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Electrode reactions of metal complexes in solution at high pressures

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Contents

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Abstract

Techniques for measuring the pressure dependencies of the electrode potentials (characterized by the cell reaction volume ΔV_{cell}) and electrode kinetics (volume of activation $\Delta V^{\ddagger}$) of metal complexes are described. Volumes of reaction ΔV for net redox reactions can be obtained by the combination of ΔV_{cell} values. We show how ΔV_{cell} can be broken down into contributions of the couple of interest and the reference electrode, and how the solvational and intrinsic components of the former can be evaluated. Values of $\Delta V^{\ddagger}$ measured for electrode reactions of aqueous metal complex couples are precisely one-half of the $\Delta V^{\ddagger}$ found for the corresponding outer-sphere self-exchange reactions, and can generally be accounted for by an extension of Marcus theory developed for the latter. When ΔV is known, the theory can be extended to $\Delta V^{\ddagger}$ for redox 'cross' reactions; thus, $\Delta V^{\ddagger}$ can serve as a criterion of a simple, adiabatic, outer-sphere reaction mechanism.

Keywords: Electrode kinetics; Electrode potentials; Marcus theory; Volume of activation; Volume of reaction

1. Introduction

The literature on the techniques of high pressure chemistry and the effects of pressure on the kinetics and equilibria of inorganic reactions in solution is extensive and has been frequently reviewed [1–18], but relatively little attention has been paid to electrode processes at high pressures. Undoubtedly, this lack of enthusiasm stems in part from the difficulty of obtaining reproducible electrochemical results from pressurized systems. This is largely because electrochemical measurements (particularly of electrode reaction kinetics) are notoriously sensitive to the condition of the electrode surfaces, and in hydraulically pressurized systems these are subject to contamination by traces of the hydraulic fluid (or impurities in it) even when a separator is used to keep it out of the reaction medium. In addition, the usual mechanical problems associated with high pressure experimentation are amplified by the fragility of reference electrode assemblies and unreliability of the feed-throughs that take the electrical signals (which may be at the nanoampere level) through the pressure vessel wall. Furthermore, electrochemically active couples may not be sufficiently stable over the time required to complete a cycle of measurements at various pressures. With care and patience, however, these problems can be overcome.

As we shall see, many useful insights into mechanistic coordination chemistry can be derived from the study of pressure effects on the kinetics and thermodynamics of reactions of metal complexes at electrodes. From a more pragmatic standpoint, the pressure dependence of redox phenomena is of interest in marine science and aqueous geochemistry, since pressures can exceed 100 MPa (1 kbar) in the ocean deeps and can be much higher within the Earth's crust. Research in hydrothermal chemistry, in which moderately high pressures maintain water in a liquid (or, above the critical temperature, liquid-like) state at temperatures above 100°C, is also gaining momentum in connection with the hydrolysis or oxidation of hazardous wastes, the synthesis of special materials (particularly for the electronics industry), the study of hot water vents on the ocean floor, the processing of minerals, and problems in electric power generation [19]. Very little has been published to date on the electrochemistry of coordination compounds under hydrothermal conditions, but complexation of metal ions by hot water is central to many geological and technologically important processes, and a brief overview of relevant recent literature on hydrothermal voltammetry is therefore included as a basis for future work on metal complexes. In this article, however, we are concerned primarily with pressure effects on electrode processes involving metal complexes in aqueous solution at *ambient* temperature. Consideration will also be given to the extension of such studies to nonaqueous systems.

2. Representation of pressure effects

The effect of pressure P on a true thermodynamic equilibrium constant K^0 is customarily represented as the *volume of reaction*, $\Delta V°$, which is the sum of the partial molar volumes of the products minus that of the reactants at the temperature T in kelvin:

$$(\partial \ln K^0/\partial P)_T = -\Delta V°/RT \tag{1}$$

For electrochemical reactions [20], this may be recast in terms of the standard electrode potential change $\Delta E°$ (the standard potential of the oxidant half-reaction minus that of the reductant half-reaction):

$$\ln K^0 = nF\Delta E°/RT \tag{2}$$

$$\Delta V° = -nF(\partial \Delta E°/\partial P)_T \tag{3}$$

where n is the number of moles of electrons transferred (normally 1) and F is the faraday (96 485 A s mol^{-1}). Although it is possible in principle to calculate $\Delta V°$ from the algebraic sum of the partial molar volumes of all the entities involved in the reaction, these quantities are often not accurately known, particularly if stable solid salts of one or more of the reacting solute species cannot be made in purity high enough for densimetric measurements. In contrast, electrochemical methods can give $\Delta V°$ directly from a single set of measurements on a solution, and cyclic voltammetry (CV) can be applied even when one of the redox partners is of limited long-term stability, since it can be generated transiently in the course of the CV cycle. Furthermore, $\Delta V°$ values obtained from partial molar volumes are valid at infinite dilution, whereas in practice it is convenient and often desirable to measure *conditional*, rather than standard, electrode potential differences and hence molar volume measurements (i.e. at some practical value of the ionic strength, etc.), in which case the zero superscripts should be dropped.

Our experience has been that ΔE is a linear function of P (i.e. that ΔV is independent of P) within experimental uncertainty over the pressure range[1] 0–200

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[1] Atmospheric pressure (0.1 MPa) is negligible in the context of this article, and is taken to be zero.

MPa for metal complex couples; the apparent nonlinearity of the dependence of ΔE on P reported for the $\mathrm{Fe(phen)_3}^{3+/2+}$ couple versus Ag/AgCl [21] has subsequently been traced to instability of the oxidized complex over the time scale of the experimental pressure cycle [22]. For pressures ranging up to 1 GPa, however (i.e. approaching the freezing pressure of aqueous solutions at ambient temperature), noticeable curvature of $\ln K$ versus P plots has been reported [23–25].

In all cases, ΔE and hence ΔV for a half-reaction of the type

$$\mathrm{ML}_n{}^{(z+1)+}(\mathrm{aq.}) + \mathrm{e}^- \rightarrow \mathrm{ML}_n{}^{z+}(\mathrm{aq.}) \tag{4}$$

can only be measured in relation to a reference half-cell such as a Ag/AgCl [21] or $\mathrm{Ag/Ag^+}$ [26] electrode (in accordance with the IUPAC convention, the half-cell of interest should be considered as a reduction as in Eq. (4), i.e. the reference half-cell may be regarded as an oxidation). Attempts [27,28] have been made to assign a volume to the electron in a metal electrode so that ΔV for a half-reaction such as Eq. (4) might be estimated from the molar volumes of $\mathrm{ML}_n^{(z+1)+}$(aq.) and ML_n^{z+} (aq.). This, however, requires some questionable assumptions and in practice is rarely necessary because, for a *net* redox reaction, subtraction of ΔV values for the constituent half-reactions relative to a common reference half-cell gives ΔE and ΔV for the net reaction, so the problem of the contribution of e^- or of the reference electrode disappears. The choice of reference electrode depends upon the system under study; the $\mathrm{Ag/Ag^+}$ electrode is robust but incompatible with chloride media, whereas the AgCl coating in Ag/AgCl/KCl(aq.) electrodes (or Ag/AgCl/NaCl(aq.), if the reaction medium contains perchlorate ion) is susceptible to damage or contamination in pressure experiments. Serendipitously, the pressure responses of the $\mathrm{Ag/Ag^+}$ and $\mathrm{Ag/AgCl/Cl^-}$ electrodes are not very different; ΔV values measured against the $\mathrm{Ag/Ag^+}$ (0.01 mol $\mathrm{l^{-1}}$)[2] electrode may be converted to ΔV relative to Ag/AgCl/KCl(4.0 mol $\mathrm{l^{-1}}$) by addition of 2.9 ± 0.4 $\mathrm{cm^3\ mol^{-1}}$ [29]. Cruañes et al. [25] have concluded that the contribution of the Ag/AgCl reference electrode to cell potentials is only slightly pressure dependent.

According to transition state theory, the pressure dependence of the rate constant of an electrode reaction at constant potential may be represented in a manner analogous to Eq. (1) as the *volume of activation*, $\Delta V^{\ddagger}_{\mathrm{el}}$:

$$(\partial \ln k_{\mathrm{el}}/\partial P)_T = -\Delta V^{\ddagger}_{\mathrm{el}}/RT \tag{5}$$

In general, however, rate constants for electrode reactions are functions of the overpotential; in this article, the symbol k_{el} is taken to mean the rate constant for a *self-exchange* reaction measured at *zero overpotential*, i.e. with the electrode operating reversibly at equilibrium. Conway and Currie [28] (see also Heusler and Gaiser [27]) give a detailed analysis of the more general case of *apparent* volumes of activation $\Delta V^{\ddagger}_{\mathrm{a}}$ for half-reactions (Eq. (4)) with particular attention to the case of

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[2] The preferred pressure- and temperature-independent unit for studies at variable pressure is mol $\mathrm{kg^{-1}}$ (molal scale), but the traditional unit, mol $\mathrm{l^{-1}}$ (molar scale), may be used so long as it is taken to refer to a particular temperature and pressure—in this article, the ambient 0.1 MPa and 22°C. For the measured quantities reported in this article, the temperature is 25°C unless otherwise stated.

hydrogen evolution, which is necessarily a multi-step process. For a simple one-step half-reaction, we have:

$$\Delta V_{el}^{\ddagger} = \Delta V_{O}^{\ddagger} + \alpha \Delta V = \Delta V_{R}^{\ddagger} - (1 - \alpha)\Delta V \qquad (6)$$

where α is the electrochemical transfer coefficient (typically ca. 0.5), $\Delta V_{O}^{\ddagger}$ and $\Delta V_{R}^{\ddagger}$ are the volumes of activation for the oxidant and reductant half-reactions, respectively, and the volume of reaction $\Delta V = \Delta V_{O}^{\ddagger} - \Delta V_{R}^{\ddagger}$. A similar expression will apply to any net redox reaction; for a self-exchange reaction, $\Delta V = 0$.

Just as with pressure effects on electrode potentials, our experience has been that, for metal complexes in aqueous solution, $\ln k_{el}$ is a linear function of P (i.e. that $\Delta V_{el}^{\ddagger}$ is constant) within the experimental uncertainty over the convenient working range 0–200 MPa. There are, however, reasons to suppose that the volume of activation $\Delta V_{ex}^{\ddagger}$ for *homogeneous* (bimolecular) electron transfer in solution (which, as we shall see, is simply related to $\Delta V_{el}^{\ddagger}$) should become numerically smaller with increasing pressure, although the effect is likely to be important only in nonaqueous solvents or, in water, when $|\Delta V_{el}^{\ddagger}|$ or $|\Delta V_{ex}^{\ddagger}|$ is large [18,30,31]. It is therefore expedient to make comparisons and theoretical analyses of $\Delta V_{el}^{\ddagger}$ or $\Delta V_{ex}^{\ddagger}$ at the midrange pressure of 100 MPa—in other words, $\ln k$ data are fitted to a linear function of P and the resulting volumes of activation are regarded as valid at 100 MPa. For the same reason, volumes of *reaction* ΔV obtained by linear regression of ΔE on P should be regarded as valid at the mid-range pressure.

3. Experimental techniques

As the specialized experimental methodology of high pressure chemistry tends (unnecessarily) to be a deterrent to its wider application, we describe in outline some of the equipment and procedures used, with emphasis on those developed in our laboratories (discussed here as 'Melbourne' and 'Calgary' cells).

3.1. Pressure generation

Methods of generating, transmitting, containing, and measuring high pressures in liquids are discussed in detail elsewhere [1–7,32]. Since water freezes at about 900 MPa at room temperature, a compressed-air-driven hydraulic pump with a fail-safe electronic controller, or a 200 MPa hand pump with a pressure intensifier, will suffice for aqueous solution studies where the internal free volume of the pressure vessel is some hundreds of millilitres. Where the volume of fluid to be compressed is only on the order of 10 ml, a screw press is more convenient. Pressure is transmitted to the pressure vessel through a separator with a free piston to keep the hydraulic fluid out of the electrochemical cell. The pressurizing fluid entering the electrochemical cell from the separator should be an electrical insulator and as free as possible from easily oxidizable or reducible impurities; hexanes, octanes or clean hydrocarbon white oil perform well.

Application of pressure with an externally supplied gas is not recommended because of safety considerations (the pressure–volume energy of a compressed gas is much greater than for a liquid at a given pressure). Jovancicevic and Bockris, however, describe a device for studying electrode kinetics at pressures up to 200 MPa that is pressurized by rapid generation of a large amount of hydrogen gas in a small volume [33]. Hydrothermal systems can often be self-pressurized by the saturated vapor pressure of the water itself in a sealed vessel, if the evaporative losses of solvent are tolerable and if pressure effects are not of interest per se, but care must be taken to allow sufficient space for the thermal expansion of the liquid phase.

3.2. *Early studies*

Early work in high pressure electrochemistry by Bridgman [32], Adams [34], and others was concerned mainly with conductimetric measurements. Pressure effects on the E.M.F. of electrochemical cells were reported by Cohen and Piepenbroek [35], who studied Tl/TlX cells ($X = Cl$, NCS), while techniques for measuring pH under pressure were developed by MacInnes et al. [36] and Hills and Kinnibrugh [37] using the $Pt,H_2/HCl//KCl/Hg_2Cl_2$ cell, and by Distèche [38,39] using a glass electrode. These and other pioneering studies have been reviewed by Hills and co-workers [40–45].

3.3. *High pressure voltammetry*

Reproducibility of voltammetric measurements at a stationary electrode in a pressurized system inevitably suffers from the difficulty of keeping the working electrode surface clean, and accordingly the dropping mercury electrode, in which the electrode surface is continually refreshed, has been developed by some workers despite the problems of drop rate regulation in a pressurized enclosure [40–47]. Hills and co-workers [40–45] have described successful adaptations of dropping mercury electrode polarography at high pressures, but the technique has not been widely applied. Hills and Kinnibrugh [37] opted instead to use a hanging drop Hg electrode to avoid the complications associated with the changing geometry of an evolving drop, and obtained a $\Delta V^{\ddagger}_{el}$ value of -3.4 cm^3 mol^{-1} for the H_2 evolution reaction. Most subsequent high pressure voltammetric studies have used stationary solid electrodes.

Which ever experimental approach is used, it is imperative to check that E.M.F. or kinetic measurements made at intervals of increasing pressure are consistent within the experimental uncertainty (not more than ± 2 mV) with measurements made on the descending leg of the pressure cycle on a given solution sample. In particular, measurements made at the lowest pressure at the start and the end of the cycle must agree. Data sets collected without this precaution must be rejected, however precise they may seem to be, as drift of the electrode response is usually steady over the day-long cycle of a typical high pressure experiment and will result in a false slope of the ΔE (or $\ln k_{el}$) versus P plot. Usually, the lowest pressure of the cycle is chosen to be in the range 1–5 MPa, rather than atmospheric pressure, as some settling of electrodes, connections, seals, etc. tends to occur over the first few MPa.

Ewald and Lim [48] were the first to report the use of a stationary Pt microelectrode for voltammetry at high pressures. Their data on the half-wave potential of the Cu^{2+}/Cu^{+} reduction relative to a saturated calomel electrode in 0.5 mol l^{-1} aqueous KCl over the range 0–303 MPa imply a volume of reaction ΔV_{SCE} (defined below) for this cell of $+23.1 \pm 0.7$ cm^3 mol^{-1} at ambient temperature. The copper species involved, however, were not precisely defined; Bard et al. [49] invoked the chloro-complexes $Cu^{II}Cl^{+}$ and $Cu^{I}Cl_3^{2-}$ as the electroactive species in a high temperature, high pressure study of this electrode reaction in aqueous KCl (0.2 mol l^{-1}) media, but did not report the pressure dependence of the E.M.F.

Nowadays, cyclic voltammetry is routinely used for electrochemical investigations in coordination chemistry. Electrode potentials relative to a reference electrode are readily obtained from a CV cycle in the form of the half-wave potential $E_{\frac{1}{2}}$ by averaging the potentials of the anodic and cathodic peaks. The CV method was first adapted for high pressure studies in 1975 by Fleischmann et al. [50], who used it to determine the volume changes accompanying the oxidation and reduction of a series of aromatic hydrocarbons in acetonitrile. Krasinski and co-workers [51] used CV and chronoamperometry to study the electroreduction of Cd^{2+}(aq.) at a static mercury electrode relative to Ag/AgCl. Cruañes and co-workers [52] have reported the pressure tuning of mass and charge transport in redox-active QPVP/$Fe(CN)_6^{3-/4-}$/KNO_3 layers on metallic electrodes over an 800 MPa range.

Ultramicroelectrodes (UMEs; electrodes with diameters on the order of 10 μm or less) offer several advantages over conventional working electrodes, including the use of very dilute supporting electrolytes and access to very fast voltammetric measurements. Faulkner and co-workers pioneered the use of high pressure CV methodology with Pt UMEs, measuring the pressure dependencies of the diffusion coefficients of $K_3Fe(CN)_6$ and O_2 in aqueous KCl [23], and of the electrode potentials of cytochrome *c* [24], $M(bpy)_3^{3+/2+}$ (M = Co, Fe) and α-(hydroxyethyl)ferrocene$^{+/0}$ [25]. An unusual feature of their design [25] is that the body of the cell as a whole is divided into working and reference/counter electrode compartments by a stainless steel frit. Stevenson and White [53] used a Pt UME to study the effects of pressure on the one-electron reductions of neat acetophenone and nitrobenzene over the pressure range 0–100 MPa, and thereby showed that the transport-limited currents for these reductions are limited solely by diffusive processes.

Redox proteins tend to bind irreversibly to untreated Pt or Au electrodes. Cruañes et al. [23] were able to measure formal potentials for redox of cytochrome *c* over the pressure range 0–500 MPa using a gold electrode that had been pre-treated with L-cysteine. Sun et al. [29] used both CV and differential pulse voltammetry (DPV) to obtain ΔV relative to Ag/AgCl for redox of horse heart cytochrome *c* at pressures up to 200 MPa, using a gold electrode modified with 4,4′-dipyridyl disulfide; the two methods gave essentially identical results.

3.3.1. *Melbourne cell*

Sachinidis et al. [26,54,55] describe the construction of a high pressure electrochemical cell and give a detailed account of procedures for high pressure voltammetry using the Ag/Ag^+ reference electrode, with the $Fe(CN)_6^{3-/4-}$ couple as an illustration. The cell is shown in Fig. 1. The Ag^+ concentration standard chosen for the reference electrode is 0.01 mol l^{-1} (as $AgNO_3$) in a solution of set total ionic strength (typically 0.1 to 1.0 mol l^{-1}, usually with KNO_3). In a recent modification of this design [110], many of the design concepts of 1 or 2 mm polished microdisk working and auxiliary electrodes of Pt or Au, with the sample solution separated from the Ag wire/$AgNO_3$ reference electrode by a Vycor frit mounted in a piston, have been maintained in a cell which has a sample volume of under 1 ml compared to around 60–70 ml in the previous cell [26]. Section drawings of this cell are shown in Fig. 2. The cell body components and electrode mounts are either Kel-F™ or Teflon™. The working and auxiliary electrodes are mounted facing one another directly across a short path of sample solution. The disk electrode assemblies are readily removed, allowing surfaces to be repolished using 1 and 0.3 μm alumina powder and then rinsed with 10% HNO_3 followed by distilled water prior to a pressure run. The sample and electrodes are prepared and the cell filled in a N_2 glove box. The cell is mounted in the same high pressure bomb used

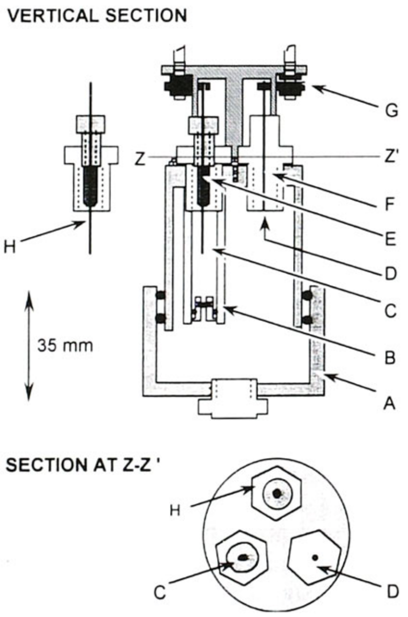


Fig. 1. Melbourne high-pressure electrochemical cell: (A) Two part Kel-F cell body to accommodate sample compression; (B) Vycor liquid junction and piston; (C) Ag reference electrode and compartment; (D) disk working electrode; (E) Teflon seal; (F) Kel-F threaded electrode mount; (G) electrical connection through to high pressure seal and detection; (H) Pt auxiliary electrode.

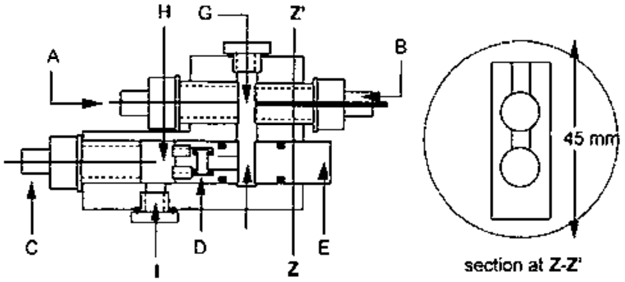


Fig. 2. Small volume high-pressure electrochemical cell: (A) Pt or Au 1 mm disk working electrode assembly; (B) Pt 2 mm disk auxiliary electrode assembly; (C) Ag wire reference electrode assembly; (D) Vycor frit liquid junction piston assembly; (E) pressure transmission/volume compensation piston; (F) cell body; (G) sample solution; (H) reference electrolyte; (I) reference electrolyte and sample solution filling caps.

for the earlier cell design and described previously [26]. Because of the low thermal transmission of the polymer materials of the cell and the unstirred oil used to generate high pressure in the steel bomb, thermostatting is slow but precise. As described for the Calgary experiments below, a pressure run, allowing for thermostatting and a stepwise increasing then decreasing set of pressures to confirm the stability of the system over the period of the experiment, typically takes a full day.

3.3.2. Calgary cell

Elsewhere [56], we give an experimental protocol for measuring the pressure dependence of electrode potentials against a Ag/AgCl electrode using CV, again with the $Fe(CN)_6^{3-/4-}$ couple as an example (see Doine et al. [21]). The electrochemical cell originally described [21,56], however, has been replaced with the cell shown in Fig. 3, in which compression of the reference electrode solution is allowed for by mounting the Vycor frit in a free piston. The reference electrode compartment is filled with 4.0 mol l^{-1} aqueous KCl, rather than the traditional saturated KCl solution in contact with solid KCl, because the solubility of KCl varies somewhat with pressure (and temperature), and slow dissolution or precipitation of KCl as the pressure is changed may cause drift of the cell E.M.F. For service with perchlorate media, NaCl solution is used in place of KCl.

The working electrode is usually a short (2–4 mm) length of Pt or Au wire (0.5 mm o.d.) or a glassy carbon fiber. The counter electrode now used is a straight 2–4 cm length of Pt or Au wire (0.5 mm o.d.) rather than the long helix of the earlier design [21,56]. Counter and working electrodes are cleaned prior to assembly of the cell by polishing with fine, wet alumina powder, followed by immersion in concentrated H_2SO_4 containing a small amount of dissolved $K_2S_2O_8$ and then washing and sonication in deionized distilled water. Solutions are deoxygenated by purging with argon before placing them in the cell under an Ar atmosphere. The same apparatus and set-up procedure are used for the measurement of pressure effects on the rate constants of electrode reactions by alternating current voltammetry (ACV) [22,57], as described below.

The pressure vessel (Fig. 4) is of heat-treated 17-4PH stainless steel, designed for a pressure ceiling of 500 MPa, but in practice has not been used above 300 MPa. Control of the temperature of the pressure vessel and its contents is achieved using a close-fitting, hollow aluminum jacket through which water is circulated rapidly from an external thermostat. Thermal equilibration to within ± 0.05°C, however, is slow, requiring some 75 min initially, and also 45–50 min after each pressure change (since adiabatic compression and decompression respectively raise and lower the temperature of the pressure vessel contents). Furthermore, before each CV or ACV measurement is made with the pressurized assembly, the working electrode must be cleaned electrochemically by cycling the potential at least three times between the most positive potential to be scanned and the hydrogen evolution potential. Consequently, a full cycle of CV and ACV measurements normally requires a full working day, placing stringent demands on the chemical stability of the couple being studied.

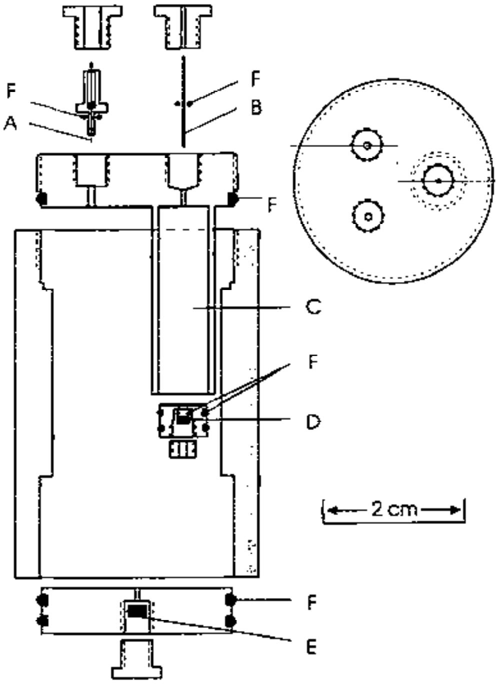


Fig. 3. The Calgary cell body is composed of virgin Teflon: (A) working electrode; (B) reference electrode (Ag wire coated with AgCl); (C) reference electrode compartment (filled usually with 4.0 mol l^{-1} KCl); (D) Vycor frit; (E) rubber disk seal; (F) rubber O-rings. Reprinted with permission from J. Am. Chem. Soc. 118 (1997) 7137. Copyright 1997 American Chemical Society.

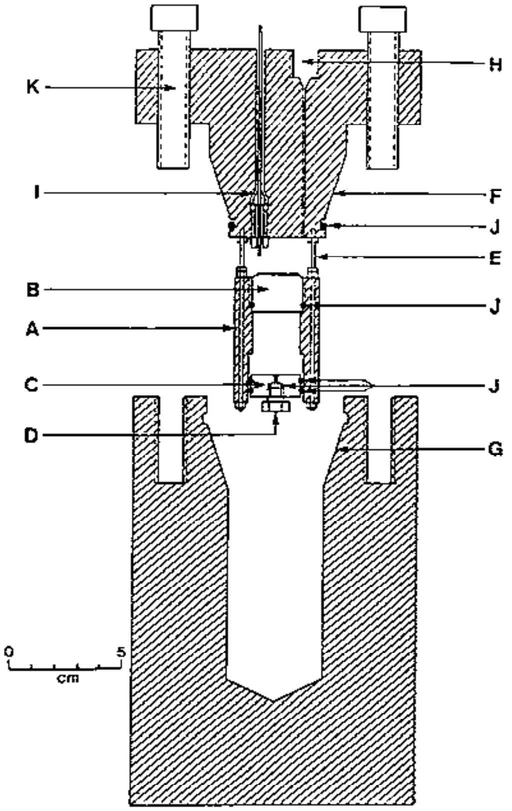


Fig. 4. Pressure vessel for Calgary cell: (A) cell; (B) Teflon plug carrying electrical connections; (C) free piston; (D) sealing plug; (E) threaded steel support rods; (F) main sealing surface of cap (39° cone); (G) main sealing surface of body (40° cone); (H) pressurizing fluid connection; (I) electrical feedthrough (brass conductor in Vespel insulating sleeve; one of four); (J) O-ring; (K) Hexhead bolt (0.625 inch NC. 2.25 inch long; eight of these, symmetrically placed). Reprinted with permission from Can. J. Chem. 70 (1992) 81. See references [21] and [56] for further details.

3.4. Aqueous voltammetry at high temperatures and pressures

With hydrothermal solutions, the problems of high pressure electrochemistry are compounded by the risk of thermoelectric effects, the corrosive nature of electrolyte solutions toward many metals, the dissolution or leaching of silica or silicate-based vessels, the softening or decomposition of many plastic structural materials such as Teflon, and the increased solubility of reference electrode components such as AgCl. Mesmer et al. [58] used a Pt,H_2/HCl,KCl//KCl,KOH/H_2,Pt system to measure the self-ionization constant of water from ambient temperature to 292°C. Problems originating with internal reference electrodes such as Ag/AgCl at high temperatures may be considerably alleviated by using an external pressure-balanced electrode at ambient temperature, but, as Lvov and Macdonald have shown [59], the thermal liquid junction potential can make major contributions to the cell potential and can vary by ±150 mV depending on the nature of the electrolyte bridge and the thermal gradient across it. Macdonald's group [59–64] has made important advances in the measurement of pH in high temperature and supercritical water in the context of power plant heat transfer chemistry and other industrial applications. The H^+ sensors they have designed and tested successfully include glass electrodes for use at moderately high temperatures (200–250°C) [60], yttrium-stabilized zirconia with an internal Hg/HgO element [61,62], and tungsten oxide [63]. They have also developed Pd–Pt electrodes for measuring dissolved H_2 in supercritical media [64].

Bard and co-workers [65] have recently described a device of small internal volume (2 ml) for voltammetric studies in near-critical or supercritical aqueous media; in such solutions, *iR* drops across the cell can be large and consequently ultramicroelectrodes (UMEs) are the sensors of choice. The Pt UMEs are mounted in a special glass (Corning 8870; 50–60% PbO, 25–35% SiO_2, 5–10% K_2CO_3, 0.1–0.5% Sb_2O_3) which, though costly, is resistant toward leaching by supercritical water at 385°C and has the same coefficient of expansion as Pt, so obviating expansion-induced leaks and protrusion (or retraction) of the electrode as the temperature is increased. The cell body is an oxidized titanium tube; earlier, less satisfactory, designs used either an alumina tube, which was subject to failure under pressure [66], or a stainless steel pressure vessel with a silica liner that was prone to dissolution by water at high temperatures [49].

3.5. Electrode kinetics at high pressures

In principle, it is possible to extract rate constants for electrode reactions from the difference in potential of the anodic and cathodic peaks of a cyclic voltammogram; for a fully reversible reaction, this separation is 59 mV, but for quasi-reversible processes limited by chemical kinetics the separation is wider. The widening, however, is not usually large enough to be measurable with the precision required for determination of $\Delta V^{\ddagger}_{el}$, and furthermore, since most $\Delta V^{\ddagger}_{el}$ values for redox processes are negative, the widening lessens as the pressure is increased [21,22,57]. Even for the alkali metal ion-mediated electrode reactions of anionic couples such as $Fe(CN)_6^{3-/4-}$, for which $\Delta V^{\ddagger}_{el}$ is strongly positive and the CV peak-to-peak separation increases with rising pressure, the increasing breadth of the peaks makes measurement of the separation imprecise, and only rough (±2 cm^3 mol^{-1} at best) values of $\Delta V^{\ddagger}_{el}$ can be obtained [21]. In any event, the peak separations tend to be increased by unidentified factors in addition to chemical kinetics.

Alternative methods of determining of k_{el} include the extrapolation of measured exchange current densities i_0 to zero overpotential by the Tafel (Butler–Volmer) relation, but this requires the presence of both $ML_n^{(z+1)+}$ and ML_n^{z+} in solution, is tedious, and is prone to error from mass transfer effects. Our preferred technique is AC voltammetry (ACV), which requires the presence of only one member of the couple in bulk solution, allows for correction for the uncompensated resistance R_u and double layer capacity C_{dl} in the calculation of k_{el}, and gives reliable k_{el} values as high as 1 cm s^{-1} with conventional electrodes. ACV also allows for calculation of the transfer coefficient α from the potential E_{dc} of the AC faradaic current peak relative to the half-wave potential $E_{\frac{1}{2}}$ of the corresponding DC cyclic voltammogram (CV):

$$E_{dc} = E_{\frac{1}{2}} + (RT/nF)\ln[\alpha/(1-\alpha)]. \qquad (7)$$

If the diffusion coefficients D_O and D_R of the oxidized (O) and reduced (R) forms of the electroactive species and the phase angle φ of the AC current relative to the true potential across the electrode-solution interface are known, then

$$[\cot\varphi]_{max} = 1 + \frac{(2D_O^{(1-\alpha)}D_R^{\alpha}\omega)^{\frac{1}{2}}}{\alpha^{-\alpha}(1-\alpha)^{-(1-\alpha)}k_{el}} \qquad (8)$$

where ω is the angular frequency of the applied AC perturbation, and k_{el} is obtainable from linear plots of $[\cot\varphi]_{max}$ against $\omega^{\frac{1}{2}}$. D_O and D_R may be taken to be the same for a given redox couple, but must be re-evaluated at each pressure from the peak currents of DC cyclic voltammograms calibrated against couples with known diffusion coefficients.

Conway and Currie [28] presented a detailed analysis of the factors to be considered in deriving a true volume of activation $\Delta V_{el}^{\ddagger}$ for an electrode reaction from the effect of pressure on current densities measured at finite over-potentials, with particular reference to the negative volume of activation reported for hydrogen evolution by Hills and Kinnibrugh [37]. Conway and Currie [28] also reported their measurements of $\Delta V_{el}^{\ddagger}$ over a 0-220 MPa range for the $Fe(CN)_6^{3-/4-}$ couple at a gold electrode in aqueous K_2SO_4 (0.5 mol l^{-1}) using a phase-sensitive AC impedance method (in effect, ACV). The reference electrode was Pd/$Fe(CN)_6^{3-/4-}$, and the counter electrode a Pt gauze. The wall of the whole cell was made of flexible Teflon tubing to accommodate compression of the contents. Sato and Yamada [67] also describe high pressure measurements on the $Fe(CN)_6^{3-/4-}$ electrode reaction in 1.0 mol l^{-1} MCl (M = Li, Na, K), using a small (2 ml capacity) Teflon electrolysis cell with a flexible silicone–rubber wall, but their experiments were limited to a 0–100 MPa range.

Franklin and Mathew measured apparent volumes of activation (0–175 MPa) for the metal electrodeposition reactions

$$M(H_2O)_6^{z+}(aq.) + ze^- \rightarrow M(s) + 6H_2O \qquad (9)$$

for M = Ni [68,69], Co and Ag [70] from a variety of electrolyte solutions. The cell body was machined out of a rod of flexible Teflon, the working electrode was of Ni wire and the counter/reference electrode was a large mercury pool covered with Hg/Hg_2SO_4 paste held in place with a glass wool plug. At a given pressure, the electrodes were cleaned in situ by cyclical sweeping of the applied voltage from 90 mV cathodic to 10 mV anodic for 6 h, after which the exchange current density i_o was determined by extrapolating the ln(current)–voltage curve from the region of cathodic overpotential -0.060 to -0.040 V to the standard electrode potential $E°$. The volumes of activation reported would seem to be apparent values, although the authors argue [69] that the contribution of ΔV according to Eq. (6) can be ignored because the rate determining step is thought to involve deaquation of the metal ion but not electron transfer.

4. Pressure effects on redox potentials of metal complexes

Volumes of reaction and of activation are conceptually more amenable to interpretation on structural and solvational grounds than are other thermodynamic and kinetic parameters, and so provide special insights into solution chemistry and reaction mechanisms. In addition to their intrinsic interest, however, volumes of reaction for electrode processes are necessary information for the extension of the well-known Marcus cross relation in rate constants for adiabatic, outer-sphere, homogeneous (bimolecular) electron transfer reactions [71,72]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}}W, \tag{10}$$

in which

$$\ln f = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z_{11}Z_{22}) + (w_{11} + w_{22})/RT]}$$

and

$$W = \exp[(w_{11} + w_{22} - w_{12} - w_{21})/2RT],$$

to a corresponding relation in volumes of activation [73]:

$$\Delta V^{\ddagger}_{12} = \tfrac{1}{2}(\Delta V^{\ddagger}_{11} + \Delta V^{\ddagger}_{22} + \Delta V_{12}) + C. \tag{11}$$

Here, the superscripts 11 and 22 refer to self-exchange reactions of, say, A with A^+ and of B with B^+, and 12 and 21 refer to the 'cross' reaction of A with B^+ and its reverse, respectively. The symbols w refer to the coulombic work required to bring the reactants together; Z_{ii} are frequency factors associated with the expression of k_{ij} in terms of a free energy of activation ΔG^{*}_{ij} and are usually taken to be 1×10^{11} l mol^{-1} s^{-1}:

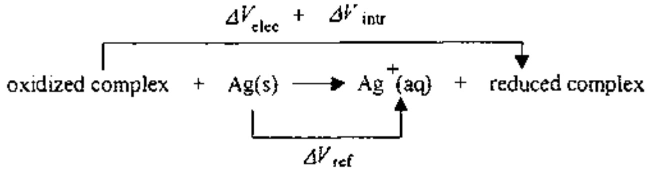
$$k_{ij} = Z_{ij} \exp(-\Delta G^{*}_{ij}/RT). \tag{12}$$

For self-exchange reactions and for cross reactions that are symmetrical with respect to the charges on the reactants, W is effectively 1 if the reactant radii are not very different, and the term C is then $-(RT/2)(\partial \ln f/\partial P)_T$ (see Grace et al. [73] for further algebraic development). For *small* 'driving forces' ΔE (in the order of 100–200 mV), $\ln f$ and therefore C can be approximated to zero. In any event, if we know $\Delta V^{\ddagger}_{ii}$ for a selection of self-exchange reactions, and can measure ΔV_{12} from the pressure dependence of ΔE (Eq. (2)) as described in this review, we can predict $\Delta V^{\ddagger}_{12}$ in so far as the adaptation of the Marcus cross relation is correct. Comparison of measured with calculated $\Delta V^{\ddagger}_{12}$ values therefore provides a check on the validity of Marcus theory for reactions known to be of the outer-sphere type, and Grace et al. [73] demonstrated this for the $Fe(H_2O)_6{}^{3+}$–$Co(ttcn)_2{}^{2+}$ reaction in water. Conversely, conformity with Eq. (11) can serve as a *criterion of the* *mechanism* of electron transfer for cross reactions—consistency of measured with theoretical $\Delta V^{\ddagger}_{12}$ values implies that the reaction is indeed adiabatic and of the outer-sphere type.

Table 1 lists experimental cell reaction volume values for various complex-ion couples. Although for experimental reasons data may have been obtained using different reference half-cells, the $\Delta V_{\mathrm{Ag/AgCl}}$ values for cells in Table 1 have all been normalised against the Ag/AgCl electrode. Whether Ag/Ag$^+$ or Ag/AgCl are used, the choice makes only a slight difference to the measured cell reaction volume. Over the range of 0–200 MPa, the potential of the cell Ag/0.01 M $AgNO_3$, 1 M KNO_3//1 M KNO_3//KCl(sat'd)/AgCl/Ag changes by around only -6 mV, corresponding to a difference in the half-cell volume contributions of only 2.9 cm^3 mol^{-1} [29]. Golas et al. [23] report values of $\Delta V_{\mathrm{Ag/AgCl}}$ for $\mathrm{Fe(CN)_6^{3-/4-}}$ that appear to be in arithmetical error by a factor of 10. The value cited in Table 1 is estimated by taking the potential data of Fig. 5 in reference [23] to be a linear function of pressure from 0 to 200 MPa., and is in satisfactory agreement with the work of others. Despite the stringent requirements for system and equipment stability, noted in Section 3, these now seem to have matured to the point where agreement between reports in Table 1 is generally good.

For any discussion of pressure effects on equilibrium redox potentials to proceed, the contributions of the separate half-cells to the experimental ΔV is among the first issues that must be resolved. Once this is achieved, the volume change associated with the reduction of the metal-complex may have contributions arising from: (a) intrinsic volume changes ΔV_{intr}, reflecting bond length and conformational changes in the structure of the complex; and, because in redox reactions there will necessarily be a change in formal charge on the complex, (b) electrostrictive volume changes ΔV_{elec}, reflecting the contraction or expansion of the surrounding solvent in response to the change in charge on the complex. These contributions are represented in Eq. (13) and schematically in Eq. 14, using the Ag/Ag$^+$ reference electrode as an exemplar.

$$\Delta V_{\mathrm{cell}} = \Delta V_{\mathrm{ref}} + (\Delta V_{\mathrm{intr}} + \Delta V_{\mathrm{elec}})_{\mathrm{complex}} \qquad (13)$$



(14)

Sachinidis et al. [54] measured redox cell volumes for a series of Fe(III)/(II) couples—$\mathrm{Fe(CN)_6^{3-/4-}}$, $\mathrm{Fe(bpy)(CN)_4^{-/2-}}$, $\mathrm{Fe(phen)(CN)_4^{-/2-}}$, $\mathrm{Fe(bpy)_2(CN)_2^{+/0}}$, $\mathrm{Fe(bpy)_3^{3+/2+}}$, and $\mathrm{Fe(phen)_3^{3+/2+}}$—chosen because, on the basis of the crystallographic data, the intrinsic volume changes, ΔV_{intr}, are expected to be negligible. In this situation Eq. (13) simplifies and, based on the proposition that the electrostrictive volume change is expected to be proportional to (charge)^2, becomes Eq. (15),

Table 1
Volumes of reaction[a] for reduction of transition metal complexes in aqueous solution at 25.0°C

Couple/electrode	Medium	Ionic strength (mol l^{-1})	$\Delta V_{Ag/AgCl}$[a] (cm^3 mol^{-1})	Ref.
$Cr(bpy)_3^{3+/2+}/Hg(Au)$	KNO_3	0.1	11.0 ± 1.0	[55]
$Mo(CN)_8^{3-/4-}/Au$	$NaClO_4$	0.5[b]	−29.8 ± 1.0	[74]
$W(CN)_8^{3-/4-}/C(gl)$	KCl	0.5	−27.5 ± 0.8	[74]
$Fe(H_2O)_6^{3+/2+}/Pt$	$HClO_4/NaClO_4$	0.5	5.5 ± 0.4	[22]
	CF_3SO_3H	0.28	5.0 ± 0.3	[21]
$Fe(H_2O)_6^{3+/2+}/Au$	$HClO_4$	1.0	4.6 ± 0.8	[55]
		0.1	2.6 ± 1.4	[55]
		0.1	7.0 ± 0.4	[111]
$Fe(phen)_3^{3+/2+}/Pt$	Na_2SO_4	0.1	15.3 ± 0.7	[22]
	NaCl	0.1	14.2 ± 0.7	[111]
$Fe(phen)_3^{3+/2+}/Au$	KNO_3	1.00	9.6 ± 1.0	[54]
		0.25	9.0 ± 0.3	[54]
$Fe(bpy)_3^{3+/2+}/Au$	KNO_3	1.00	10.9 ± 0.3	[54]
		0.10	11.2 ± 0.5	[54]
$Fe(bpy)_3^{3+/2+}/Pt$	KNO_3	0.10	18[c,d]	[25]
$Fe(bpy)_2(CN)_2^{+/0}/Au$	KNO_3	1.00	−3.7 ± 0.5	[54]
		0.010	−3.6 ± 0.6	[54]
$Fe(bpy)(CN)_4^{-/2-}/Au$	KNO_3	1.00	−22.8 ± 0.6	[54]
		0.010	−26.7 ± 0.6	[54]
$Fe(phen)(CN)_4^{-/2-}/Au$	KNO_3	1.00	−22.6 ± 0.8	[54]
$Fe(phen)_2(CN)_2^{+/0}/Pt$	NaCl	0.1	0	[111]
$Fe(CN)_6^{3-/4-}/Pt$	KCl	1.0	−38.3 ± 1.0	[21]
		0.51	−36.6 ± 0.7	[21]
		0.28	−36.2 ± 0.8	[21]
		0.1	ca. −34[c,e]	[23]
	LiCl	0.28	−37.1 ± 1.3	[21]
	K_2SO_4	0.28	−34.4 ± 0.6	[21]
$Fe(CN)_6^{3-/4-}/Au$	KNO_3	1.00	−34.6 ± 0.4	[26]
			−35.8 ± 0.5	[54]
		0.33	−38.7 ± 0.9	[54]
		0.30	−37.6 ± 0.6	[26]
		0.10	−39.3 ± 0.5	[26]
			−39.9 ± 0.6	[54]
		0.030	−38.4 ± 0.6	[26]
			−39.6 ± 0.6	[54]
		0.010	−35.0 ± 1.2	[26]
			−36.1 ± 1.3	[54]
	$NaNO_3$	0.10	−42.4 ± 0.7	[54]
	$Ba(NO_3)_2$	0.81	−42.0 ± 1.4	[54]
		0.30	−38.9 ± 0.6	[54]
		0.03	−42.3 ± 1.0	[54]
	$Sr(NO_3)_2$	0.30	−41.6 ± 0.8	[54]
	$La(NO_3)_3$	6.0	−23.6 ± 0.7	[54]
		0.60	−29.5 ± 0.4	[54]
		0.06	−30.4 ± 0.5	[54]
		0.01	−32.3 ± 0.5	[54]
	(Li,Na,K)Cl	1.0	−35	[67]
Cyt $c^{III/II}$	NaCl[g]	0.1	23[c,h]	[24]
	$NaClO_4$[i]	0.1	−14.0 ± 0.5	[29]
$L(NH_3)_4Ru^{III}Cyt^{II} \leftrightarrow L(NH_3)_4Ru^{II}Cyt^{III}$				
$L = NH_3$	$NaClO_4$[i]	0.1	31.7 ± 1.2	[29]
L = *trans*-isn	$NaClO_4$[i]	0.1	21.1 ± 1.0	[29]

Table 1 (*Continued*)

Couple/electrode	Medium	Ionic strength (mol l^{-1})	$\Delta V_{\mathrm{Ag/AgCl}}$[a] (cm^3 mol^{-1})	Ref.
L = *trans*-py	$NaClO_4$[i]	0.1	23.3 ± 0.6	[29]
L = *trans*-(3,5-lut)	$NaClO_4$[i]	0.1	21.1 ± 0.8	[29]
$Fe(C_5H_5)_2^{+/0}$/SAM/Au	$NaClO_4$	1.0	−10 to −22	[112]
$CH_3CHOH(C_5H_4)$	KNO_3	0.1	−0.8[c,j]	[25]
$Ru(H_2O)_6^{3+/2+}$/Au	$NaClO_4$	0.1	2.4 ± 0.7	[55]
	$HClO_4$	0.1	3.0 ± 0.6	[55]
$Ru(NH_3)_6^{3+/2+}$/Au	KNO_3	0.1	20.2 ± 0.4	[55]
$Ru(NH_3)_6^{3+/2+}$/Hg(Au)	$NaClO_4$	0.1	19.7 ± 0.6	[55]
$Ru(en)_3^{3+/2+}$/Hg(Au)	KNO_3	0.1	16.9 ± 0.6	[55]
$Os(CN)_6^{3-/4-}$/Pt	KCl	0.6	−33.4 ± 0.9	[74]
$Co(phen)_3^{3+/2+}$/Au	KNO_3	0.1	24.3 ± 1.1	[55]
$Co(phen)_3^{3+/2+}$/Pt	NaCl	0.1	27.3 ± 1.1	[22]
			27.0 ± 1.0	[29]
			28.4 ± 1.4	[111]
$Co(bpy)_3^{3+/2+}$/Au	KNO_3	0.1	23.9 ± 0.9	[55]
$Co(bpy)_3^{3+/2+}$/Pt	KNO_3	0.1	29.2[c,k]	[25]
	NaCl	0.1	27.1 ± 1.4	[111]
$Co(terpy)_2^{3+/2+}$/Pt	NaCl	0.1	30.8 ± 1.5	[111]
$Co(en)_3^{3+/2+}$/Pt	KCl[l]	0.5	26.7 ± 0.7	[22]
$Co(en)_3^{3+/2+}$/Hg(Au)	KNO_3[m]	0.1	29.8 ± 1.4	[55]
$Co(diamsar)^{3+/2+}$/Au	$NaClO_4$[n]	0.1	17.4 ± 0.5	[75]
$Co(diamsarH_2)^{5+/4+}$/Au	$HClO_4$/ $NaClO_4$[o]	0.13	19.5 ± 0.8	[75]
$Co(sep)^{3+/2+}$/Pt	KCl	1.0	13.5 ± 0.4	[21]
		0.28	13.9 ± 0.5	[21]
		0.5	15.8 ± 0.5	[22]
$Co(ttcn)_2^{3+/2+}$/Pt	$NaClO_4$	0.1	24.4 ± 1.0	[22]
	CF_3SO_3K	0.26	21.1 ± 0.3[p]	[73]
	KCl	0.26	20.6 ± 0.2[p]	[73]
		1.1	21.8 ± 0.5[p]	[73]
	NaCl	0.3	21.4 ± 1.1	[111]
$Ni(tacn)_2^{3+/2+}$/Pt	NaCl	0.1	24.7 ± 1.2	[111]
$Cu(aq.)^{2+/0}$/Cu[q]	$NaNO_3$[r]	0.1	2.8	[26,54]
$Cd^{2+/0}$/Hg	NaCl	4.0	10.7	[51]
$Eu(aq.)^{3+/2+}$/Cu	$HClO_4/NaClO_4$	1.0	11.3	[113]

[a] Relative to Ag/AgCl/KCl (4.0 mol l^{-1}) and assumed to be independent of pressure, 0–200 MPa, except as indicated.

[b] pH 2.7.

[c] Pressure dependent; value at 100 MPa.

[d] Ranges from 39.5 cm^3 mol^{-1} at 0 MPa to 4.0 cm^3 mol^{-1} at 1 GPa.

[e] See text.

[f] Horse heart cytochrome *c*.

[g] Buffer solution (pH 7) containing 10 mmol l^{-1} *cis*-tris–buffer and 1.0 mmol l^{-1} cysteine.

[h] Ranges from −27 cm^3 mol^{-1} at 0 MPa to −3 cm^3 mol^{-1} at 500 MPa.

[i] Buffer solution (pH 7) containing 0.08 mol l^{-1} $NaClO_4$, 0.01 mol l^{-1} tris, 0.01 mol l^{-1} NaN_3, and 0.1 mmol l^{-1} 4,4′-dipyridyl disulfide.

[j] Ranges from 1.9 cm^3 mol^{-1} at 0 MPa to −3.8 cm^3 mol^{-1} at 500 MPa; nearly constant at −3.7 ± 0.1 cm^3 mol^{-1} from 0.5 to 1.0 GPa.

[k] Ranges from 55.1 cm^3 mol^{-1} at 0 MPa to 12.5 cm^3 mol^{-1} at 1.0 GPa.

[l] 0.2 mol l^{-1} en

[m] 0.01 mol l^{-1} en

[n] pH 5.4

[o] $[H^+] = 0.10$ mol l^{-1}.

[p] Relative to Ag/AgCl/KCl (saturated).

[q] High pressure potentiometry [26].

[r] pH 4–6.

where $\Delta z^2 = z^2_{\mathrm{oxid}} - z^2_{\mathrm{red}}$.

$$\Delta V_{\mathrm{cell}} = \Delta V_{\mathrm{ref}} + (\Delta V_{\mathrm{elec}})_{\mathrm{complex}} = \Delta V_{\mathrm{ref}} + B\Delta z^2/r \tag{15}$$

For this series of Fe(III)/(II)–cyanodiimine complexes, the cell reaction volumes obtained from the pressure dependence of the cell potential are indeed a linear function of Δz^2 (Fig. 5) and, by interpolating the data to a point where Δz^2 is zero, a measure can be obtained of ΔV_{ref}. For the Ag/Ag$^+$ half cell (0.01 mol l^{-1} Ag$^+$, ionic strength 1.0 mol l^{-1}), the volume change is -11.9 ± 0.5 cm^3 mol^{-1}; from data at ionic strength 0.1 mol l^{-1}, ΔV_{ref} is estimated as -13 cm^3 mol^{-1} [54]. From the observations of Sun et al. [29] on the Ag/Ag$^+$//AgCl/Ag cell, the ΔV_{ref} half-cell contribution for a Ag/AgCl/KCl reference electrode is therefore -9.0 ± 1 cm^3 mol^{-1}. As a useful working rule the electrostrictive volume changes by around 4 cm^3 mol^{-1} per unit of Δz^2 for these systems.

With the complex-ion couple contribution to the cell volume change identified, attention has been addressed to the breakdown of the intrinsic and electrostrictive contributions to the complex-ion reduction volume, $\Delta V_{\mathrm{complex}}$ [55]. Where the intrinsic volume change is anticipated to be zero, such as for Fe(bpy)$_3^{3+\ 2+}$ [54], Fe(phen)$_3^{3+\ 2+}$ [54], or Cr(bpy)$_3^{3+\ 2+}$ [55], the $\Delta V_{\mathrm{complex}}$ values are very similar and attributed to ΔV_{elec} alone. Assuming that this will be the electrostrictive contribution to $\Delta V_{\mathrm{complex}}$ for complexes such as Co(phen)$_3^{3+\ 2+}$ or Co(bpy)$_3^{3+\ 2+}$, intrinsic changes contribute around half of the +34 cm^3 mol^{-1} associated with these reductions [55]. Different approaches, using the effects of bond-length on the partial molar volumes of various M(phen)$_3$ salts or collating measurements on M(phen)$_3^{3+\ 2+}$ in acetonitrile, form a consistent estimate of the intrinsic and electrostrictive contributions for this Co(III)/Co(II) system. These data are summarized in Table 2.

The magnitude of ΔV_{elec} is expected to be affected by a number of factors. The Drude–Nernst expressions predict a change inversely proportional to the complex ion radius and dependent on (charge)^2 [12–18]. The effect of change in charge is the basis of the ΔV_{ref} assignment above [54]. The data in Table 2 all relate to complex couples with a 3+ to 2+ charge reduction. The electrostrictive volume change is around +20 cm^3 mol^{-1} for the larger tris–phen and tris–bpy systems, increasing to around +27 cm^3 mol^{-1} for the smaller tris–en and hexaammine complexes.

The change in metal–carbon bond lengths for the reductions Fe(CN)$_6^{3-\ 4-}$, Os(CN)$_6^{3-\ 4-}$, Mo(CN)$_8^{3-\ 4-}$, W(CN)$_8^{3-\ 4-}$ is negligibly small [74], so here also $\Delta V_{\mathrm{complex}}$ essentially only reflects electrostrictive contributions. Allowing for the reference electrode contribution to the data in Table 1 for these cyano-systems, the trend in $\Delta V_{\mathrm{complex}}$ values of -27.6 [21], -24.4, -20.8 and -18.7 cm^3 mol^{-1} [74], respectively (all for 0.5 or 0.6 mol l^{-1} electrolyte) again support the idea that high pressure electrochemical measurements are sensitive enough to detect and reflect these differences in size.

The types of ligand in the first coordination sphere may affect the nature of interactions with the surrounding solvent and therefore ΔV_{elec}. While results for the phen, bpy, en and ammine complexes in Table 2 can be accommodated in a simple

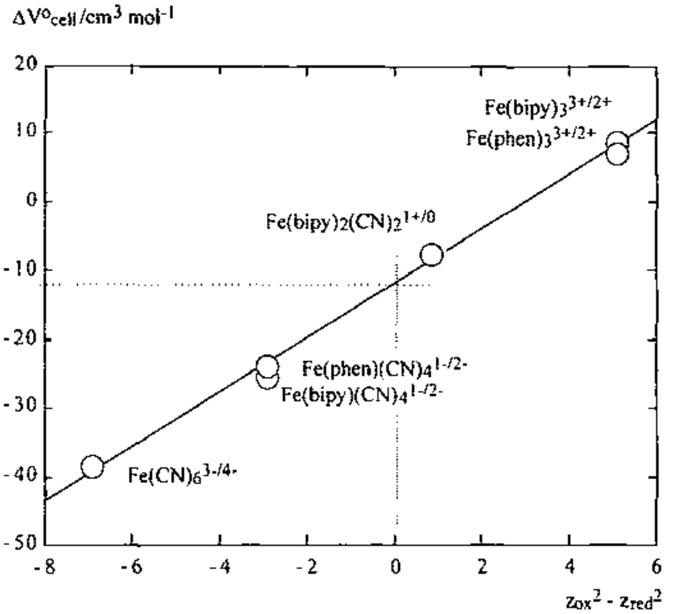


Fig. 5. A Plot of $\Delta V°_{cell}$ as a function of Δz^2 for various $Fe^{III/II}$ complexes; ionic strength 1.0 mol l^{-1}, 25°C. Reprinted with permission from Inorg. Chem. 33 (1994) 6180. Copyright 1994 American Chemical Society.

trend of ion size, the $Ru(H_2O)_6^{3+/2+}$ and $Fe(H_2O)_6^{3+/2+}$ data indicate that for aqua-ligands other factors may also come into play. Using the change in M–O bond length to estimate the contribution due to ΔV_{intr} (+6.7 and +9.6 cm^3 mol^{-1}, respectively for the Ru and Fe aqueous systems), the values of ΔV_{elec} are dramatically lower than expected on the basis of charge and size compared to, say, the $Ru(NH_3)_6^{3+/2+}$ system. The sensitivity of ΔV_{elec} to change in charge is reduced to only 1 cm^3 mol^{-1} per (charge)^2. It has been proposed [55], in an argument similar to that used to rationalize differences in reduction entropies in these systems, that electrostrictive ordering of water around aqua-ions is a combination of specific hydrogen bonding to the adjacent solvent layers and longer range general ion-dipole interactions. When aqua-ligands are present and the charge on the ion is reduced, the loss of highly structured H-bonded H_2O around $M(H_2O)_6^{3+}$ might be expected to lead to a reduction in volume as it collapses, analogous to the reduction in volume when water melts, offset and slightly outweighed by the longer range release of electrostricted solvent leading to small positive ΔV_{elec}.

Volumes of reaction for transition metal complexes measured at various total ionic strengths with different supporting electrolytes are reported in Table 1. Considerable data are available for the ferri/ferrocyanide couple [21,26,54] and $\Delta V_{complex}$ seems remarkably insensitive to the nature and concentration of electrolyte. For example, the change in ΔV_{cell} between 0.01 and 1.00 mol l^{-1} KNO_3 is smooth, but only a few cm^3 mol^{-1}. This contrasts with the dramatic effects of cations in catalysing the kinetics of electron exchange for this couple as discussed in the next section. There can be no doubt that the highly charged ferri- or ferrocyanide ions are significantly, even entirely, associated with cations and it seems reasonable to expect that the effective net charge of the species to be reduced at the electrode would be modified. A net change in (charge)^2 from 7 for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ to 5 for $[K^+,Fe(CN)_6^{3-}]/[K^+,Fe(CN)_6^{4-}]$ or 3 for $[K^+,Fe(CN)_6^{3-},K^+]/[K^+,Fe(CN)_6^{4-},K^+]$ should be readily observed in the measured electrostrictive volume change, expected to be around 4 cm^3 mol^{-1} per Δz^2 for these systems. This does not appear to be so. Only at high concentrations of La^{3+} is the reduction volume of $Fe(CN)_6^{3-}$ significantly affected [54]. The presence of the nearby cations generally seems to have only a minor effect.

This seems true also for the reduction of $Co(diamsar)^{3+/2+}$ ($\Delta V_{cell} = 17.4$ cm^3 mol^{-1} [75]) and $Co(diamsarH_2)^{5+/4+}$ ($\Delta V_{cell} = 19.5$ cm^3 mol^{-1} [75]); double

Table 2
Electrostrictive and intrinsic contributions to various M(III)/(II)-complex reduction volumes (cm^3 mol^{-1}) in aqueous solution at 298 K[a]

Redox couple	$\Delta V_{complex}$	ΔV_{elec}	ΔV_{intr}
$Fe(phen)_3^{3+/2+}$	+19.1[b]	*+19.1*	0
$Fe(bipy)_3^{3+/2+}$	+21.3[c]	*+21.3*	0
$Cr(bipy)_3^{3+/2+}$	+21.1[d]	*+21.1*	0
$Co(phen)_3^{3+/2+}$	+34.4[d,e]	+19.1[f]	*+15.3*
			+16.5[g]
	+34.4[d,e]	*+20.7*	+13.7[h]
$Co(bipy)_3^{3+/2+}$	+34.0[d,e]	+21.3[f]	*+12.7*
$Co(en)_3^{3+/2+}$	+39.9[d,e]	*+28.0*	+11.9[h]
$Ru(en)_3^{3+/2+}$	+27.0[d,e]	*+25.9*	+1.1[h]
$Ru(NH_3)_6^{3+/2+}$	+30.3[d,e,i]	*+27.7*	+2.6
	+29.8[d,e,j]	*+27.2*	+2.6
$Ru(H_2O)_6^{3+/2+}$	+12.5[e]	*+6.8*	+6.7
	+13.1[e,i]	*+6.4*	+6.7
$Fe(H_2O)_6^{3+/2+}$	+13.6[k]	*+4.0*	+9.6
	+12.7[e,j]	*+3.1*	+9.6
	+14.5[l]	*+4.9*	+9.6
	+14.0[m]	*+4.4*	+9.6

[a] Italicized data are calculated from the other two sets of data for that system.

[b] $I = 0.25$ mol l^{-1} KNO_3 [54].

[c] $I = 0.10$ mol l^{-1} KNO_3 [54].

[d] $I = 0.10$ mol l^{-1} KNO_3 [55].

[e] Assumes $\Delta V_{ref}(Ag/Ag^+)$ of -13 cm^3 mol^{-1} [54].

[f] Assumes Fe(III)/(II) value.

[g] Based on difference in Co(III)/(II) and Fe(III)/(II) cell values in acetonitrile [55].

[h] Assumes value based on molar volume data [55].

[i] Using Au(Hg) working electrode.

[j] $I = 0.1$ mol l^{-1} $HClO_4$.

[k] $I = 1.0$ mol l^{-1} $HClO_4$; assumes ΔV_{ref} $(Ag/Ag^+) = -11.9$ cm^3 mol^{-1} [55].

[l] $I = 0.5$ mol l^{-1} $HClO_4/NaClO_4$; assumes ΔV_{ref} $(Ag/AgCl) = -9$ cm^3 mol^{-1} [22].

[m] $I = 0.28$ mol l^{-1} CF_3SO_3H; assumes ΔV_{ref} $(Ag/AgCl) = -9$ cm^3 mol^{-1} [21].

Table 3
Cell reaction volumes for complex-ion couples in non-aqueous solvents[a]

Couple/electrode	Solvent$_{\text{cmpx}}$	Solvent$_{\text{ref}}$	ΔV_{cell} (cm^3 mol^{-1})	Ref.
Fe(cp)$_2^{+/0}$/Au	CH_3CN	CH_3CN	-9.9 ± 0.5	[55]
Fe(phen)$_3^{3+/2+}$/Au	CH_3CN	CH_3CN	-1.5 ± 1.1	[55]
Co(phen)$_3^{3+/2+}$/Au	CH_3CN	CH_3CN	$+15.0 \pm 0.9$	[55]
Co(bipy)$_3^{3+/2+}$/Au	CH_3CN	CH_3CN	$+14.0 \pm 1.4$	[55]
$Ag^{+/0}$/Ag	H_2O[a]	CH_3CN	7.7 ± 0.5	[110]
$Ag^{+/0}$/Ag	H_2O[b]	CH_3CN	7.9 ± 0.8	[110]
$Ag^{+/0}$/Ag	H_2O[c]	CH_3CN	7.8 ± 1.3	[110]
$Ag^{+/0}$/Ag	H_2O[a]	DMSO	-4.1 ± 0.5	[110]
$Ag^{+/0}$/Ag	H_2O[a]	DMF	1.3 ± 0.5	[110]
$Ag^{+/0}$/Ag	H_2O[a]	Acetone	12.2 ± 0.7	[110]
$Ag^{+/0}$/Ag	CH_3CN	DMSO	-11.7 ± 0.6	[110]
$Ag^{+/0}$/Ag	CH_3CN	DMF	-6.5 ± 0.7	[110]
$Ag^{+/0}$/Ag	CH_3CN	PhCN	5.5 ± 0.6	[110]

[a] 0.1 mol l^{-1} Et_4NClO_4 supporting electrolyte, 298 K.

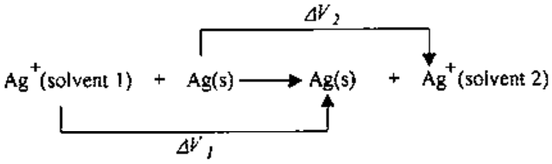
[b] 0.1 mol l^{-1} KNO_3 supporting electrolyte, 298 K.

[c] 0.01 mol l^{-1} Et_4NClO_4 supporting electrolyte, 298 K.

protonation of the amines outside the cage ligand has a negligible effect on the volume change associated with the Co reduction. We are currently investigating other systems to probe the apparent very localized nature of these electrostrictive interactions.

Some high pressure electrochemical data are now becoming available in solvents other than water and are given in Table 3. In all cases these have been measured using a Ag/Ag$^+$ reference electrode. While the absolute magnitude of ΔV_{cell} values for the Fe(phen)$_3^{3+/2+}$, Co(phen)$_3^{3+/2+}$ and Co(bpy)$_3^{3+/2+}$ reductions are substantially different from the same systems in water, the Co(phen)$_3^{3+/2+}$ and Co(bpy)$_3^{3+/2+}$ values are again similar to one another and subtracting the reaction volume of -1.5 ± 1.1 cm^3 mol^{-1} for the Fe(phen)$_3^{3+/2+}$ couple from that for the Co(phen)$_3^{3+/2+}$ couple ($+15.0 \pm 0.9$ cm^3 mol^{-1}) leads to an estimate of ΔV_{intr} for the Co(phen)$_3^{3+/2+}$ couple of $+16.5 \pm 2.0$ cm^3 mol^{-1}, which is in good agreement with the difference of $+15.3 \pm 1.4$ cm^3 mol^{-1} found in aqueous solution.

Any more detailed treatment of high pressure voltammetry in non-aqueous media requires experiments by which ΔV_{ref} can be separated and assigned. Boyd et al. [110] have carried out a series of high pressure potentiometric measurements in the cell shown in Fig. 2, modified for two Ag-electrode operation with the working electrode replaced by a silver wire and the auxiliary electrode position blanked off. For a series of cells Ag/$AgClO_4$ (0.01 mol l^{-1}), Et_4ClO_4 (0.1 mol l^{-1}) in Solvent$_1$// Et_4ClO_4 (0.1 mol l^{-1}), $AgClO_4$ (0.01 mol l^{-1}) in Solvent$_2$/Ag, equilibrium potentials were measured as a function of pressure to obtain the ΔV_{cell} values in Table 3. The experiment is summarized in Eq. 16, where $\Delta V_{\text{cell}} = \Delta V_1 + \Delta V_2$ and corresponds to the molar volume of transfer of Ag^+ from Solvent$_1$ to Solvent$_2$.



(16)

Building from ΔV_{ref} for the Ag/Ag$^+$ reference electrode in water of -13 cm^3 mol^{-1} [54], ΔV_{ref} in acetonitrile can be established as -20.7 ± 2 cm^3 mol^{-1} and hence ΔV_{ref} for the other solvent systems developed. An implicit assumption in the approach is that any liquid junction potential developed between the two solvent systems has no pressure dependence. The internal consistency and additivity of the volumes of transfer from, for example, water to acetonitrile (7.7 cm^3 mol^{-1}), then acetonitrile to DMSO (-11.7 cm^3 mol^{-1}), compared with the direct transfer experiment water to DMSO (-4.1 cm^3 mol^{-1}) seems to support this. In a Ag/AgCl system, Sun et al. [29] have demonstrated that between aqueous half cells where significant liquid junction potentials were intentionally set up, the pressure dependence of this potential was negligible.

Biological redox reagents, notably metalloproteins such as the cytochromes and plastocyanins, present special electrochemical problems because of a tendency to adsorb irreversibly on electrodes and possibly become denatured in so doing. This can be avoided by coating the working electrode with a strongly adsorbed monolayer of a suitable electron transfer promoter—for example, cysteine [24] or dipyridyl disulfide [29] for cytochrome *c*. Two conflicting reports of pressure effects on the redox potential of the iron(III)/(II) center in horse heart cytochrome *c* relative to Ag/AgCl have been published [24,29]. As noted in Table 1, the earlier study by Cruañes et al. [24] covered a wide pressure range (0–500 MPa) but yielded a markedly curved plot of ΔE versus P, the interpretation of which is further complicated by the possibility raised by the same group [25] that the properties of the Ag/AgCl reference electrode undergo a sharp change at about 300 MPa. Sun et al. [29] avoided the issue of a possible change in response of the reference electrode around 300 MPa by confining their attention to the range 0–200 MPa, over which any curvature $(\partial \Delta V / \partial P)_T$ of the plot of ΔE versus P was smaller than that reported by Cruañes et al. [24] by a factor of 3–4 and was probably not significant outside the experimental uncertainty. Discrepancies between the reports of Cruañes et al. [24] and Sun et al. [29] may have originated partly in medium effects such as the use of L-cysteine as the electrode modifying agent in the former study and 4,4′-dipyridyl disulfide in the latter [29], but a discrepancy of some 9 cm^3 mol^{-1} remains unaccounted for. Similar discrepancies were noted [29] between results obtained with UMEs and with conventional electrodes for the $Co(bpy)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ couples (Table 1). It is not clear from the published account [24] that the pressure-cycle reversibility criterion given in Section 3.3 was satisfied; thus, some systematic error could have existed in the UME measurements. The results of Sun et al. [29] are therefore regarded as definitive for our purposes.

Sun et al. [29] use the Sachinidis–Shalders–Tregloan principle [54] to estimate the contribution of the reduction of cytochrome c^{III} to cytochrome c^{II} to $\Delta V_{Ag/AgCl}$, It transpires that the absolute volume of cytochrome c^{III} is actually 5 cm^3 mol^{-1} *larger* than cytochrome c^{II}, which is at first sight surprising since most reductions of metal complexes lead to a lengthening of the metal–ligand bonds and hence an expected expansion. In the case of cytochrome *c*, however, it is thought that lengthening of the Fe–N bonds leads to a clamshell-like opening of the heme cleft in the protein, permitting ingress of water molecules and a net decrease in the volume of the system.

5. Pressure effects on the kinetics of electrode reactions of metal complexes

5.1. *The ferri/ferrocyanide couple*

The $Fe(CN)_6^{3-/4-}$ couple has received much attention from electrochemists, as the electrode potential is conveniently midrange, the reagents are inexpensive and readily available in high purity off the shelf, and ligand substitution occurs only very slowly (except on exposure to ultraviolet light). Not surprisingly, then, Conway and Currie [28] selected this couple for the first detailed high pressure kinetic study of an electrode reaction of complex ions. Conway and Currie used an AC impedance method to obtain a value of $\Delta V^{\ddagger}_{el}$ of +1.9 cm^3 mol^{-1} for the $Fe(CN)_6^{3-/4-}$ couple at a gold electrode in 0.5 mol l^{-1} K_2SO_4, but this seems too small in the light of later work [22,57,67]. Sato and Yamada [67] measured k_{el} for $Fe(CN)_6^{3-/4-}$ at a Pt electrode by cyclic galvanostatic method over only a limited range of pressure (0.1, 40, and 100 MPa) and found $\Delta V^{\ddagger}_{el}$ ca. +41, +30 and +13 cm^3 mol^{-1} in 1.0 mol l^{-1} LiCl, NaCl and KCl, respectively; these values seem to err on the large side, but the $\Delta V^{\ddagger}_{el}$ value for a KCl medium is in reasonable agreement with recent ACV (Table 4 [22,57]) and CV [81] results. More importantly, the point emerges that the kinetics of the $Fe(CN)_6^{3-/4-}$ electrode reaction are very sensitive to the nature of added salts [74], so that the result of Conway and Currie may reflect an electrolyte effect. Furthermore, Conway and Currie [28] corrected their concentration data for compression; in general, such corrections are neither necessary nor desirable in high-pressure studies [82]. The credibility of the $\Delta V^{\ddagger}_{el}$ value of +11 cm^3 mol^{-1} (average of values at two [KCl]) for the $Fe(CN)_6^{3-/4-}$ couple in Table 4 is enhanced by the fact that it is *precisely one-half* the volume of activation $\Delta V^{\ddagger}_{ex}$ for the corresponding self-exchange reaction in K^+ media (see discussion below).

5.2. *Electrodeposition of metals*

Franklin and Mathew [68–70] studied the kinetics of electrodeposition of metallic Co, Ni, and Ag from solutions of $Co(H_2O)_6^{2+}$, $Ni(H_2O)_6^{2+}$, and $Ag(aq.)^+$, respectively, at Hg/Hg_2Cl_2 or Hg/Hg_2SO_4 anodes up to 180 MPa. Rate constants were derived from exchange current densities obtained by extrapolation of Tafel plots to the equilibrium electrode potential. In dilute solutions, $\Delta V^{\ddagger}_{el}$ was on the order of +13 cm^3 mol^{-1} for Co and Ni and +10 cm^3 mol^{-1} for Ag, becoming

Table 4
Rate constants and volumes of activation for self-exchange reactions at electrodes and in homogeneous aqueous solution at 25.0°C

Couple/electrode	Medium (mol l^{-1})[a]	k^0_{el} (cm s^{-1})	$\Delta V^{\ddagger}_{el}$	k^{0}_{ex},[b] (l mol^{-1} s^{-1})	$\Delta V^{\ddagger}_{ex}$,[c] (cm^3 mol^{-1})	Ref.
A: $\mathrm{Co(phen)_3}^{3+/2+}$/Pt	0.1 NaCl	0.108 ± 0.002	-9.1 ± 0.4	6.7 (0.10)	-17.6 ± 0.7	[22,76]
B: $\mathrm{Co(en)_3}^{3+/2+}$/Pt[d]	0.5 KCl	0.036 ± 0.001	-8.3 ± 0.5	8×10^{-5} (0.5)	-15.5 ± 0.8	[22,57,77]
C: $\mathrm{Fe(H_2O)_6}^{3+/2+}$/Pt	0.5 $\mathrm{HClO_4/NaClO_4}$	0.0207 ± 0.0005	-5.5 ± 0.2	4.8 (0.5)	-11.1 ± 0.4	[22,78]
D: $\mathrm{Co(diamsar)}^{3+/2+}$/Au	0.1 $\mathrm{NaClO_4}$ (pH 9)	0.0162 ± 0.0007	-3.5 ± 0.2	0.48 (0.14)	-10.4 ± 0.5	[22,75]
E: $\mathrm{Co(diamsarH_2)}^{5+/4+}$/Au	0.13 $\mathrm{HClO_4/NaClO_4}$	0.010 ± 0.001	-3.8 ± 0.3	0.05 (0.4)	-9.6 ± 0.8	[22,75]
F: $\mathrm{Co(sep)}^{3+/2+}$/Pt	0.5 KCl	0.091 ± 0.001	-3.0 ± 0.4	5.0 (0.2)	-6.4 ± 0.2	[22,57,73,79]
G: $\mathrm{Co(ttcn)_2}^{3+/2+}$/Pt	0.1 $\mathrm{NaClO_4}$	0.27 ± 0.02	-2.8 ± 0.7	9.5×10^4 (0.1)	-4.8 ± 0.2	[22,73,79]
H: $\mathrm{Fe(phen)_3}^{3+/2+}$/Pt	0.1 $\mathrm{Na_2SO_4}$	0.300 ± 0.003	-1.6 ± 0.1	1.4×10^7 (0.3)	-2.2 ± 0.1	[22,80]
I: $\mathrm{Fe(CN)_6}^{3-/4-}$/Pt	0.5 KCl	0.072 ± 0.005	$+11.9 \pm 1.3$	2.6×10^{4e}	$+22 \pm 2$	[22,57,81]
	0.2 KCl	0.047 ± 0.004	$+10.4 \pm 1.4$			
J: $\mathrm{Os(CN)_6}^{3-/4-}$/C(gl)	0.6 KCl	0.040 ± 0.005	$+9.7 \pm 0.7$	3.1×10^{4f}	$+18.5 \pm 0.8$	[74]
K: $\mathrm{Mo(CN)_8}^{3-/4-}$/Au	0.5 $\mathrm{NaClO_4}$ (pH 2.7)	0.053 ± 0.001	$+7.3 \pm 0.7$	3.1×10^{4g}	$+14.6 \pm 0.5$	[74]
L: $\mathrm{Mo(CN)_8}^{3-/4-}$/C(gl)	0.5 $\mathrm{[Et_4N]Cl}$	0.18 ± 0.03	-4.4 ± 0.5	6×10^{4h}	-8.2 ± 0.6	[74]
M: $\mathrm{W(CN)_8}^{3-/4-}$/Pt	0.5 KCl	0.161 ± 0.008	$+10.8 \pm 0.4$	1.0×10^{5i}	$+22.5 \pm 1.1$	[74]

[a] Medium for k^0_{el} and $\Delta V^{\ddagger}_{el}$ measurements.
[b] Ionic strength (mol l^{-1}) in parenthesis.
[c] See reference for details of medium and temperature.
[d] A total of 0.2 mol l^{-1} en present.
[e] 0.08 mol l^{-1} $\mathrm{K_4Fe(CN)_6}$, 0.002 mol l^{-1} $\mathrm{K_3Fe(CN)_6}$.
[f] 0.19 mol l^{-1} $\mathrm{K_4Os(CN)_6}$, 0.01 mol l^{-1} $\mathrm{K_3Os(CN)_6}$.
[g] 0.078 mol l^{-1} $\mathrm{K_4Mo(CN)_8}$, 0.05 mol l^{-1} $\mathrm{K_3Mo(CN)_8}$.
[h] 0.069 mol l^{-1} $\mathrm{[Et_4N]_4Mo(CN)_8}$, 0.007 mol l^{-1} $\mathrm{[Et_4N]_3Mo(CN)_8}$.
[i] 0.23 mol l^{-1} $\mathrm{K_4W(CN)_8}$, 0.014 mol l^{-1} $\mathrm{K_3W(CN)_8}$.

smaller as the concentration of supporting electrolyte (e.g. KCl) was increased. Franklin and Mathew argued, by analogy with the volumes of activation for water exchange on $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ (+6.1 and +7.2 $cm^3\ mol^{-1}$, respectively [83]), that the activation process for electrodeposition involved the removal of *two* water molecules (one from the electrode surface, one from the first coordination sphere of the aqueous ion) as the rate-determining first step en route to formation of a desolvated atom of elemental metal.

In fact, volumes of activation for water exchange on metal aqua ions in homogeneous solution probably reflect an *interchange* process, in which the movements of the incoming and outgoing waters are to some degree coupled, rather than a limiting dissociative process. According to an empirical equation relating molar volumes of aqua-ions to coordination number [84,85], the volume change expected for *complete removal* of one water molecule from the first coordination sphere of a metal aqua-ion to bulk solution is about +13 $cm^3\ mol^{-1}$, with only slight dependence on ionic charge or size. Thus, the results of Franklin and Mathew [68–70] suggest that removal of one aqua ligand from the metal ion, without dehydration of the electrode surface, allows a sufficiently close approach of the central metal ion to the electrode for electron transfer to occur. When significant concentrations of chloride, thiocyanate, or azide ions are present, these anions become coordinated to the metal ion and provide efficient bridged (inner-sphere) pathways for electron transfer from the electrode, so that $\Delta V^{\ddagger}_{el}$ becomes very small [69]. Conversely, for Ag^+, complexation with NH_3, which cannot act as a bridge for electron transfer, increases $\Delta V^{\ddagger}_{el}$ to +21 $cm^3\ mol^{-1}$ [70].

5.3. The 'fifty-percent rule' linking electrode and homogeneous self-exchange kinetics

Table 4 lists rate constants k^0_{el} (i.e. k_{el} at atmospheric or 'zero' pressure) and volumes of activation $\Delta V^{\ddagger}_{el}$ for electrode reactions of some transition metal complexes, obtained in our Calgary laboratories by AC voltammetry. Choices of electrode material and supporting electrolyte varied from one couple to another because of problems with specific interactions with the electrodes, solubility, and redox stability. The key to making reproducible measurements of k_{el} over a series of pressures is potential cycling between measurements at different pressures to restore the cleanliness of the electrode surface, as outlined in Section 3.3 [22,57]. For the couples listed in Table 4, the transfer coefficient α was 0.45–0.50, except in the cases of the slowest Co complexes (0.27 for $Co(diamsar)^{3+/2+}$, 0.41 for $Co(diamsarH_2)^{5+/4+}$, and 0.42 for $Co(en)_3^{3+/2+}$).

In Table 4, k^0_{el} and $\Delta V^{\ddagger}_{el}$ values for electrode reactions of transition metal complexes are compared with analogous quantities for the corresponding homogeneous self-exchange reactions in bulk solution. Marcus [86] has argued that the free energy of activation ΔG^*_{el} for an electrode reaction of a couple $ML_n^{(z+1)+/z+}$ should be just *one-half* that for the corresponding self-exchange reaction, ΔG^*_{ex}—if, however, the separation σ_{el} between the metal center and the electrode is more than half the M–M distance σ_{ex} in the bimolecular encounter, e.g. because of an adsorbed layer of molecules on the electrode surface, then $\Delta G^*_{el} \geq \frac{1}{2}\Delta G^*_{ex}$. The reason for this relationship may be understood in terms of the Marcus–Hush–Sutin theory of outer-sphere electron transfer reaction rates [86,87], according to which ΔG^*_{ex} is determined largely by the reorganizations of the metal–ligand bond lengths and the solvation environments of both $ML_n^{(z+1)+}$ and ML_n^{z+} to a common configuration or 'half-way-house' so that electron transfer between the two colliding complexes can occur. In the corresponding electrode reaction, however, only *one* complex molecule is involved, and so the reorganization energy to reach the half-way-house is just one-half that of the bimolecular reaction. Similar considerations apply to the coulombic work terms affecting the mutual approach of the complexes. In the simplest treatment, ΔG^*_{el} and ΔG^*_{ex} govern the corresponding rate constants through the equations

$$k_{el} = Z_{el}\exp(-\Delta G^*_{el}/RT) \tag{17}$$

$$k_{ex} = Z_{ex}\exp(-\Delta G^*_{ex}/RT) \tag{18}$$

where Z_{el} and Z_{ex} are the respective frequency factors, so that, in the limiting case of $\Delta G^*_{el} = \frac{1}{2}\Delta G^*_{ex}$, we may anticipate

$$k_{el}/Z_{el} = \sqrt{(k_{ex}/Z_{ex})}. \tag{19}$$

Thus, if Z_{el} and Z_{ex} were approximately constant from one couple to another (as seems to be the case for Z_{ex}, which is usually assumed to be about 10^{11} l mol^{-1} s^{-1} at 298 K), we would expect a plot of ln k_{el} versus ln k_{ex} for a selection of couples to be linear with slope 0.5. There have been several attempts to test Eq. (19) experimentally [88–96] for transition metal complexes, but generally ln k_{el} versus ln k_{ex} plots are only roughly linear, and the slope is rarely 0.5, unless rather elaborate corrections are applied [95]. Indeed, a ln k_{el} versus ln k_{ex} plot of the data of Table 4 shows extreme scatter and no statistically meaningful relationship. The reason for this apparent failure of Eq. (19) is the marked sensitivity of electrode kinetics to the composition and condition of the electrode surface. For example, McCreery [97] lists k_{el} values for $Fe(CN)_6^{3-/4-}$ at 298 K that range from $< 10^{-7}$ cm s^{-1} on cleaved basal surfaces of highly ordered pyrolytic graphite (HOPG) to 0.24 cm s^{-1} on Pt. The mode of pretreatment of an electrode surface, however, is probably of greater importance than the identity of the bulk material; thus, values of k_{el} for $Fe(CN)_6^{3-/4-}$ can reach 0.10 cm s^{-1} on laser-treated *edges* of HOPG, and may be as low as 0.002 cm s^{-1} on Pt cleaned by potential cycling in 1.0 mol l^{-1} LiCl [97]. In our own experience with the $Mo(CN)_8^{3-/4-}$ couple in tetraethylammonium chloride media [74], k_{el} was 0.01 cm s^{-1} on Pt (which became slowly poisoned) but 0.18 cm s^{-1} on glassy carbon (which showed no deterioration over a pressure cycle).

On the other hand, the nature of the surface of an electrode is unlikely to change significantly with pressure. Consequently, it may be anticipated that Z_{el} will be insensitive to pressure, or at least that any small pressure dependence that it shows will be effectively cancelled by that of Z_{ex} in Eq. (19). Thus, combining Eq. (19)

with Eq. (5) (and the analogous equation for k_{ex}), we predict that, if the Marcus concept holds good,

$$\Delta V^{\ddagger}_{\mathrm{el}} = \tfrac{1}{2}\Delta V^{\ddagger}_{\mathrm{ex}}. \tag{20}$$

In fact, a plot of $\Delta V^{\ddagger}_{\mathrm{el}}$ versus $\Delta V^{\ddagger}_{\mathrm{ex}}$ from Table 4 (Fig. 6) is accurately linear ($r^2 = 0.992$) with zero intercept, within the experimental uncertainty, and has a slope of 0.497 ± 0.014—in effect, *precisely one-half*, just as predicted. It is rare in inorganic kinetics to find a correlation as tight as this; it is all the more remarkable when one considers the differences in experimental methodology (ACV for $\Delta V^{\ddagger}_{\mathrm{el}}$, NMR spectroscopy, radioisotope exchange, and stopped-flow circular dichroism spectroscopy for $\Delta V^{\ddagger}_{\mathrm{ex}}$) and the problems noted above in obtaining definitive values for k_{el}. In a cycle of pressure measurements, it does not matter what the absolute value of k^{0}_{el} is, so long as that same value is recovered accurately at the end of the cycle; the resulting $\Delta V^{\ddagger}_{\mathrm{el}}$ will be the same.

We refer to Eq. (20) as the 'fifty-percent rule'. It applies with remarkable accuracy in all cases studied to date except for the $\mathrm{MnO_4}^{-/2-}$ couple, but in that instance no consistent results could be obtained because the strongly alkaline solutions necessary to protect the manganate(VI) ion dissolved the Vycor frit in the reference electrode (Fig. 3). The fifty-percent rule can be used with confidence to estimate $\Delta V^{\ddagger}_{\mathrm{ex}}$ values from $\Delta V^{\ddagger}_{\mathrm{el}}$ in many cases where direct measurements of the former are not feasible—for example, where both partners in a couple are paramagnetic, so precluding the use of NMR methods, or where one of the partners is too unstable for methods requiring its use in significant concentrations for protracted periods (a solution of only one partner is needed for AC voltammetry).

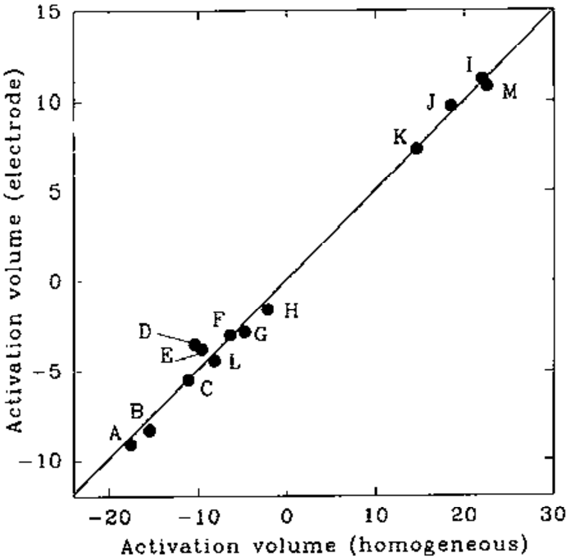


Fig. 6. Relationship between volumes of activation ($\mathrm{cm^3\ mol^{-1}}$) for electrode reactions and homogeneous self-exchange reactions. Letter code as in Table 4. Linear regression line has slope 0.50.

The success of the fifty-percent rule also implies that $\Delta V^{\ddagger}_{\mathrm{el}}$ values can be calculated theoretically via $\Delta V^{\ddagger}_{\mathrm{ex}}$ from solvent properties (dielectric constant D, refractive index n, isothermal compressibility β) and reactant dimensions (effective radii r_1 and r_2; the separation σ at which electron transfer occurs is usually taken to be $r_1 + r_2$), using an adaptation developed elsewhere [18,30,31,98] of the Marcus theory of homogeneous electron transfer rates [71,72]. For adiabatic electron transfer of the outer-sphere type in homogeneous solution, $\Delta V^{\ddagger}_{\mathrm{ex}}$ comprises contributions from inner-sphere reorganization (usually taken to mean metal–ligand bond length changes), solvent reorganization, the coulombic work of bringing the reactants together, and the pressure dependence of the ionic activity coefficients (of necessity, expressed in terms of the extended Debye–Hückel theory):

$$\Delta V^{\ddagger}_{\mathrm{ex}} = \Delta V^{\ddagger}_{\mathrm{IR}} + \Delta V^{\ddagger}_{\mathrm{SR}} + \Delta V^{\ddagger}_{\mathrm{COUL}} + \Delta V^{\ddagger}_{\mathrm{DH}} \tag{21}$$

Of these contributions, $\Delta V^{\ddagger}_{\mathrm{IR}}$ is calculated to be between 0 and $+1$ cm^3 mol^{-1} for rigid transition metal complexes [98], and may be set to 0.6 cm^3 mol^{-1} for most couples or to zero when metal–ligand bond lengths are essentially the same in the reduced and oxidized states (as is the case for $\mathrm{Fe(phen)_3}^{3+/2+}$). The other contributions can be calculated from Eqs. (22)–(24), in which z_1 and z_2 are the charge numbers of the reactants, a is the mean close approach distance of the reagents to their counterions, B and C are the Debye–Hückel parameters (the pressure dependence of which is precisely calculable from those of D and the solvent density), and the remaining undefined symbols have their usual meanings in SI.

$$\Delta V^{\ddagger}_{\mathrm{SR}} = (N_{\mathrm{A}}e^2/16\pi\varepsilon_0)[(2r_1)^{-1} + (2r_2)^{-1} - \sigma^{-1}]\{\partial(n^{-2} - D^{-1})/\partial P\}_T \tag{22}$$

$$\Delta V^{\ddagger}_{\mathrm{COUL}} = (N_{\mathrm{A}}z_1z_2e^2/4\pi\varepsilon_0\sigma)(\partial D^{-1}/\partial P)_T \tag{23}$$

$$\Delta V^{\ddagger}_{\mathrm{DH}} = \{RTz_1z_2CI^{1/2}/(1 + BaI^{1/2})^2\}[(\partial \ln D/\partial P)_T(3 + 2BaI^{1/2}) - \beta)] \tag{24}$$

A further term $\Delta V^{\ddagger}_{\mathrm{PREC}}$ ($= \beta RT$, $= +1.1$ cm^3 mol^{-1} for water at 298 K), originating in pressure dependence of the pre-exponential part of the formation constant of the precursor complex, should be added to the right hand side of Eq. (21) if electron transfer occurs without hard contact between the reactants, i.e. if $\sigma > (r_1 + r_2)$ [30] and compresses with the linear compression of the solvent. In that event, however, a term $-N_{\mathrm{A}}e^2(n^{-2} - D^{-1})\beta/48\pi\varepsilon_0\sigma$ should be added to the right hand side of Eq. (22), and a term $N_{\mathrm{A}}z_1z_2e^2\beta/12\pi\varepsilon_0 D\sigma$ to the right hand side of Eq. (23). In practice, for aqueous solutions at ordinary temperatures, these corrections are not large and they tend to cancel each other out. Furthermore, for practical values of the ionic strength I (say, 0.1–0.5 mol l^{-1}), $\Delta V^{\ddagger}_{\mathrm{DH}}$ and $\Delta V^{\ddagger}_{\mathrm{COUL}}$ are of opposite sign but similar magnitude, and so these terms also tend to offset each other, leaving $\Delta V^{\ddagger}_{\mathrm{SR}}$ as the dominant component of $\Delta V^{\ddagger}_{\mathrm{ex}}$.

As shown elsewhere [18,31], $\Delta V^{\ddagger}_{\mathrm{ex}}$ is accurately predicted by Eqs. (21)–(24) for couples **C**–**H** in Table 4. It follows that $\Delta V^{\ddagger}_{\mathrm{el}}$ is also accurately predictable in these cases by the fifty-percent rule. In other words, we may say that *the effect of pressure on the rates of simple electrode reactions of typical metal complex couples such as* **C** *through* **H** *is well understood*. The $\mathrm{Mo(CN)_8^{3-/4-}}$ couple also appears to fall in this category when the counterion is tetraethylammonium (couple **L** in Table 4), as the calculated $\Delta V_{\mathrm{el}}^{\ddagger}$ value is -3 ± 1 cm^3 mol^{-1}, depending on the choice of ionic radii. The question then remains as to why $\Delta V_{\mathrm{el}}^{\ddagger}$ is excessively negative for $\mathrm{Co(en)_3}^{3+/2+}$ and $\mathrm{Co(phen)_3}^{3+/2+}$, and so strongly *positive* for the cyanometallates **I**, **J**, **K** and **M** for alkali metal cations—in no case does our adaptation [18,30,31] of the Marcus theory predict positive values for $\Delta V_{\mathrm{el}}^{\ddagger}$. The fact that all these couples do conform well to the fifty-percent rule implies that neither the homogeneous self-exchange nor the electrode reaction are 'anomalous', but rather that the simple two-sphere model on which Eqs. 16–19 are based needs refinement.

5.4. *Cobalt(III/II) couples*

Most $\mathrm{Co^{II}}$ complexes (in Table 4, all except $\mathrm{Co(ttcn)_2}^{2+}$) have a high-spin $3d^7$ electronic configuration (three unpaired electrons, ground state $^4\mathrm{T}_{1g}$ in O_h symmetry), whereas $\mathrm{Co^{III}}$ complexes are almost always spin-paired ($^1\mathrm{A}_{1g}$ ground state), so that, somewhere along the oxidation reaction coordinate from high-spin $\mathrm{Co^{II}}$ to low-spin $\mathrm{Co^{III}}$, spin-pairing must occur. One consequence of this change is that there are large Co–ligand bond length changes in oxidations of high-spin $\mathrm{Co^{II}}$, leading to large internal reorganization contributions to the free energy of activation, and certainly the much higher k_{ex} for the low-spin/low-spin $\mathrm{Co(ttcn)}_2^{3+/2+}$ self-exchange relative to the other values in Table 4 attests to this (k_{el} is a less reliable criterion because of electrode surface effects, as noted above).

It has been less clear, however, whether the spin-state change per se can influence self-exchange rates directly, that is, whether intermolecular electron transfer might be 'spin forbidden' in the manner of transitions in electronic spectroscopy. There has been much debate [75,76,99–105] over two basic alternative mechanisms for $\mathrm{Co^{III/II}}$ redox processes. In terms of $\mathrm{Co^{III/II}}$ self-exchange, the alternatives are a nonadiabatic 'spin forbidden' electron transfer from the $^4\mathrm{T}_{1g}$ ground state of $\mathrm{Co^{II}}$ to the ground state of the $\mathrm{Co^{III}}$ partner coupled with spin-state change, and a fast but unfavorable pre-equilibrium between $^4\mathrm{T}_{1g}$ and $^2\mathrm{E}_g$ states of $\mathrm{Co^{II}}$ with relatively rapid adiabatic electron transfer from the latter to the $\mathrm{Co^{III}}$. Although the nonadiabatic alternative was favored in earlier interpretations of $\Delta V_{\mathrm{ex}}^{\ddagger}$ results [76,77], more recent data showing that Co cage complexes exhibit 'normal' adiabatic $\Delta V_{\mathrm{ex}}^{\ddagger}$ values leave little doubt that the excessively negative $\Delta V_{\mathrm{ex}}^{\ddagger}$ values for $\mathrm{Co(en)_3}^{3+/2+}$ and $\mathrm{Co(phen)_3}^{3+/2+}$ reflect a fast $\mathrm{Co^{II}}(^4\mathrm{T}_{1g}) \Leftrightarrow \mathrm{Co^{II}}(^2\mathrm{E}_g)$ equilibrium with an estimated reaction volume on the order of -10 cm^3 mol^{-1} (see the $\mathrm{Co(terpy)}_2^{2+}$ spin equilibrium [106]) followed by adiabatic electron transfer from $\mathrm{Co^{II}}(^2\mathrm{E}_g)$ to the oxidant [18,75,105]. A key point here is that cage complexes such as $\mathrm{Co(sep)}^{3+}$ are somewhat larger than $\mathrm{Co(en)}_3^{3+}$ but structurally related to it (indeed, they are synthesized by capping it); thus, since any tendency toward nonadiabaticity should increase with increasing metal–metal atom separation σ for comparable couples, the $\mathrm{Co(en)_3}^{3+/2+}$ exchange must be adiabatic if $\mathrm{Co(sep)}^{3+/2+}$ and $\mathrm{Co(diamsar)}^{3+/2+}$ are. Electron transfer in the cage couples must also entail a spin change pre-equilibrium, but the volume changes due to Jahn–Teller type distortions that accompany spin change in the flexible $\mathrm{Co(en)_3}^{2+}$ and $\mathrm{Co(phen)_3}^{2+}$ species will be suppressed in the rigid cage complexes.

From the standpoint of the electrode reactions, application of these same arguments to $\Delta V_{\mathrm{el}}^{\ddagger}$ leads to the conclusion that the electrode reactions of couples **A** through **H** are adiabatic, and that a $\mathrm{Co^{II}}$ spin pre-equilibrium precedes electron transfer for the $\mathrm{Co^{III/II}}$ couples. Furthermore, following Marcus' original argument [86], the fact that $\Delta V_{\mathrm{el}}^{\ddagger}$ is precisely $0.50\Delta V_{\mathrm{ex}}^{\ddagger}$ (and hence $\Delta G_{\mathrm{el}}^{*}$ is precisely $0.50\Delta G_{\mathrm{ex}}^{*}$) implies that there is no layer of adsorbed molecules separating the electroactive species from the electrically conducting surface of the electrode, although this surface itself may be an adsorbed layer of some sort. This conclusion echoes our foregoing reinterpretation of Franklin and Mathew's data for electrodeposition of metals from metal aqua ions—$\Delta V_{\mathrm{el}}^{\ddagger}$ is entirely accounted for by the removal of one aqua ligand from the metal ion, and no dehydration of the electrode need occur.

5.5. *Cyanometalate complexes*

The strongly positive $\Delta V_{\mathrm{el}}^{\ddagger}$ and $\Delta V_{\mathrm{ex}}^{\ddagger}$ values for the hexa- and octa-cyanometallate couples listed in Table 4 are associated with the presence of *alkali metal* cations M. Added MCl causes acceleration of the self-exchange reaction, in the order $\mathrm{M = Li < Na < K < Rb < Cs}$ [74,107–109], but $\Delta V_{\mathrm{ex}}^{\ddagger}$ remains positive and large [74], as does $\Delta V_{\mathrm{el}}^{\ddagger}$. When the only cation present is tetramethyl- or tetraethylammonium (Table 4), however, the volumes of activation become 'normal' (i.e. they follow the predictions of Eqs. (21)–(24)). The simplest explanation for these facts is that cations assist the transfer of the (negatively charged) electron by acting as bridges, providing a region of positive potential between the reactant anions, but must be partly desolvated first. The contributions of hydration enthalpy to free energies of activation decrease in the sequence $\mathrm{Li > Na > K > Rb > Cs}$, consistent with the sequence of catalytic effects. Furthermore, the excess of about 20–28 $\mathrm{cm^3\ mol^{-1}}$ in $\Delta V_{\mathrm{ex}}^{\ddagger}$ over that calculated from theory (Eqs. (21)–(24)) corresponds to the removal of two water ligands from the first coordination spheres of the alkali metal ions [84,85], as might be expected for a bridging metal cation. The hydrophobic quaternary ammonium cations, however, are already poorly hydrated and so $\Delta V_{\mathrm{ex}}^{\ddagger}$ is close to the theoretical value for a simple two-sphere model of outer-sphere electron transfer. A detailed interpretation of the nature of the involvement of the cations in the absence of added electrolyte is complicated by the lack of exact knowledge of the degree of ion pairing, which must be extensive [81,107], but evidently this is inconsequential in the context of pressure effects since $\Delta V_{\mathrm{el}}^{\ddagger}$ and $\Delta V_{\mathrm{ex}}^{\ddagger}$ are insensitive to the addition of further cations of the kind already present.

The $\Delta V_{\mathrm{el}}^{\ddagger}$ values for cyanometallate electrode reactions can be understood in an analogous way, in the light of the fifty-percent rule, but the effect of cations is more clearly seen in homogeneous self-exchange through k_{ex}, because k_{el} is also sensitive to the nature of the electrode surface, which in turn is susceptible to electrolyte effects. The $\Delta V_{\mathrm{el}}^{\ddagger}$ data are important, however, in that they authenticate the $\Delta V_{\mathrm{ex}}^{\ddagger}$ values and confirm that there is no fundamental difference in mechanism between outer-sphere self-exchange redox reactions in homogeneous solution and the corresponding reactions at electrodes. Furthermore, the implication is that the *energetics*

(ΔG^*_{el} and ΔG^*_{ex}) as well as the volumes of activation of the two reaction classes are related by the fifty-percent rule.

6. Concluding remarks

We have shown that reliable volumes of reaction ΔV and of activation $\Delta V^{\ddagger}_{el}$ for electrode reactions of transition metal complexes are obtainable from high-pressure adaptations of modern electrochemical techniques such as cyclic and alternating-current voltammetry. Although in practice ΔV can only be measured with respect to a reference electrode (ΔV_{cell}), differences between ΔV_{cell} values for pairs of couples referred to a common reference electrode, as in Tables 1 and 3, give ΔV for a wide range of redox reactions of transition metal complexes. For a particular couple, the Sachinidis–Shalders–Tregloan principle permits separation of the contributions to ΔV_{cell} of the reference electrode and the couple of interest. In principle, this separation should be possible through algebraic summation of the molar volumes of the chemical species involved, but these are ideal parameters and do not relate accurately to working cell conditions. Once the separation is effected, it becomes possible to break ΔV for the couple into electrostrictive and intrinsic components, so providing much otherwise inaccessible information on the solvational and structural changes accompanying redox processes. This applies to both aqueous and nonaqueous solutions.

For aqueous solutions, we have also shown that $\Delta V^{\ddagger}_{el}$ for a given couple is *precisely one-half* that for the corresponding self-exchange reaction ($\Delta V^{\ddagger}_{ex}$) in homogeneous solution. This observation vindicates a prediction of Marcus concerning the relationship between these two types of electron transfer reaction. It also permits reliable indirect estimation of $\Delta V^{\ddagger}_{ex}$ values for couples for which this parameter cannot be directly measured, such as fast exchange reactions between two paramagnetic partners for which the NMR method is inapplicable. Since $\Delta V^{\ddagger}_{ex}$ for uncomplicated outer-sphere processes can be accounted for by an extension of Marcus theory, it follows that $\Delta V^{\ddagger}_{el}$ can be similarly interpreted or predicted. Finally, if ΔV for a *net* redox reaction together with $\Delta V^{\ddagger}_{el}$ (and hence $\Delta V^{\ddagger}_{ex}$) for the two contributing couples are obtained as described above, it becomes possible to calculate (through an adaptation of the Marcus 'cross relation') a value of $\Delta V^{\ddagger}$ for the reaction on the assumption that it is of the *adiabatic, outer-sphere* type. Thus, comparison of calculated with measured values of $\Delta V^{\ddagger}$ can serve as a mechanistic criterion for any redox process between metal complexes.

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Abbreviations

ACV	alternating current voltammetry/voltammogram
bpy	2,2′-bipyridine
CV	cyclic voltammetry/voltammogram
diamsar	1,8-diamino-3,6,10,13,16,19-hexaaazabicyclo[6.6.6]eicosane (diaminosarcophagine)
en	1,2-diaminoethane (ethylenediamine)
isn	isonicotinamide
3,5-lut	3,5-lutidine
phen	1,10-phenanthroline
py	pyridine
QPVP	quaternized poly(4-vinylpyridine)
SAM	self-assembled monolayer
sep	1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane (sepulchrate)
tacn	1,4,7-triazacyclononane ([9]aneN_3)
terpy	2,2′:6′,2″-terpyridine
ttcn	1,4,7-trithiacyclononane ([9]aneS_3)
UME	ultramicroelectrode

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