Relationship between Heterogeneous and Homogeneous Kinetics of Electron Transfer between Transition Metal Complexes in Aqueous Solution: Volumes of Activation

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Abstract: Electrochemical rate constants k_{el} and volumes of activation $\Delta V_{el}^{\ddagger}$ for self-exchange at an electrode of the aqueous couples $Co(phen)_3^{3+/2+}$, $Co(en)_3^{3+/2+}$, $Fe(H_2O)_6^{3+/2+}$, $Co(diamsar)^{3+/2+}$, $Co(diamsarH_2)^{3+/2+}$, $Co(sep)^{3+/2+}$, $Co(ttcn)_2^{3+/2+}$, $Fe(phen)_3^{3+/2+}$, $Mo(CN)_8^{3-/4-}$, and $Fe(CN)_6^{3-/4-}$ have been measured by high-pressure AC voltammetry over the range 0.1−200 MPa at 25 °C; the respective values of $\Delta V_{el}^{\ddagger}$ are −9.1, −8.3, −5.5, −3.5, −3.8, −3.0, −2.8, −1.6, +7.3, and +11 cm³ mol⁻¹. Although the theory of Marcus (*Electrochim. Acta* **1968**, *13*, 1005) suggests that $\ln k_{el}$ should be linearly related to $^1/_2 \ln k_{ex}$, where k_{ex} is the rate constant of the corresponding homogeneous (bimolecular) self-exchange reaction, $\ln k_{el}$ is often sensitive to the nature of the working electrode and the supporting electrolyte and is only weakly correlated with $\ln k_{ex}$, with slope ≈0.1. In contrast, $\Delta V_{el}^{\ddagger} = (0.50 \pm 0.02)\Delta V_{ex}^{\ddagger}$, in precise agreement with an extension of Marcus' theory, regardless of the nature of the electrode and the supporting electrolyte. This result implies that electron transfer in these couples occurs adiabatically on direct ion−ion and ion−electrode contact (i.e., within the outer Helmholtz plane), and also that $\Delta V_{el}^{\ddagger}$ values are predictable in the manner described elsewhere (*Can. J. Chem.* **1996**, *74*, 631) for $\Delta V_{ex}^{\ddagger}$. Conversely, where $\Delta V_{ex}^{\ddagger}$ cannot be measured for technical reasons (e.g., where paramagnetism of both reactants precludes NMR measurements of k_{ex}), it can be reliably estimated as $2\Delta V_{el}^{\ddagger}$.

Introduction

It has long been recognized[1-7] that a relationship should exist between the rate constant for bimolecular self-exchange by electron transfer in a metal complex couple $ML_n^{(z+1)+/z+}$ in homogeneous solution (k_{ex}) and that for heterogeneous electron transfer involving the same couple at an electrode (k_{el}). Following the approach of Marcus in its simplest form,[1] the rate constants can be expressed in terms of the corresponding free energies ΔG_i^* of activation and collision frequency factors Z_i:

$$k_{ex} = Z_{ex} \exp(-\Delta G_{ex}^*/RT) \qquad (1)$$

$$k_{el} = Z_{el} \exp(-\Delta G_{el}^*/RT) \qquad (2)$$

Marcus showed that, in general, $\Delta G_{el}^* \geq {}^1/_2\Delta G_{ex}^*$, or, in the limiting case where the M-electrode distance σ_{el} is just one-half the M−M distance σ_{ex} for the bimolecular reaction (i.e., where there is no intervening layer of adsorbed solvent or other molecules on the electrode surface to increase σ_{el}) at the respective instants of electron transfer, $\Delta G_{el}^* = {}^1/_2\Delta G_{ex}^*$. In essence, this is so because the barrier to bimolecular electron transfer involves the internal (M−L bond lengths, reorganization energy λ_i) and outersphere (solvation sheath, reorganization energy λ_o) reorganization of *two* complexes $ML_n^{(z+1)+}$ and

ML_n^{z+}, whereas in the electrode process only *one* complex and its environment have to be reorganized—$ML_n^{(z+1)+}$ or ML_n^{z+} forms its own redox partner. For self-exchange reactions, if the coulombic work w of bringing the reactants together is disregarded, ΔG_{el}^* is given by $(\lambda_i + \lambda_o)/8$ and ΔG_{ex}^* by $(\lambda_i + \lambda_o)/4$.[1-4,7] Thus, in the limiting case, we may expect:

$$k_{el}/Z_{el} = (k_{ex}/Z_{ex})^{1/2} \qquad (3)$$

Several authors[7-17] have sought to test eq 3 experimentally, with or without corrections for double-layer and other effects, but the results have not been clear-cut, largely because of problems in defining Z_{el} and Z_{ex} or their equivalents. Generally, simple plots of $\ln k_{el}$ vs $\ln k_{ex}$ are scattered but roughly linear with slope about 0.5, as predicted, up to $k_{el} \approx 10^{-2}$ cm s⁻¹, but the slope decreases on going to faster reactions, with k_{el} appearing to tend to a limit on the order of 10 cm s⁻¹.[8-10,12,13] On the other hand, for some very fast electrode reactions of organic molecules, Peover[11] found a *direct proportionality* between k_{el} and k_{ex}, as predicted by Hush[5,6] for cases in which λ_i is negligible if swamping of charge-imaging at the electrode

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by a supporting electrolyte permits the σ_{el}-dependent term in λ_o to be disregarded. The dimensional incompatibility of k_{el} and k_{ex} (cm s^{-1} and L mol^{-1} s^{-1}) is symptomatic of the difficulties underlying attempts to correlate them; Weaver[16] tackled this problem by converting work-corrected k_{el} values to "equivalent second-order" rate constants with unit dimensions L mol^{-1} s^{-1}. Nonetheless, a simple, universal relationship between uncorrected k_{el} and k_{ex} values remains elusive.

In contrast, we report here a simple, very close correlation between the *volumes of activation* $\Delta V_j^{\ddagger}$ $[=-RT(\partial \ln k_j/\partial P)_T$, with j standing for ex or el] of heterogeneous and the corresponding homogeneous self-exchange reactions. In a preliminary communication[18] concerning three cases chosen in early work for their wide spread of $\Delta V_j^{\ddagger}$ values, we noted that, within the experimental uncertainty,

$$\Delta V_{el}^{\ddagger} = {}^1/_2 \Delta V_{ex}^{\ddagger} \tag{4}$$

as expected from the pressure derivative of $\ln k_j$ in eq 3 *if*, as we will argue below, Z_{el} and Z_{ex} are sensibly independent of pressure. We now report in full the results of high pressure electrochemical kinetic studies of ten aqueous self-exchange reactions, for which values of $\Delta V_{ex}^{\ddagger}$ are available,[19] that confirm that eq 4 holds with remarkable precision, despite a very poor correlation between $\ln k_{el}$ and $\ln k_{ex}$. High pressure studies of redox phenomena at electrodes are not common,[20–40] and reports of high-pressure kinetic measurements are particularly sparse,[18,41–45] probably because of problems with reproducibility

Figure 1. Schematic structures of Co cage complexes.

due to contamination of electrodes in high-pressure equipment. We describe here procedures that yield reliable values of k_{el} and $\Delta V_{el}^{\ddagger}$ from AC voltammetry.

Experimental Section

Materials. Supporting electrolytes (NaCl, KCl, Na$_2$SO$_4$, and NaClO$_4$·H$_2$O; BDH Assured), HClO$_4$ (Baker Analyzed, 69.9%), Fe(ClO$_4$)$_3$·9H$_2$O (Aldrich, low in chloride), and K$_3$[Fe(CN)$_6$] (BDH Analar) were used as received. Negative precipitation tests with concentrated AgNO$_3$ solution indicated that the chloride contents of the NaClO$_4$·H$_2$O, 69.9% HClO$_4$, and Fe(ClO$_4$)$_3$·9H$_2$O were less than 1 × 10^{-7}%, 5 × 10^{-9}%, and 1 × 10^{-7}%, respectively. Literature methods were used to make [Co(en)$_3$]Cl$_3$,[46] [Co(diamsarH$_2$)]Cl$_5$·1.5H$_2$O,[39] and [Co(sep)]Cl$_3$[47] (prepared by R. D. Shalders), [Co(phen)$_3$](ClO$_4$)$_3$·2H$_2$O[48] (prepared by M. R. Grace), K$_4$[Mo(CN)$_8$][49] (prepared by P. D. Metelski), [Co(ttcn)$_2$](ClO$_4$)$_2$,[50,51] and [Fe(phen)$_3$]SO$_4$.[52,53] Figure 1 shows the structures of the Co complexes of the "cage" ligands sep and diamsar. Distilled water was further purified by passage through a Barnstead NANOpure train. In this article, concentrations are expressed in units of mol L^{-1} valid at 22 °C and 0.1 MPa.

Apparatus. Cyclic and AC voltammograms were obtained with an EG&G Princeton Applied Research (PARC) Model 173 potentiostat/galvanostat controlled by a PARC Model 175 universal programmer. A PARC Model 124A lock-in amplifier with a Model 117 differential preamplifier were used to impose a sine-wave potential perturbation on the output of the potentiostat and to detect the AC response at the perturbation frequency. The perturbation amplitude was preset by using an oscilloscope, and its frequency was measured with a Tektronix Model DC 503 universal counter. The voltammograms were recorded with a PARC Model RE0074 X–Y recorder.

Voltammetric data were collected by using a working electrode of Pt or Au wire (Φ 0.5 mm) flame sealed inside polyethylene tubes, a Pt or Au wire counter electrode of area much larger than the working electrode, and a reference electrode of Ag wire (Φ 2 mm) coated with AgCl and immersed in aqueous KCl or NaCl (4 mol L^{-1} for high pressure, or saturated for ambient pressure, experiments). The pressure vessel and the electrochemical cell were similar to those previously described[37] except that the lid of the cell and the mounting of the electrodes in it were modified as shown in Figure 2, largely to improve isolation of the cell contents from the pressurizing fluid (mixed hexanes), and the Vycor frit that provides electrical communication

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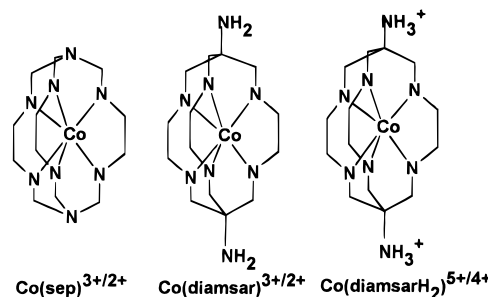
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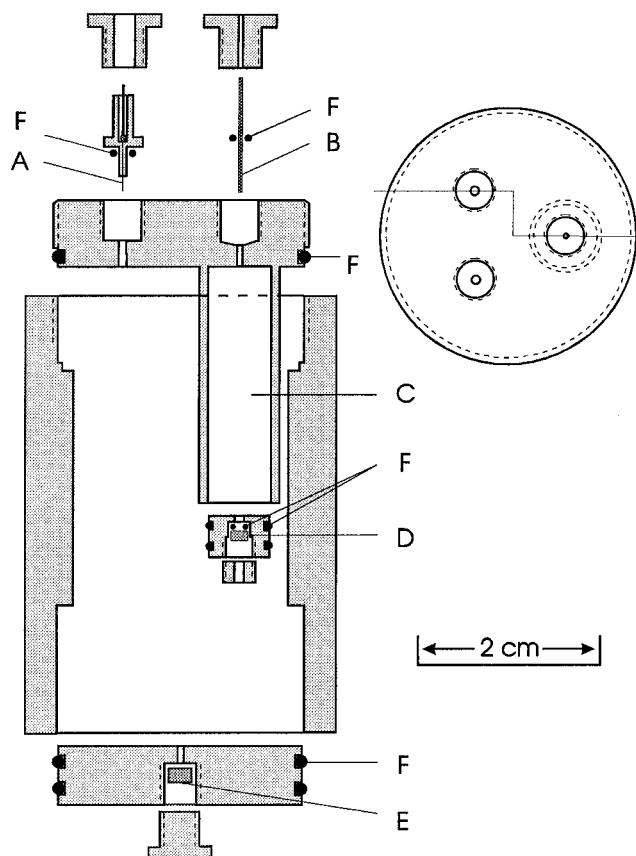
Figure 2. Electrochemical cell for use in the pressure vessel described in ref 37. Lightly shaded components are machined from virgin Teflon; A, working electrode; B, reference electrode (Ag wire coated with AgCl); C, reference electrode compartment (filled with 4.0 mol L^{-1} KCl, in use); D, Vycor frit; E, rubber disk seal; F, O-rings.

between the reference electrode fluid and the bulk solution was mounted in a free Teflon piston, sealed at the reference compartment wall with two O-rings.

Voltammetric Measurements. All solutions were degassed with water-saturated N$_2$ for at least 40 min before the cell was closed. The assembled pressure vessel containing the cell was placed in a thermostated waterjacket, and about 45 min was allowed for the thermal equilibration (25.0 ± 0.05 °C) of the cell after assembly and after each change of pressure P. At each pressure, a DC cyclic voltammogram (CV) was first recorded at a sweep rate $v = 50$ mV s^{-1} to determine the half-wave potential $E_{1/2}$. Then, the uncompensated resistance R_u was measured at a high frequency (8 kHz) and a potential at least 300 mV removed from the $E_{1/2}$ value of the redox couple to be studied; the double-layer capacitance C_{dl} was determined by the method of Smith.[54] Finally, AC voltammograms (ACVs) were run at each of three frequencies, recording the in-phase and 90° out-of-phase voltammograms sequentially. The in-phase and out-of-phase faradaic peak currents were obtained after correction for R_u and C_{dl}, and the phase angle φ of the AC peak current relative to the true AC potential across the electrode-solution interface was calculated.[54−56]

The key to obtaining reproducible ACV data was cleanliness of the electrode surfaces. Pretreatment of working electrode surfaces included gentle polishing with 0.05 μm Al$_2$O$_3$ powder followed by sonication

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(55) In AC voltammetry, it is possible to compensate for the potential drop iR_u by using the positive feedback circuitry of the PARC 173 potentiostat, but in practice this is tedious (especially since R_u is slightly pressure dependent, requiring readjustment of the compensation at each pressure), and moreover a small R_u is necessary for accurate operation of the apparatus. Since the iR_u drop is less than 5% of the applied AC potential, Smith's procedure[54] of measuring R_u directly and correcting for it was adopted here.

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in a K$_2$S$_2$O$_8$/concentrated H$_2$SO$_4$ bath for 15−30 s and then in water for 5 min. For measurements on couples other than Co(ttcn)$_2^{3+/2+}$ (which reduces to Co(ttcn)$_2^+$ with some apparent decomposition before the H$_2$ evolution potential is reached), the electrode was further cleaned *in situ* in the assembled pressure apparatus by sweeping the potential negatively from near $E_{1/2}$ to the point of vigorous H$_2$ evolution and back three times; it was important to repeat this at each pressure, as a cycle of measurements, nominally 0 to 200 and back to 0 MPa, typically extended over 10 h.

Results

Our previous attempts[37] to obtain $\Delta V_{el}^{\ddagger}$ values by cyclic voltammetry (the Nicholson method[57]) at high pressures gave usable results only in the Fe(CN)$_6^{3-/4-}$ case, in which the peak separation increases with pressure, so facilitating measurement. Even so, precision was poor because of the effect of uncompensated resistance. Determination of k_{el} from exchange current densities i_o measured by Tafel (Butler−Volmer) extrapolation to zero overpotential 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. AC voltammetry, on the other hand, requires the presence of only one member of the couple in bulk solution, allows for correction for R_u and C_{dl} in the calculation of k_{el}, and gives reliable k_{el} values as high as 1 cm s^{-1} with conventional electrodes. It is also possible to extract the transfer coefficient α from the potential E_{dc} of the AC faradaic current peak relative to the half-wave potential $E_{1/2}$ of the corresponding DC cyclic voltammogram (CV):

$$E_{dc} = E_{1/2} + (RT/nF) \ln[\alpha/(1 - \alpha)] \tag{5}$$

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[18] are known, then

$$[\cot \varphi]_{max} = 1 + \frac{(2D_O^{(1-\alpha)}D_R^{\alpha}\omega)^{1/2}}{\alpha^{-\alpha}(1 - \alpha)^{-(1-\alpha)}k_{el}} \tag{6}$$

where ω is the angular frequency of the applied AC perturbation, and k_{el} is obtainable from linear plots of $[\cot \varphi]_{max}$ against $\omega^{1/2}$. In this work, D_O and D_R were taken to be the same for a given redox couple, but had to be re-evaluated at each pressure from the peak currents of DC cyclic voltammograms calibrated against couples with known diffusion coefficients. Values of k_{el} measured at variable pressure are given in the Supporting Information.

The results are summarized in Table 1, in which the k_{el}^0 values listed are the zero-pressure intercepts of plots of ln k_{el} vs pressure, and the diffusion coefficients D^0 and half-wave potentials $E_{1/2}$ similarly refer to zero (ca. atmospheric) pressure. These plots, of which Figure 3 is typical, were in all cases linear within the experimental uncertainty. For all couples except Co(ttcn)$_2^{3+/2+}$ (see below), only those pressure cycles for which the final (lowest-pressure) k_{el} value coincided with the first, within the experimental uncertainty, were accepted. Table 1 also lists values of the equilibrium reaction volume $\Delta V_{AgCl/Ag}$ of the ML$_n^{(z+1)+/z+}$ couple relative to the AgCl/Ag/4.0 mol L^{-1} KCl reference electrode, obtained for the pressure dependence of $E_{1/2}$; these data are byproducts of the high-pressure CV measurements and are not intended to be definitive−values from other studies are cited where they are clearly more reliable.

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Table 1. Electrochemical Parameters for Self-Exchanging Couples in Aqueous Solution at 25.0 °C[a]

couple/electrode	medium/mol L^{-1}	$E_{1/2}$[b]/mV	$D^0/10^{-6}$ cm^2 s^{-1}	$\Delta V_{AgCl/Ag}$/cm^3 mol^{-1}	α[c]	k_{el}^0/cm s^{-1}	$\Delta V_{el}^{\ddagger}$/cm^3 mol^{-1}
A: Co(phen)$_3$$^{3+/2+}$/Pt	0.1 NaCl	+330	5.96	27.3 ± 1.1	0.50	0.108 ± 0.002	−9.1 ± 0.4
B: Co(en)$_3$$^{3+/2+}$/Pt[d]	0.5 KCl	−290	6.17	26.7 ± 0.7	0.42	0.036 ± 0.001	−8.3 ± 0.5
C: Fe(H$_2$O)$_6$$^{3+/2+}$/Pt	0.5 HClO$_4$/NaClO$_4$	+675	6.21	5.5 ± 0.4	0.45	0.0207 ± 0.0005	−5.5 ± 0.2
D: Co(diamsar)$^{3+/2+}$/Au	0.1 NaClO$_4$ (pH 9)	−410	5.85	17.4 ± 0.5[e]	0.27	0.0162 ± 0.0007	−3.5 ± 0.2
E: Co(diamsarH$_2$)$^{5+/4+}$/Au	0.13 HClO$_4$/NaClO$_4$	−35	5.21	19.5 ± 0.8[e]	0.41	0.010 ± 0.001	−3.8 ± 0.3
F: Co(sep)$^{3+/2+}$/Pt	0.5 KCl	−535	6.57	15.8 ± 0.5	0.50	0.091 ± 0.001	−3.0 ± 0.4
G: Co(ttcn)$_2$$^{3+/2+}$/Pt	0.1 NaClO$_4$	+230	5.69	24.4 ± 1.0	0.50	0.27 ± 0.02	−2.8 ± 0.7
H: Fe(phen)$_3$$^{3+/2+}$/Pt	0.1 Na$_2$SO$_4$	+1040	3.99	15.3 ± 0.7	0.50	0.300 ± 0.003	−1.6 ± 0.1
I: Mo(CN)$_8$$^{3-/4-}$/Au[f]	0.5 NaClO$_4$ (pH 2.7)	+618	5.47	−29.8 ± 1.0	0.50	0.053 ± 0.001	+7.3 ± 0.7
J: Fe(CN)$_6$$^{3-/4-}$/Pt[f]	0.5 KCl	+340	7.63	−36.6 ± 0.7[g]	0.50	0.072 ± 0.005	+11.9 ± 1.3
	0.2 KCl					0.047 ± 0.004	+10.4 ± 1.4

[a] See text for details of conditions. [b] ±5 mV, vs AgCl/Ag in saturated KCl. [c] ±0.02. [d] 0.2 mol L^{-1} en present. [e] Reference 39. [f] The counterion of octacyanomolybdate is K$^+$. [g] Reference 37.
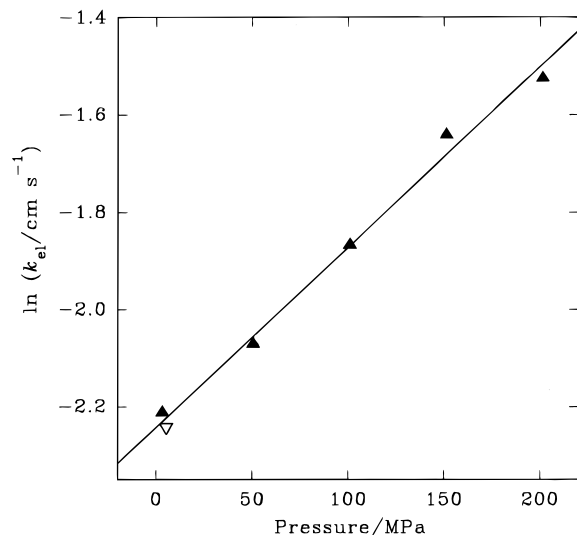

Figure 3. Pressure dependence of ln k_{el} for Co(phen)$_3$$^{3+/2+}$ at a Pt wire electrode in 0.100 mol L^{-1} aqueous NaCl at 25 °C; [Co(phen)$_3$(ClO$_4$)$_3$] = 0.100 mmol L^{-1}. Solid triangles: pressure increasing. Open triangle: pressure decreasing.

Values of $E_{1/2}$ at atmospheric pressure agreed satisfactorily with recommended values, where these are available,[58] after allowance for differences in the media and the reference electrodes. Atmospheric pressure values of k_{el}, however, typically depend markedly on the nature of the medium and the working electrode, and some disagreement with literature data may be expected.

Couple A: Tris(1,10-phenanthroline)cobalt(III)/(II). The perchlorate salt of Co(phen)$_3$$^{3+}$ was used; solubility limited the working concentration to 1.0 mmol L^{-1}, at which level no precipitation of KClO$_4$ in the reference electrode interface occurred. As the electrode reaction in 0.5 mol L^{-1} KCl or NaCl (our usual choices of supporting electrolyte) was a little too fast to give reliable k_{el} values, high pressure rate measurements were made in 0.1 mol L^{-1} NaCl with use of a Pt wire working electrode, a Pt wire counter electrode, and, as in all experiments described below, AgCl/Ag/4.0 mol L^{-1} NaCl as the reference electrode. At atmospheric pressure, k_{el} values of 0.12 ± 0.02, 0.15 ± 0.01, and 0.21 ± 0.04 cm s^{-1} were obtained at [NaCl] = 0.104, 0.200, and 0.505 mol L^{-1}, respectively; thus, k_{el}, like k_{ex},[48] exhibits a marked medium dependence in the case of Co(phen)$_3$$^{3+/2+}$. The pressure dependence of k_{el} for one of the duplicate pressure cycles is shown in Figure 3. The value of $\Delta V_{AgCl/Ag}$ agrees satisfactorily with that of Tregloan et al.[36] (24.3 ± 1.1 cm^3 mol^{-1}, after addition of 2.9 cm^3 mol^{-1} to the latter value to convert from an Ag$^+$/Ag to an AgCl/Ag/4.0 mol L^{-1} KCl reference electrode[33]) for a KNO$_3$ rather than a NaCl medium.

Table 2. Medium Dependence of Heterogeneous Exchange Rate Constants for Fe(H$_2$O)$_6$$^{3+/2+}$ in Aqueous HClO$_4$/NaClO$_4$[a]

ionic strength/mol L^{-1}	[H$^+$]/mol L^{-1}	[Na$^+$]/mol L^{-1}	k_{el}/cm s^{-1}
0.70	0.70	0	0.062
	0.35	0.35	0.030
	0.20	0.50	0.029
	0.10	0.60	0.025
0.50	0.40	0.10	0.055
	0.20	0.30	0.032
	0.10	0.40	0.027
	0.05	0.45	0.025
0.40	0.20	0.20	0.063
0.30	0.20	0.10	0.11
0.25	0.20	0.05	0.12
0.20	0.20	0	0.14

[a] 25.0 °C, 0.1 MPa.

Couple B: Co(en)$_3$$^{3+/2+}$. Solutions contained [Co(en)$_3$]Cl$_3$ (2.0 mmol L^{-1}) and KCl (0.5 mol L^{-1}), together with free en (0.2 mol L^{-1}) to suppress decomposition of the labile, transiently formed Co(en)$_3$$^{2+}$ and so ensure reversible redox behavior. The working and counter electrodes were of Pt and Au wire, respectively. The value of $\Delta V_{el}^{\ddagger}$ given in Table 1 is the mean of two independent determinations. Agreement between the $\Delta V_{AgCl/Ag}$ value and the converted value of Tregloan et al.[36] (29.8 ± 1.4 cm^3 mol^{-1}, 0.1 mol L^{-1} KNO$_3$) is acceptable, given the difference in media. The value of k_{el} at atmospheric pressure (0.036 ± 0.001 cm s^{-1}) in 0.5 mol L^{-1} KCl compares favorably with measurements by Sahami and Weaver[59] (0.03 and 0.05 cm s^{-1} in 0.1 and 0.4 mol L^{-1} KPF$_6$, respectively, at an Hg electrode) despite differences in the medium and the working electrode.

Couple C: Fe(H$_2$O)$_6$$^{3+/2+}$. The electrochemical measurements reported for this couple in Tables 1 and 2 were made in perchlorate media with 2.0 mmol L^{-1} [Fe(H$_2$O)$_6$](ClO$_4$)$_3$, Pt wire working and counter electrodes, and a NaCl/AgCl/Ag reference electrode. Because the kinetics of the Fe$^{3+/2+}$(aq) electrode reaction are sensitive to traces of chloride ion (see Discussion), it was demonstrated that replacement of the NaCl/AgCl/Ag electrode with a similar non-chloride reference electrode (internal electrolyte 0.0l mol L^{-1} AgNO$_3$/0.5 mol L^{-1} NaNO$_3$) gave essentially the same ACV results; thus, for a 0.2 mol L^{-1} HClO$_4$/0.3 mol L^{-1} NaClO$_4$ medium, k_{el} = 0.032 and 0.034 cm s^{-1}, respectively. Some AC voltammograms were obtained with CF$_3$SO$_3$H (0.2 mol L^{-1}) as supporting electrolyte as a non-chlorine alternative to perchlorates, but they showed distortion, even though the DC CVs appeared normal. Perchlorate media were therefore used in all Fe$^{3+/2+}$(aq) experiments reported in Tables 1 and 2 since, in all these cases, the chloride content introduced with the reagents was <3 nmol L^{-1}.

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Since the rate of homogeneous $Fe(H_2O)_6^{3+/2+}$ self-exchange is $[H^+]$ dependent,[60,61] the variation of k_{el} with $[HClO_4]$ was investigated with the ionic strength I maintained with $NaClO_4$. The results in Table 2 show, however, that the main influence on k_{el} is $[Na^+]$ rather than $[H^+]$ or I; at constant $[H^+]$ of 0.20 mol L^{-1}, k_{el} falls essentially linearly as $[Na^+]$ is increased from zero, but k_{el} reaches a plateau at about 0.030 cm s^{-1} for $[Na^+]$ $\geq$ 0.3 mol L^{-1}. When $[H^+]$ is varied with $[Na^+] \geq 0.3$ mol L^{-1}, k_{el} remains constant at about 0.030 cm s^{-1} above $[H^+] = 0.2$ mol L^{-1} and declines slightly with decreasing $[H^+]$ below this concentration. The high-pressure experiments were therefore carried out with $[H^+] = 0.20$ mol L^{-1} and $[Na^+] = 0.30$ or 0.50 mol L^{-1} (two independent runs at each $[Na^+]$), with excellent consistency in $\Delta V_{el}^{\ddagger}$ (-5.5 ± 0.3 cm^3 mol^{-1}, four runs). Weaver et al.[62] reported $k_{el} = 9 \times 10^{-6}$ cm s^{-1} for this couple at a mercury electrode in 0.4 mol L^{-1} KPF_6, which confirms the strong influence of the reaction environment in this case.

Couple D: $Co(diamsar)^{3+/2+}$. Solutions were made up with 5 mmol L^{-1} $[Co(diamsarH_2)]Cl_5 \cdot 1.5H_2O$ in 0.1 mol L^{-1} $NaClO_4$, and the pH was adjusted to 9.0 with NaOH to ensure deprotonation of both $-NH_3^+$ functions; in cyclic voltammograms, redox peaks due to $Co(diamsarH)^{4+}$ did not completely disappear until the pH reached 8.5, beyond which the CVs remained unchanged up to pH 11 at least. The supporting electrolyte concentration was adjusted to 0.1 mol L^{-1} with $NaClO_4$. AC voltammograms were obtained with a gold wire working electrode and a Pt counter electrode. The value of the transfer coefficient (0.27) was smaller than expected, but was fully reproducible. The volume of reaction obtained from CVs at high pressure was 23.7 ± 0.8 cm^3 mol^{-1}; this value is 6 cm^3 mol^{-1} larger than that reported earlier,[39] which is considered the more reliable and is cited in Table 1.

Couple E: $Co(diamsarH_2)^{5+/4+}$. High acidity is required to ensure protonation of both amino groups,[39] with the result that electrochemical measurements must be made close to the potential for H_2 evolution. For this reason, gold wire, which is more susceptible to contamination than Pt but has a higher overpotential for H_2 evolution, was chosen as the working electrode, with Pt wire as the counter electrode. The transfer coefficient α (0.41) was within the preferred range, but measurements of $\Delta V_{AgCl/Ag}$ were subject to large uncertainties and the value obtained earlier[39] was taken as definitive (Table 1). ACV measurements of $\Delta V_{el}^{\ddagger}$ with 5.0 mmol L^{-1} $Co(diamsarH_2)^{5+/4+}$ in 0.100 mol L^{-1} $HClO_4$/0.025 mol L^{-1} $NaClO_4$ and in 0.020 mol L^{-1} $HClO_4$/0.105 mol L^{-1} $NaClO_4$ solutions gave closely similar results (-3.7 ± 0.5 and -3.8 ± 0.3 cm^3 mol^{-1}, respectively).

Couple F: $Co(sep)^{3+/2+}$. The working and counter electrodes were Pt and Au wire, respectively. The value of $\Delta V_{AgCl/Ag}$ obtained (Table 1) was in satisfactory agreement with a previous determination.[37] The average $\Delta V_{el}^{\ddagger}$ from three independent runs was -3.0 ± 0.4 cm^3 mol^{-1}.

Couple G: $Co(ttcn)_2^{3+/2+}$. Cyclic voltammograms of $[Co(ttcn)_2](ClO_4)_2$ (1.0 mmol L^{-1}) in NaCl solution (0.1 mol L^{-1}), using Pt wire working and counter electrodes, showed features at $E_{1/2} = 365$ and -520 mV, due to the $Co(ttcn)_2^{3+/2+}$ and $Co(ttcn)_2^{2+/+}$ couples, respectively. For the former couple, $\Delta V_{AgCl/Ag}$ (Table 1) was in satisfactory agreement with a previously reported value.[38] In ACV measurements, k_{el} for

$Co(ttcn)_2^{3+/2+}$ decreased very slowly with time, apparently because of some decomposition, so that the final (lowest pressure) k_{el} of a pressure cycle was significantly lower than the first; this decrease, however, was regular and reproducible, and k_{el} values over a pressure cycle were corrected for this small effect. Addition of excess ttcn ligand had no effect on k_{el}, and $\Delta V_{el}^{\ddagger}$ values of -2.7 ± 0.6 and -2.8 ± 0.8 cm^3 mol^{-1} were obtained for runs with and without added ttcn (saturated, ca. 5 mmol L^{-1}), respectively, in $NaClO_4$ (0.100 mol L^{-1}; chloride was avoided as a possible contributor to the presumed decomposition process, although there was no evidence for such interference).

Couple H: $Fe(phen)_3^{3+/2+}$. $[Fe(phen)_3]SO_4$ (1.0 mmol L^{-1}) was studied in both 0.100 mol L^{-1} H_2SO_4 and 0.100 mol L^{-1} Na_2SO_4 (i.e., ionic strength $I \approx 0.3$ mol L^{-1}), but spectrophotometric measurements showed slow ligand dissociation in the acidic solution, and decomposition may account for the curved $E_{1/2}$ vs P plots reported previously.[37] In the present work, high-pressure CV measurements on the Na_2SO_4 solutions, using Pt working and counter electrodes, gave accurately linear $E_{1/2}$ vs P plots with $\Delta V_{AgCl/Ag} = 15.3 \pm 0.7$ cm^3 mol^{-1}, 5$-$6 cm^3 mol^{-1} more positive (after correction for the different reference electrode) than those reported by Tregloan et al.[35,36] for KNO_3 media. A single series of high-pressure ACV measurements on the very fast $Fe(phen)_3^{3+/2+}$ electrode reaction was made, giving $\Delta V_{el}^{\ddagger} = -1.6 \pm 0.1$ cm^3 mol^{-1}. At atmospheric pressure, $k_{el} = 0.300 \pm 0.003$ cm s^{-1}, which may be compared with 0.7 cm s^{-1} reported by Aoyagui et al.[9] for a Pt electrode but a different medium (0.5 mol L^{-1} LiCl).

Couple I: $Mo(CN)_8^{3-/4-}$. Literature values of k_{el} for $Mo(CN)_8^{3-/4-}$ range from 2×10^{-4} cm s^{-1} at a polymer-modified graphite electrode in 0.2 mol L^{-1} CF_3COOH/CF_3COONa (pH 1.5)[63] to 0.5 cm s^{-1} at a Pt sphere in 0.2 mol L^{-1} KF;[9] for the conditions chosen here (2.0 mmol L^{-1} $K_4[Mo(CN)_8]$ in 0.5 mol L^{-1} KCl), k_{el} lay toward the upper end of this range and was sensitive to the nature of the electrode (0.10 $\pm$ 0.01 cm s^{-1} for Pt wire working and counter electrodes, and 0.18 $\pm$ 0.01 cm s^{-1} with a gold working electrode, under neutral conditions). The value of $E_{1/2}$ (618 mV vs AgCl/Ag) was in satisfactory agreement with the generally accepted value for 0.5 mol L^{-1} KCl (811 mV vs NHE).[58,64] Some inconsistency of k_{el} values obtained in ACV measurements on *neutral* solutions over a 200 MPa pressure cycle was noted and attributed to slow formation of a Pt oxide film. Accordingly, a gold working electrode was used for the definitive high-pressure runs, and in some cases the solutions were acidified; however, $\Delta V_{el}^{\ddagger}$ values obtained from initial readings with the Pt electrode were in good agreement with those obtained with Au. With Au, the dependence of ln k_{el} on P was reproducible and linear, giving $\Delta V_{el}^{\ddagger} = +7.4 \pm 1.1$ cm^3 mol^{-1} for 0.5 mol L^{-1} KCl and, better, $\Delta V_{el}^{\ddagger} = +7.2 \pm 0.7$ cm^3 mol^{-1} for 0.001 mol L^{-1} $HClO_4$/0.5 mol L^{-1} $NaClO_4$ at Au. Under the latter conditions, $E_{1/2}$ was accurately a linear function of P, giving $\Delta V_{AgCl/Ag} = -29.8 \pm 1.0$ cm^3 mol^{-1}. For the *homogeneous* $Mo(CN)_8^{3-/4-}$ exchange, Metelski[65] found it difficult to obtain fully reproducible values of k_{ex} from one atmospheric-pressure experiment to another by ^{13}C-NMR line broadening because of photochemical or other losses of the Mo^V anion during sample preparation and an undetermined dependence of k_{ex} on cation concentration and ionic strength, but for a given cycle of high-pressure NMR measurements (in which the sample was isolated and in darkness) plots of the apparent ln k_{ex} vs P were satisfactorily

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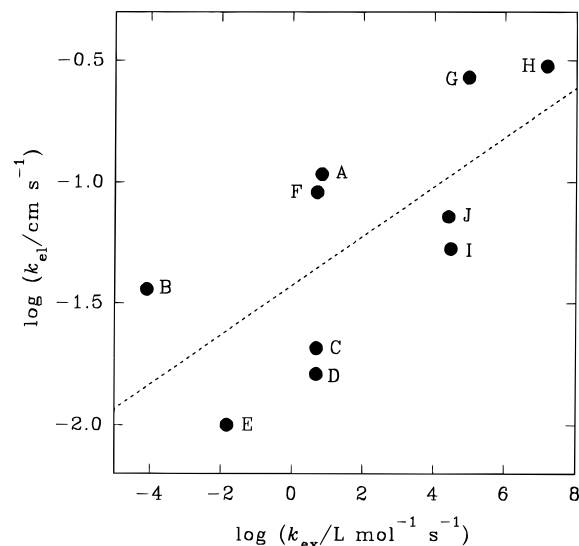(65) Metelski, P. D.; Swaddle, T. W. Forthcoming publication.

Figure 4. Plot of ln k_{el} (this work) against ln k_{ex} (refs 39, 45, 52, 60, and 66 and this work) at 25 °C for comparable ionic strengths in the range 0.1–0.5 mol L^{-1}. See Results section for letter code. The broken line is a least-squares fit, slope = 0.10 ± 0.04.

Figure 5. Plot of $\Delta V_{el}^{\ddagger}$ (this work) against $\Delta V_{ex}^{\ddagger}$ (ref 20 and this work) at 25 °C for comparable ionic strengths in the range 0.1–0.5 mol L^{-1}. See Results section for letter code. The solid line is a least-squares fit, slope = 0.50 ± 0.02.

linear with reproducible slopes, giving $\Delta V_{ex}^{\ddagger} = +14.7 \pm 1.5$ cm^3 mol^{-1} (mean of three experiments) with $k_{ex} = 3 \times 10^4$ L mol^{-1} s^{-1} at atmospheric pressure (identical with that obtained indirectly from the Marcus cross-relation by Sutin and co-workers[66]).

Couple J: Fe(CN)$_6^{3-/4-}$. Electrochemical measurements were made on freshly prepared solutions containing 2 mmol L^{-1} K$_3$[Fe(CN)$_6$], using a Pt wire working electrode and a gold counter electrode and excluding light. Contamination of the working electrode surface, probably by deposition of Prussian blue-like films through decomposition of the hexacyanoferrates,[67] led to erratic results in experiments lasting half a day or more, but the contaminants were adequately removed in situ by potential cycling. Cyclic voltammetry gave $\Delta V_{AgCl/Ag} = -34.2 \pm 1.2$ cm^3 mol^{-1}, in satisfactory agreement with earlier work regarded as definitive (Table 1).[35,37] Electrochemical rate constants reported for this much-studied couple range from <0.01 to 0.24 cm s^{-1}, being markedly influenced by both the supporting electrolyte and the nature, dimensions, and mode of cleaning of the working electrode.[67-69] The k_{el} values of Table 1, however, are in good agreement with careful measurements[68,70] using conventional Pt electrodes at the same or interpolated K$^+$ concentrations, and the high-pressure techniques described here were therefore developed by using this conveniently available couple. Homogeneous electron transfer kinetics for aqueous Fe(CN)$_6^{3-/4-}$ are similarly subject to marked counterion effects.[45] Three independent pressure experiments gave an average $\Delta V_{el}^{\ddagger} = +11.9 \pm 1.3$ cm^3 mol^{-1} in 0.5 mol L^{-1} KCl, and a single cycle in 0.2 mol L^{-1} KCl gave $\Delta V_{el}^{\ddagger} = +10.4 \pm 1.4$ cm^3 mol^{-1}.

Discussion

Figure 4 shows that there is at best only a very weak correlation (correlation coefficient $r^2 = 0.49$) between ln k_{el} and ln k_{ex} in comparable aqueous media for the 10 outer-sphere electron exchange couples A–J considered in this study.

Furthermore, the slope of the dubious linear least-squares regression line is only 0.10 ± 0.04, as against 0.50 expected from eq 3. The lack of conformity to eq 3 is perhaps to be expected, since k_{el} and k_{ex} are not dimensionally compatible, no corrections[12-16] for factors such as the work terms or for double layer effects have been applied, and in any event the results described above show that medium effects and the nature of the working electrode can affect the value of k_{el} substantially. There is, however, no obvious pattern of medium or electrode material effects that might account for the scatter of the data. There is good evidence, coming in part from $\Delta V_{ex}^{\ddagger}$ data,[19] that the self-exchange reactions considered here are essentially adiabatic, and if the electrode reactions are also adiabatic (see below), k_{el} values should be independent of the nature of the electrode;[71] in reality, k_{el} can clearly be markedly influenced by the environment of the couple during electron transfer, adiabatic or not, and this may show up as an apparent electrode effect. It might be argued that the measured k_{el} values are not, in fact, "true" electrochemical rate constants because of the effects of uncompensated resistance R_u, *inter alia*; however, R_u was specifically taken into account in our measurements, and besides Weaver and co-workers[72,73] have shown that realistic k_{el} values are indeed obtainable from ACV methods so long as $k_{el} \leq 1$ cm s^{-1}, as was always the case in this study. In short, then, eq 3 as such seems not to hold for the couples A–J in aqueous solution.

In contrast, Figure 5 shows a remarkably close correlation between $\Delta V_{el}^{\ddagger}$ and $\Delta V_{ex}^{\ddagger}$ ($r^2 = 0.988$) with slope 0.50 ± 0.02 and intercept essentially zero (0.1 ± 0.3 cm^3 mol^{-1}), just as predicted by eq 4, which we refer to as the "fifty percent rule".[18] Here again, no corrections of the experimental data have been made,[74] but the quantities being compared are dimensionally compatible (units of cm^3 mol^{-1} for both), and eq 4 holds with

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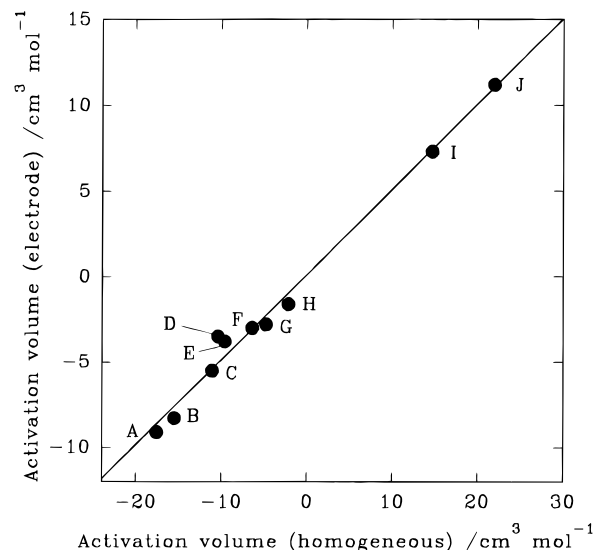(70) Hinman, A. S. Ph.D. Thesis, University of Alberta, 1983.

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(74) Throughout this study, ln k_{el}, ln k_{ex}, and $E_{1/2}$ are taken to be linear functions of P over the experimental range of 0 to 200 MPa. Since some curvature of the ln k_{ex} vs P plot is predicted (and, in a few cases such as the homogeneous Co(en)$_3^{3+/2+}$ exchange, actually observed),[20] this practice amounts to comparing $\Delta V_{el}^{\ddagger}$ with $\Delta V_{ex}^{\ddagger}$ values for the midrange pressure of 100 MPa.

impressive accuracy. It follows that the assumptions implicit in eq 4 must be valid, that is, that the electrode and homogeneous reactions alike are adiabatic and that Z_{el} and Z_{ex} are indeed independent of pressure to within the experimental uncertainty. The absence of any detectable dependence of $\Delta V_{el}^{\ddagger}$ on the nature of the electrode is understandable, since solid electrode surfaces will be negligibly affected by a 200 MPa pressure cycle.

The reason for the apparent absence of electrolyte or double layer effects on $\Delta V_{el}^{\ddagger}$, even when k_{el} is strongly influenced, is less obvious. The fact that the slope of the $\Delta V_{el}^{\ddagger} - \Delta V_{ex}^{\ddagger}$ correlation is precisely 0.50 implies that the M-electrode distance σ_{el} is indeed just one half the M–M distance σ_{ex} in homogeneous electron transfer. The simplest interpretation of this is that the complex ion undergoes redox in direct contact with the electrode surface; that being so, the absence of specific double layer effects on $\Delta V_{el}^{\ddagger}$ is understandable. On the other hand, k_{el} may show a marked dependence on the nature of the double layer, since the electroactive complexes must compete with species making up the double layer for sites on the electrode surface in an essentially statistical fashion that is unlikely to be significantly affected by pressure.

Volumes of activation for adiabatic homogeneous self-exchange of $ML_n^{(z+1)+/z+}$ couples in aqueous solution can be predicted quantitatively from an adaptation of Marcus–Hush theory (Stranks–Hush–Marcus–Swaddle or SHMS theory), except where there is specific involvement of the counterion or of a spin-change pre-equilibrium in the mechanism, or where the reaction proceeds by an innersphere pathway; the theory is less successful for nonaqueous systems, for reasons that can be identified.[19] The theory treats $\Delta V_{ex}^{\ddagger}$ as the sum of contributions $\Delta V_{IR}^{\ddagger}$ from internal reorganization (related to λ_i), $\Delta V_{SR}^{\ddagger}$ from solvent or outersphere reorganization (related to λ_o), $\Delta V_{DH}^{\ddagger}$ from medium (Debye–Hückel) effects, $\Delta V_{COUL}^{\ddagger}$ from the coulombic work of bringing the reactants together, and $\Delta V_{PREC}^{\ddagger}$ from the pressure dependence of the pre-exponential part of the work terms governing formation of the $ML_n^{(z+1)+/z+}$ precursor complex. Inclusion of $\Delta V_{PREC}^{\ddagger}$ (which is in any event only +1 to +2 cm^3 mol^{-1}) is appropriate only if σ_{ex} is pressure dependent, i.e., if electron transfer occurs over a *range* of close-encounter M–M separations; as noted above, however, the present results suggest that σ_{ex} and σ_{el} correspond to "hard" ion–ion and ion–electrode contacts, respectively, in which case $\Delta V_{PREC}^{\ddagger}$ is redundant. Furthermore, $\Delta V_{IR}^{\ddagger}$ is small, because shrinkage of ML_n^{z+} offsets expansion of $ML_n^{(z+1)+}$ as the precursor complex goes to the transition state—this applies even though the corresponding ΔG_{IR}^* may be very large, since the displacement of the reactants from their equilibrium configurations requires input of energy to *both*. Finally, at the ionic strengths at which $\Delta V_{ex}^{\ddagger}$ is usually measured, $\Delta V_{DH}^{\ddagger}$ and $\Delta V_{COUL}^{\ddagger}$, which are of opposite sign, tend to cancel, so that $\Delta V_{SR}^{\ddagger}$ emerges as the dominant contributor to $\Delta V_{ex}^{\ddagger}$.

The implication of the success of the "fifty percent rule" is that $\Delta V_{el}^{\ddagger}$ is also predictable from SHMS theory.[19] The fortuitous cancellation of $\Delta V_{DH}^{\ddagger}$ and $\Delta V_{COUL}^{\ddagger}$ at ionic strengths in the range (0.1–0.5 mol L^{-1}) covered by our electrochemical experiments may appear in a slightly different guise in electrode kinetics; little is known about the effects of pressure on the properties of the diffuse double layer,[75] but without resort to a detailed analysis, the formal similarity between the Gouy–Chapman–Stern treatment of the double layer and the Debye–Hückel theory of ion activities in solution leads us to expect approximate cancellation of double-layer contributions to the kinetic pressure effect by the work terms in the heterogeneous, as in the homogeneous, case. In any event, double layer effects

are not evident in the $\Delta V_{el}^{\ddagger} - \Delta V_{ex}^{\ddagger}$ correlation. The lack of marked electrolyte effects on $\Delta V_{el}^{\ddagger}$ mirrors the absence of significant dependence of $\Delta V_{ex}^{\ddagger}$ on ion strength in the range 0.1–1.0 mol L^{-1} even when k_{ex} is substantially affected.[48]

Interestingly, the most deviant points in Figure 5, the Co(diamsar)$^{3+/2+}$ and Co(diamsarH$_2$)$^{5+/4+}$ exchanges, fit the "fifty percent rule" very closely if the theoretical, rather than the experimental, $\Delta V_{ex}^{\ddagger}$ values are used, thus giving added credence to the SHMS theory of $\Delta V_{ex}^{\ddagger}$. As SHMS theory stands, however, *negative* $\Delta V_{ex}^{\ddagger}$ values are predicted for all likely outersphere self-exchange reactions, and so it fails badly for the Fe(CN)$_6^{3-/4-}$ and Mo(CN)$_8^{3-/4-}$ couples, for which $\Delta V_{ex}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$ are strongly *positive*, apparently because the counterions are intimately involved in the transition states.[45,65] Yet these anion–anion couples obey eq 4 closely; the implication here is that they are not "anomalous", and that it should be possible to modify SHMS theory to cover these cases too. The fit of the Fe(CN)$_6^{3-/4-}$ data to the "fifty percent rule" also gives us confidence that our $\Delta V_{el}^{\ddagger}$ value of +11 cm^3 mol^{-1} for this couple is correct; agreement with Sato and Yamada's value of $\Delta V_{el}^{\ddagger}$ = +13 cm^3 mol^{-1} for Fe(CN)$_6^{3-/4-}$ in 1.0 mol L^{-1} KCl (from three data points over a 100 MPa pressure range)[43] is satisfactory, but Conway and Currie[41] obtained $\Delta V_{el}^{\ddagger}$ = +1.9 cm^3 mol^{-1} for this couple in 0.5 mol L^{-1} K$_2$SO$_4$ at a gold electrode. The reason for the disagreement, other than the difference in the supporting electrolyte, is not clear; we note, however, that Sato and Yamada[43] found a marked sensitivity of $\Delta V_{el}^{\ddagger}$ to the nature of the medium, and that Conway and Currie[41] unnecessarily corrected their concentration data for compression.[76]

Figure 5 covers all but one of the simple outersphere self-exchange reactions for which experimental $\Delta V_{ex}^{\ddagger}$ data are available in aqueous solution.[19] The exception is the MnO$_4^{-/2-}$ couple,[77] for which we have been unable to obtain a reliable $\Delta V_{el}^{\ddagger}$ value because the Vycor frit of the reference electrode was destroyed by the high alkalinity necessary to protect the manganate(VI) ion. Preliminary results suggest, however, that $\Delta V_{el}^{\ddagger}$ may be quite strongly positive for this couple, which would be consistent with the behavior of the other anion–anion couples discussed here but not reconcilable with the strongly negative $\Delta V_{ex}^{\ddagger}$ deduced for the exchange of the "naked" MnO$_4^{-/2-}$ ions or the near-zero $\Delta V_{ex}^{\ddagger}$ values found for the Na$^+$- and K$^+$-dependent pathways. Possibly, there is a greater involvement of the cations in the electrode reaction than in the homogeneous self-exchange in this case, but in any event we note that the $\Delta V_{ex}^{\ddagger}$ data themselves are not readily interpretable in terms of the SHMS theory without additional assumptions.[77]

Of all the couples examined in this study, only Fe(H$_2$O)$_6^{3+/2+}$ is substitutionally labile in both the oxidized and reduced forms on the time scale of the electrochemical measurements and is therefore subject to the incursion of innersphere electron transfer pathways that are not amenable to direct detection. The conformity of our $\Delta V_{el}^{\ddagger} - \Delta V_{ex}^{\ddagger}$ data for this couple to the "fifty percent rule" would seem to imply an adiabatic *outersphere* mechanism for both the homogeneous[61] and heterogeneous electron transfer processes, since the Marcus theory assumes outer-sphere behavior. It has been reported,[78–80] however, that k_{el} values as large as those of Tables 1 and 2, though consistent with the findings of many workers,[81,82] are

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about 10^3-fold larger than the true value for the $Fe(H_2O)_6^{3+/2+}$ couple, and may reflect catalysis of the electrode process by adventitious chloride ions. The reagents used in our experiments contributed less than 3 nmol L^{-1} Cl^- to the solutions, and the consistency of k_{el} values before and after pressure cycles as well as from experiment to experiment would seem to eliminate contamination from fingerprints or AgCl/Ag electrode leakage as sources of error. (Decomposition of perchlorate ion itself seems not to be a significant source of Cl^- in these systems even at 275 °C.[80]) Nevertheless, a 1.5 nmol L^{-1} level of chloride in our cell would be sufficient to form a monolayer of Cl^- on the working electrode (if all Cl^- were adsorbed). Nagy et al.[79,80] used two methods to remove adsorbed chloride (potential cycling to the point of H_2 evolution—as in this study—followed by a potential pulse to commence measurement of k_{el}, and prior scavenging of adsorbed Cl^- by $Cr^{2+}(aq)$ as $Cr(H_2O)_5Cl^{2+}$) and obtained consistent k_{el} values of about 2×10^{-5} cm s^{-1} for the $Fe(H_2O)_6^{3+/2+}$ electrode reaction. Unfortunately, we are unable to use these methods with our present resources, not least because such rate constants are too low for accurate measurement by AC voltammetry.

Thus, the possibility exists that the $\Delta V_{el}^{\ddagger}$ reported here for the $Fe^{3+/2+}(aq)$ couple refers to a Cl^--mediated process, possibly of the innersphere type. We plan to determine whether, contrary to expectations, known innersphere reactions also conform to the "fifty percent rule", but $\Delta V_{ex}^{\ddagger}$ values as well as $\Delta V_{el}^{\ddagger}$ are generally lacking for suitable couples and a major effort will be required to get them. We note, however, that the absence of an inverse dependence of k_{el} on $[H^+]$ (Table 2) shows that the conjugate base pathway involving $Fe(H_2O)_5OH^{2+}$ and $Fe(H_2O)_6^{2+}$, though important in homogeneous solution because it proceeds an *innersphere* mechanism,[61] does *not* participate measurably in the electrode reaction. As an interim hypothesis, then, we conclude that our $\Delta V_{el}^{\ddagger}$ and $\Delta V_{ex}^{\ddagger}$ measurements on the $Fe^{3+/2+}(aq)$ couple do indeed refer to outersphere electron transfer between the hexaaqua ions, but that differences in the electrical properties of the Pt surface account for the discrepancies in k_{el} between various studies, surface properties being relatively insensitive to pressure. Platinum oxide films[7,81] form

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at potentials slightly more anodic than $E_{1/2}$ for $Fe(H_2O)_6^{3+/2+}$, and were presumably present in our experiments on this couple since our sweeps began at more positive potentials to observe reduction of iron(III). Significantly, Galus and Adams[83] found low k_{el} values (8.5×10^{-5} to 2.3×10^{-4} cm s^{-1}) for the $Fe^{3+/2+}(aq)$ couple at a carbon-paste rotating disk electrode in media with chloride contents ranging from 0.1 to 4.0 mol L^{-1}, so that an innersphere mechanism involving chloride ion can be ruled out in this case and presumably also at a Pt electrode. The very low k_{el} found by Weaver et al.[62] with a PF_6^- medium at an Hg electrode lends support to the view that high k_{el} values reflect a surface property specific to Pt.

The effect of $[Na^+]$ on k_{el} for $Fe^{3+/2+}(aq)$ at atmospheric pressure (Table 2) suggests that the electroactive species must compete with Na^+ for sites at the electrode surface, but that Na^+ coverage of the surface is saturated at $[Na^+] \geq 0.3$ mol L^{-1}.

Finally, the success of the "fifty percent rule" means that high-pressure electrochemical measurements of $\Delta V_{el}^{\ddagger}$ may permit indirect estimation of $\Delta V_{ex}^{\ddagger}$ in cases where direct determination is impossible, e.g., for rapidly exchanging couples in which both partners are paramagnetic and so not amenable to NMR line-broadening rate measurements. Since $\Delta V_{ex}^{\ddagger}$ values can be combined with volumes of reaction (also determinable from high-pressure electrochemistry through $\Delta V_{AgCl/Ag}$) to predict volumes of activation $\Delta V_{12}^{\ddagger}$ for adiabatic, outersphere "cross" reactions,[38] comparison of predicted and measured $\Delta V_{12}^{\ddagger}$ values can provide an important criterion of mechanism for virtually any redox process in aqueous solution.

Supporting Information Available: Table of values of k_{el} as a function of pressure for couples A−J (5 pages). See any current masthead page for ordering and Internet access instructions.

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