

THE ELUCIDATION OF INORGANIC REACTION MECHANISMS BY HIGH PRESSURE STUDIES

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ABSTRACT

Recent studies of the effect of high pressure upon the rates of redox, solvent exchange, nucleophilic substitution and hydrolysis reactions are reviewed. Quantitative predictions of volumes of activation for outer-sphere electron transfer processes are used to interpret redox reactions of uncertain mechanism. Both the volume of activation, and its pressure dependence, may be used to diagnose dissociative and associative substitution processes and also to ascertain the participation of solvent molecules in transition states.

INTRODUCTION

The effect of pressure upon the rate of a chemical reaction in solution is attributed to a volume change which occurs in the activation step of that reaction. If the change in volume on activation is negative, then the reaction is accelerated by an increase of pressure; if the volume change is positive, then the reaction is retarded by an increase of pressure.

This review aims to show how such volume changes can be interpreted to yield information on the detailed molecular rearrangements which make up the reaction mechanisms of inorganic complexes. Authoritative and comprehensive reviews of the application of these ideas to organic systems are available¹⁻⁷ but little is available for inorganic systems. A major reason for this is that only in the last four years has any body of systematic data begun to accumulate for inorganic reactions in solution.

In principle, the interpretation of a volume change is based on inferred changes in nuclear positions. This involves a structural concept which should be intrinsically simpler to handle than the alternative concept of an entropy change which depends on inferred changes in *both* nuclear positions and energy. Traditionally, reaction mechanisms have been interpreted in terms of enthalpies and entropies of activation because the effect of temperature on reaction rates is readily investigated in the laboratory. However, simplifications in modern high pressure techniques and equipment now make volumes of activation readily accessible and these volumes may now be used routinely to interpret reaction mechanisms.

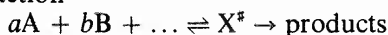
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EVALUATION OF VOLUMES AND COMPRESSIBILITIES OF ACTIVATION

In dilute solution, the change in chemical potential of any species i with pressure is equal to the partial molar volume of that species:

$$(\partial\mu_i/\partial P)_T = \bar{V}_i \quad (1)$$

This fundamental relation may be applied, with the transition state theory, to the generalized reaction



The effect of pressure on the observed rate coefficient k is attributed to the pressure variation of the concentration quotient K^\ddagger describing the assumed equilibrium between the activated complex X^\ddagger in the transition state and the initial reactant state. Then it follows⁸ that

$$-RT(\partial \ln k/\partial P)_T = -RT(\partial \ln K^\ddagger/\partial P)_T = \Delta\bar{V}^\ddagger \quad (2)$$

where the *volume of activation*, $\Delta\bar{V}^\ddagger$, is defined by

$$\Delta\bar{V}^\ddagger = \bar{V}_{X^\ddagger} - a\bar{V}_A - b\bar{V}_B \dots = \bar{V}_{X^\ddagger} - \sum_A a\bar{V}_A \quad (3)$$

The volume of activation is thus the excess of the partial molar volume of the transition state over the combined partial molar volumes of the initial reactant species. When molar concentrations are employed by the experimenter, the rate coefficient k is most conveniently evaluated at different pressures with solutions whose molar concentrations are all constant at 1 atmosphere pressure. Otherwise a small solvent compressibility term ($1.1 \text{ cm}^3 \text{ mol}^{-1}$ for water at 25°C) must be applied to equation 2.

Equation 2 sets one limit to the accuracy with which $\Delta\bar{V}^\ddagger$ may be determined. For $\Delta\bar{V}^\ddagger = -1 \text{ cm}^3 \text{ mol}^{-1}$, the rate coefficient will be increased by only 4% when pressure is increased from 1 to 1000 bar (1 bar = 10^5 pascal = 0.9869 atm). A reliable evaluation of such a small $\Delta\bar{V}^\ddagger$ value thus requires measurements at least up to 3 kbar. Many inorganic reactions require the use of techniques such as spectrophotometry and isotopic tracer analysis and even skilled experimenters obtain rate coefficients with variances of $\pm 2\%$. Fortunately many reactions involve much larger volumes of activation, ranging from +20 to $-20 \text{ cm}^3 \text{ mol}^{-1}$, and evaluation of $\Delta\bar{V}^\ddagger$ usually entails uncertainties of $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$ or less.

It is instructive to compare the accuracy with which ΔS^\ddagger and ΔV^\ddagger can be evaluated. The errors in entropies of activation are derived from those in enthalpies of activation and a rate coefficient. Thus recent work^{9,10} in Caldin's laboratories on the rapid reaction of metal ions with the nitrogen base PADA (pyridine-2-azodimethylaniline) yields the data in Table 1. It

Table 1. Activation parameters for the reaction:
 $M_{\text{aq}}^{2+} + \text{PADA} \rightarrow \text{M-PADA}^{2+}$

System	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta\bar{V}^\ddagger$ $\text{cm}^3 \text{ mol}^{-1}$
$\text{Ni}^{2+} + \text{PADA}$	56.8 ± 4.6	4 ± 8	7.7 ± 0.3
$\text{Co}^{2+} + \text{PADA}$	43.0 ± 2.1	-8 ± 8	7.2 ± 0.2

is difficult to decide on whether these ΔS^\ddagger values are equivalent but the values of $\Delta \bar{V}^\ddagger$ yield an immediately consistent picture. This problem is fairly general with ΔS^\ddagger values close to zero where even the sign of ΔS^\ddagger is in doubt.

A second limitation on the accuracy of evaluating $\Delta \bar{V}^\ddagger$ is that frequently, *but not always*, the volume of activation itself exhibits a pressure dependence; plots of $\ln k$ versus P are not linear as predicted by equation 2. In general, the slope of such graphical plots, proportional to $\Delta \bar{V}^\ddagger$, decreases with increasing pressure. This is shown in *Figure 1* for three reactions, one involving a large negative $\Delta \bar{V}^\ddagger$ (the base hydrolysis of the selenitopentaamminecobalt(III) ion) and the others large positive $\Delta \bar{V}^\ddagger$ (the *trans* \rightarrow *cis* isomerization of diaquo-bis-ethylenediaminecobalt(III) and the base hydrolysis of sulphatopentaammine cobalt(III)).

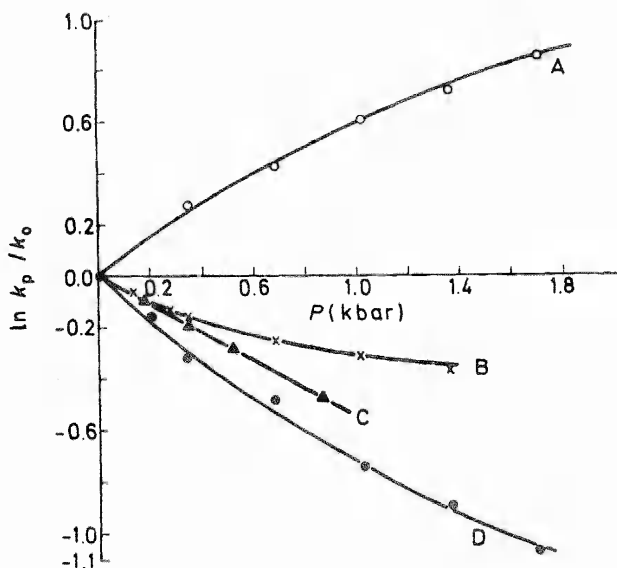


Figure 1. Pressure dependence of volume of activation.

- A (○—○) Base hydrolysis of $\text{Co}(\text{NH}_3)_5\text{OSeO}_2^+$
 B (×—×) *trans* \rightarrow *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ (1M HClO_4)
 C (▲—▲) *trans* \rightarrow *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ (0.05M HClO_4)
 D (●—●) Base hydrolysis of $\text{Co}(\text{NH}_3)_5\text{OSO}_3^+$

The problem is to estimate the limiting slope of such a plot at zero pressure in order to evaluate the *volume of activation at zero pressure*, $\Delta \bar{V}_0^\ddagger$. This has been a topic of some controversy⁷ since the functional pressure dependence of $\ln k$ is unknown. More recently careful analysis by Hyne¹¹ has shown that a quadratic expression

$$\ln k_p = \ln k_0 + bP + cP^2 \quad (4)$$

most accurately describes a variety of reactions and this view is supported by a number of studies in the author's laboratories. Studies in Swaddle's laboratories¹² suggest that an empirical relation based on the Tait equation

may be marginally better in representing the data. However, the difference in estimating $\Delta\bar{V}_0^\ddagger$ is rather small from the two methods; for the aquation of halopentaamminechromium(III) ions typical values^{1,2} are $\Delta\bar{V}_0^\ddagger = -10.6 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ (equation 4) and $\Delta\bar{V}_0^\ddagger = -10.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ (modified Tait equation). Equation 4 will be assumed for subsequent discussion even though it is clear that higher terms are clearly required properly to describe the variation of $\ln k_p$ at very high pressures. The point here is that the present inaccuracies in k_p do not justify a more exhaustive analysis.

The fitting of the experimental data with equation (4) necessitates a careful multiple regression analysis of the statistical significance of the coefficients b and c . A number of separate rate determinations below 2 kbar is especially important in obtaining a reliable value of $\Delta\bar{V}_0^\ddagger$.

The volume of activation at any pressure P , $\Delta\bar{V}_p^\ddagger$, is then given from equation (4) as

$$\Delta\bar{V}_p^\ddagger = -bRT - 2RTcP \quad (5)$$

and the volume of activation at zero pressure is

$$\Delta\bar{V}_0^\ddagger = -bRT \quad (6)$$

We may now define a new quantity representing the pressure dependence of the volume of activation. This will be designated *the compressibility coefficient of activation*, $\Delta\beta^\ddagger$, defined by:

$$\Delta\beta^\ddagger = -(\partial\Delta\bar{V}^\ddagger/\partial P)_T = 2RTc \quad (7)$$

The use of the Δ operator is important since

$$\Delta\beta^\ddagger = (-\partial\bar{V}^\ddagger/\partial P)_T - \sum_A -a(\partial\bar{V}_A/\partial P)_T = \beta^\ddagger - \sum_A a\beta_A \quad (8)$$

The compressibility coefficient of activation is thus the excess of the compressibility coefficient for the transition state over that for the combined initial reactant species. For inorganic systems in water values of $\Delta\beta^\ddagger$ can range from zero to $\pm 20 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ and should be even higher in solvents like methanol whose compressibility is three times that of water. Hyne¹¹ has shown for a number of reaction types analysed with equation (4), that values of $\Delta\bar{V}_0^\ddagger$ are associated with a precision of 1–15% whilst values of $\Delta\beta^\ddagger$ have a precision of 2–41% depending on the magnitude of the pressure effects.

The compressibility coefficient of activation should be distinguished from the related *compressibility of activation*, $\Delta\kappa^\ddagger$, defined by

$$\Delta\kappa^\ddagger = -(\partial\Delta\bar{V}^\ddagger/\partial P)_T/\Delta\bar{V}^\ddagger = \Delta\beta^\ddagger/\Delta\bar{V}^\ddagger \quad (9)$$

Values of $\Delta\kappa^\ddagger$ need to be quoted when comparing different reactions but unlike the compressibility coefficient, $\Delta\kappa^\ddagger$ cannot be separated into a linear combination of terms from the transition state and the initial state.

The non-linear dependence of $\ln k_T$ upon pressure has often been treated rather as a hindrance in estimating $\Delta\bar{V}_0^\ddagger$. However, in some of the examples which follow the thesis will be developed that the values of the compressibility coefficient offer more supplementary mechanistic information than has been used hitherto. This information is analogous to that deduced from ΔC_p^\ddagger

values derived from the temperature dependence of ΔH^\ddagger . However, it is argued here that the sign and magnitude of $\Delta\beta^\ddagger$ is more reliably deduced from pressure studies than is ΔC_p^\ddagger from temperature studies.

THE VOLUMES AND COMPRESSIBILITIES OF COMPLEX IONS

The different stereochemistries and dimensions of most coordination complexes of metal ions are well recognised. However, in the present context all complexes, regardless of their actual coordination numbers, will be assumed to be spherical species, each with a characteristic average radius. This assumption is not too extreme since only changes in volume in passing from the reactant state to the transition state are under discussion, rather than absolute volumes. Thus a five-coordinate intermediate will be assumed to sweep out the same volume in solution as its six-coordinate precursor. In the limit, formation of a dissociated activated complex should then involve a positive $\Delta\bar{V}_0^\ddagger$ value equal to the effective volume of the leaving ligand (Figure 2). However, these expectations would be invalid if the compressibility of the transition state were much greater than the reactant state; dissociation would then be accompanied with a significant decrease in the radius of the 'spherical' activated complex.

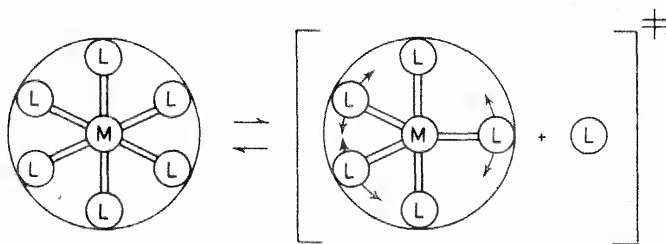


Figure 2. Volume of activation for a limiting dissociative reaction.

A reasonable estimate of the compressibility of a complex may be derived from the potential function¹³ in which a metal ion of charge Ze is visualized as surrounded by n dipoles of permanent dipole moment μ with a metal-ligand distance, d ,

$$U(d, z) = -nZe\mu/d^2 + B/d^m \quad (10)$$

Hush¹³ has shown that the repulsive exponent m may be calculated from the relation

$$m = 2 + \log(z/z - 1)/\log(d_{z-1}/d_z) \quad (11)$$

where d_{z-1} and d_z are the metal-ligand distances in complexes of oxidation state $(z - 1)$ and (z) respectively. The repulsive constant B may be readily eliminated to yield the potential energy U for an equilibrium metal-ligand bond distance d_0 :

$$U = nZe\mu(1 - 2/m)/d_0^2 \quad (12)$$

The compressibility of the complex ion is defined by

$$\kappa = -(\partial V/\partial P)_T/V \quad (13)$$

where V is the intrinsic volume of the complex ion. Thence it follows that

$$\kappa = 6\pi d_0^4 r/nZe\mu(m-2) \quad (14)$$

where r is the radius of the spherical complex ion and the change in this radius with pressure is

$$(\partial r/\partial P)_T = -\kappa r/3 \quad (15)$$

In the case of a crystal-field-stabilized ion it may be shown that

$$\kappa = 6\pi d_0^4 r/\{nZe\mu(m-2) + 3(m-6)C\Delta/d_0^4\} \quad (16)$$

where Δ is the crystal-field splitting and the quantity C is defined in terms of the number of electrons, $n(\epsilon)$ of symmetry $d(\epsilon)$ and $n(\gamma)$ of symmetry $d(\gamma)$, as

$$C = 4n(\epsilon) - 6n(\gamma) \quad (17)$$

For a typical case, the compressibility of the $\text{Ni}(\text{NH}_3)_6^{2+}$ cation may be calculated from equation 16 as $\kappa = 2.2 \times 10^{-6} \text{ bar}^{-1}$. Hush¹³ has deduced from the observed pressure dependence of electronic absorption bands of crystalline $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ that $\kappa = 1.45 \times 10^{-6} \text{ bar}^{-1}$. The agreement is satisfactory (especially so when the polarizability of the NH_3 ligands is not included in the potential function in equation 10) and establishes the magnitude of $\partial r/\partial P = -0.6 \times 10^{-3} \text{ \AA kbar}^{-1}$ for the metal-ligand bond; this represents a negligible change in physical volume over a large pressure range. Likewise the contraction of a dipolar ligand of radius r_L is readily estimated from a known stretching force constant, k , as

$$(\partial r_L/\partial P)_T = 4\pi r_L^4/k \quad (18)$$

For the case of an NH_3 ligand with $k = 6.25 \times 10^5 \text{ dyn cm}^{-1}$ then $(\partial r_L/\partial P)_T = -1.3 \times 10^{-4} \text{ \AA kbar}^{-1}$, which is even less than the contraction in the metal-ligand bond.

We are now in a position to estimate the probable volume change when the six-coordinate $\text{Ni}(\text{NH}_3)_6^{2+}$ cation generates a five-coordinate transition state of dissociation of one ammine ligand. The reactant $\text{Ni}(\text{NH}_3)_6^{2+}$ cation with a calculated $\kappa = 2.2 \times 10^{-6} \text{ bar}^{-1}$ has an intrinsic volume of $138 \text{ cm}^3 \text{ mol}^{-1}$. The transition state species $\text{Ni}(\text{NH}_3)_5^{2+}$ with $\kappa = 1.8 \times 10^{-6} \text{ bar}^{-1}$ (equation 16) is estimated to have an intrinsic volume of $137.9 \text{ cm}^3 \text{ mol}^{-1}$ based on an estimated metal-ligand bond contraction of 0.0005 \AA at 1 kbar pressure. This small volume change ($\sim 0.1 \text{ cm}^3 \text{ mol}^{-1}$) is less than present-day experimental errors in $\Delta \bar{V}_0^\ddagger$ and in any case is likely to be an overestimate because of the neglect of polarizabilities in the potential function.

In general cases, for complex ions of charge 2+ and 3+ with metal-ligand distances ranging from 2.0 to 2.4 \AA , the calculated compressibility values of κ range from $0.9 \times 10^{-6} \text{ bar}^{-1}$ to $2.8 \times 10^{-6} \text{ bar}^{-1}$. *These low compressibilities imply that these complex ions may be reasonably treated as incompressible spheres in their reactions.* These compressibilities are significantly less than the value assumed for a 1+ ion by Whalley¹⁴, $\kappa = 5 \times 10^{-6} \text{ bar}^{-1}$, in

discussing electrostatic interactions of ions in solution. Larger compressibilities of this order are calculated only to arise with 1+ ions with large ionic radii, as in the case of $\text{Ti}(\text{OH}_2)_6^+$ discussed later.

The discussion so far has considered only the intrinsic volume of a complex ion, \bar{V}_{int} , in terms of its first coordination sphere. The partial molar volume of a complex ion in solution contains a second major contribution, \bar{V}_{el} , from the electrostatic interaction of the charged ion with the solvent such that $\bar{V} = \bar{V}_{\text{int}} + \bar{V}_{\text{el}}$. The introduction of an ion into a solvent causes a significant contraction of the system. This phenomenon may be discussed¹⁵ in terms of the electrostriction of the solvent, as a homogeneous dielectric of bulk dielectric constant ϵ , by an ion of charge Ze and radius r :

$$\bar{V}_{\text{el}} = \frac{-Z^2 e^2}{2r\epsilon^2} \left(\frac{\partial \epsilon}{\partial P} \right)_T + \frac{Z^2 e^2}{2r^2} \left(1 - \frac{1}{\epsilon} \right) \left(\frac{\partial r}{\partial P} \right)_T \quad (19)$$

Equation (19), with the term in $(\partial r/\partial P)_T$ omitted, is the original Drude-Nernst equation. For complex ions of charges 2+ and 3+, the estimates of $(\partial r/\partial P)_T$ provided by equation 15 show that the first term is at least four times the size of the second term in solvent water. Omission of the second term may involve larger errors for ions of charge 1+.

Equation 19 is important in the interpretation of reactions involving charged reactants (as for redox reactions below) or the generation or removal of charge (as in substitution and solvolysis reactions). In all cases, the dependence of the electrostrictive effect on Z^2 involves contributions to $\Delta \bar{V}_0^\ddagger$ ranging up to $\pm 20 \text{ cm}^3 \text{ mol}^{-1}$ in solvent water. Since this electrostrictive effect is operating on the solvent outside the first coordination sphere of the complex ion ($r \sim 3.5 \text{ \AA}$), it is reasonable to assume the bulk dielectric properties of the solvent operate and polarization effects in the first sphere are irrelevant.

A consequence of the electrostrictive effect is the formation of ordered layers of solvent molecules about a highly charged complex ion and these layers may be visualized as successive solvation spheres. The electrostatic field of the ion generates a strong centro-symmetrical pressure in the solvent dielectric proportional to the second power of the electric field strength

$$P = \{(\epsilon - 1)/8\pi\} \{Ze/\epsilon r^2\}^2 \quad (20)$$

Whalley¹⁴ has calculated that this pressure has a maximum value of 14 kbar at 3 Å from the centre of an ion of charge 1+. For a complex ion with a first coordination sphere of radius 3–3.5 Å and charge 3+, this pressure is about 32 kbar at the point where the first hydration sphere (or the second coordination sphere) of the complex ion is located (*Figure 3*). Water in this first hydration sphere of such a complex ion will therefore have a molar volume characteristic of water at about 32 kbar. This is $15 \text{ cm}^3 \text{ mol}^{-1}$, compared with $18 \text{ cm}^3 \text{ mol}^{-1}$ at 1 bar. At this high pressure, solvent water has virtually no free volume. Furthermore the compressibility of water in this first hydration (second coordination) sphere will have a value characteristic of solvent water at $\sim 30 \text{ kbar}$, namely $8.0 \times 10^{-6} \text{ bar}^{-1}$, compared with a bulk compressibility of $46.4 \times 10^{-6} \text{ bar}^{-1}$ at 1 bar pressure. Likewise the compressibility coefficient of water in the first hydration sphere should be

$\beta = 0.12 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ compared with $\beta = 0.84 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ for bulk water at 1 bar.

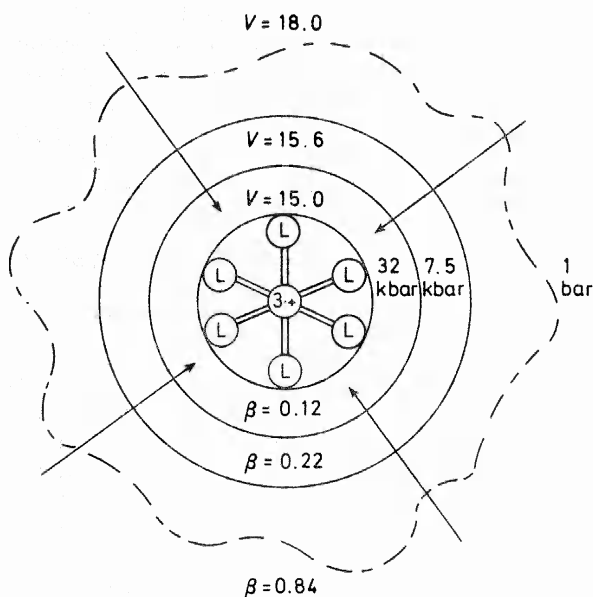


Figure 3. Spheres of electrostricted water about a charged complex ion.

This centro-symmetrical pressure falls off rapidly with distance but it is readily shown for a complex ion of charge $3+$ that the second hydration (third coordination) sphere is still subject to a pressure of ~ 7.5 kbar. At this pressure the molar volume of water in this sphere will be $15.6 \text{ cm}^3 \text{ mol}^{-1}$, with $\kappa = 1.4 \times 10^{-6} \text{ bar}^{-1}$ and $\beta = 0.22 \text{ cm}^3 \text{ mol}^{-1}$. The third hydration sphere, however, even for a $3+$ complex ion, will resemble closely the properties of bulk solvent water.

A general conclusion is that *surrounding a charged complex ion there are two layers of electrostricted water in which the water molecules have molar volumes and compressibilities which are distinctly less than those of the bulk solvent*. Exchanges of water in an activation step between these hydration spheres and the bulk solvent should therefore involve contributions to the volumes and compressibilities of activation.

OXIDATION-REDUCTION REACTIONS

One mechanism for oxidation-reduction involves electron transfer in an outer-sphere transition state in which chemical bonds are neither broken nor formed. The quantitative adiabatic theories of Marcus¹⁶ and Hush¹⁷ and the non-adiabatic dielectric continuum theory of Levich and Dogonadze¹⁸ may all be adapted to the calculation of volumes of activation for outer-sphere reactions. We shall use Hush's treatment here since it continues the formalism just developed above for estimating the compressibility of com-

plex ions. Moreover Hush's potential function leads to a more satisfactory estimate of internal rearrangement effects than a simple harmonic oscillator approximation.

The free energy for activation for an outer-sphere electron exchange reaction ($\Delta G^0 = 0$) may be separated as follows

$$\Delta G^\ddagger = \Delta G_{\text{coul}}^\ddagger + \Delta G_{\text{SR}}^\ddagger + \Delta G_{\text{IR}}^\ddagger + \Delta G_{\text{DH}}^\ddagger \quad (21)$$

where these separate terms represent in turn the free energy barrier for coulombic work in bringing charged reactants to the transition state ($\Delta G_{\text{coul}}^\ddagger$), the solvent rearrangement on formation of the charged transition state ($\Delta G_{\text{SR}}^\ddagger$), the internal rearrangement of the metal-ligand bonds to an intermediate configuration ($\Delta G_{\text{IR}}^\ddagger$) and the change in activity due to interionic interactions in a reaction medium of finite ionic strength ($\Delta G_{\text{DH}}^\ddagger$).

From equation (21) it follows that

$$\Delta V_0^\ddagger = \Delta V_{\text{coul}}^\ddagger + \Delta V_{\text{SR}}^\ddagger + \Delta V_{\text{IR}}^\ddagger + \Delta V_{\text{DH}}^\ddagger \quad (22)$$

We have argued above that complex ions, at least of charge 2+ and 3+, are almost incompressible and, based on that assumption, it may be shown that for electron exchange between ions of charge Z_1e and Z_2e and of radii r_1 and r_2 then

$$\Delta V_{\text{coul}}^\ddagger = \frac{Z_1 Z_2 e^2}{(r_1 + r_2)} \frac{\partial}{\partial P} \left(\frac{1}{\varepsilon} \right)_T \quad (23)$$

$$\Delta V_{\text{SR}}^\ddagger = \frac{e^2}{4} \left\{ \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{\sigma} \right\} \frac{\partial}{\partial P} \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon} \right)_T \quad (24)$$

In these equations, ε is the bulk dielectric constant of the solvent and ε_0 is the dielectric constant at optical frequencies; the latter term allows for electronic polarization of the solvent as the instantaneous charge distribution on each ion alters. For ions of finite compressibility, additional explicit terms can be added to equations 23 and 24 but these are minor in size and opposite in sign in the two cases as we shall see shortly.

For incompressible complex ions $\Delta V_{\text{IR}}^\ddagger = 0$ but for complex ions of compressibilities κ_1 and κ_2

$$\Delta V_{\text{IR}}^\ddagger = \frac{ne\mu}{6(m-2)} \left[\frac{\kappa_1 r_1}{Z_1 d_1^3} + \frac{\kappa_2 r_2}{Z_2 d_2^3} \right] \quad (25)$$

where the remaining terms have been already defined in deducing equation 16.

We may use the extended Debye-Hückel expression for the relation between rate coefficients at finite ionic strength, k_μ , and zero ionic strength, k_0 ,

$$\ln k_\mu = \ln k_0 + \frac{2Z_1 Z_2 A \sqrt{\mu}}{1 + B a \sqrt{\mu}} + 0.2 |Z_1 Z_2| \mu \quad (26)$$

where the parameters A and B are both pressure dependent since $A \propto (\varepsilon T)^{-\frac{3}{2}}$

and $B \propto (\epsilon T)^{-\frac{1}{2}}$ as is μ itself. Thence to an adequate approximation:

$$\Delta V_{\text{DH}}^{\ddagger} = -RT \cdot Z_1 Z_2 \frac{A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \left(\frac{3}{\epsilon} \frac{\partial \epsilon}{\partial P} - \kappa_s \right) \quad (27)$$

Equation 27 predicts that at 25°C and for the Debye-Hückel parameter $a = 3.5 \text{ \AA}$, then $\Delta V_{\text{DH}}^{\ddagger} = 0.35 Z_1 Z_2 \text{ cm}^3 \text{ mol}^{-1}$ at $\mu = 0.1\text{M}$; at $\mu = 0.5\text{M}$, $\Delta V_{\text{DH}}^{\ddagger} = 0.63 Z_1 Z_2 \text{ cm}^3 \text{ mol}^{-1}$; and at $\mu = 1.0\text{M}$, $\Delta V_{\text{DH}}^{\ddagger} = 0.78 Z_1 Z_2 \text{ cm}^3 \text{ mol}^{-1}$. Hence ionic strength effects should contribute significantly to the observed value of ΔV_0^{\ddagger} for electron exchange involving 2+ and 3+ complex ions. The magnitude of the temperature variation of the $\Delta V_{\text{DH}}^{\ddagger}$ contribution is shown below to be small but significant.

Table 2 summarizes some calculated volumes of activation for typical electron exchange studies. It should be noted that these calculations have allowed for finite compressibilities of ions but in all cases the contribution from this effect is only about $+0.07 \text{ cm}^3 \text{ mol}^{-1}$ to $\Delta V_{\text{coul}}^{\ddagger}$ and -0.12 to $\Delta V_{\text{SR}}^{\ddagger}$.

Table 2. Calculated volumes of activation for typical electron exchange systems ($\mu = 0.5\text{M}$; 25°C)

Exchange system	$\Delta V_{\text{coul}}^{\ddagger}$	$\Delta V_{\text{SR}}^{\ddagger}$	$\Delta V_{\text{IR}}^{\ddagger}$ $\text{cm}^3 \text{ mol}^{-1}$	$\Delta V_{\text{DH}}^{\ddagger}$	$\Delta V_{\text{calc}}^{\ddagger}$
$\text{V}(\text{OH}_2)_6^{2+} + \text{V}(\text{OH}_2)_6^{3+}$	-7.12	-5.71	0.41	-3.78	-16.2
$\text{Cr}(\text{OH}_2)_6^{2+} + \text{Cr}(\text{OH}_2)_6^{3+}$	-7.12	-5.66	0.57	-3.78	-16.0
$\text{Fe}(\text{OH}_2)_6^{2+} + \text{Fe}(\text{OH}_2)_6^{3+}$	-7.06	-5.67	0.47	-3.78	-16.0
$\text{Co}(\text{OH}_2)_6^{2+} + \text{Co}(\text{OH}_2)_6^{3+}$	-7.13	-5.73	0.46	-3.78	-16.2
$\text{Co}(\text{en})_3^{2+} + \text{Co}(\text{en})_3^{3+}$	-6.11	-4.92	0.60	-3.78	-14.2
$\text{Co}(\text{en})_3^{2+} + \text{Co}(\text{en})_3^{3+*}$	-8.10	-6.55	0.60	-4.38	-18.4
$\text{Co}(\text{EDTA})^{2-} + \text{Co}(\text{EDTA})^{-}$	-2.02	-4.93	0.60	-0.80	-7.2
$\text{Co}(\text{OH}_2)_6^{3+} + \text{Ce}(\text{OH}_2)_6^{4+}$	-13.31	-5.30	0.12	-7.56	-26.1

*Values calculated at 65°C.

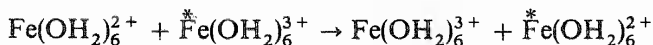
Table 2 shows that for these relatively incompressible ions, $\Delta V_{\text{IR}}^{\ddagger}$ is understandably small. The major contributions to the calculated volumes of activation stem from electrostatic repulsions and electrostrictive processes *outside* the primary coordination spheres. The effect of charge type is apparent when the $\text{Ce}^{3+}/\text{Ce}^{4+}$ and $\text{Co}(\text{EDTA})^{2-}/\text{Co}(\text{EDTA})^{-}$ systems are compared with the $\text{M}_{\text{aq}}^{2+}/\text{M}_{\text{aq}}^{3+}$ system. The effect of ionic size is significant as seen by comparing $\text{Co}(\text{en})_3^{2+}/\text{Co}(\text{en})_3^{3+}$, for which $(r_1 + r_2) = 8.1 \text{ \AA}$, with $\text{Co}_{\text{aq}}^{2+}/\text{Co}_{\text{aq}}^{3+}$, for which $(r_1 + r_2) = 7.1 \text{ \AA}$. Since the solvent dielectric properties are temperature sensitive, there is a predicted significant change in ΔV^{\ddagger} with temperature. For example, the quantity $\partial/\partial P (1/\epsilon)_T$ increases by 32% from 25°C to 65°C and this is a major cause of the $4 \text{ cm}^3 \text{ mol}^{-1}$ difference for $\text{Co}(\text{en})_3^{2+}/\text{Co}(\text{en})_3^{3+}$ at 25°C and 65°C.

These predictions have been tested in our laboratories¹⁹ first with the known outer-sphere electron exchange reaction between Co(en)_3^{2+} and Co(en)_3^{3+} . At 65°C in perchlorate media with $\mu = 0.5\text{M}$, there is a marked acceleration in rate with increasing pressure and $\Delta V_0^\ddagger = -19.8 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. The value calculated on the basis of radii of 4.13 Å for Co(en)_3^{2+} and 3.98 Å for Co(en)_3^{3+} is $-18.4 \text{ cm}^3 \text{ mol}^{-1}$. The agreement is within the experimental uncertainty. Furthermore measured values of $\ln k_p$ exhibit a non-linear dependence on pressure and the measured compressibility coefficient of activation is $\Delta\beta^\ddagger = -(4 \pm 1) \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$. Equations 23–27 can all be differentiated with respect to pressure since the pressure dependences of solvent dielectric properties are also non-linear with pressure. Substitution of known values of $\partial^2/\partial P^2 (1/\epsilon)_T$ and $\partial^2/\partial P^2 (1/\epsilon_0)_T$ yields a calculated value $\Delta\beta^\ddagger = -3.3 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ which is again in good agreement with the measured value. This suggests that the curvature in $\ln k_p$ vs. P plots for these electron exchange reactions is wholly attributable to the changing dielectric properties of the solvent as it is subjected to electrostriction by the highly charged reactants forming the transition state.

Since internal rearrangement is only a minor contributor to ΔV_0^\ddagger , uncertainties from spin-multiplicity restrictions and bond rearrangement energies are not important. By contrast, the Hush treatment yields a calculated value for the $\text{Co(en)}_3^{2+}/\text{Co(en)}_3^{3+}$ reaction of $\Delta S^\ddagger = -100 \text{ J K}^{-1} \text{ mol}^{-1}$ (24 cal $\text{K}^{-1} \text{ mol}^{-1}$) whereas the value derived via the experimental ΔH^\ddagger value is $\Delta S^\ddagger = -130 \text{ J K}^{-1} \text{ mol}^{-1}$ (31 cal $\text{K}^{-1} \text{ mol}^{-1}$). The success of these deduced relations in reproducing ΔV_0^\ddagger and $\Delta\beta^\ddagger$ values justifies using the calculations to interpret redox systems which react by uncertain mechanisms.

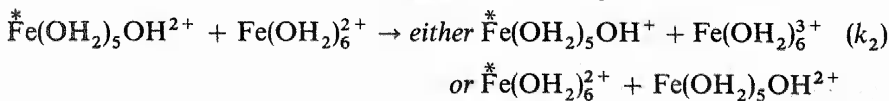
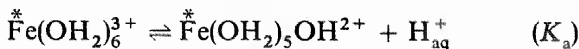
The $\text{Fe}^{\text{II}}-\text{Fe}^{\text{III}}$ exchange system in perchlorate media proceeds by two concurrent mechanisms. The rate of one pathway is pH independent and this is attributed to electron exchange between the hexa-aquo cations. The rate of the other pathway is inversely proportional to $[\text{H}^+]$ and this is attributed to exchange between $\text{Fe}(\text{OH})_2)_5\text{OH}^{2+}$ and $\text{Fe}(\text{OH})_2)_6^{2+}$. Despite the relatively short half-times and the more difficult tracer separations, we have been able¹⁹ to measure rates up to 2 kbar over a range of $[\text{H}^+]$ and evaluate volumes of activation for both pathways.

At 2°C, the pathway



is accelerated by increasing pressure and $\Delta V^\ddagger = -12.2 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. A reliable estimate of $\Delta\beta^\ddagger$ was not obtained since the more difficult experimental procedures entail larger variances of measured rates. The calculated value for an outer-sphere mechanism at 2°C is $\Delta V_0^\ddagger = -14.4 \text{ cm}^3 \text{ mol}^{-1}$ and the fair agreement suggests that the mechanism for the hexa-aquo pathway is indeed outer-sphere in character.

The hydroxo pathway involves the steps



The first set of alternative products arises from an outer-sphere mechanism and the second set of products from an inner-sphere mechanism with hydroxo-ligand transfer. In either case $k_{\text{obs}} = k_2 K_a$ and hence $\Delta V_{\text{obs}}^{\ddagger} = \Delta V_2^{\ddagger} + \Delta V_a^0$. We have measured²⁰ ΔV_a^0 separately by spectrophotometric evaluation of K_a as a function of pressure and find $\Delta V_a^0 = -1.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$. The observed rate coefficient hardly changes over a 2 kbar range and $\Delta V_{\text{obs}}^{\ddagger} = -0.4 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ so that $\Delta V_2^{\ddagger} = +0.8 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$. The calculated value for an outer-sphere mechanism is $\Delta V_2^{\ddagger} = -11.4 \text{ cm}^3 \text{ mol}^{-1}$. *The distinctly more positive value observed for ΔV_2^{\ddagger} is strong evidence that the hydroxo path proceeds by an inner-sphere mechanism.* This pathway involves no overall chemical change and $\Delta G^0 = 0$ for this mechanism. The excess positive value for ΔV_2^{\ddagger} , namely $12.2 \text{ cm}^3 \text{ mol}^{-1}$, is consistent with dissociative release of one aquo-ligand from $\text{Fe}(\text{OH}_2)_6^{2+}$ in generating the activated complex as in *Figure 4*. The same calculated electrostatic, electrostrictive and ionic strength contributions are likely to apply to the bridged transition state as for an outer-sphere transition state and the volume excess of $12.2 \text{ cm}^3 \text{ mol}^{-1}$ applies to the dissociated aquo-ligand.

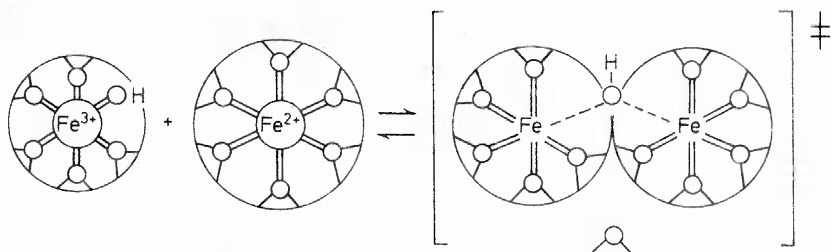
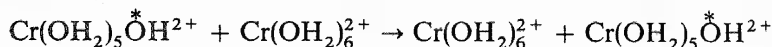


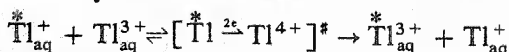
Figure 4. Activated complex for inner-sphere $\text{FeOH}^{2+} + \text{Fe}_{\text{aq}}^{2+}$ electron exchange.

A very similar result for the $\text{FeOH}^{2+} - \text{Fe}^{2+}$ pathway is being found in a current study of the $\text{Cr}^{3+} - \text{Cr}^{2+}$ electron exchange which proceeds with ligand transfer:

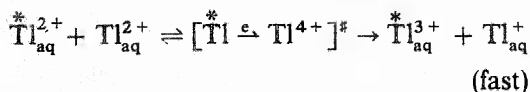
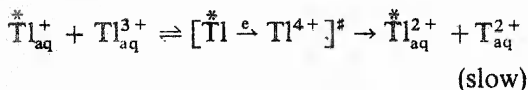


For this rate-determining step, $\Delta V^{\ddagger} = +4.2 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$ and this is $15.8 \text{ cm}^3 \text{ mol}^{-1}$ more positive than the value predicted for an outer-sphere transfer ($-11.6 \text{ cm}^3 \text{ mol}^{-1}$).

Formal two-electron transfer processes, as in the $\text{Tl}^{\text{I}} - \text{Tl}^{\text{III}}$ exchange system may proceed either by simultaneous two-electron transfer:



or by two successive one-electron transfers:



For the two-electron alternative, the Hush treatment is readily adapted to

outer-sphere multiple electron transfer and this yields a predicted value $\Delta V_0^\ddagger = -25.2 \text{ cm}^3 \text{ mol}^{-1}$ at 30°C and in 1.1M perchloric acid. This prediction differs markedly from our measured²¹ value $\Delta V_0^\ddagger = -13.2 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$.

The slow one-electron formation of Ti^{2+} involves a positive free-energy change, estimated from rate data as 86 kJ mol^{-1} . The corresponding molar volume change can be estimated with reasonable confidence from well-established correlations²² of partial molar volumes of ions with ionic radii; for the $\text{Ti}^{3+} + \text{Ti}^+ \rightarrow 2\text{Ti}^{2+}$ reaction, ΔV^0 is estimated as -9.3 cm^3 . In order to allow for the free energy and molar volume changes, the expression for ΔV_0^\ddagger , equation (22), must be modified by the addition of an extra term:

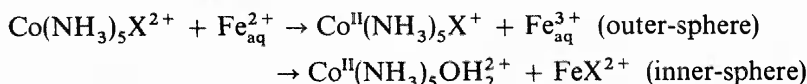
$$\Delta V_0^\ddagger = \Delta V_{\text{coul}}^\ddagger + \Delta V_{\text{SR}}^\ddagger + \Delta V_{\text{IR}}^\ddagger + \Delta V_{\text{DH}}^\ddagger + \lambda^\ddagger \Delta V^0 \quad (28)$$

where the parameter λ^\ddagger is defined by

$$\lambda^\ddagger = \frac{1}{2} + \Delta G^0/2(G_{\text{R}} + \Delta G_{\text{IR}}) \quad (29)$$

For the $\text{Ti}^{\text{I}}-\text{Ti}^{\text{II}}$ one-electron transfer $\lambda^\ddagger = 0.719$ leading to a calculated value $\Delta V_0^\ddagger = -13.7 \text{ cm}^3 \text{ mol}^{-1}$ which is in remarkable agreement with the measured value $\Delta V_0^\ddagger = -13.2 \pm 1.0$. This seems to constitute evidence for considering that *the thallium exchange reaction proceeds by a slow outer-sphere one-electron transfer*. The subsequent fast electron transfer could well occur in a solvent cage between geminate partners without the Ti^{2+} ions being scavengable by other reagents. The solvent rearrangement necessary for forming the transition state is, however, characteristic of a one-electron transfer. It should be noted that the compressibility of the large $\text{Ti}(\text{OH}_2)_6^+$ ion, assumed in these calculations, contributes overall $+3.25 \text{ cm}^3 \text{ mol}^{-1}$ to ΔV_0^\ddagger .

Equation 28 may be applied to consider *net redox reactions* of the type studied by Candlin and Halpern²²



where $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-$ or N_3^- .

Since these reactions have relatively long half-times and the initial Co^{II} and Fe^{III} products are quite labile, it is not possible to distinguish between mechanisms on the basis of final product analysis. It is readily shown from equation (28) that the ΔV_0^\ddagger values expected from these reactions, if they were involved in an outer-sphere mechanism, will range from -10.6 to $-12.8 \text{ cm}^3 \text{ mol}^{-1}$ depending on the overall size of ΔG^0 . The observed values are $+11$ ($\text{X} = \text{F}^-$), $+8$ (Cl^-, Br^-), $+14$ (N_3^-). Evidently the mechanism is inner-sphere with the release of water in the transition state (approx. $+14 \text{ cm}^3 \text{ mol}^{-1}$) overcoming the opposing negative volume effects of electrostatic repulsion and solvent electrostriction. The theoretical treatment of these inner-sphere reactions must now be refined to allow for the influence of the negatively charged ligand in a transition state which has a net positive charge. The reactant state is probably best regarded as an ion pair, e.g. $\text{M}^{3+} - \text{X}^-$, rather than as a spherical species of net charge $2+$, whilst the transition state is probably best viewed as an ion-triplet, e.g. $\text{M}^{3+} - \text{X}^- - \text{M}^{2+}$. This is especially important with extended ligands like N_3^- and large

conjugated organic ligands. The calculations of volume changes may then be treated as a classical electrostatic problem despite the significant orbital overlap existing between oxidant and reductant.

These recent studies suggest then that comparison of measured and predicted volumes of activation may be very useful in diagnosing the mechanism of oxidation-reduction processes.

WATER EXCHANGE WITH HYDRATED CATIONS

The lability of solvent-ligands coordinated to metal cations is the key to the general substitution properties of solvated cations. In particular, an understanding of the mechanism of water exchange is a necessary prelude to mechanistic studies of substitution reactions in this chemically and bio-chemically important solvent. Until quite recently, however, the mechanisms of water exchange have been based on deductions from measured enthalpies and entropies of activation and from solvent competition studies. For example, the recent ideas of Bennetto and Caldin²³ on the role of the solvent in substitution have (necessarily) been cast in terms of enthalpies and entropies of activation.

Solvent exchange is not accompanied by any change in formal charge of the ion and since these hydrated cations are relatively incompressible, the effects of electrostriction are virtually constant throughout the course of the reaction. The interpretation of observed volumes of activation is therefore comparatively straightforward. Table 3 summarizes a number of ΔV_0^\ddagger values which have accumulated recently and which provide us with a spectrum of values in charge and sign.

Table 3. Measured volumes of activation for water exchange with aquo-metal cations

Aquo-cation	ΔV_0^\ddagger cm ³ mol ⁻¹ (temp, °C)	$\Delta\beta^\ddagger$ cm ³ mol ⁻¹ kbar ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	Ref.
Cr(OH ₂) ₆ ³⁺	-9.3 ± 0.3 (45)	≤ 0.7	+1.3 ± 4.2	24
Cr(NH ₃) ₅ (OH ₂) ³⁺	-5.8 ± 0.2 (25)	≤ 0.7	0.0 ± 6.7	25
Rh(NH ₃) ₅ (OH ₂) ³⁺	-4.1 ± 0.4 (35)	~ 0	+3.3 ± 4.6	25
Co(NH ₃) ₅ (OH ₂) ³⁺	+1.2 ± 0.2 (25, 35)	~ 0	+17.5 ± 4.2	26
<i>trans</i> -Co(en) ₂ (SeO ₃)(OH ₂) ⁺	+7.6 ± 0.7 (15)	< 0.6		20
<i>trans</i> -Co(en) ₂ (SeO ₃ H)(OH ₂) ²⁺	+8.0 ± 0.6 (25)	< 0.6	+53.1 ± 4.2	20
<i>trans</i> -Co(en) ₂ (OH ₂) ³⁺	+14.3 ± 0.2 (35, 46) ^a	1.1 ± 0.3	+92 ± 5	20
<i>trans</i> -Co(en) ₂ (OH ₂) ³⁺	+13.1 ± 0.8 (45, 50) ^b	8 ± 2	+51.5 ± 4.5	20
<i>trans</i> -Co(en) ₂ (OH ₂) ³⁺	+13.7 ± 0.5 (45) ^c	8 ± 2		20

^a $\mu = 0.05M$ (HClO₄). ^b $\mu = 1.0M$ (HClO₄). ^c $\mu = 1.0M$ (NaClO₄).

The *trans*-Co(en)₂(SeO₃)OH₂⁺ and *trans*-Co(en)₂(OH₂)₂³⁺ systems have been studied by following the *trans* → *cis* isomerization, a process which simultaneously leads to aquo-ligand exchange.

The compressibility of aquo-cations has already been shown to be quite low and very small volume changes of the aquo-cations themselves, both intrinsic and electrostrictive, can be anticipated for both dissociative and associative aquo-exchange. Moreover the very compact structure of these aquo-cations¹⁰ appears to preclude compensatory bond contraction by second water molecules when bond stretching occurs in the primary coordi-

nation sphere (and vice versa). Consequently the negative $\Delta\bar{V}_0^\ddagger$ values listed in Table 3 are directly diagnostic of associative reactions of a water nucleophile with the aquo-cation and the positive values diagnostic of dissociative reactions with release of an aquo-ligand.

There is a contrast then between the associative reactions of chromium(III) and rhodium(III) with the dissociative reactions of cobalt(III). Since the molar volume of an aquo-ligand is estimated¹² to be $14.0 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$, and that in the first hydration sphere has been estimated above to be $15.0 \text{ cm}^3 \text{ mol}^{-1}$, then dissociative interchange of an aquo-ligand from the first to second coordination sphere should yield $\Delta V_0^\ddagger = +1.0 \text{ cm}^3 \text{ mol}^{-1}$. This value is observed with the $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ system. The larger random errors in ΔS^\ddagger and a possible systematic error in ΔS^\ddagger due to the unknown molecularity of water do not permit such an unequivocal description of mechanism based on the corresponding entropies of activation.

The dissociative release of an aquo-ligand from the first to the second coordination sphere is described as an I_d mechanism. We have argued that a five-coordinate complex should define the same intrinsic volume as a six-coordinate complex and hence ΔV_0^\ddagger should approach in the limit $+15 \text{ cm}^3 \text{ mol}^{-1}$, the molar volume of water in the second sphere about a $3+$ complex ion. This value is closely approached with the $\text{trans-Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ ion. Likewise an associative interchange, I_a , mechanism could exhibit $\Delta V_0^\ddagger = -15 \text{ cm}^3 \text{ mol}^{-1}$. This value is not approached as closely with the aquocations of Cr and Rh probably because of the substantial steric crowding in the seven-coordinate activated complex. Compensatory dissociation of an aquo-ligand almost certainly is needed to offset the incoming water nucleophile and a less negative ΔV_0^\ddagger results.

The dissociative mechanism (D) entails synchronous release of electrostricted water to the bulk of the solvent. Correspondingly, the associative (A) mechanism entails synchronous entry of bulk water into the electrostricted zone. The D and A mechanisms should involve similar limiting V_0^\ddagger values ($\pm 18 \text{ cm}^3 \text{ mol}^{-1}$) as for the I_d and I_a mechanisms. However, the D and A mechanisms involve the movement of water molecules between regions of quite different compressibilities. The D mechanism of a $3+$ cation should yield for one water molecule $\Delta\beta^\ddagger = (0.84 - 0.12) = 0.72 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ and for one water molecule in an A mechanism, $\Delta\beta^\ddagger = -0.72 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$.

The experimental $\ln k_p$ vs. P plots for most of these aquo-exchanges show no detectable curvature but the magnitude of $\Delta\beta^\ddagger$ is within the experimental error for most systems. A reliable distinction cannot be drawn between I_a and A mechanisms. However, for the $\text{trans-Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ marked curvature in $\ln k_p$ vs. P plots is observed (Figure 1) and $\Delta\beta^\ddagger$ is quite large. At 0.05M ionic strength, the value of $\Delta\beta^\ddagger$ implies that at least one water molecule is released to the bulk solvent and a D mechanism seems likely, as argued earlier by Kruse and Taube²⁷. At 1M ionic strength, the value of $\Delta\beta^\ddagger$ suggests at least eight water molecules being released into the bulk solvent. The change in molar volume when a water molecule moves from an outer electrostricted zone to the bulk is approximately $(18-15.6) = 2.4 \text{ cm}^3 \text{ mol}^{-1}$. The measured ΔV_0^\ddagger value, which is known to higher accuracy, suggests that $(13.7/2.4) \approx 6$ water molecules are released. The agreement is not too unreasonable when

all the approximations are recognized. This analysis confirms the recent expectations of El'yanov and Gonikberg²⁸ that there should be a correlation between ΔV_0^\ddagger and $\Delta\beta^\ddagger$. The probable reason for the changed mechanistic details at 1M ionic strength is the formation of $\text{Co(en)}_2(\text{OH}_2)_2^{3+} \cdot \text{ClO}_4^-$ ion pairs. The water structure in these ion pairs could be so heavily ordered that in order to create a defect in the structure to allow release of an aquo-ligand, the whole hydrated ion-pair aggregate must be broken. There are corresponding changes in ΔH^\ddagger and ΔS^\ddagger when the ionic strength is increased but the ΔV_0^\ddagger and $\Delta\beta^\ddagger$ values give a better guide to mechanism.

Further advances in evaluating ΔV_0^\ddagger values for highly labile systems must await the adaptation of high pressure techniques notably in the n.m.r. area.

SUBSTITUTION OF HYDRATED CATIONS

Nucleophilic substitution of an aquated cation is a more general case of solvent exchange; indeed substitution by nucleophiles competes with exchange by solvent molecules. An additional complication, however, is that many nucleophiles are charged and microreversibility considerations require that any postulated mechanism must encompass outer-sphere ion-pairing. Thus the commonly observed second-order rate coefficient for formation of a metal complex, k_f , is often related to the rate of water loss and/or nucleophile entry, $k_{\text{H}_2\text{O}}$, by the equation

$$k_f = K_{\text{os}} k_{\text{H}_2\text{O}} \quad (30)$$

where K_{os} is the equilibrium quotient for formation of the outer-sphere ion-pair. Accordingly

$$\Delta V_{\text{obs}}^\ddagger = \Delta V_{\text{os}}^0 + \Delta V_{\text{H}_2\text{O}}^\ddagger \quad (31)$$

For labile systems ΔV_{os}^0 usually needs to be estimated from an electrostatic model for the ion-pair and Hemmes²⁹ has shown that

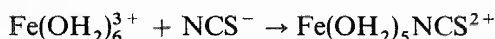
$$\Delta V_{\text{os}}^0 = RT(Z_+ Z_- e^2 / \epsilon kT) [\partial(\ln \epsilon) / (\partial P)_T - \kappa_s] \quad (32)$$

provided activity coefficients are ignored. There is experimental evidence, however, that reveals a very large variation of ΔV_{os}^0 with ionic strength³⁰. Nevertheless ΔV_{os}^0 is likely to be of the order of +2 to +5 $\text{cm}^3 \text{mol}^{-1}$ for commonly encountered ionic systems at normal ionic strengths.

Grant³¹ has assumed a value $\Delta V_{\text{os}}^0 = +3 \text{ cm}^3$ for $\text{M}_{\text{aq}}^{2+}$ + glycinate reactions to derive values of $\Delta V_{\text{H}_2\text{O}}^\ddagger$ and compare these with those observed¹⁰ for dipolar nitrogen bases. The comparisons are summarized in *Table 4*.

The striking feature of the data is the complete lack of correlation between $\Delta V_{\text{H}_2\text{O}}^\ddagger$ and the overall volume change for a reaction, ΔV^0 , in both magnitude and sometimes sign. On the other hand for each metal $\Delta V_{\text{H}_2\text{O}}^\ddagger$ is sensibly constant regardless of the nucleophile, suggesting that the common process is dissociative release of an aquo-ligand. A value of $\Delta V_{\text{H}_2\text{O}}^\ddagger = +7 \text{ cm}^3 \text{mol}^{-1}$ corresponds¹⁰ to between 20 and 50% stretching of the metal-oxygen bond in the aquated cation, depending on the radius assigned to the aquo leaving group. It is likely that a similar mechanistic picture will emerge for substitution of $\text{Fe}(\text{OH}_2)_6^{3+}$. Brower³¹ has reported $\Delta V^\ddagger = +5 \text{ cm}^3 \text{mol}^{-1}$ and

$\Delta V^0 = +17.5 \text{ cm}^3 \text{ mol}^{-1}$ for the reaction



consistent with an I_d mechanism involving an ion-pair.

Table 4. Volume changes for the substitution reaction:
 $M_{\text{aq}}^{2+} + L^{n-} \rightarrow ML^{(2-n)}$

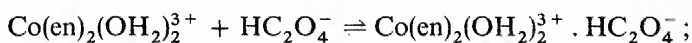
Metal ion	Nucleophile	$\Delta V_{\text{H}_2\text{O}}^\ddagger$ $\text{cm}^3 \text{ mol}^{-1}$	ΔV^0 cm^3
Co	PADA	7.2 ± 0.2	5.8 ± 0.4
	NH_3	4.8 ± 0.7	-8.6 ± 1.6
	$\text{NH}_2\text{CH}_2\text{COO}^-$	5 ± 2	7.3 ± 1.8
Ni	PADA	7.7 ± 0.3	0.9 ± 0.7
	NH_3	6.0 ± 0.3	-2.3 ± 0.7
	$\text{NH}_2\text{CH}_2\text{COO}^-$	7 ± 1	2.1 ± 0.6
Cu	$\text{NH}_2\text{CH}_2\text{COO}^-$	9 ± 1	13.4 ± 0.4
Zn	$\text{NH}_2\text{CH}_2\text{COO}^-$	4 ± 1	5.2 ± 0.8

The importance of electrostrictive effects is shown³¹ in the following successive stages of substitution of aquo-ligands of chromium(III) by HC_2O_4^- :

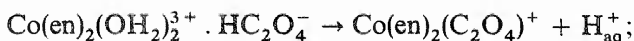
- (1) $\text{Cr}(\text{OH}_2)_6^{3+} + \text{HC}_2\text{O}_4^- \rightarrow \text{Cr}(\text{OH}_2)_4(\text{C}_2\text{O}_4)^+ + \text{H}_{\text{aq}}^+$;
 $\Delta V_1^\ddagger = -2.2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$
- (2) $\text{Cr}(\text{OH}_2)_4(\text{C}_2\text{O}_4)^+ + \text{HC}_2\text{O}_4^- \rightarrow \text{Cr}(\text{OH}_2)_2(\text{C}_2\text{O}_4)_2^- + \text{H}_{\text{aq}}^+$;
 $\Delta V_2^\ddagger = -8.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$
- (3) $\text{Cr}(\text{OH}_2)_2(\text{C}_2\text{O}_4)_2^- + \text{HC}_2\text{O}_4^- \rightarrow \text{Cr}(\text{C}_2\text{O}_4)_3^{3-} + \text{H}_{\text{aq}}^+$;
 $\Delta V_3^\ddagger = -10.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$

Step (1) should cause substantial solvent release on forming the 2+ transition state. Offsetting this is probably the associative involvement of the oxalate nucleophile. Step (2) should involve a slight positive electrostrictive contribution to ΔV_2^\ddagger whilst step (3) should involve a negative contribution to ΔV_3^\ddagger . These measured volumes seem consistent with associative interchange of water with $\text{Cr}(\text{OH}_2)_6^{3+}$ for which $\Delta V_0^\ddagger = -9.3 \text{ cm}^3 \text{ mol}^{-1}$.

The associative nature of $\text{Cr}(\text{OH}_2)_6^{3+}$ reactions is in contrast with the dissociative character of comparable reactions of aquo-cobalt(III) cations. Substitution of $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$ by HC_2O_4^- proceeds²⁰ through an ion-pair mechanism:



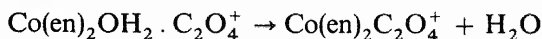
$$\Delta V^0 = +2.6 \pm 1.2 \text{ cm}^3$$



$$\Delta V^\ddagger = +4.7 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$$

The small positive value $\Delta V^\ddagger = 4.7$ is markedly less than that for water exchange of $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$, namely $\Delta V^\ddagger = +13.4$. The water exchange has

been assigned a dissociative, *D*, mechanism and substitution by oxalate in the ion-pair is then very likely a dissociative interchange, *I_d*, mechanism. Since $\Delta\beta^\ddagger \leq 0.4 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ for this oxalate reaction, it seems very likely that there is little desolvation of the free carboxylate group in the transition state. A similar mechanism also probably holds²⁰ for the ring-closing reaction



for which $\Delta V^\ddagger = +3.5 \text{ cm}^3 \text{ mol}^{-1}$.

HYDROLYSIS REACTIONS OF COMPLEX IONS

The contrast between the dissociative reactions of cobalt(III) complex ions and the associative reactions of chromium(III) is well illustrated by recent work in Swaddle's laboratories.

Data for the aquation of pentaamminecobalt(III) ions³² are summarized in *Table 5*. There is a very close linear correlation between ΔV_0^\ddagger and the overall volume change for the aquation reaction ΔV^0 . This indicates that in the transition state the activated complex resembles the ionic products presumably as $[\text{Co}(\text{NH}_3)_5^{3+} \dots \text{X}^{n-}]$ in which electrostriction of the solvent is the origin of the negative volumes. Furthermore quite large $\Delta\beta^\ddagger$ values are exhibited. If the difference in the compressibility coefficients for bulk water and electrostricted water is taken to be $0.72 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ (see above) then the number of water molecules $\Delta x_{\text{H}_2\text{O}}^\ddagger$ drawn into the activated complex will be $\Delta x_{\text{H}_2\text{O}}^\ddagger = \Delta\beta^\ddagger/0.72$. These are listed in *Table 5* together with Swaddle's estimates from an entirely different deduction based on a modified Tait equation. Considering the different approaches, the correspondence is reasonable. A better description of the activated complex would then include several water molecules about the separating ionic fragments in a dissociative interchange mechanism.

Table 5. Volume changes for the aquation reaction:
 $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+} + \text{H}_2\text{O} \rightarrow \text{Co}(\text{NH}_3)_5\text{OH}_2^{3+} + \text{X}^{n-}$
 (Ref. 32)
 (25°C; $\mu = 0.1\text{M}$)

X^{n-}	ΔV_0^\ddagger $\text{cm}^3 \text{ mol}^{-1}$	ΔV^0 $\text{cm}^3 \text{ mol}^{-1}$	$\Delta\beta^\ddagger$ $\text{cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$	$\Delta x_{\text{H}_2\text{O}}^\ddagger$ (see text)
SO_4^{2-}	-17.0 ± 0.6	-19.2	-4 ± 0.5	-5.5 (8.0)
Cl^-	-9.9 ± 0.5	-11.6	-2.1 ± 0.2	-2.9 (4.1)
Br^-	-8.7 ± 0.2	-10.8	-2.0 ± 0.2	-2.8 (3.9)
NO_3^-	-5.9 ± 0.4	-7.2	-1.0 ± 0.2	-1.4 (1.9)
H_2O	$+1.2 \pm 0.1$	0.0	0.0 ± 0.1	0 (0)

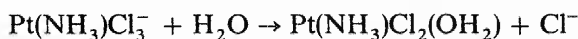
An analogous study¹² of the aquation of pentaamminechromium(III) species is summarized in *Table 6*. There is again a linear relation between ΔV_0^\ddagger and ΔV^0 but the slope is only 0.59; for the cobalt(III) system the slope is 0.98. This suggests that the separation of ionic charge is much less complete

with the chromium(III) system and it is striking that the number of water molecules brought into the transition state, as estimated from $\Delta\beta^\ddagger$ values, is much less than for the cobalt(III) analogue. The solvent exchange with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ falls precisely in the $\Delta V_0^\ddagger/\Delta V^0$ correlation and, since this reaction involves an uncharged leaving group, the negative ΔV_0^\ddagger values seem to be indicative of an associative interchange I_a mechanism.

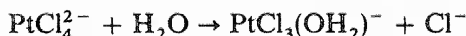
Table 6. Volume changes for the aquation reaction:
 $\text{Cr}(\text{NH}_3)_5\text{X}^{(3-n)+} + \text{H}_2\text{O} \rightarrow \text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+} + \text{X}^{n-}$
 (Ref. 12)
 (25°C; $\mu = 0.1\text{M}$)

X^{n-}	ΔV_0^\ddagger $\text{cm}^3 \text{mol}^{-1}$	ΔV^0 $\text{cm}^3 \text{mol}^{-1}$	$\Delta\beta^\ddagger$ $\text{cm}^3 \text{mol}^{-1} \text{kbar}^{-1}$	$\Delta x_{\text{H}_2\text{O}}^\ddagger$
Cl^-	-10.6 ± 0.3	-8.4	-1.0 ± 0.2	$-1.4 (1.9)$
Br^-	-9.9 ± 0.3	-7.2	-1.0 ± 0.1	$-1.4 (2.0)$
I^-	-9.2 ± 0.2	-6.0	-0.96 ± 0.13	$-1.3 (1.7)$
H_2O	-5.8 ± 0.2	0	0.0 ± 0.3	0

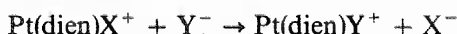
Associative mechanisms arise also in the aquation of platinum(II) complexes³³. For the reaction



$\Delta V^\ddagger = -14 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$ whilst for the reaction



$\Delta V^\ddagger = -17 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$. Compressibility coefficients are unknown for these reactions however. Associative mechanisms are also suggested by the work of Kelm and Palmer³⁴ reported at this Conference for both the solvent and direct nucleophilic paths in the general reaction

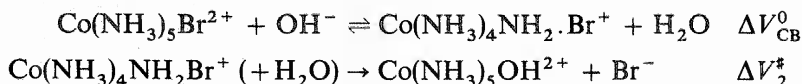


The base hydrolysis of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (Table 7) exhibits a positive ΔV_0^\ddagger value which Burris and Laidler³⁵ correlated with charge neutralization with release of electrostricted water. The OH^- ion has an unusually large volume of electrostriction³⁸ ($\bar{V}_{\text{el}} \sim 22 \text{ cm}^3 \text{ mol}^{-1}$) and this large positive contribution would need to be offset by a negative contribution from released Br^-

Table 7. Volumes of activation for the base hydrolysis reaction:
 $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+} + \text{OH}^- \rightarrow \text{Co}(\text{NH}_3)_5\text{OH}_2^{2+} + \text{X}^{n-}$
 ($\mu = 0.5\text{M}$)

Complex ion	ΔV_0^\ddagger $\text{cm}^3 \text{mol}^{-1}$	$\Delta\beta^\ddagger$ $\text{cm}^3 \text{mol}^{-1} \text{kbar}^{-1}$	Temp. °C	Ref.
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	$+8.5$		25	35
$\text{Co}(\text{NH}_3)_5\text{OSO}_3^+$	$+19.5 \pm 1.1$	$+9.5 \pm 2.2$	15	36
$\text{Co}(\text{NH}_3)_5\text{OSeO}_2^+$	-17.1 ± 1.0	-19 ± 2	25	36
$\text{Co}(\text{NH}_3)_5\text{OPO}_3^0$	$+28.9 \pm 2.2$	$+7.7 \pm 2.1$	55	36

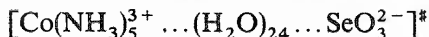
to yield $\Delta V_0^\ddagger = +8.5$. An alternative interpretation is in terms of the conjugate-base mechanism



such that $\Delta V_0^\ddagger = \Delta V_{\text{CB}}^0 + \Delta V_2^\ddagger$. There are grounds^{30, 38} for assigning $\Delta V_{\text{CB}}^0 \simeq +18 \text{ cm}^3 \text{ mol}^{-1}$ since ions such as $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ have similar partial molar volumes as $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ due probably to the charge separation in the complex ion. Consequently $\Delta V_2^\ddagger \simeq -10 \text{ cm}^3 \text{ mol}^{-1}$, suggesting a dissociative interchange mechanism, as for the aquation of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ for which $\Delta V^\ddagger = -8.7$.

The base hydrolysis of the O-bonded sulphato and phosphato complexes exhibit very large positive ΔV_0^\ddagger and $\Delta\beta^\ddagger$ values. This is incompatible with a simple neutralization of formal charge but it is consistent with release of electrostricted water (about 13 water molecules from the value of $\Delta\beta^\ddagger$) in a conjugate-base pre-equilibrium. On the other hand, the values of ΔV_2^\ddagger are zero or positive, suggesting *either* that there is slight dissociative release of the highly charged SO_4^{2-} and PO_4^{3-} in the transition state *or* that these ligands are exerting electrostrictive effects on the solvent which are almost as great as those of the non-coordinated free ion.

The mechanism for base hydrolysis of the O-bonded selenito complex is evidently quite different. Our ¹⁸O studies show that this hydrolysis proceeds by O—Se bond rupture and not Co—O bond rupture. The reaction exhibits an unusually low value of $\Delta H^\ddagger = 48.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -121 \text{ J K}^{-1} \text{ mol}^{-1}$. These values are compatible with the large negative values $\Delta V_0^\ddagger = -17.1 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta\beta^\ddagger = -19 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$. The last quantity emphasises the very great hydration of selenite ions that occurs and the transition state probably has the approximate composition



with the structure closely resembling that of the final products.

CONCLUSIONS

We have seen that substantial advances have been made in accounting for the volumes of activation of redox reactions and interpreting uncertain redox mechanisms. In these cases electrostrictive effects are dominant. In the case of substitution reactions, both the volume of activation and the compressibility coefficient of activation provide mechanistic insights not only into the structure of the reactants in the transition but also into the participation of the solvent. One can anticipate extensions to non-aqueous solvents and progress in the study of faster reactions. Simplifications in the interpretation of mechanism using volume changes merit close attention to these approaches in the future and offer more detailed insights into the molecular rearrangements which make up reaction mechanisms.

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