⁺ _{aq}	8.8	3.0		-19	5.8	1.6	-14
Fe ³⁺ _{aq}	U ³⁺ _{aq}	6.7	1.2		-18	2.7	-1.2	-13
Np ⁴⁺ _{aq}	V ²⁺ _{aq}	14.0	9.6		-14	12.7	9.5	-11
V ³⁺ _{aq}	Eu ²⁺ _{aq}	17.0	11.0		-20	16.3	10.4	-20
V ³⁺ _{aq}	U ³⁺ _{aq}	11.4	9.4		-7	11.6	5.1	-22
Ru(NH ₃) ₆ ³⁺	V ²⁺ _{aq}	8.8	-0.8		-32	9.4	2.3	-24
Ru(NH ₃) ₆ ³⁺	Np ³⁺ _{aq}	14.3	3.0		-38	13.8	3.0	-36
Ru(NH ₃) ₆ ³⁺	U ³⁺ _{aq}	6.6	-1.8		-28	5.1	-2.8	-26

Table 22. (cont.)

Oxidant	Reductant	$(\Delta G_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	$(\Delta H_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	$(\Delta S_{12}^*)_{\text{corr}}$ e.u.	$(\Delta G_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	$(\Delta H_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	$(\Delta S_{12}^*)_{\text{calc}}$ e.u.
Ru(en)_3^{3+}	$\text{Np}_{\text{aq}}^{3+}$	12.5	0.5	-40	12.4	1.0	-38
Ru(en)_3^{3+}	$\text{U}_{\text{aq}}^{3+}$	5.7	-0.8	-21	4.2	-3.6	-26
$\text{Ru(NH}_3)_5\text{py}^{3+}$	$\text{V}_{\text{aq}}^{2+}$	6.5	-0.4	-23	6.1	-0.1	-21
$\text{Ru(NH}_3)_5\text{py}^{3+}$	$\text{Eu}_{\text{aq}}^{2+}$	7.6	-0.4	-27	6.0	-1.1	-24
$\text{Fe}_{\text{aq}}^{3+}$	$\text{Ru(NH}_3)_6^{2+}$	5.5	2.0	-12	4.3	2.5	-6
$\text{Fe}_{\text{aq}}^{3+}$	Ru(en)_3^{2+}	6.0	2.4	-12	5.2	4.0	-4
$\text{Fe}_{\text{aq}}^{3+}$	$\text{Ru(NH}_3)_5\text{py}^{2+}$	7.6	4.4	-10	5.4	4.5	-3
Co(phen)_3^{3+}	$\text{Ru(NH}_3)_6^{2+}$	7.9	3.2	-15	6.6	1.2	-18
Co(phen)_3^{3+}	$\text{Ru(NH}_3)_5\text{py}^{2+}$	9.5	8.0	-5	8.2	3.5	-16
Co(en)_3^{3+}	$\text{Yb}_{\text{aq}}^{2+}$	9.2	-0.4	-32	8.2	2.3	-20
Co(phen)_3^{3+}	$\text{V}_{\text{aq}}^{2+}$	9.2	3.4	-19	8.0	0.9	-24
Co(bpy)_3^{3+}	$\text{V}_{\text{aq}}^{2+}$	10.2	3.4	-23	8.8	2.6	-21
Ru(bpy)_3^{3+}	$\text{Fe}_{\text{aq}}^{2+}$	6.1	-0.8	-23	2.2	-3.2	-18

Notes to Table 22.

- ^a"Debye-Hückel corrected" free energy of activation, taken from Tables 18 and 20.
- ^b"Debye-Hückel corrected" enthalpy of activation, obtained from experimental activation enthalpies $\Delta H^\ddagger$ by using eqn (13) to obtain $(\Delta H^\ddagger_{12})_{app}$ and then assuming $(\Delta H^\ddagger_{12})_{corr} = (\Delta H^\ddagger_{12})_{app} - (\Delta G^W_{DH})$ (see text). Data sources are the same as those given in Tables 17 and 19.
- ^cEntropy of activation, obtained for experimental activation entropies by using eqn (12). See Tables 17 and 19 for data sources.
- ^dFree energy of activation for cross reaction, calculated by using eqn (6) with the $(\Delta G^\ddagger_{11})_{corr}$ and $(\Delta G^\ddagger_{22})_{corr}$ values from Table 16 and the ΔG°_{12} values from Table 21, along with the value of α determined from eqn (6a) by assuming that $\Delta G^W_s = 0$.
- ^eEnthalpy of activation for cross reaction, determined from the activation enthalpies of the corresponding self-exchange reactions given in Table 16 by using eqn (15), the assumption that $\Delta H^W_s = 0$ (see text).
- ^fEntropy of activation for cross reaction, calculated from eqn (14) by using the activation entropies for the corresponding self-exchange reactions listed in Table 16, by assuming that $\Delta S^W_s = 0$, and by calculating α from eqn (6a) with the assumption that $\Delta G^W_s = 0$ (see text).

-20 e.u., since these values are more compatible with cross-reaction data (see below). Although these estimates are admittedly somewhat arbitrary, the actual, experimentally determined values of $(\Delta S_{11}^*)_{\text{corr}}$ for such small cationic reactants tend to fall within the narrow range between ca. -15 to -20 e.u. (see Table 16). Such values are also suggested by the experimental values of $(\Delta S_{12}^*)_{\text{corr}}$ for cross reactions with small driving forces (see below). For $\text{Ru}(\text{bpy})_3^{3+/2+}$, $(\Delta S_{11}^*)_{\text{corr}}$ was assumed to be ~ 0 e.u. (134).

In order to compare the experimental parameters for cross reactions with the predictions of eqns (14) and (15), values of the entropic and enthalpic driving forces, ΔS_{12}° and ΔH_{12}° , are required. The former can be obtained from the expression: $\Delta S_{12}^\circ = (\Delta S_{\text{rc}}^\circ)^{\text{red}} - (\Delta S_{\text{rc}}^\circ)^{\text{ox}}$ where $(\Delta S_{\text{rc}}^\circ)^{\text{red}}$ and $(\Delta S_{\text{rc}}^\circ)^{\text{ox}}$ are the reaction entropies of the couples undergoing reduction and oxidation, respectively. The $\Delta S_{\text{rc}}^\circ$ values were taken from Table 15 and were determined at ionic strengths comparable to those used for the kinetic measurements. The ΔS_{12}° values are listed in Table 21, along with the corresponding values of ΔH_{12}° which were obtained from the relation: $\Delta H_{12}^\circ = \Delta G_{12}^\circ + T\Delta S_{12}^\circ$ with $T = 298^\circ\text{K}$.

For each cross reaction in Table 22, the experimental activation parameters $(\Delta G_{12}^*)_{\text{corr}}$, $(\Delta H_{12}^*)_{\text{corr}}$, and $(\Delta S_{12}^*)_{\text{corr}}$ are listed alongside the calculated parameters $(\Delta G_{12}^*)_{\text{w=0}}^{\text{calc}}$, $(\Delta H_{12}^*)_{\text{w=0}}^{\text{calc}}$, and $(\Delta S_{12}^*)_{\text{w=0}}^{\text{calc}}$. The calculated values were obtained by inserting the appropriate self-exchange parameters from Table 16 into eqns (6), (15), and (14), setting $\Delta S_{\text{s}}^{\text{W}}$ and $\Delta H_{\text{s}}^{\text{W}}$ equal to zero, and determining α from eqn (6a) by assuming that $\Delta G_{\text{s}}^{\text{W}} = 0$.

Inspection of Tables 21 and 22 reveals that when the cross reactions have small values of ΔS_{12}° and ΔH_{12}° , good agreement occurs between the experimental quantities, $(\Delta S_{12}^*)_{\text{corr}}$ and $(\Delta H_{12}^*)_{\text{corr}}$, and the corresponding calculated parameters $(\Delta S_{12}^*)_{w=0}^{\text{calc}}$ and $(\Delta H_{12}^*)_{w=0}^{\text{calc}}$. Naturally the small ΔH_{12}° and ΔS_{12}° values for these reactions yield small ΔG_{12}° values, and the good agreement between the calculated and experimental entropies and enthalpies dictates a similar relation between $(\Delta G_{12}^*)_{\text{corr}}$ and $(\Delta G_{12}^*)_{w=0}^{\text{calc}}$. As the magnitude of the free energy driving force increases, the progressively smaller values of $(\Delta G_{12}^*)_{w=0}^{\text{calc}}$ that are seen relative to $(\Delta G_{12}^*)_{\text{corr}}$ are typically reflected in values of $(\Delta H_{12}^*)_{w=0}^{\text{calc}}$ that are markedly smaller than $(\Delta H_{12}^*)_{\text{corr}}$ and values of $(\Delta S_{12}^*)_{w=0}^{\text{calc}}$ that are less negative than $(\Delta S_{12}^*)_{\text{corr}}$.

It remains to be seen if the difference between experimental and calculated activation parameter can be traced to an enthalpic or entropic work term. The determination of ΔH_s^W and ΔS_s^W is more difficult than that of ΔG_s^W due to the greater complexity of eqns (14) and (15) relative to eqn (6). However, it is possible to fit the predictions of eqns (14) and (15) with the experimental quantities $(\Delta S_{12}^*)_{\text{corr}}$ and $(\Delta H_{12}^*)_{\text{corr}}$ by trying various values of ΔS_s^W , ΔH_s^W , and ΔG_s^W . This procedure will be effective only in those cases where the work terms have a significant effect on the values of the calculated activation parameters. Inspection of eqns (14) and (15) shows that this will be true when ΔG_{12}° is sufficiently large so that α is significantly greater than zero (eqn (6a)). Table 23 lists the

Table 23. Activation Parameters for some Cross Reactions Having Large Driving Forces. Effect of Including Entropic and Enthalpic Work Terms on Marcus Predictions.

Oxidant	Reductant	$(\Delta G_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	^a $(\Delta H_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	^b $(\Delta S_{12}^*)_{\text{corr}}$ e.u.	^c $(\Delta S_{12}^*)_{\text{corr}}$ e.u.	^d $(\Delta G_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	^e $(\Delta H_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	^f $(\Delta S_{12}^*)_{\text{calc}}$ e.u.
1 Co _{aq} ³⁺	Fe _{aq} ²⁺	11.7	8.0	-13	-13	6.0	0.3 5.5	-19 - 2
2 Co _{aq} ³⁺	Cr _{aq} ²⁺	8.6	9.2	2	2	6.1	-0.3 7.3	-21 4
3 Co _{aq} ³⁺	U _{aq} ³⁺	5.9	1.2	-16	-16	11.0	2.6 21.5	-28 35
4 Fe _{aq} ³⁺	V _{aq} ²⁺	8.2	3.4	-16	-16	7.2	2.5 4.9	-16 - 8
5 Fe _{aq} ³⁺	Eu _{aq} ²⁺	8.8	3.0	-19	-19	7.3	2.0 4.4	-18 -10
6 Fe _{aq} ³⁺	U _{aq} ³⁺	6.7	1.2	-18	-18	6.0	0 5.8	-20 - 1
7 Ru(NH ₃) ₆ ³⁺	U _{aq} ³⁺	6.6	-1.8	-28	-28	6.1	-1.1 0.7	-24 -18
8 Ru(en) ₃ ³⁺	U _{aq} ³⁺	5.7	-0.8	-21	-21	5.6	-1.3 1.2	-23 -15
9 Ru(NH ₃) _{5py} ³⁺	Eu _{aq} ²⁺	7.6	-0.4	-27	-27	6.8	0.2 1.5	-22 -18

Table 23. (cont.)

Oxidant	Reductant	$(\Delta G_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	^a $(\Delta H_{12}^*)_{\text{corr}}$ kcal mol ⁻¹	^b $(\Delta S_{12}^*)_{\text{corr}}$ e.u.	^c $(\Delta G_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	^d $(\Delta H_{12}^*)_{\text{calc}}$ kcal mol ⁻¹	^e $(\Delta S_{12}^*)_{\text{calc}}$ e.u.	^f
10 Fe _{aq} ³⁺	Ru(NH ₃) ₆ ²⁺	5.5	2.0	-12	5.6	1.8 4.2	-13 - 5	
11 Fe _{aq} ³⁺	Ru(en) ₃ ²⁺	6.0	2.4	-12	6.1	3.2 4.8	-10 - 4	
12 Co(en) ₃ ³⁺	Yb _{aq} ²⁺	9.2	-0.4	-32	8.9	2.7 3.7	-21 -18	
13 Ru(bpy) ₃ ³⁺	Fe _{aq} ²⁺	6.1	-0.8	-23	5.5	0.3 11.7	-18 21	

^a"Debye-Hückel corrected" free energy of activation (from Tables 18 and 20).

^b"Debye-Hückel corrected" enthalpy of activation (from Table 22).

^cEntropy of activation (from Table 22).

^dCalculated free energy of activation for cross reaction, obtained with eqns (6) and (6a) by using

$(\Delta G_{11}^*)_{\text{corr}}$ and $(\Delta G_{22}^*)_{\text{corr}}$ from Table 16, ΔG_{12}° from Table 21, and the assumptions that $\Delta G_s^W = 6$ kcal mol⁻¹ for aquo-aquo reactions and that $\Delta G_s^W = 5$ kcal mol⁻¹ for nonaquo-aquo reactions (see text).

^eCalculated enthalpy of activation for cross reaction. For each pair of values listed, the upper one is obtained from eqns (15) and (6a) by assuming that $\Delta G_s^W = -T\Delta S_s^W$, while the lower values were calculated by using the same equations and changing the assumption to $\Delta G_s^W = H_s^W$ (see text).

^fCalculated entropy of activation for cross reaction, obtained from eqns (14) and (6a). The upper value of each pair is calculated by using the assumption $\Delta G_s^W = -T\Delta S_s^W$, while the lower one results from assuming that $\Delta G_s^W = \Delta H_s^W$.

cross reactions from Tables 21 and 22 for which this condition holds. Two sets of activation parameters are given for each system in Table 23. The first set contains experimental values that are taken from Table 22. The other activation parameters in Table 23, labelled $(\Delta G_{12}^*)^{\text{calc}}$, $(\Delta H_{12}^*)^{\text{calc}}$, and $(\Delta S_{12}^*)^{\text{calc}}$, are determined from eqns (6), (6a), (15), and (14) by including trial estimates of the appropriate work terms, ΔG_s^W , ΔH_s^W , and ΔS_s^W . For the aquo-aquo reactions, ΔG_s^W was taken to be 6 kcal mol⁻¹, whereas for the nonaquo-aquo reactions ΔG_s^W was chosen to be 5 kcal mol⁻¹. (The larger ΔG_s^W value for the aquo-aquo reactions is in keeping with the trends found in Tables 18 and 20.) The estimates of $(\Delta G_{12}^*)^{\text{calc}}$ which result from the inclusion of these work terms are seen to agree much more closely with $(\Delta G_{12}^*)^{\text{corr}}$ than did the $(\Delta G_{12}^*)^{\text{calc}}_{w=0}$ values listed in Table 22. Pairs of $(\Delta H_{12}^*)^{\text{calc}}$ and $(\Delta S_{12}^*)^{\text{calc}}$ values are given for each reaction in Table 23. The upper values were determined by assuming that $\Delta G_s^W = -T\Delta S_s^W$, and the lower values by assuming that $\Delta G_s^W = \Delta H_s^W$. These results are also given in graphical form in Figures 5 and 6 which are plots of $(\Delta H_{12}^*)^{\text{corr}}$ versus $(\Delta H_{12}^*)^{\text{calc}}$ and of $(\Delta S_{12}^*)^{\text{corr}}$ versus $(\Delta S_{12}^*)^{\text{calc}}$, respectively. Apart from the $\text{Co}_{\text{aq}}^{3+} - \text{Fe}_{\text{aq}}^{2+}$ and $\text{Co}_{\text{aq}}^{3+} - \text{Cr}_{\text{aq}}^{2+}$ reactions, it is seen that considerably better agreement between the experimental and calculated activation parameters is obtained using the former assumption (i.e., the closed rather than open points in Figures 5 and 6). Essentially the same results were obtained by choosing different values of ΔG_s^W within the range of the estimates given in Tables 18 and 20. Reasonable concordance was also obtained by assigning both entropic

Figure 5. Experimental $(\Delta H_{12}^*)_{\text{corr}}$ for cross reactions corrected for Debye-Huckel work terms plotted against $(\Delta H_{12}^*)^{\text{calc}}$.

Key: $(\Delta H_{12}^*)^{\text{calc}}$ was calculated from eqn (15). Data are taken from Table 23. The labels for each point follow the numbering scheme in Table 23. The calculated activation parameters were obtained by assuming that $\Delta G_s^W = -T\Delta S_s^W$ (closed circles) and $\Delta G_s^W = \Delta H_s^W$ (open circles). Reactions 1-3 involving $\text{Co}_{\text{aq}}^{3+/2+}$ were omitted for clarity. The solid straight line has unit slope and passes through the origin.

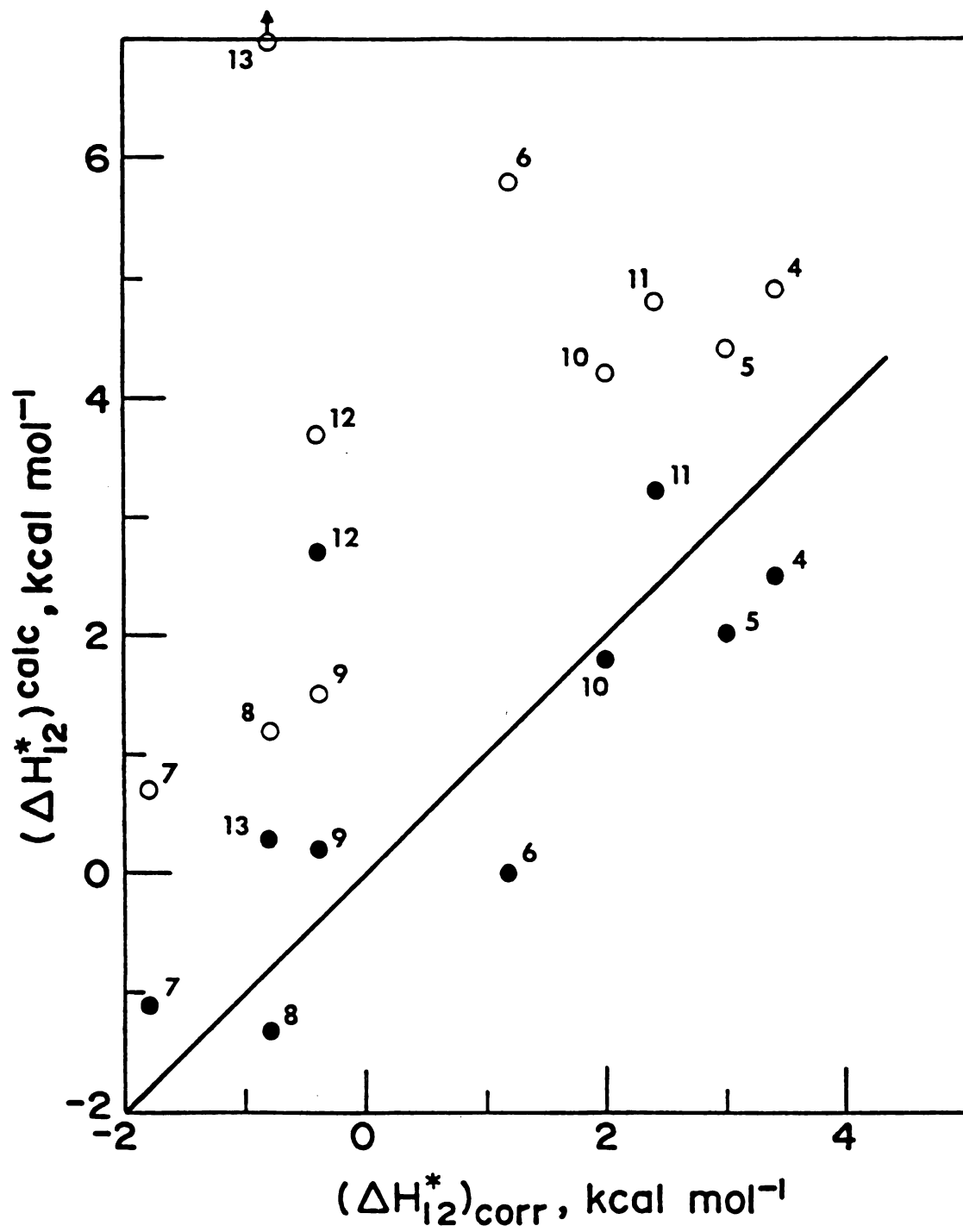


Figure 5.

Figure 6. Experimental $(\Delta S_{12}^*)_{\text{corr}}$ for cross reactions corrected for Debye-Hückel work terms plotted against $(\Delta S_{12}^*)^{\text{calc}}$.

Key: $(\Delta S_{12}^*)^{\text{calc}}$ was calculated from eqn (14).

Other details are as given in the Key to Figure 5.

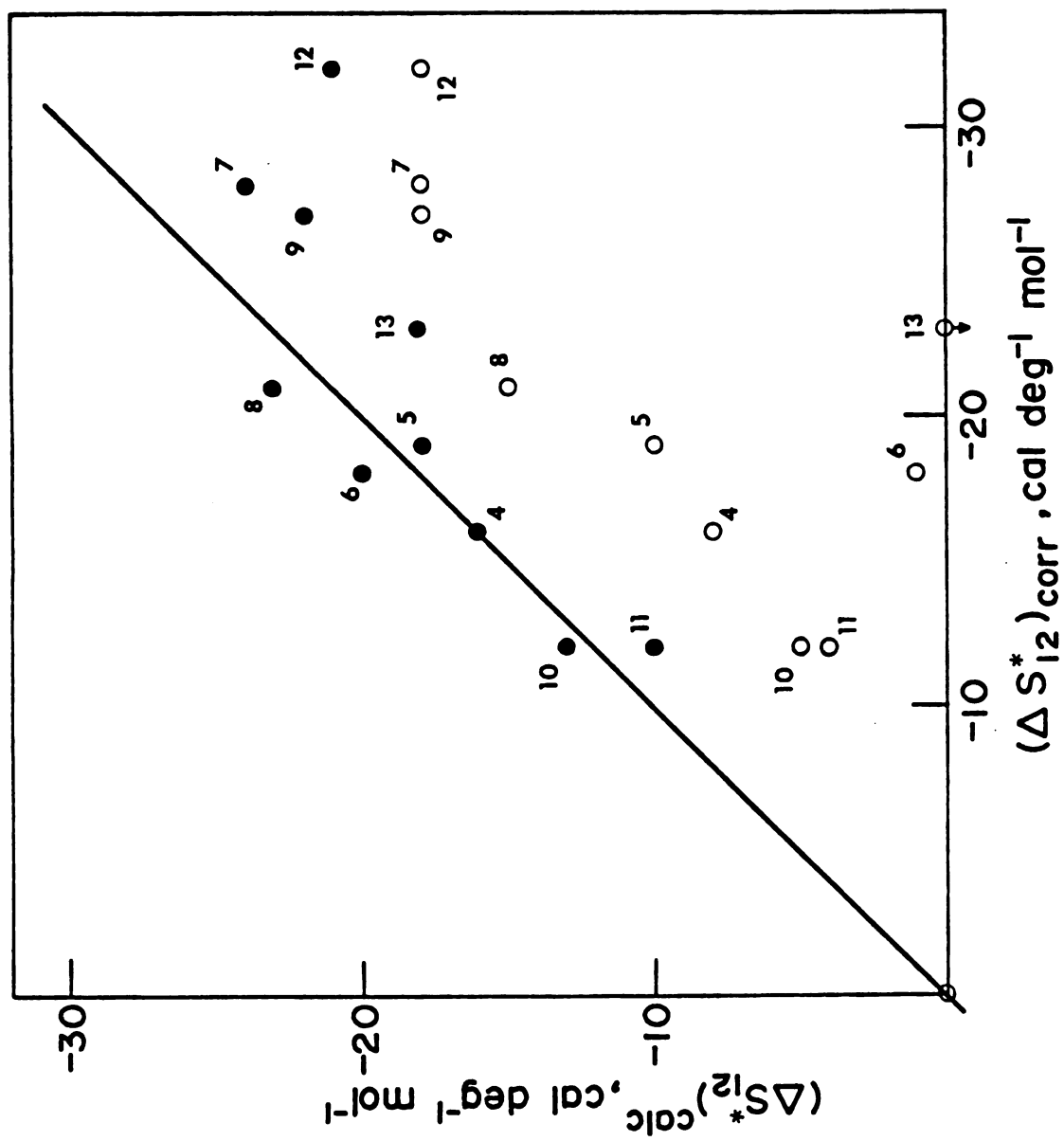


Figure 6.

and enthalpic components to ΔG_s^W , but only when the predominant contributor was assumed to be ΔS_s^W .

C. Discussion

It was noted in the introduction that increasingly marked discrepancies between the experimental rate constants of outer-sphere cross reactions and the predictions of eqn (1) are observed as the thermodynamic driving force becomes extremely large. The foregoing results indicate that such behavior is consistent with the presence of a significant component of the overall free energy of activation which does not respond to changes in the driving force. A simple, albeit not the only, explanation of such behavior is that this part of the activation free energy is associated with the work ΔG^W of forming the binuclear collision complex prior to the rate-determining electron-transfer step. This consideration results in eqns (6), (6a), (14), and (15). However, the derived values of ΔG^W are typically much larger than the Debye-Hückel estimates $(\Delta G^W)_{DH}$ and appear to arise chiefly from unexpectedly large and negative values of the entropic component ΔS^W (ca. -15 to -25 e.u.). It is tempting to speculate that this entropy term has the same origin as the similarly large and negative entropies of activation ΔS^* that are typically observed for self-exchange reactions ($\sim$ -15 to -20 e.u.). Since the reorganization entropy within the binuclear complex is theoretically predicted (60,146) and experimentally confirmed (173) to be close to zero for self-exchange processes, the observed negative values of ΔS^* in these bimolecular reactions could also reflect the unfavorable entropic

work required to form the binuclear complex from the separated reactants.

It remains to consider the possible origins of such large entropic terms. A common feature of all the reactions considered here is that they involve small multi-charged cationic reactants. Consequently, it has been suggested that the negative activation entropies are largely the result of concentrating charge in the dielectric medium (173). Furthermore, the ionic entropy of the transition state appears to be related to its net charge (140a,174). Thus the high polarizing field within the vicinity of the collision complex could result in a substantial local ordering of solvent molecules when this complex is formed from the separated reactants. Such a notion is supported by the observation that the values of the reaction entropies for the redox couples of interest here are frequently much larger than the values predicted from the dielectric-continuum (Born) model (see Chapter IV).

For a number of cross reactions with extremely large driving forces, the derived estimates of ΔG_s^W are close to the overall free energy of activation $(\Delta G_{12}^*)_{\text{corr}}$ (Tables 18 and 20). This suggests that the rate-determining step under these conditions is the formation of the collision complex rather than the electron-transfer step itself (83). In this case estimates of ΔG_s^W would refer to the formation of the transition state prior to the ground-state collision complex, so that the actual values of ΔG_s^W could be substantially smaller than these estimates.

A major assumption that was made in obtaining eqns (5) and (6) and also eqns (14) and (15) from eqn (3) is that the work terms for the corresponding self-exchange and cross reactions are the same. Although this should be approximately the case for cross reactions between structurally similar reactants such as the aquo-aquo reactions considered here, this assumption is less likely to be valid for the amine-aquo cross reactions since amine ligands appear to induce less solvent ordering in the vicinity of multi-charged cations than aquo ligands (see Chapter IV). However, from the form of eqn (3) it is seen that if the work terms for the cross reactions, ΔG_{12}^W and ΔG_{21}^W , are both equal to the mean of the analogous quantities for the self-exchange reactions, ΔG_{11}^W and ΔG_{22}^W , then work terms of any sort will still only appear in the quadratic driving force terms in eqns (5) and (6). (It should be noted that if this cancellation of work terms does not occur, eqn (1) will prove to be significantly in error. This failure will be found even at low driving forces as long as the work terms are sufficiently large.) The fact that the values of ΔG^W for aquo-amine reactions are typically smaller than for aquo-aquo reactions may reflect a smaller degree of solvent ordering around the amine redox center. Such findings are consistent with the markedly larger values of ΔS_{rc}° observed for aquo couples (Chapter IV). These ΔS_{rc}° values had suggested that the aquo complexes induce an unusual degree of solvent ordering in the trivalent oxidation state. Substantial differences have also been observed in the degree of solvent ordering in the transition states for heterogeneous electron transfer for otherwise similar aquo and ammine complexes (124,175).

These large and negative apparent entropies of activation are also expected if nonadiabatic mechanisms are followed; i.e., if the probability κ of electron tunneling in the transition state is small (74,80,140b). Such an effect would indeed appear as an apparent negative entropic work term in eqn (14) if the values of κ for self-exchange and cross reactions are comparable. This possibility has been discussed by Chou et al (134). Nonadiabatic pathways have been suggested to explain the especially slow electron-transfer rates of reactions involving lanthanide and actinide redox couples since the transferred f electrons are shielded from the surrounding environment and therefore are expected to have greater difficulties in tunneling (80). However, cross reactions between f- and d-electron reactants do not exhibit any obviously larger discrepancies with eqns (6), (14), and (15) compared to reactions involving electron transfer between d-acceptor and donor orbitals (Tables 17-23). This provides one argument against the occurrence of strongly nonadiabatic pathways and suggests that cross reactions involving f-electron couples are adiabatic or not especially nonadiabatic. However, non-adiabatic factors may be responsible for some of the large apparent values of ΔG_s^W observed for reactions involving Co(III)/(II) couples (131).

An extensive comparison of experimental rate constants for outer-sphere reactions with the predictions of eqn (1) and of some experimental activation parameters with the predictions of eqns (10) and (11) has recently been given by Chou, Creutz, and Sutin (134).

These workers found discrepancies between the experimental rate parameters and the Marcus predictions which were similar to those noted in the present work. A number of possible explanations for these discrepancies were considered by Chou et al., including non-cancellation of work terms and nonadiabatic factors. On the basis of a comparison of the experimental activation parameters with the values calculated from eqns (10) and (11) using the limited ΔS_{rc}° data then available, Chou et al. tentatively concluded that the unexpectedly small rate constants for the cross reactions originate primarily from the enthalpic rather than the entropic component of the activation free energies (134). This apparent disparity with the present conclusions arises partly from the use of different values of ΔS_{rc}° in ref. 134 and in the present work. The ΔS_{rc}° data employed here are considered to be more reliable as a consequence of the experimental precautions described in Chapter IV. However, the chief reason for the discord arises from the hypothesis embodied in eqns (14) and (15) that the discrepancies between the calculated and observed activation parameters arise entirely from work terms that are independent of the driving force. The observation that a major portion of the differences between a set of observed activation parameters and the values calculated from eqns (14) and (15) lies in the enthalpic (or entropic) terms does not necessarily imply that the factor responsible for the difference is of enthalpic (or entropic) origin. (This connection was made in ref. 134.) Such reasoning is fallacious because a contribution to α arising from either an entropic or enthalpic contribution to ΔG_s^W (eqn (6a)) will affect *both* the activation entropies $(\Delta S_{12}^*)^{calc}$

and enthalpies $(\Delta H_{12}^*)^{\text{calc}}$ calculated from eqns (14) and (15). Although both $(\Delta H_{12}^*)_{w=0}^{\text{calc}}$ and $(\Delta S_{12}^*)_{w=0}^{\text{calc}}$ typically display pronounced differences from the experimental quantities $(\Delta H_{12}^*)_{\text{corr}}$ and $(\Delta S_{12}^*)_{\text{corr}}$ (see Table 22), insertion of an entropic rather than enthalpic work term usually leads to a significantly better fit between the calculated and experimental activation parameters.

Because the Marcus model assumes the barriers to electron transfer to be harmonic, it was reasonable for Chou et al. to consider the possibility that the observed differences between the experimental results and the Marcus predictions are due to anharmonicity of the potential energy barriers. However, it was concluded that the expected magnitude of this effect was insufficient to account for the observed size of the discrepancies (134). One piece of evidence which prompts further consideration of anharmonicity factors is obtained from some recently observed kinetic data for the electrooxidations of $\text{Cr}_{\text{aq}}^{2+}$, $\text{Eu}_{\text{aq}}^{2+}$, and $\text{V}_{\text{aq}}^{2+}$ at the mercury-aqueous interface (176). It was found that all three reactions are accelerated with increasing anodic overpotential (i.e., thermodynamic driving force) to a strikingly smaller extent than predicted by the harmonic Marcus model (176). In other words, these systems exhibit the same type of driving-force-dependent deviations from theory seen for homogeneous reactions. On the other hand, discrepancies between experiment and theory that are substantially smaller and in the opposite direction were observed for the electroreduction rates of $\text{Cr}_{\text{aq}}^{3+}$ and $\text{Eu}_{\text{aq}}^{3+}$ at cathodic overpotentials (176,177). The observed anodic electrochemical behavior could be due to the

presence of strongly anharmonic *free* energy surfaces, apparently arising from the need for additional orientation of solvent molecules in the vicinity of the dipositive aquo reactant prior to electron transfer (176). It is interesting to note that most of the homogeneous cross reactions listed in Tables 17-20 that have rate constants markedly smaller than anticipated from the Marcus model also involve the oxidation of aquo cations.

The present results therefore suggest that the conventional dielectric-continuum models of electron transfer provide an incomplete description of the role of the solvent in some outer-sphere reactions. These models presume that at high ionic strengths essentially all of the solvent reorganization that is required for electron transfer occurs after formation of the precursor complex. In contrast, the present findings suggest that a sizable solvent contribution to the overall activation free energy arises from the formation of the precursor complex from the separated reactants, although the estimates of ΔG_s^W obtained from eqns (6) and (6a) will be markedly oversized if nonadiabatic and anharmonic factors are indeed important. Whatever the detailed reasons for the observed behavior, it seems plausible that specific solvation factors can play an important role in determining the kinetics of cationic redox reactions in aqueous solution. The further acquisition of kinetic and thermodynamic data, both in solution and at electrode surfaces for redox reactions involving systematic variations in ligand structure and thermodynamic driving force should provide valuable additional information on this important question.

CHAPTER VI
HOMOGENEOUS REDOX KINETICS OF THE EUROPIUM CRYPTATES

A. Introduction

The electrochemical results in Chapter III demonstrated that the heterogeneous charge-transfer rates of $\text{Eu(2.2.1)}^{3+/2+}$ and $\text{Eu(2.2.2)}^{3+/2+}$ were at least two orders of magnitude greater than that for $\text{Eu}_{\text{aq}}^{3+/2+}$. It would be of interest to learn if similar rate enhancements take place in the homogeneous electron-transfer reactions of these cryptates. For a wider perspective, one can attempt to ascertain how and why the kinetic behavior of the Eu(III)/(II) couple is altered by encapsulation within a cryptate cavity.

These objectives may be realized by determining the reaction mechanisms and rate constants for redox reactions between the Eu cryptates and other one-electron reductants or oxidants. The rate constants for the outer-sphere cross reactions can then be used in the Marcus cross-relation to obtain the self-exchange rate constants for the Eu cryptates. These rate parameters will provide a good index of the intrinsic redox reactivity of the $\text{Eu(2.2.1)}^{3+/2+}$ and $\text{Eu(2.2.2)}^{3+/2+}$ couples.

Other data from Chapter III have a bearing on this procedure. The studies of the ligation kinetics indicate that the dissociation of the Eu cryptates is a relatively slow process. Thus, these complexes will retain their structural integrity for a considerable period of time. This substitutional inertness of the Eu cryptates will play an important role in determining which electron-transfer mechanisms are available to the cross reactions. The values of the cross-reaction equilibrium constants employed in the Marcus

cross-relation can be calculated by using the thermodynamic data from Chapters III and IV.

The literature does not appear to contain any studies on the homogeneous redox kinetics of any cryptate couple. Some work has been done on the $\text{Co}(\text{sep})^{3+/2+}$ couple (88). The sep (sepulchrate) ligand is an octaaza analog of (2.2.2) except that the bridgehead nitrogens in sep are joined to the other heteroatoms by methylene linkages. The self-exchange rate constant for $\text{Co}(\text{sep})^{3+/2+}$ has been determined to be $5 \text{ M}^{-1} \text{ s}^{-1}$, although the interpretation of this result has not been straightforward (88b).

B. Results

Rate constants at 25°C were determined for the following reactions:
 $\text{Eu}(2.2.1)^{3+} + \text{Eu}_{\text{aq}}^{2+}$, $\text{Eu}(2.2.1)^{3+} + \text{V}_{\text{aq}}^{2+}$, $\text{Eu}(2.2.1)^{2+} + \text{Co}(\text{NH}_3)_6^{3+}$,
 $\text{Eu}(2.2.2)^{3+} + \text{Eu}_{\text{aq}}^{2+}$, and $\text{Eu}(2.2.2)^{3+} + \text{V}_{\text{aq}}^{2+}$. In each case, the progress of the reaction was followed by periodically recording the polarographic limiting current of the cryptate reactant. Pseudo first-order conditions were employed with the noncryptate reactant present in at least a ten-fold excess. Linear plots of $\ln i$ vs. time (where i is the polarographic limiting current corrected for background) were obtained which indicate that a first-order rate law is operative under these conditions. Since the cryptate concentration is directly proportional to i (see eqn (6) in Chapter III), the slope of the $\ln i$ vs. t plot will be the same as that for a $\ln [\text{cryptate}]$ vs. time plot. The slope of either plot yields an experimental rate constant k_{exp} which describes the overall rate of disappearance of the cryptate

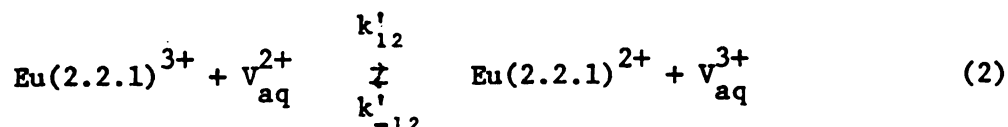
reactant. Since this rate is the sum of the rates of cryptate consumption via the electron-transfer and dissociation reactions, one must sometimes subtract out the contribution of the latter process in order to obtain the rate constant for the redox reaction. This is not difficult since the dissociation rate constants of the cryptates have already been determined under a wide range of conditions (Chapter III). The dissociation process was found to be a minor but significant contributor to the observed rates of consumption of $\text{Eu}(2.2.2)^{3+}$ and $\text{Eu}(2.2.1)^{2+}$. On the other hand, the dissociation rate of $\text{Eu}(2.2.1)^{3+}$ is quite slow and has a negligible ($< 1\%$) influence on the k_{exp} values of the reactions which involve this cryptate.

The dissociation-corrected rate constant can be determined as a function of the concentration of the noncryptate reactant. (This last quantity can be calculated from the appropriate diffusion-limited polarographic current.) A first-order relation is obtained, which enables one to conclude that the overall rate law for these cryptate redox reactions is:

$$\text{Rate} = k'_{12}[\text{oxidant}][\text{reductant}] \quad (1)$$

This rate law was followed by all reactions except the one between $\text{Eu}(2.2.1)^{3+}$ and $\text{V}_{\text{aq}}^{2+}$. The rate of this reaction decayed more rapidly than predicted by eqn (1), and one did not find the usual decrease in the cryptate current when this reaction was carried out in concentrated perchlorate media ($\sim 0.1\text{--}0.2 \text{ M}$). A slight decrease followed by an increase in current was observed instead. This last problem

was eliminated by the use of PF_6^- electrolytes, but the unexpectedly slow reaction rates were still encountered. A method of treating the slow kinetics of the $\text{Eu(2.2.1)}^{3+} - \text{V}_{\text{aq}}^{2+}$ reaction was obtained by considering the following scheme:



Because the equilibrium constant for this reaction is small ($K=7$) the back reaction will have a significant effect on the observed rate. The current-time behavior was then found to conform to a modified form of eqn (1) which includes a correction for the back reaction:

$$\text{Rate} = k'_{12} [\text{Eu(2.2.1)}^{3+}] [\text{V}_{\text{aq}}^{2+}] - \frac{k'_{12}}{K} [\text{Eu(2.2.1)}^{2+}] [\text{V}_{\text{aq}}^{3+}] \quad (3)$$

where K is the equilibrium constant for reaction (2). The other redox reactions have large equilibrium constants or are chemically irreversible, so no back-reaction corrections are needed in these cases.

The source of the problems encountered in perchlorate media is unclear. The observed current-time behavior indicates that $\text{V}_{\text{aq}}^{3+}$ is being produced by some means besides the cryptate reaction. While ClO_4^- slowly oxidizes $\text{V}_{\text{aq}}^{2+}$ to $\text{V}_{\text{aq}}^{3+}$ (160,178), the rate of this reaction appears to be too slow to explain the results obtained. However, these earlier studies were performed at significantly higher acid concentrations ($[\text{H}^+] \approx 0.5 \text{ M}$) than the present study, so an inverse-acid catalysis may be producing the faster rates found in the latter.

Studies of the acid dependence of k'_{12} , the experimental cross-reaction rate constant, revealed a relation of the form

$$k'_{12} = k_{12} + k_H/[H^+] \quad (4)$$

for the $\text{Eu(2.2.1)}^{3+} - \text{Eu}_{\text{aq}}^{2+}$ and $\text{Eu(2.2.2)}^{3+} - \text{Eu}_{\text{aq}}^{2+}$ reactions. The other reactions did not show any significant $[H^+]$ dependence for H^+ concentrations in the 1-50 mM range. (Work involving Eu(2.2.2)^{3+} was limited to 1-20 mM H^+ in order to minimize the acid-catalyzed dissociation of this cryptate.) Because of the low precision of the k'_{12} values for $\text{Eu(2.2.1)}^{3+} - \text{Eu}_{\text{aq}}^{2+}$ reaction, one could only obtain estimates of the quantities in eqn (4) ($k_{12} \approx 0.2 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_H \approx 0.4 \pm .02 \text{ s}^{-1}$). The k'_{12} values for the $\text{Eu(2.2.2)}^{3+} - \text{Eu}_{\text{aq}}^{2+}$ reaction also suffered from poor reproducibility, but it was possible to determine that $k_{12} = 1.4 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_H = (1.6 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$. (These problems in reproducibility do not appear to be specific to these cryptate - $\text{Eu}_{\text{aq}}^{2+}$ reactions. Similar results have been found for other redox reactions which involve two lanthanide ions; e.g., $\text{Eu}_{\text{aq}}^{3+} + \text{Yb}_{\text{aq}}^{2+}$ (179).)

Reactions which show an inverse-acid dependence (and other redox reactions as well) have been known to be accelerated by the presence of anions such as Cl^- , Br^- , and SCN^- (59, 140a, 157). The reactions in the present study did not display any discernible rate increases in the presence of Cl^- , even though chloride concentrations of up to 50-100 mM were used.

After performing the various analyses described above, one can

obtain values of k_{12} , the acid-independent cross-reaction rate constant. These are given in Table 24. The k_{12} value for the $\text{Eu(2.2.1)}^{3+} - \text{Eu}_{\text{aq}}^{2+}$ reaction was not included on account of its poor relative precision. The $\text{Co(NH}_3)_6^{3+} - \text{Eu(2.2.1)}^{2+}$ reaction was conducted at an ionic strength of $\mu = 0.066$ due to the limited solubility of the cobalt complex in concentrated perchlorate media. The rate constants for this reaction were corrected to $\mu = 0.1$ by using the following expression (165):

$$\log k = \log k_0 + \frac{2A Z_A Z_B \mu^{1/2}}{1 + B a \mu^{1/2}} \quad (5)$$

where k_0 is the value of the rate constant at $\mu = 0$, Z_A and Z_B are the charges of the reactants, a is the internuclear separation in the precursor complex, and A and B are Debye-Hückel parameters with values of .512 and $3.29 \times 10^{-9} \text{ cm}^{-1}$, respectively, at 25°C (82,180). Approximations for a were obtained from the sum of the radii of the reactants. An estimate for the radius of Eu(2.2.1)^{3+} (5.3 Å) was calculated from the sum of the ligand thickness and the cavity radius (3) while a value of 3.5 Å for $\text{Co(NH}_3)_6^{3+}$ was obtained by assuming the radius of this complex to be closely similar to that given for $\text{Ru(NH}_3)_6^{3+}$ in Chapter IV.

The values of the self-exchange rate constants for the Eu cryptates were then calculated from the k_{12} values in Table 24 by means of the Marcus cross-relation:

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \quad (6)$$

where k_{11} and k_{22} are the self-exchange rate constants for the non-cryptate and cryptate couples, respectively, K_{12} is the equilibrium

Table 24. Rate Constants and Equilibrium Constants
for Cross Reactions Involving Europium Cryptates

Oxidant	Reductant	k_{12} ($\underline{M}^{-1} \text{ s}^{-1}$)	Ionic Strength	K_{12}
$\text{Eu}(2.2.1)^{3+}$	$\text{V}_{\text{aq}}^{2+}$	0.5 ± 0.1	0.10	7.0
$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Eu}(2.2.1)^{2+}$	$.043 \pm .004$	0.066	--
$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Eu}(2.2.1)^{2+}$	$.055 \pm .005$	0.10	--
$\text{Eu}(2.2.2)^{3+}$	$\text{V}_{\text{aq}}^{2+}$	1.5 ± 0.2	0.10	3.7×10^4
$\text{Eu}(2.2.2)^{3+}$	$\text{Eu}_{\text{aq}}^{2+}$	1.4 ± 0.3	0.10	1.3×10^7

constant for the cross reaction and f_{12} is given by

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log(k_{11}k_{22}/Z^2)} \quad (7)$$

where Z , the bimolecular collision frequency in solution, has a value of $6 \times 10^{10} \underline{M}^{-1} \text{ s}^{-1}$ at 25°C (see Chapter V). The k_{11} values used for these calculations are given in Table 25. These values are those for k_{11}^{obs} from Table 15. The k_{11} for $\text{V}_{\text{aq}}^{3+/2+}$ was corrected to $\mu=0.1$ by using eqn (5) with $a = 8 \text{ \AA}$. The $\text{Eu}_{\text{aq}}^{3+/2+}$ value was obtained from the k_{11}^{corr} in Table 15 by subtracting the appropriate Debye-Hückel work term (see note d to Table 15). The formal potentials given in Chapters III and IV were used to calculate K_{12} by using

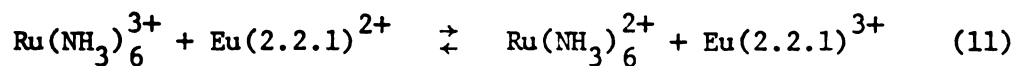
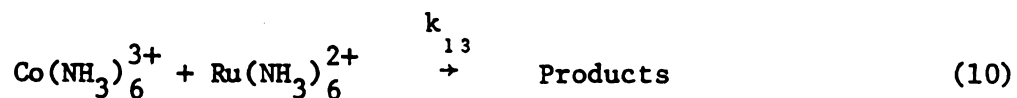
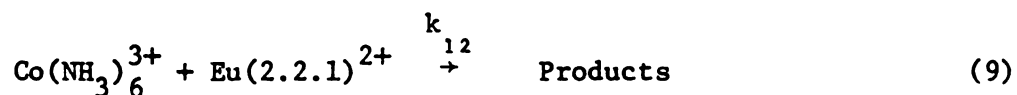
$$K_{12} = \exp\left[\frac{F}{RT}(E_f^{\text{red}} - E_f^{\text{ox}})\right] \quad (8)$$

where E_f^{red} and E_f^{ox} are the formal potentials of the species undergoing reduction and oxidation, respectively. Table 24 summarizes these K_{12} values.

Table 25. Self-Exchange Rate Constants
for Selected Noncryptate Couples

Redox Couple	k_{11} ($\text{M}^{-1} \text{s}^{-1}$)
$\text{V}_{\text{aq}}^{3+/2+}$	2×10^{-3}
$\text{Eu}_{\text{aq}}^{3+/2+}$	1×10^{-5}
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	3×10^3

The analysis of the $\text{Co}(\text{NH}_3)_6^{3+} - \text{Eu}(2.2.1)^{2+}$ reaction is more complicated. An accurate formal potential for the $\text{Co}(\text{NH}_3)_6^{3+/2+}$ couple is not available due to the instability of the $\text{Co}(\text{NH}_3)_6^{2+}$ complex. Fortunately, the calculation of the $\text{Eu}(2.2.1)^{3+/2+}$ self-exchange rate constant is possible if the following series of reactions is considered:



One can then write the Marcus expressions for cross reactions (9) and (10) and obtain:

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (12)$$

$$k_{13} = (k_{11}k_{33}K_{13}f_{13})^{1/2} \quad (13)$$

where k_{11} , k_{22} , and k_{33} are the self-exchange rate constants of $\text{Co}(\text{NH}_3)_6^{3+/2+}$, $\text{Eu}(2.2.1)^{3+/2+}$, and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, respectively. When the ratio k_{12}^2/k_{13}^2 is calculated, k_{11} and the E_f for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ will cancel, yielding

$$k_{12}^2/k_{13}^2 = K_{23}k_{22}/k_{33} \quad (14),$$

provided that $f_{12} \approx f_{13}$. In eqn (14), K_{23} is the equilibrium constant for reaction (11) and can be calculated from the formal potentials of $\text{Eu}(2.2.1)^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ by means of eqn (8). A value of $k_{13} = 0.01 \text{ M}^{-1} \text{ s}^{-1}$ (corrected to $\mu = 0.1$ by using $a = 7 \text{ \AA}$ in eqn (5)) was obtained from reference 164. Thus eqn (14) can be used to compute a value of k_{22} for $\text{Eu}(2.2.1)^{3+/2+}$.

By employing the procedures described above, values of the cryptate self-exchange rate constants could be calculated. The results are presented in Table 26.

Table 26. Self-Exchange Rate Constants for
 $\text{Eu(2.2.1)}^{3+/2+}$ and $\text{Eu(2.2.2)}^{3+/2+}$

Redox Couple	k_{22} ($\text{M}^{-1} \text{ s}^{-1}$)	Cross reaction used to calculate k_{22}
$\text{Eu(2.2.1)}^{3+/2+}$	13	$\text{Eu(2.2.1)}^{3+} + \text{V}_{\text{aq}}^{2+}$
$\text{Eu(2.2.1)}^{3+/2+}$	6.1	$\text{Co(NH}_3)_6^{3+} + \text{Eu(2.2.1)}^{2+}$
$\text{Eu(2.2.2)}^{3+/2+}$	3.9×10^{-2}	$\text{Eu(2.2.2)}^{3+} + \text{V}_{\text{aq}}^{2+}$
$\text{Eu(2.2.2)}^{3+/2+}$	4.2×10^{-2}	$\text{Eu(2.2.2)}^{3+} + \text{Eu}_{\text{aq}}^{2+}$

C. Discussion

1. Reliability of the Self-Exchange Parameters of the Eu Cryptates

Some variation is observed in the k_{22} values in Table 26. The two values for $\text{Eu(2.2.2)}^{3+/2+}$ agree quite well, considering the precision of the cross-reaction rate constants used to calculate them. In fact, this concurrence is probably fortuitous to a certain degree. The self-exchange rate constants listed for $\text{Eu(2.2.1)}^{3+/2+}$ differ from each other by a factor of two. This is of no great moment if one notes the uncertainties involved in the calculations. The k_{11} value of $\text{V}_{\text{aq}}^{3+/2+}$ was determined at $\mu = 2$ (135), and its correction to $\mu = 0.1$ is probably the most error-prone of all of the ionic-strength corrections performed in this work. The validity of the k_{22} value determined from the data of the $\text{Co(NH}_3)_6^{3+} - \text{Eu(2.2.1)}^{2+}$ reaction depends on the soundness of the assumption that was used in deriving eqn (14). Furthermore, the predictions of the Marcus cross-reaction are not

absolutely accurate. It is not uncommon to find that calculated and observed cross-reaction rate constants are only within about an order of magnitude of each other (see Chapter V and reference 60). Therefore, it is not surprising that the same sort of small disparities appear when self-exchange parameters are obtained from cross-reaction data. Thus, reasonable compromise k_{22} values are $10 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Eu}(2.2.1)^{3+/2+}$ and $0.04 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Eu}(2.2.2)^{3+/2+}$.

2. Mechanistic Implications of the Inverse-Acid Dependence of k'_{12}

The above self-exchange parameters were calculated with the assumption that the acid-independent cross-reaction rate constants corresponded to outer-sphere electron transfer. At the outset, one might think that the encapsulation of the Eu(III) or Eu(II) ion within the cryptate cavity would rule out inner-sphere reactions by preventing the formation of ligand bridges. However, the $[\text{H}^+]^{-1}$ dependences of the experimental cross-reaction rate constant (such as those seen for the $\text{Eu}(2.2.1)^{3+} - \text{Eu}_{\text{aq}}^{2+}$ and $\text{Eu}(2.2.2)^{3+} - \text{Eu}_{\text{aq}}^{2+}$ reactions) have usually been ascribed to the presence of an inner-sphere mechanism which proceeds via a hydroxide bridge. Contrary to initial impressions, this type of mechanism is possible for the cryptate reactions. As noted in Chapter III, $\text{Eu}(2.2.1)^{3+}$ and $\text{Eu}(2.2.2)^{3+}$ associate strongly with OH^- . Thus one can conceive of a reaction intermediate in which a hydroxide ion is shared by the trivalent cryptate and $\text{Eu}_{\text{aq}}^{2+}$. This is not necessarily a classical ligand-bridged intermediate. A species of this kind would require the hydroxide to penetrate between the strands of the cryptate and to coordinate directly to the Eu(III) ion.

This arrangement may aid the conduction of the electron between the redox centers. Such an effect would be especially important if one believes electron transfer involving f orbitals to be nonadiabatic (80). However, as pointed out in Chapter V, the degree of nonadiabaticity for lanthanide reactions appears to be no greater than that for other types of reactions. In addition, the inspection of molecular models shows that the formation of a direct bridge will come at the expense of a considerable distortion of the ligand configuration. This alteration in the ligand conformation could result in an increase in the inner-shell reorganizational barrier to electron transfer. Therefore, a direct bridge is normally a reasonable explanation for an inverse-acid pathway, but under the present circumstances, one finds a number of structural arguments against the formation of such species.

The interaction between the trivalent cryptate and OH^- need not be the direct complexation discussed above. It is possible that the hydroxide ion could displace one of the water molecules immediately adjacent to the cryptate. If this hydroxide were also to coordinate with the $\text{Eu}_{\text{aq}}^{2+}$ coreactant, one would obtain an "indirect" bridge. The formation of this species would seem more facile than that of the direct bridge since no distortion of the cryptate would be necessary. However, the indirect bridge does not supply unbroken communication between the redox centers. Thus, it is more difficult to see how this arrangement would significantly alter the probability of electron transfer in the activated complex. It could be possible that the

indirect bridge catalyzes the redox reactions by other means. The presence of the hydroxide ion reduces the electrostatic repulsions which are associated with the convergence of the two cationic reactants to form the precursor complex. Because the anion bridge lowers the overall charge of the precursor complex, one could suspect that the change in local solvent ordering that is required to reach the activated complex will be less than that needed in the case where the bridge is absent.

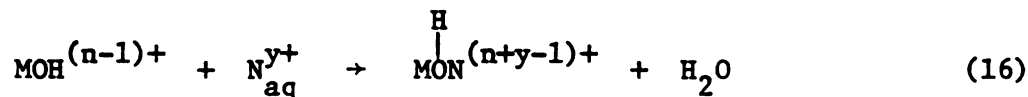
The factors discussed above could account for the observed inverse-acid catalyses of the reactions involving $\text{Eu}_{\text{aq}}^{2+}$, but there is no obvious reason why this effect is not found when $\text{V}_{\text{aq}}^{2+}$ is a co-reactant. (Of course, no $[\text{H}^+]^{-1}$ effect is expected for the $\text{Co}(\text{NH}_3)_6^{3+} - \text{Eu}(2.2.1)^{2+}$ reaction since a hydroxide bridge cannot be formed with the substitutionally inert cobalt complex). The rate constants for some reactions between $\text{V}_{\text{aq}}^{2+}$ and certain aquo-cation oxidants are acid independent (181-183), but these reactions are rapid ($k_{12} \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$). The rate of electron transfer is greater than that for ligand displacement on $\text{V}_{\text{aq}}^{2+}$, which is a relatively substitution-inert species. Thus, the redox reaction takes place before a potential bridging ligand has a chance to displace one of the aquo ligands on $\text{V}_{\text{aq}}^{2+}$. However, when electron transfer is slower, some hydroxide-bridged inner-sphere reactions should be found since there will be an opportunity for ligand substitution to occur on $\text{V}_{\text{aq}}^{2+}$. For example, the $\text{Np}_{\text{aq}}^{4+} - \text{V}_{\text{aq}}^{2+}$ reaction is relatively slow ($k_{12} = 1.3 \text{ M}^{-1} \text{ s}^{-1}$; see Table 17) and has been found to have a $[\text{H}^+]^{-1}$ term in its rate law (159). The rate constants for the cryptate- $\text{V}_{\text{aq}}^{2+}$ reactions are

comparable to that for $\text{Np}_{\text{aq}}^{4+} - \text{V}_{\text{aq}}^{2+}$ and are certainly not fast enough to rule out OH^- bridges on the basis of substitution-inertness arguments.

In order to formulate explanations for the lack of a detectable inner-sphere pathway in the $\text{V}_{\text{aq}}^{2+}$ -cryptate reactions, it is worthwhile to consider the formation of the bridge in greater detail. The usual description of this process begins with the deprotonation of an aquo ligand on one of the reactants which yields a hydroxo complex:



This hydroxide then displaces a ligand on the other reactant N^{y+} while remaining complexed to the original reactant:



Thus, the hydroxide bridge is formed. The deprotonation is customarily assumed to occur on the more highly charged reactant since this species tends to have the larger K_a value. By using the β_1 value for $\text{Eu(2.2.1)}^{3+} - \text{OH}^-$ from Chapter III in conjunction with $K_a = K_w \beta_1$, one can calculate that $\text{p}K_a = 8.5$ for Eu(2.2.1)^{3+} . A value of $\text{p}K_a = 2.3$ has been determined for $\text{Np}_{\text{aq}}^{4+}$ (184,185). Thus the deprotonation of an aquo ligand on $\text{Np}_{\text{aq}}^{4+}$ is greatly favored over that of a water molecule immediately adjacent to Eu(2.2.1)^{3+} . In fact, $\text{V}_{\text{aq}}^{2+}$ ($\text{p}K_a = 6.5$ (186)) has a stronger inclination to deprotonate than Eu(2.2.1)^{3+} . In any case, the less favorable deprotonation equilibria of the reactants in the $\text{Eu(2.2.1)}^{3+} - \text{V}_{\text{aq}}^{2+}$ reaction yield

relatively low concentrations of potential bridge-forming species. Therefore, the concentrations of the intermediates can determine if an effective inner-sphere pathway exists (as for the $\text{Np}_{\text{aq}}^{4+} - \text{V}_{\text{aq}}^{2+}$ reaction) or if electron transfer will be restricted to outer-sphere processes (as in $\text{Eu}(2.2.1)^{3+} - \text{V}_{\text{aq}}^{2+}$). An analogous argument would use the pK_a value for $\text{V}_{\text{aq}}^{3+}$ ($\text{pK}_a \approx 2.7$ (187,188)) to account for the presence of an inverse-acid dependence in the $\text{V}_{\text{aq}}^{3+/2+}$ self-exchange rate (135).

Although the β_1 value for $\text{Eu}(2.2.2)^{3+} - \text{OH}^-$ has not been determined, it should be comparable to that for $\text{Eu}(2.2.1)^{3+} - \text{OH}^-$, if the similarities of the β_1 values of $\text{Eu}(2.2.1)^{3+} - \text{F}^-$ and $\text{Eu}(2.2.2)^{3+} - \text{F}^-$ (see Table 2) are indicative of a general trend. Therefore, the lack of a $[\text{H}^+]^{-1}$ dependence for the $\text{Eu}(2.2.2)^{3+} - \text{V}_{\text{aq}}^{2+}$ reaction could be explained in a manner similar to that used for $\text{Eu}(2.2.1)^{3+} - \text{V}_{\text{aq}}^{2+}$.

The lack of any chloride catalysis of the cryptate reaction rates can also be ascribed to an unfavorable preceding equilibrium. It was noted in Chapter III that neither $\text{Eu}(2.2.1)^{3+}$ nor $\text{Eu}(2.2.2)^{3+}$ associates strongly with Cl^- . Thus, the concentrations of species such as $\text{Eu}(2.2.1)^{3+} - \text{Cl}^-$ and $\text{Eu}(2.2.2)^{3+} - \text{Cl}^-$ will be too low to have any appreciable effect on the observed rates. (While the rate enhancements afforded by the chloride-bridged pathways may be substantial, it is assumed that they are not so phenomenally large that they overcome the effects of the extremely low concentrations of the Cl^- -bridged intermediates.)

The above discussion clarifies some of the observed rate behavior

but does not shed any light on the difference between the cryptate - V_{aq}^{2+} and the cryptate - Eu_{aq}^{2+} reactions. While no K_a value for Eu_{aq}^{2+} appears to be available, it should be less than that for V_{aq}^{2+} , if one assumes that a smaller tendency towards hydrolysis follows from the larger radius (18) and lower charge density of Eu_{aq}^{2+} . Thus on the basis of the deprotonation equilibria, inverse-acid terms would be expected in the rate laws of the cryptate - V_{aq}^{2+} reactions.

One possible clue to the presence or absence of a hydroxide-bridged pathway could reside in the disparate reaction entropies of $Eu_{aq}^{3+/2+}$ ($\Delta S_{rc}^\circ = 48$ e.u.) and $V_{aq}^{3+/2+}$ ($\Delta S_{rc}^\circ = 38$ e.u.). The ΔS_{rc}° value for $V_{aq}^{3+/2+}$ is one of the smallest found for any aquo couple and is an indication that a relatively limited solvent reorganization is necessary to reach the transition state for electron transfer. (This rearrangement may be quite substantial on an absolute scale but it should be considerably less than that for $Eu_{aq}^{3+/2+}$.) As noted above, one of the principal reasons for inverse-acid catalysis is that the formation of the hydroxide bridge decreases the extent of solvent reorganization required in the activation process (i.e., the outer-shell component of the activation free energy is smaller for the inner-sphere reaction). However, if this outer-shell term is relatively small for the outer-sphere pathway in the cryptate - V_{aq}^{2+} reactions (as suggested by the ΔS_{rc}° for $V_{aq}^{3+/2+}$), the hydroxide-bridged mechanism may not offer a great advantage over the outer-sphere route. On the assumption that such circumstances exist, the inverse-acid catalysis may not be detected since the rate enhancement

associated with the hydroxide bridge is not enough to compensate for the unfavorable position of the preceding deprotonation equilibrium (reaction (15)) in acidic solution.

3. The Effect of Cryptate Formation on the Intrinsic Redox Reactivity of the Eu(III)/(II) Couple

From the self-exchange rate constants for the Eu cryptates ($k_{22} = 10 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Eu}(2.2.1)^{3+/2+}$ and $k_{22} = 0.04 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Eu}(2.2.2)^{3+/2+}$), it is obvious that the intrinsic barriers to electron transfer in these complexes are much smaller than the corresponding quantity for $\text{Eu}_{\text{aq}}^{3+/2+}$ ($k_{11} = 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$). Both outer-shell and inner-shell factors contribute to the enhanced reactivity of the Eu cryptates. The reaction entropies for the cryptate and aquo couples ($\Delta S_{\text{rc}}^{\circ} = 48, 27.5, \text{ and } 21 \text{ e.u.}$ for $\text{Eu}_{\text{aq}}^{3+/2+}$, $\text{Eu}(2.2.1)^{3+/2+}$, and $\text{Eu}(2.2.2)^{3+/2+}$, respectively) indicate that the outer-shell component, ΔG_{out}^* , of the activation free energy ΔG_{22}^* should be smaller for the cryptate self-exchange reactions than for the corresponding $\text{Eu}_{\text{aq}}^{3+/2+}$ process. This conclusion stems from the relationship between $\Delta S_{\text{rc}}^{\circ}$ and ΔG_{out}^* which was described in Chapter IV. The $\Delta S_{\text{rc}}^{\circ}$ value of a transition metal redox couple is determined by the interactions between its ligands and the surrounding solvent. The encapsulation of Eu(III)/(II) in the cryptate cavity largely precludes the formation of an extensive, hydrogen-bonded network of "frozen" solvent such as that around $\text{Eu}_{\text{aq}}^{3+}$. This substantial solvent structuring in the vicinity of $\text{Eu}_{\text{aq}}^{3+}$ yields the large $\Delta S_{\text{rc}}^{\circ}$ value for $\text{Eu}_{\text{aq}}^{3+/2+}$ and also gives rise to the considerable solvent-reorganization barrier to electron transfer.

In contrast, the smaller ΔS_{rc}° values of the cryptates demonstrate that the differences in solvent ordering around the trivalent and divalent states are comparatively small, as are the solvent rearrangements needed to reach the activated complexes.

The redox reactivities of the Eu aquo and cryptate couples can also be discussed in terms of ΔG_{in}^* , the inner-shell component of the activation free energy. In most cases, ΔG_{in}^* is associated with the changes in the metal-ligand bond distances which are needed to reach the activated complex. As noted in Chapter III, the ionic radii of Eu^{3+} and Eu^{2+} are 0.95 and 1.17 Å, respectively, so sizable differences are anticipated between the M-L bond lengths in Eu_{aq}^{3+} and Eu_{aq}^{2+} . This implies that large changes in the bond distances are required to go from the reactants to the transition state. On the other hand, the relatively rigid structure of the cryptate should restrict the elongation or compression which the M-L bonds can undergo. While one cannot expect the cryptands to be totally inflexible when complexed to Eu(III) or Eu(II) , they almost certainly represent a more constrained ligand environment than the aquo ligands around $\text{Eu}_{aq}^{3+/2+}$. The restraint placed on the metal-ligand bonds in the cryptates should yield smaller ΔG_{in}^* values for these complexes. Thus, the faster self-exchange rates for the Eu cryptates can be traced to these systems' smaller solvent- and ligand-reorganizational barriers to electron transfer.

The preceding arguments did not make any special attempts to distinguish $\text{Eu(2.2.1)}^{3+/2+}$ from $\text{Eu(2.2.2)}^{3+/2+}$ since the major goal was to point out the qualitative differences between the Eu aquo and

cryptate couples. However, it is clear that the redox reactivities of the two cryptates are quite dissimilar. The k_{22} value of $\text{Eu}(2.2.1)^{3+/2+}$ is over two hundred times greater than that for $\text{Eu}(2.2.2)^{3+/2+}$. The former couple has a $\Delta S_{\text{rc}}^\circ$ value of 27.5 e.u. while $\Delta S_{\text{rc}}^\circ = 21$ e.u. for the latter. Therefore it does not appear that the outer-shell reorganization is less for the (2.2.1) complex. It remains to consider the inner-shell barriers.

The crystal structure of $\text{Eu}(2.2.2)^{3+}$ has been determined (5b). A certain degree of ligand distortion was found, as evidenced by the nonsymmetric arrangement of the donor atoms of the ligand. (This deformation may be an attempt by the ligand to accommodate the highly charged and relatively small Eu^{3+} ion by twisting its diether strands in a manner which increases donor-acceptor interactions.) The crystal structure for $\text{Eu}(2.2.2)^{2+}$ is not available, although one may surmise that it is similar to the corresponding structures of $\text{Ca}(2.2.2)^{2+}$ (189) and $\text{Pb}(2.2.2)^{2+}$ (5e) since the ionic radii of Ca^{2+} and especially Pb^{2+} are comparable to that of Eu^{2+} . The ligand distortions in the Ca and Pb cryptates are less severe and the distributions of the donor atoms are closer to being symmetric. Thus, it seems reasonable that the ligand conformation in $\text{Eu}(2.2.2)^{3+}$ is quite different from that in $\text{Eu}(2.2.2)^{2+}$. Since the ligand configuration in the activated complex is intermediate to those of the trivalent and divalent cryptates, a sizable change in the ligand structure will be included in the activation process. This also means that ΔG_{22}^* will contain a relatively large inner-shell component. The ligand distortions in the $\text{Eu}(2.2.1)^{3+/2+}$ should be less. The smaller cavity of (2.2.1) is more

closely matched to the radius of Eu^{3+} , and favorable interactions between the cation and the donor atoms could be achieved without large deformations in the ligand structure. Furthermore, the (2.2.1) cryptand should be more rigid than (2.2.2) since the monoether strand in the former reduces its flexibility. Thus, the very structure of $\text{Eu}(2.2.1)^{3+/2+}$ may prevent this cryptate from undergoing the kind of conformational changes assumed for $\text{Eu}(2.2.2)^{3+}$. (Unfortunately, the relevant crystallographic data for the (2.2.1) systems are not available, so the above statements are credible but unproven at present.) These considerations indicate that the slower self-exchange in the $\text{Eu}(2.2.2)^{3+/2+}$ system is due to a larger ΔG_{in}^* term which arises from the ligand reorganization needed to reach the activated complex. This inner-shell barrier for $\text{Eu}(2.2.2)^{3+/2+}$ is sufficiently large to overcome the effect of the smaller ΔG_{out}^* for this couple.

The Eu cryptate results do not conform to the correlation between $\Delta S_{\text{rc}}^\circ$ and ΔG_{22}^* which was noted in Chapter IV. The couple with the smaller $\Delta S_{\text{rc}}^\circ$ value ($\text{Eu}(2.2.2)^{3+/2+}$) does not have the larger self-exchange rate. Some understanding of this apparent anomaly can be gained by considering the factors which determine the $\Delta S_{\text{rc}}^\circ$ and k_{22} values. The smaller $\Delta S_{\text{rc}}^\circ$ for $\text{Eu}(2.2.2)^{3+/2+}$ can be ascribed to the larger radii of the trivalent and divalent forms of the couple. The charge density and the tendency to induce local solvent ordering will be less for a $\text{Eu}(2.2.2)$ cryptate than for the $\text{Eu}(2.2.1)$ complex of the same charge. It seems reasonable that this disparity in structuring effects will be greater in the trivalent state, assuming that the square of the charge is the relevant parameter in this situation.

Thus, the relatively lower degree of solvent order around Eu(2.2.2)^{3+} is a major contributor to the smaller $\Delta S_{\text{rc}}^\circ$ for the (2.2.2) couple.

The correlation between reaction entropies and free energies of activation was observed for systems which were significantly different from the cryptates. The redox couples in Chapter IV had much simpler ligand structures (except for $\text{Co(sep)}^{3+/2+}$). In these complexes, the factors which determine the solvent-reorganizational (or outer-shell) barrier to electron transfer also influence $\Delta S_{\text{rc}}^\circ$. The inner-shell barriers associated with compressing or stretching metal-ligand bonds will also be reflected in the reaction entropies since the expansion or contraction of an ionic species will affect the solvent structure in its vicinity. However, inner-shell components to the activation energy which arise from changes in ligand conformation are less likely to be mirrored in $\Delta S_{\text{rc}}^\circ$. It is plausible that the radii of Eu(2.2.2)^{3+} and Eu(2.2.2)^{2+} are quite similar. The alterations in ligand configuration which accompany the interconversion of the trivalent and divalent forms of Eu(2.2.2) will modify some of the internal dimensions of the ligand, but its overall size will remain relatively unchanged. Thus, the $\Delta S_{\text{rc}}^\circ$ for $\text{Eu(2.2.2)}^{3+/2+}$ only corresponds to the outer-shell portion of the activation free energy. The reaction entropy lacks an analog for the large change in ligand conformation in $\text{Eu(2.2.2)}^{3+/2+}$. Therefore, the $\Delta S_{\text{rc}}^\circ - k_{22}$ correlation does not appear to be appropriate for the Eu cryptates.

CHAPTER VII
MISCELLANEOUS EXPERIMENTS

A. Electrochemistry of Other Transition Metal Cryptates

The electrochemistry of several other cryptates was studied. A sample of $\text{Cu}(2.2.1)(\text{NO}_3)_2$ was obtained from Dr. Gansow's group, and cyclic voltammograms of this cryptate in neutral 0.5 M NaClO_4 at 25°C had sweep-rate-independent peak separations of 60 mV. This is quite close to the 57 mV value which is expected for electrochemically reversible, one-electron couples (92). Thus, the encapsulation of Cu(I) in the cryptate cavity stabilizes this oxidation state to a point where it is easily observed in aqueous solution. In contrast, the cyclic voltammograms of $\text{Cu}(\text{NO}_3)_2$ in 0.5 M NaClO_4 had peak separations which were appropriate for a two-electron couple, indicating that $\text{Cu}_{\text{aq}}^{2+}$ is reduced directly to Cu^0 and that the existence of a Cu(I) state is at most transitory under these conditions.

The formal potential of the $\text{Cu}(2.2.1)^{2+}/^+$ couple ($E_f = -0.103 \text{ V}$) was obtained from the mean of the cathodic and anodic peak potentials. By comparing this potential with $E_f \approx -0.085 \text{ V}$ for $\text{Cu}_{\text{aq}}^{2+}/^+$ (190), one concludes that the Cu(II) state is slightly stabilized relative to Cu(I) by the formation of the cryptate. According to equation (1) from Chapter III, the difference between the free energies of complexation of $\text{Cu}(2.1.1)^+$ and $\text{Cu}(2.1.1)^{2+}$ is quite small (only about 0.4 kcal/mole).

Although no detailed studies were performed, the dissociation of $\text{Cu}(2.1.1)^{2+}$ appears to be quite slow. After one month in neutral 0.5 M NaClO_4 at ambient temperature ($\sim 23^\circ\text{C}$), about 75% of the complex remains intact. This result allows a value of $k_d \approx 1 \times 10^{-7} \text{ s}^{-1}$ to be estimated for the dissociation rate constant.

The techniques described in Chapter IV were used to obtain a value of $\Delta S_{rc}^{\circ} = 12.5$ e.u. for $\text{Cu}(2.1.1)^{2+/+}$ in 0.5 M NaClO_4 . This rather low reaction entropy is comparable to those found for other $2+/+$ redox couples. For example, $\Delta S_{rc}^{\circ} = 15$ e.u. for $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+/+}$ and $\Delta S_{rc}^{\circ} = 10$ e.u. for $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+/+}$ (see Chapter IV). These last two systems may not be exact analogs to the $\text{Cu}(2.1.1)^{2+/+}$ since the Ru couples have significantly different ligand structures compared to the cryptate. However, at present it appears that the overall charges of these couples are the main influences on the reaction entropies.

A number of cryptate deposition (i.e., amalgam-formation) reactions were also investigated in aqueous media. Solutions of $\text{Cd}(2.2.1)^{2+}$, $\text{Tl}(2.2.1)^{+}$, $\text{Pb}(2.2.1)^{2+}$, $\text{Cd}(2.2.2)^{2+}$, and $\text{Pb}(2.2.2)^{2+}$ were made by combining a ten-fold excess of the cryptand with an appropriate salt of the metal ion in $0.1 \text{ M Et}_4\text{NClO}_4$. The cyclic voltammograms of each of these cryptates were obtained using a HMDE. All of the current-voltage curves had large, sweep-rate-dependent peak separations. For example, the peak separations for $\text{Pb}(2.2.2)^{2+}$ were 530 mV and 490 mV for scan rates of 200 and 50 mV/sec, respectively. The smallest peak separations (250 mV at a sweep rate of 200 mV/sec) were found for $\text{Tl}(2.2.1)^{+}$. Even with these large peak separations, it was easily seen that the voltammetric waves of the cryptates were shifted to more negative potentials than those of the free metal ions. These results indicate that the metal ions are stabilized by cryptate formation, although these effects cannot be quantified since thermodynamic information cannot be extracted from the irreversible cyclic voltammograms.

The electrochemical irreversibility of these cryptates stems from the involvement of the metallic state in the electrode reactions. Two mechanisms are available to the electroreduction of the cryptates. The so-called EC mechanism consists of the electrochemical reduction of the cryptate (e.g., $\text{Pb(2.2.2)}^{2+} + 2\text{e}^- \rightarrow \text{Pb(2.2.2)}^0$) followed by a chemical step in which the reduction product dissociates to yield the free cryptand and a metal amalgam. The other possibility is the CE mechanism in which the chemical step precedes the electrochemical one. Thus, the dissociation of the cryptate gives the free ligand and metal ion, and this last species is then reduced to the amalgam in a subsequent step.

An explanation of the observed voltammetric behavior in terms of the EC mechanism could face some difficulties, especially if one makes the assumption that the electroreduction of the cryptate yields a metal atom inside the ligand cavity. Given that the atomic radii of Pb, Tl, and Cd are 1.80, 1.90, and 1.55 Å, respectively (191), it is unclear how the cavities of the (2.2.1) and (2.2.2) cryptands are able to accommodate these atoms. The application of the EC mechanism becomes more tenable if some modifications are made in the structure which is assumed for the reduction product. It is conceivable that the activation process for the electrode reaction involves a distortion of the ligand to a point where the metal ion is no longer completely encapsulated. Such an arrangement would allow the metal ion to be reduced without constraining the resulting metal atom to fit inside the cryptate cavity. The reduction product in this case

would be some sort of loose association between the metal atom and ligand which would fall apart easily in the following chemical step. The ligand reorganization in this mechanism would give rise to a substantial inner-shell component to the activation barrier to electron transfer. The large activation energies for the electrode reactions would then be reflected in slow heterogeneous charge-transfer kinetics and electrochemically irreversible behavior.

The slow dissociation rates of the cryptates pose some problems to the application of the CE mechanism to the present electrode reactions. For example, the stability constant of $\text{Pb}(2.2.2)^{2+}$ is 5×10^{12} (15). From Table 8, it is apparent that most divalent (2.2.2) cryptates have formation rate constants of about $10^4 - 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Thus, the dissociation rate constant for $\text{Pb}(2.2.2)^{2+}$ is in the neighborhood of 10^{-9} s^{-1} . This seems to indicate that the dissociation of the cryptate (i.e., the first step of the CE mechanism) occurs too slowly to be seen on the cyclic voltammetric time scale. However, it must be remembered that the estimates made above apply only to bulk solution. The strong electric fields in the interfacial region may bring about field-assisted cryptate dissociation rates which are compatible with the observed electrochemistry.

The slow cryptate dissociation rates and the CE mechanism can also be reconciled if one assumes a somewhat different chemical step. Instead of the complete dissociation of the cryptate, this step would now consist of the partial removal of the metal ion from

the cryptate cavity. The rate of this step or the reduction rate of the intermediate formed in this step would have to be slow enough to account for the observed electrochemical irreversibility, but at the same time, these rates would be much faster than the extremely slow dissociation rates of the cryptates. It should be noted that this new CE mechanism is rather similar to the modified EC mechanism discussed earlier. The main difference is that the distortion of the cryptate yields an activated complex in the latter mechanism while it produces a reaction intermediate in the former. At the present either mechanism appears to be adequate for explaining the observed voltammetric behavior.

At the outset of this work, there had been some hope that the formation of a cryptate would stabilize an uncommon oxidation state of the encapsulated metal ion. This proved to be the case in the $\text{Cu}(2.1.1)^{2+}/+$ couple. On the other hand, no evidence for the existence of $\text{Cd}(2.2.1)^+$ or $\text{Cd}(2.2.2)^+$ was found, although Cd(I) state has been seen in the solid state (192). Evidently the stabilization which Cd(I) would gain through complexation with a cryptand is not sufficient to overcome the strong tendency of this oxidation state to disproportionate to Cd(II) and Cd metal.

B. The $\text{Tl}(2.2.2)^+/\text{Tl(Hg)}$ Couple as a Probe of Cryptate Thermodynamics in Nonaqueous Solvents

While the amalgam-forming electroreductions of the Cd^{2+} and Pb^{2+} cryptates were irreversible, the corresponding reaction for $\text{Tl}(2.2.2)^+$ was found to be electrochemically reversible in a variety of solvents

(namely water, acetonitrile (MeCN), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), and methanol). Cyclic voltammograms of solutions containing Tl^+ and at least a ten-fold excess of (2.2.2) had sweep-rate-independent peak separations of about 60 mV, which is quite close to the value expected for a reversible one-electron process (92). Reversible voltammetric behavior was also obtained for the $Tl(I)/Tl(Hg)$ couple in the absence of (2.2.2) in each of the five solvents listed above. In all cases, the voltammetric half-wave potential $E_{1/2}$ was obtained from the mean of the cathodic and anodic peak potentials. The dependence of $E_{1/2}$ upon the cryptand concentration was found to be in accordance with the Ligane equation, which applies to the reversible amalgam-forming reduction of labile complexes of high stability (193):

$$E_{1/2}^{TlC} - E_{1/2}^{Tl} = -(RT/F)(\ln K_s^{Tl} + m \ln [C]_t) \quad (1)$$

In eqn (1), $E_{1/2}^{Tl}$ and $E_{1/2}^{TlC}$ are the half-wave potentials of the $Tl(I)/Tl(Hg)$ couple in non-complexing media and in the presence of a large excess of cryptand, respectively, $[C]_t$ is the total (analytical) concentration of (2.2.2) cryptand, and K_s^{Tl} is the stability constant of the thallium (I) cryptate, TlC_m .

Data for the dependence of $E_{1/2}^{TlC}$ on $[C]_t$ were analyzed using eqn (1). It was found that $m = 1$ in all solvents; i.e., Tl^+ and (2.2.2) form a 1:1 complex, as expected. A value of $\log K_s^{Tl} = 6.4$ was obtained in aqueous media ($\mu = 0.05$) at 25°C. This agrees quite well with an earlier value of 6.3 which was determined using a potentiometric titration (6).

The reversible electroreduction of the $\text{Tl}(2.2.2)^+/\text{Tl}(\text{Hg})$ couple indicates that the exchange between Tl^+ and $\text{Tl}(2.2.2)^+$ is rapid on the time scale of cyclic voltammetry. This finding is in harmony with the rapid exchange rates obtained from NMR measurements (3,19). It is noteworthy that the previous electrochemical study of $\text{Tl}(2.2.2)^+$ found irreversible behavior for this complex in propylene carbonate (34). Only a stoichiometric amount of the cryptand was present in the experiments described in reference 34. These conditions render the interpretation of the results difficult since the conventional treatment of labile complex-forming systems requires the ligand to be present in a large excess relative to the electroactive metal ion (11). In the present investigation, the concentration of (2.2.2) was always at least ten times that of Tl^+ .

From the form of eqn (1), it can be seen that the $\text{Tl}^+/\text{Tl}(\text{Hg})$ and $\text{Tl}(2.2.2)^+/\text{Tl}(\text{Hg})$ couples provide a direct means of monitoring the activity (or concentration) of free cryptand. Systems of this kind can be classified as electrodes of the second kind and have been labeled "metal complex" electrodes (194,195). Such couples can be combined with competitive complexation methods to allow the determination of the stability constants of the complexes of electroinactive cations (194,195). A method of this type can be employed to determine a wide range of stability constants by using the following procedure. The half-wave potential, $E_{1/2}$, for the $\text{Tl}(\text{I})/\text{Tl}(\text{Hg})$ couple was determined in solutions containing 0.5 mM Tl^+ ($E_{1/2}^{\text{Tl}}$), and then after successive additions of 5-10 mM (2.2.2) cryptand ($E_{1/2}^{\text{TlC}}$) and 15-50 mM of

the electroinactive metal cation M ($E_{1/2}^{TlMC}$). The ionic strength was maintained at 0.05 or 0.1 M using tetraethylammonium perchlorate (TEAP). Reversible cyclic voltammograms were obtained in each case, at least when M was an alkali metal cation. In general, it was observed that $-E_{1/2}^{Tl} < -E_{1/2}^{TlMC} < -E_{1/2}^{TlC}$. The proximity of $E_{1/2}^{TlMC}$ to $E_{1/2}^{Tl}$ or $E_{1/2}^{TlC}$ was dependent on how effectively M could compete with Tl^+ for the cryptand. In order to determine K_s^M , the stability constant for the $M(2.2.2)$ complex, it is necessary to know the equilibrium concentrations of the metal cryptate $[MC]$, the metal ion $[M]$, and the free cryptand in the presence of M , $[C]_M$. As outlined below, $[C]_M$ can be determined from the electrochemical data. Knowing $[C]_M$, the remaining terms $[MC]$ and $[M]$ can be found directly since $[MC] \approx [C]_t - [C]_M$ and $[M] = [M]_t - [MC]$, where $[M]_t$ is the analytical concentration of M . (Strictly speaking, $[MC] = [C]_t - [C]_M - [TlC]$, but the last term is usually quite small relative to the others and its neglect represents an error of 3-5%. If necessary, $[TlC]$ can be calculated from $[C]_M$, K_s^{Tl} , and the analytical concentration of Tl^+ , $[Tl^+]_t$.)

The determination of $[C]_M$ can be accomplished by noting that Buck's equation for the effect of complexation upon reversible voltammetric waves (196) can be written for the competition experiment as

$$E_{1/2}^{TlMC} - E_{1/2}^{Tl} = -\frac{RT}{F} \ln(K_s^{Tl}[C]_M) - \frac{RT}{F} \ln \frac{K_s^{Tl}[C]_M + 1}{K_s^{Tl}[C]_M} \quad (2)$$

(The activity coefficient terms are omitted from eqns (1) and (2) and

elsewhere for simplicity.) Although Buck's equation normally only applies to the case where the free ligand is present in a large excess (197), it should apply in the present case even though the free ligand concentration $[C]_M$ is typically less than $[Tl]_t$. This is because the cryptand concentration will be "buffered" provided that $[C]_t \gg [Tl]_t$ and the equilibrium $M + C \rightleftharpoons MC$ is maintained during the cyclic voltammogram. (If this is not the case, then the shape of the voltammogram will be severely distorted since the concentration of cryptand increases during the cathodic part of the cycle.) Consequently, by obtaining K_s^{Tl} from eqn (1) in the absence of metal ion M and then inserting K_s^{Tl} into eqn (2), one can determine $[C]_M$ and hence K_s^M . In particular, it is interesting to note that when $K_s^{Tl}[C]_M \gg 1$ (i.e., when the stability of the thallium cryptate is sufficiently greater than that for the competing metal cryptate so that $E_{1/2}^{Tl} - E_{1/2}^{TlMC} \gtrsim 100$ mV), the last term in eqn (2) can be neglected, which allows eqn (1) to be subtracted from eqn (2) to yield

$$E_{1/2}^{TlMC} - E_{1/2}^{TlC} = \frac{RT}{F}(\ln[C]_t - \ln[C]_M) \quad (3)$$

In this case, $[C]_M$ and K_s^M can be determined directly from eqn (3). This procedure does not require a knowledge of K_s^{Tl} . Therefore, under these conditions, the Tl(I)/Tl(Hg) couple responds only to the decrease in free cryptand concentration which results when an excess of metal ion M is added. It is noteworthy that K_s^{Tl} is not needed for a determination of K_s^M under these circumstances. In nonaqueous solvents, it is possible that the small concentration of Tl^+ (0.5 mM) is preferentially complexed by water and other impurities, which could

lead to false values of K_s^{Tl} . These incorrect Tl stability constants will not affect the K_s^M measurements unless the impurities vary in concentration upon the addition of M, or if they are capable of binding significantly to the much higher (10-50 mM) concentrations of M that were present in these experiments. It is also important to note that $[C]_M$ can be calculated using eqn (2) or (3) even when $[C]_M \ll [C]_t$, and that the method is generally capable of allowing K_s^M to be obtained even when $K_s^M \ll K_s^{Tl}$. In fact, the practical lower limit of K_s^M that can be determined using this method is simply that which corresponds to appreciable cryptate formation at the concentrations of M and C chosen. Since we find that K_s^{Tl} lies in the range $10^6 - 10^{10}$ in the solvents studied to date, the method described here allows values of K_s^M in the range ca. 10^2 to 10^{10} to be accurately evaluated. (It is difficult to obtain K_s^M values when $K_s^M > K_s^{Tl}$ since the Tl^+ ceases to be an effective competitor. In practice, the difference between $E_{1/2}^{Tl}$ and $E_{1/2}^{TlMC}$ becomes too small to be measured reliably.)

Table 27 lists some preliminary results for K_s^M in DMSO and MeCN. It is seen that good agreement is obtained between the present and earlier determinations of K_s^M for $Cs(2.2.2)^+$ in DMSO (198). Potassium and thallium cations were uniformly found to exhibit the largest values of K_s^M in each solvent, which is in harmony with the judicious fit of these bare cations into the (2.2.2) cryptate cavity.

This simple electrochemical method therefore appears to provide a powerful approach to the exploration of the thermodynamics of cryptate and other macrocyclic complexation in a range of solvents.

Table 27. Formal Stability Constants ($\log K_g$) for Univalent (2.2.2) Cryptates in Dimethylsulfoxide and Acetonitrile at 25°C.

Cryptate	DMSO ^a	MeCN ^b
Li(2.2.2) ⁺	< 1	7.3
Na(2.2.2) ⁺	5.3	10.6
K(2.2.2) ⁺	6.0	11.1
Cs(2.2.2) ⁺	1.6	--
Tl(2.2.2) ⁺	6.2	12.3

^aDetermined at $\mu = 0.05$.

^bDetermined at $\mu = 0.1$.

While its requirement of electrochemically reversible systems may seem restrictive, the Tl probe does offer an advantage over the principal alternative, potentiometry. Because the Tl technique is not a zero-current method, it is less likely to be affected by impurity currents. Thus, the Tl probe can be considered an important complement to the well-established potentiometric methods.

CHAPTER VIII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A. Conclusions

1. Transition Metal Cryptates

A recurrent theme in the studies of transition metal cryptates is the important influence of ion hydration. The relatively low stability constants of the trivalent Eu cryptates result from the enthalpic destabilization associated with the extensive (or at least partial) desolvation of the aquo cations upon their encapsulation within the cryptate cavity. The surprising kinetic stabilities of these trivalent cryptates stem from the large changes in solvent structure which are needed to attain the transition states in the dissociation reactions. One of the primary reasons for the enhanced redox reactivities of the Eu cryptate couples relative to $\text{Eu}_{\text{aq}}^{3+/2+}$ is a smaller solvent-reorganization barrier to electron transfer in the former species. The comparatively weak hydration of the trivalent cryptates could well be the explanation for the tendencies of these ions to associate strongly with F^- and OH^- .

The variations seen in the standard potentials of the $\text{Eu}(2.2.1)^{3+/2+}$, $\text{Eu}(2_{\text{B}}.2.1)^{3+/2+}$, and $\text{Eu}(2.2.2)^{3+/2+}$ couples indicate that the structure of ligand can have a strong influence on the relative stabilities of the encapsulated Eu(III) and Eu(II) oxidation states. Therefore, it would seem that the appropriate alterations in ligand structure could yield a cryptate couple which has a specified oxidizing or reducing ability. The cryptands could be modified by replacing some of the ether oxygens with nitrogen or sulfur donor

atoms, by binding various functional groups to the ethylene bridges, by lengthening or shortening these bridges, or by introducing substituents into the aromatic ring of (2_B.2.1). This last approach could yield a series of structurally similar redox couples with varying standard potentials. These cryptates could be useful in studies of homogeneous electron-transfer kinetics since the intrinsic components of the activation barriers of these complexes could well be reasonably constant while the driving-force components obviously have to vary. One could then investigate the driving-force dependence of homogeneous cross-reaction rate constants. A study of this kind could also be undertaken with structurally dissimilar reactants, but some sort of model would have to be employed in order to account for the effects of the disparate intrinsic terms.

The rate data from Chapter VI appear to support the analysis of Chapter V which suggested that electron transfer involving f orbitals was not especially nonadiabatic. The cross-reaction rate constants in Chapter VI conform to the Marcus cross-relation within the limits of experimental uncertainty. Thus the electron-transfer reactions of the Eu cryptates do not show any indications of nonadiabaticity. In fact, if the $\text{Eu}_{\text{aq}}^{3+/2+}$ couple were nonadiabatic, one would expect the cryptates to be even more so since the encapsulation of Eu(III) or Eu(II) inside the cavity of a large organic ligand should significantly diminish the already low probability for electron transfer within the activated complex. (In other words, one would anticipate that the transferred electron would have to tunnel over a greater distance in the cryptate reactions.) On the basis of the present evidence, the Eu(III)/(II) couples in this study are no less

adiabatic than couples which transfer electrons to and from d orbitals.

2. Reaction Entropies

The effects of hydration also pervade the reaction entropy study. The large ΔS_{rc}° values for M(III)/(II) aquo couples are due to the extensive solvent structure which forms around the trivalent ion as the result of field-assisted hydrogen bonding involving the protons on the aquo ligands. The lower ΔS_{rc}° values of the ammine couples presumably result from the weaker hydrogen bonding between the ammine protons and the surrounding solvent. Thus, interactions between the ligands and the solvent play a major role in determining the ΔS_{rc}° for a transition metal couple. Under certain circumstances, the ligand effects predominate to such an extent that the reaction entropy of a couple can be obtained simply by considering individual contributions from each ligand in the complex. For example, the similar ΔS_{rc}° values of the $\text{Fe}(\text{bpy})_3^{3+/2+}$ and $\text{Ru}(\text{bpy})_3^{3+/2+}$ couples or of the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Os}(\text{NH}_3)_6^{3+/2+}$ couples can be explained in these terms. Perhaps the most graphic instance of the ligand influence is in the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Ru}(\text{NH}_3)_4\text{bpy}^{3+/2+}$, $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$, and $\text{Ru}(\text{bpy})_3^{3+/2+}$ series, where the ΔS_{rc}° values can be obtained by adding together separate components for each bpy and NH_3 ligand. However, the reaction entropy is not always solely dependent on the ligands in the redox couple. The different ΔS_{rc}° values for analogous Co and Ru couples (see Table 11) indicate that the central metal ion can also have a significant effect on the reaction entropy. It would appear that two redox couples will have comparable reaction entropies when

they have the same ligand composition and when the electronic structures of the two central metal ions are similar. These conditions are restrictive but some useful generalizations might be made. The Ru(III)/(II) systems could serve as models for analogous couples in which an electron is transferred to or from a nonbonding orbital, and the appropriate Co(III)/(II) couples may be representative of those systems where an antibonding orbital is involved in the electron transfer. Unfortunately, only a limited number of metal ion couples are suitable for studying the above assertions, so these will remain largely untested at the present.

The reaction entropies provide a convenient means of calculating the entropy of reaction for homogeneous redox processes. These quantities can also be obtained from the temperature dependence of the appropriate equilibrium cell potentials. The potentiometric method has a number of drawbacks. The cell potential of each reaction has to be measured separately. In contrast, a relatively small number of ΔS_{rc}° values can be used to calculate the thermodynamic driving forces of a host of homogeneous reactions. The potentiometric method frequently requires the maintenance of stable concentrations of reactants and products. This can be difficult considering that many of the species in these reactions are unstable with respect to oxidation or aquation, especially at high temperatures. In the ΔS_{rc}° method, these species only need to be present for the duration of a cyclic voltammogram (i.e., a few seconds). Finally, the uncertainties in the ΔS_{rc}° values which stem from extrathermodynamic assumptions will cancel when the difference between two reaction entropies

is taken to calculate the ΔS_{12}° value for a cross reaction. In essence, these advantages of the ΔS_{rc}° method enabled the study performed in Chapter V to scrutinize a wide range of reactions. It would have been impossible, or at best laborious, to obtain the driving-force parameters by means of direct potentiometry.

The correlation between ΔS_{rc}° and ΔG_{11}^* , the activation free energy for self-exchange, proved to be effective in explaining certain patterns in redox reactivity. However, this correlation cannot be applied indiscriminately. It appears to retain general validity when it is employed with relatively simple redox couples, but the problems which are encountered when the correlation is applied to the Eu cryptates may indicate that the correspondence between ΔS_{rc}° and ΔG_{11}^* is not as firm when more complex ligand structures are under consideration. Large changes in ligand conformation can occur in the electron-transfer activation process for such systems. These changes will be reflected in ΔS_{rc}° only if the alteration in ligand conformation has a significant effect on the ability of the solvent to approach the redox center. Therefore, it may well be that the correlation is only useful to a limited degree for complex ligand systems such as those seen in many biological redox couples. On the whole, the $\Delta S_{rc}^\circ - \Delta G_{11}^*$ correlation is best used for interpreting the trends shown by a large number of redox couples (Figure 4 is one example of this use.) The correlation is not exact, so one cannot expect consistent success when applying it to pairs or trios of redox couples unless these systems are very similar to each other.

B. Suggestions for Further Work

Because the hydration of metal cations has emerged as a crucial factor in the cryptate and reaction entropy studies, it will be of interest to determine if similar investigations in nonaqueous solvents yield the same sort of results. The different dielectric constants and specific solvating abilities of these solvents should produce a wide range of ΔS_{rc}° values. These reaction entropies should contain useful information on the solvent structure and the ligand-solvent interactions in nonaqueous solution. One can also expect some changes in the thermodynamics and kinetics of the Eu and Yb cryptates when these complexes are studied in a nonaqueous solvent. Some increases in the cryptate dissociation rates might be found in weakly solvating media. The difference in the formal potentials of the Eu cryptate and solvated Eu couples will be related to the extent of solvation of Eu(III) relative to that of Eu(II).

A number of further investigations on the homogeneous redox kinetics of cryptates could be performed. Information on the reactivity of $\text{Yb(2.2.1)}^{3+/2+}$ would be useful for comparison with the Eu cryptates and also for its own sake. Because the $\text{Yb(2.2.1)}^{3+/2+}$ couple has a very negative standard potential, the reactions of this species with most commonly employed redox reagents will have large driving forces. The relevant reactions in Chapter V all had substantial driving forces and at least one aquo reactant. It would be interesting to determine if the reactions between the Yb cryptate

and some appropriate nonaquo coreactants contain the same solvent-related work terms (ΔG_s^W) found in Chapter V. The presence of the ΔG_s^W term was ascribed to the solvent reorientation needed to form the highly charged precursor complex. It seems likely that much of the solvent structure in these complexes is induced by the aquo ligands on one or both of the reactants. Because nonaquo complexes are less strongly hydrated, it might be expected that a redox reaction between two such species would have a lower ΔG_s^W value. Unfortunately, the extremely negative standard potential of $\text{Yb}(2.2.1)^{3+/2+}$ will cause some difficulties in the determination of the self-exchange rate constants for this couple. The Marcus cross-relation begins to break down when the driving force of a cross reaction is large. This will be the case for the reactions between the Yb cryptate and most well-characterized coreactants. Therefore, one must employ redox couples which also have particularly negative E° values; e.g., $\text{U}_{\text{aq}}^{4+/3+}$ or $\text{Yb}_{\text{aq}}^{3+/2+}$.

The homogeneous redox kinetics of the $\text{Cu}(2.1.1)^{2+/+}$ couple would be worthy of examination. The low $\Delta S_{\text{rc}}^\circ$ value of this couple and the more rigid structure of the (2.1.1) ligand relative to (2.2.1) and (2.2.2) suggest that the self-exchange rate for $\text{Cu}(2.1.1)^{2+/+}$ should be rapid. Studies of the dissociation kinetics of the divalent and monovalent Cu cryptates and the characterization of any anion effects (such as those observed for the Eu(III) cryptates) would be useful preliminaries for the investigation of the electron-transfer reactions of $\text{Cu}(2.1.1)^{2+/+}$.

The range of formal potentials shown by the $\text{Eu}(2.2.1)^{3+/2+}$, $\text{Eu}(2_{\text{B}}.2.1)^{3+/2+}$, and $\text{Eu}(2.2.2)^{3+/2+}$ couples demonstrates that the E_f value of the $\text{Eu}(\text{III})/(\text{II})$ couple can be altered considerably by changes in the cryptand structure. Further insight into this kind of ligand effect could be obtained by determining the formal potentials for complexes formed between $\text{Eu}(\text{III})/(\text{II})$ and the various polyaza and polythia analogs of the (2.2.1), (2.2.1), and (2.1.1) cryptands. The replacement of the oxygen atoms in the cryptands by nitrogen and sulfur should produce large changes in the relative stabilities of the $\text{Eu}(\text{III})$ and $\text{Eu}(\text{II})$ complexes. The nitrogen and sulfur donor atoms could well stabilize the $\text{Eu}(\text{III})$ state via covalent bonding and modify the ligation and electron-transfer kinetics of the trivalent and divalent complexes.

The technique of determining stability constants for (2.2.2) complexes by means of a competition with Tl^+ should prove to be applicable to a large number of solvents. As noted in Chapter VII, this method can be employed when the $\text{Tl}^+/\text{Tl}(\text{Hg})$ and $\text{Tl}(2.2.2)^+/\text{Tl}(\text{Hg})$ couple are electrochemically reversible and when $\text{Tl}(2.2.2)^+$ and the other (2.2.2) complexes under study are substitutionally labile. Since $\text{Tl}(2.2.2)^+$ is quite stable, the Tl^+ competition method can be utilized to determine stability constants which are too large to be obtained from spectrophotometric techniques. This aspect of the Tl^+ method takes on special significance in those nonaqueous solvents where pH titrations cannot be used to determine cryptate stability constants. Thus, the K_s values for a number of (2.2.2) complexes can be obtained in a range of solvents by means of this Tl^+ competition technique.

The enthalpies and entropies of complexation can then be calculated from the temperature dependences of the stability constants. These studies will furnish useful insights into the influences of the solvent on cryptate stability. The Tl^+ method should be easily applicable to univalent cryptates, but some obstacles could be encountered with divalent complexes. As noted in Chapters I and III, a divalent cryptate has a larger stability constant and slower dissociation rate constant than the corresponding univalent complex. Therefore, the Tl^+ ion may not be capable of competing effectively with alkaline earth ions for the (2.2.2) ligand. In other cases, thermodynamic information will not be available since the voltammetric waves will be distorted by the slow ligand exchange kinetics of the divalent cryptate. Despite these possible limitations, the Tl^+ competition method represents a simple and convenient means for probing cryptate stabilities in a variety of solvents.

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96. The (2_B.2.1) cryptand is similar to (2.2.1) except that one of the central dioxyethylene groups is replaced by the analogous catechol (3).
97. Although the determination of ΔS_{rc}° requires at least one extrathermodynamic assumption to be made (see Chapter IV), this uncertainty will cancel when differences in ΔS_{rc}° are considered as in eqn (2).
98. It is important to note that the time required to attain true equilibrium will be determined by the ligand exchange rate (i.e., the first-order rate constant for dissociation of the complex) irrespective of whether the complex is allowed to aquate spontaneously or the free metal ion is allowed to complex with added ligand.
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