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# Measurement of Redox Reaction Volumes for Iron(III/II) Complexes Using High-Pressure Cyclic Staircase Voltammetry. Half-Cell Contributions to Redox Reaction Volumes

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Redox reaction volumes for a series of iron complexes of the type $Fe(L\text{-}L)_{3-0.5x}(CN)_x$, where L-L is either 1,-10-phenanthroline or 2,2′-bipyridine and $x = 0, 2, 4,$ or 6, have been measured using high-pressure cyclic staircase voltammetry. For these Fe(III/II) systems, where there are no significant bond length changes associated with the change in oxidation state, changes in the intrinsic volume for the complex ions are minimal and changes in the reaction volume therefore primarily reflect electrostrictive changes associated with the Fe(III/II) reduction. Estimates of the volume changes for individual Fe(III/II) half-cell reductions require an assignment of the molar volume change associated with the reference half-cell. From the charge dependence of the cell reaction volume for a series of Fe(III/II) reactions using a constant $Ag/AgNO_3$ reference half-cell, we have estimated the reference half-cell volume change for the oxidation of Ag(s) to $Ag^+(aq)$ at 298 K and an ionic strength of 1.0 M to be $-11.9 \pm 0.5$ $cm^3$ $mol^{-1}$. The assignment is independent of any previously determined molar volumes for the reactants. Addition of supporting electrolyte, necessary for the electrochemical measurement and normal for most kinetic and mechanistic studies, has some effect on the volume changes.

## Introduction

The use of reaction and activation volumes is a conceptually simple and useful probe to reaction mechanism and solute-solvent interactions in general.[1] However, for homogeneous and heterogeneous electron transfer reactions the number of data is relatively small. Of the various experimental techniques used to study electron transfer processes at high pressure, such as stopped-flow, NMR, pulse radiolysis and circular dichroism, application is often constrained by specific requirements of the chemical system to be studied. In light of this we have developed a high pressure voltammetric method which may be useful for extending the range of redox couples which can be measured and hence exploring the factors influencing the molar volume changes accompanying redox reactions.

Recently, some applications of high-pressure cyclic voltammetric methods for the measurement of molar volume changes associated with redox processes involving coordination complexes have been presented.[2–6] From the pressure dependence of the formal potential, $E^{\circ\prime}$, for a redox couple, the cell reaction volume, $\Delta V^{\circ}_{cell}$, can be obtained from $-nF(d(E^{\circ\prime})/dP$. The basis for such measurements has been established for some time;[7–12] however very few of these electrochemical studies have involved cyclic voltammetric procedures and indeed many were concerned with the activation volume for the electrode kinetics rather than the pressure dependence of the electrode potential. We have chosen to probe these thermodynamic aspects before undertaking kinetic studies. Also, as discussed by Faulkner *et al.*,[5] the earlier studies involved the use of a reference electrode with unknown behavior at high pressures. If this technique is to provide useful information concerning the molar volume changes accompanying electron transfer processes of particular redox couples, a determination of the volume change for the reference half-cell is essential.

Using the hexacyano Fe(III/II) couple in eq 1 as an example, the volume changes associated with the reaction can be analyzed in various ways as shown in eq 2, where $\phi$ is the molar volume

$$Fe(CN)_6^{\ 3-}(aq) + Ag(s) \rightarrow Ag^+(aq) + Fe(CN)_6^{\ 4-}(aq) \qquad (1)$$

$$\begin{aligned}\Delta V^{\circ}_{cell} &= \sum V^{\circ}_{prod} - \sum V^{\circ}_{react} \\ &= \phi_{Ag^+} + \phi_{Fe(CN)_6{}^{4-}} - \phi_{Ag(s)} - \phi_{Fe(CN)_6{}^{3-}} \\ &= \phi_{AgNO_3} + \phi_{K_4Fe(CN)_6} - \phi_{Ag(s)} - \phi_{K_3Fe(CN)_6} - \\ &\qquad \phi_{KNO_3} \qquad (2)\end{aligned}$$

for each species. In some cases, it is therefore possible to estimate reaction volumes from the molar volumes of the formal reactant compounds involved in the reaction, although these will generally have been determined at concentration conditions far

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from the solutions of interest in a typical kinetic or mechanistic study. In many other cases, such an estimation is impossible due to the reactivity or unavailability of one of the oxidation states of the couples under investigation. This is one of the attractive features of obtaining redox reaction volume data from direct electrochemical measurements, only requiring that both oxidation states of the couples are stable and unaffected by possible side reactions on the electrochemical time scale.

For a redox reaction, the overall volume change can be analysed in terms of the two half-cell components, as shown in Equation 3, for example. A reliable measure of $\Delta V^\circ_{\mathrm{ref}}$ would

$$\Delta V^\circ_{\mathrm{cell}} = \Delta V^\circ_{\mathrm{Fe(III/II)}} + \Delta V^\circ_{\mathrm{Ag(s)/Ag^+}} = \Delta V^\circ_{\mathrm{Fe(III/II)}} + \Delta V^\circ_{\mathrm{ref}} \tag{3}$$

permit the volume changes for the complex-ion couples to be determined. Of course, the thermodynamic properties of individual ions cannot be measured;[13a] however, in practice useful data have been obtained by invoking extrathermodynamic assumptions. In the case of separate ionic contributions to molar volumes, a scale referenced to an assumption for $\phi_{\mathrm{H+(aq)}}$ is generally used. In our study too, any such extrathermodynamic assumption will be central to the assignment of the molar volume change for the reference half-cell, $\Delta V^\circ_{\mathrm{ref}}$ ($\phi_{\mathrm{Ag^+}} - \phi_{\mathrm{Ag(s)}}$).

For solution reactions involving ionic species, the volumes and changes in volume may be separated into intrinsic, $\Delta V^\circ_{\mathrm{int}}$, and electrostrictive, $\Delta V^\circ_{\mathrm{elec}}$, contributions as shown by eq 4.

$$\Delta V^\circ = \Delta V^\circ_{\mathrm{int}} + \Delta V^\circ_{\mathrm{elec}} \tag{4}$$

Intrinsic contributions to the volume arise from the atomic volume and for monoatomic species is usually determined from $4/3\pi$(ionic crystal radius)$^3$.[13b] For irregularly shaped molecules or ions such a simple approach is not possible and computational models of varying complexity have been employed.[14,15] These models typically involve summation of the van der Waals volumes with some account of atomic overlap and the voids resulting from the packing of the individual atoms. Electrostrictive contributions to the molar volume of an ion arise from interaction of polar solvent molecules with the ionic charge of the solute.[16−19] The quantitative separation of the two components is difficult.

In this study, redox reaction volumes for a series of metal-complex ions which do not undergo any appreciable intrinsic volume change upon electron transfer are investigated in anticipation of obtaining the electrostrictive volume changes for reduction of these complexes. These solvational contributions to the volume changes accompanying electron transfer processes are an integral aspect of the descriptions using Marcus−Hush theory and its extensions.[20−25] The use of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) in various combinations with cyanide ligands allows systematic variation in the complex-ion charge. The objective of the study is an estimate of the separate contributions to the reaction volume from the complex couple and the reference half-cell obtained under the experimental solution conditions.

## Experimental Section

**Reagents.** $K_3Fe(CN)_6$ (BDH, AnalaR), $KNO_3$ (Ajax, AR), $Ba(NO_3)_2$ (Ajax, AR), $Sr(NO_3)_2$ (Anax, AR), $La(NO_3)_3$ (Fluka, AR), $AgNO_3$ (Ajax, LR), $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (BDH, AnalaR), 1,10-phenanthroline (Aldrich, 99+%) and 2,2′-bipyridine (Aldrich, 99+%) were all used as received. $K_2Fe(CN)_4(phen){\cdot}4H_2O$, $K_2Fe(CN)_4(bipy){\cdot}3H_2O$, *cis*-$Fe(CN)_2(phen)_2{\cdot}2H_2O$ and *cis*-$Fe(CN)_2(bipy)_2{\cdot}3H_2O$ were prepared according to Schilt's method.[26] $Fe(bipy)_3SO_4$ was prepared using a procedure analogous to that used for the preparation of $Fe(phen)_3SO_4{\cdot}9H_2O$.[27] All complexes were characterized using UV−vis spectrophotometry.[26,28] Solutions of $Fe(ox)_3^{3-}$ were generated *in situ* by mixing a 0.001 M solution of ferrous ammonium sulfate with 0.1 M $NH_4HC_2O_4{\cdot}H_2O$ (Hopkin & Williams, AR).

**High-Pressure Electrochemical Measurements.** The high-pressure voltammetric apparatus and technique has been described recently.[2] A schematic diagram of the cell used in these measurements is shown in Figure 1. The three electrode cell configuration consisted of (a) either a 1 mm gold disk or gold amalgam disk working electrode, (b) a platinum wire auxiliary electrode and (c) a Ag/$AgNO_3$ in $KNO_3$ reference electrode separated from the working solution by a liquid junction incorporating a Vycor glass frit. Ionic strength of the reference electrode was identical to that of the working solution. Preparation of the gold amalgam disk working electrode involved rubbing the surface of a gold disk electrode, which had been abraded using fine emery paper, into a pool of mercury metal. Within 10 min, sufficient mercury had amalgamated to produce an electrode which allowed significantly more negative potentials to be achieved compared to those at either a gold or platinum surface.

Scan rates were optimized for each system so as to obtain quasi-reversible behavior with peak separations of around 60−80 mV. In some experiments, typically those involving low supporting electrolyte concentrations, larger peak separations were observed, however this has been found to have no influence on the reaction volume obtained.[2] All measurements were recorded at a temperature of 298 K. Formal potentials for each solution were determined from the mean of the oxidation and reduction cyclic voltammetric peaks.

The complex-ion concentration was typically 0.001 M in 1.0 M or 0.1 M $KNO_3$ supporting electrolyte. The Ag/$AgNO_3$ (0.01 M) reference electrode also contained $KNO_3$ set to the same ionic strength of the Fe(III/II) test solution for reasons described previously.[2] For the $Fe(ox)_3^{3-/4-}$ measurements, the reference cell contained 0.1 M $KNO_3$ while the 0.1 M $NH_4HC_2O_4{\cdot}H_2O$, used in excess with 0.001 M ferrous ammonium sulfate in a previously aerated aqueous solution to form the $Fe(ox)_3^{3-}$ *in situ*, acted as the supporting electrolyte for the test solution. For the study of supporting electrolyte type and ionic strength effects on reaction volume for the $Fe(CN)_6^{3-/4-}$ couple, both the reference and test cells contained identical supporting electrolyte. Solutions were deoxygenated with water saturated nitrogen for at least 10 min before sealing the cell and placing it into the high-pressure bomb.

## Results

As an example of the use of the technique, cyclic voltammograms at various pressures are shown in Figure 2 for (a) $Fe(phen)CN_4^{1-/2-}$ and (b) $Fe(ox)_3^{3-/4-}$. These are typical of the study. The pressure dependences of formal potential for all of the cyano/bipyridine Fe(III/II) systems at 25 °C and an ionic strength of 1.0 M are collected together in Figure 3. Reaction volumes derived for all of the complexes used for the charge dependence study of redox reaction volume at various ionic strengths are summarized in Table 1.

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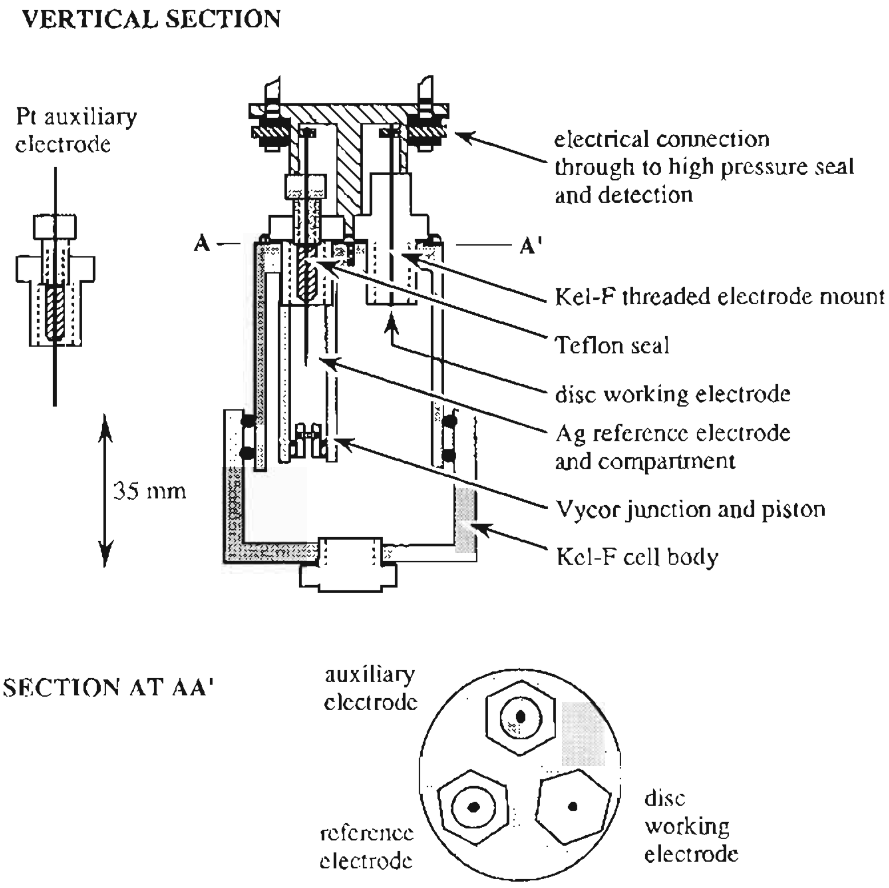

**Figure 1.** Schematic of the high-pressure electrochemical cell.

**Table 1.** Redox Reaction Volumes for Fe(III/II) Couples of Different Charge Types in $KNO_3$ Supporting Electrolyte at 298 K[a]

| redox couple | $\mu$ (mol dm$^{-3}$) | $\Delta V°_{cell}$ (cm$^3$ mol$^{-1}$) |
|---|---|---|
| $Fe(CN)_6^{3-/4-}$ | 1.00 | −38.7 (0.5) |
| | 0.10 | −42.8 (0.6) |
| $Fe(phen)(CN)_4^{1-/2-}$ | 1.00 | −25.5 (0.8) |
| $Fe(bipy)(CN_4)^{1/2-}$ | 1.00 | −25.7 (0.6) |
| | 0.10 | −29.6 (0.6) |
| $Fe(bipy)_2(CN)_2^{1+/0}$ | 1.00 | −6.6 (0.5) |
| | 0.10 | −6.5 (0.6) |
| $Fe(phen)_3^{3+/2+}$ | 1.00 | +6.7 (1.0) |
| | 0.25 | +6.1 (0.3) |
| $Fe(bipy)_3^{3+/2-}$ | 1.00 | +8.0 (0.3) |
| | 0.10 | +8.3 (0.5) |

[a] Reference electrode: $Ag/AgNO_3$ (0.01 M), *x* M $KNO_3$; ionic strength identical to that of test solution.

**Effects of Fe(III/II)-Complex Charge on Reaction Volume.** Quasi-reversible voltammograms were obtained for the $Fe(CN)_6^{3-/4-}$ couple using a gold disk working electrode over the potential range +150 to −500 mV and a scan rate of 0.045 V s$^{-1}$. The formal electrode potential for a 0.001 M ferricyanide solution of −192 mV at 0.1 MPa was within the region expected using a $Ag/AgNO_3$ reference electrode at $\mu = 1.0$ M.[29] The values of formal potentials and peak separations for all of the systems at measured pressures are available as supplementary data. The value of $\Delta V°_{cell} = -38.7 \pm 0.5$ cm$^3$ mol$^{-1}$, obtained from the slope of the data in the Figure 3, is in good agreement with the value reported previously for this couple under the same ionic conditions[2] and is similar to values reported in an independent study by Swaddle *et al.*[3] at comparable ionic strengths but with different supporting electrolytes and a Ag/AgCl, KCl (saturated) reference electrode. For the ferri-/ferrocyanide system both oxidized and reduced forms of the complex are stable. This allowed high pressure potentiometric measurements[2] on the cell Ag(s)/$AgNO_3$(aq) (0.010 M), $KNO_3$(aq) (0.100 M)//$K_3Fe(CN)_6$(aq) (0.001 M), $K_4Fe(CN)_6$(aq) (0.001 M), $KNO_3$(aq) (0.100 M)/Pt(s) to be carried out. From the pressure dependence of the potential for this cell, the reaction volume of $-44.0 \pm 0.7$ cm$^3$ mol$^{-1}$ at $\mu = 0.1$ M agreed well with the $-42.8 \pm 0.8$ cm$^3$ mol$^{-1}$ from the cyclic voltammetric experiments at the same ionic strength.

Substitution of a bipy or phen ligand for two of the cyanide ligands causes a positive shift in formal electrode potential for the $Fe(phen)CN_4^{1-/2-}$ and $Fe(bipy)CN_4^{1-/2-}$ couples, relative to the $Fe(CN)_6^{3-/4-}$ couple, due to changes in the metal environment.[30] Cyclic staircase voltammograms were recorded over a potential range of +250 to −400 mV at a gold disk electrode with a scan rate of 0.055 V s$^{-1}$. Cell redox reaction volumes were $-25.5 \pm 0.8$ and $-25.7 \pm 0.6$ cm$^3$ mol$^{-1}$ for the $Fe(phen)CN_4^{1-/2-}$ and $Fe(bipy)CN_4^{1-/2-}$ couples, respectively. For the $Fe(bipy)_2CN_2^{1+/0}$ couple, potential limits were 350 and −100 mV. The pressure dependence of $E°'$ for this couple (Figure 3) corresponds to a $\Delta V°_{cell}$ of $-6.6 \pm 0.5$ cm$^3$ mol$^{-1}$. Low peak currents observed for this couple are a consequence of the low solubility of the neutral iron(II) salt in aqueous solution. The formal potential at 0.1 MPa (+108 mV) continues the shift to more positive potentials as the cyanide ligands are replaced by a diimine ligand. The analogous phenanthroline complex could not be studied due to its low solubility in water. Voltammograms for both the $Fe(phen)_3^{3+/2+}$ and $Fe(bipy)_3^{3+/2+}$ were recorded over the potential range 600–200 mV. Cell redox reaction volumes were $+6.7 \pm 1.0$ and $+8.0 \pm 0.3$ cm$^3$ mol$^{-1}$ for the $Fe(phen)_3^{3+/2+}$ and $Fe(bipy)_3^{3+/2+}$ couples, respectively. For all of these complexes involving diimine ligands, a scan rate of 0.055 V s$^{-1}$ was used.

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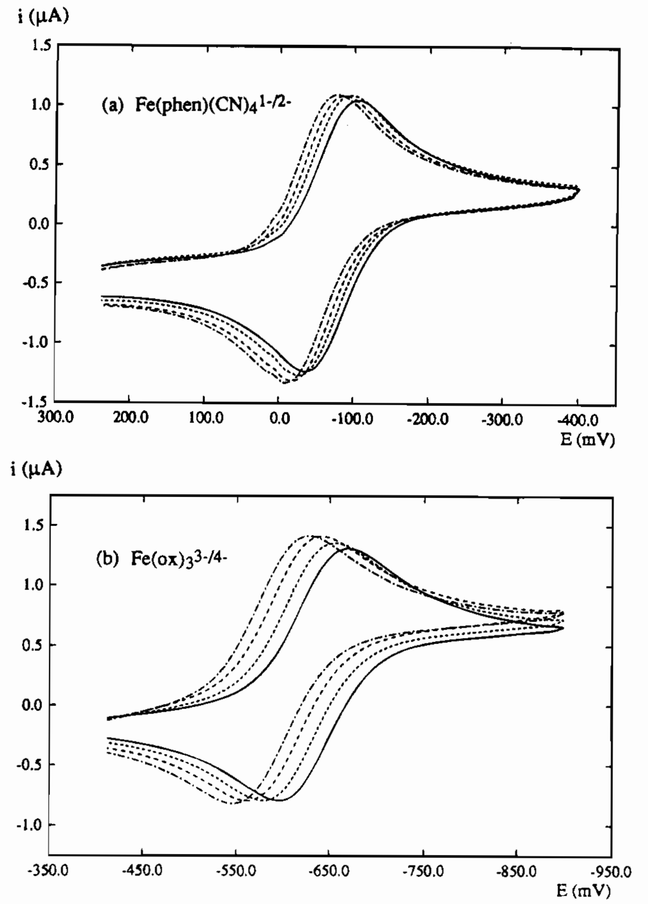

**Figure 2.** (a) Voltammograms of the $Fe(phen)CN_4{}^{1-/2-}$ couple in 1.00 M $KNO_3$ at 0.1 MPa(—), 36.2 MPa (•••), 70.3 MPa (- - -), and 105.2 MPa (— • — •) at a gold disk electrode using a $Ag/AgNO_3$ (0.01 M), 1.0 M $KNO_3$ reference cell. Scan rate = 0.057 V $s^{-1}$; $T = 298$ K. (b) Voltammograms of the $Fe(ox)_3{}^{3-/4-}$ couple in 0.10 M $NH_4HC_2O_4$ at 0.1 MPa (—), 35.7 MPa (•••), 69.7 MPa (- - -), and 104.5 MPa (— • — •) at a gold amalgam disk electrode using a $Ag/AgNO_3$ (0.01 M), 0.10 $KNO_3$ reference cell. Scan rate = 0.057 V $s^{-1}$; $T = 298$ K.

For the $Fe(ox)_3{}^{3-/4-}$ couple, special care was taken to avoid photochemical decomposition of the complex prior to enclosure in the bomb. For this couple, a gold amalgam disk working electrode was used since the voltammetric signal for this system occurs beyond the solvent imposed cathodic limit of the gold disk electrode. At 0.1 MPa with a scan rate of 0.055 V $s^{-1}$, a quasi-reversible voltammogram with a formal potential of −632 mV was observed between the potential limits of −900 and −400 mV. From the pressure dependence, the cell reaction volume was −43.3 ± 0.6 $cm^3$ $mol^{-1}$.

**Effects of Supporting Electrolyte and Ionic Strength.** We have reported[2] that ionic strength, set with $KNO_3$ supporting electrolyte, has only a small effect on the redox reaction volume for the $Fe(CN)_6{}^{3-/4-}$ couple. To investigate these effects further, particularly for the complexes of different charge type, high-pressure voltammograms were measured for the $Fe(bipy)CN_4{}^{1-/2-}$, $Fe(bipy)_2CN_2{}^{1+/0}$, $Fe(phen)_3{}^{3+/2+}$ and $Fe(bipy)_3{}^{3+/2+}$ couples in different concentrations of $KNO_3$. These data are included in Table 1.

With the exception of the potential limits for the $Fe(bipy)CN_4{}^{1-/2-}$ couple, voltammograms for the $Fe(bipy)CN_4{}^{1-/2-}$ and $Fe(bipy)_2CN_2{}^{1+/0}$ systems were measured with experimental parameters identical to studies performed in 1.0 M $KNO_3$ supporting electrolyte described previously. A shift in formal potential for the $Fe(bipy)CN_4{}^{1-/2-}$ couple upon decreasing the supporting electrolyte ionic strength from 1.0 to 0.1 M required potential limits of 200 and −400 mV to be used in 0.10 M $KNO_3$. Cell reaction volumes were measured as −29.6 ± 0.6 $cm^3$ $mol^{-1}$ for the $Fe(bipy)CN_4{}^{1-/2-}$ couple and −6.5 ± 0.6 $cm^3$ $mol^{-1}$ for the $Fe(bipy)_2CN_2{}^{1+/0}$ couple. Redox reaction volumes for the $Fe(phen)_3{}^{3+/2+}$ and $Fe(bipy)_3{}^{3+/2+}$ couples were measured in 0.25 and 0.10 M $KNO_3$, respectively. At lower supporting electrolyte concentration the $Fe(bipy)_3{}^{2+}$ concentration was increased to 0.003 M and the $Fe(phen)_3{}^{2+}$ concentration was increased to 0.004 M for the respective pressure studies. Pressure dependences of the formal potentials gave reaction volumes of +6.1 ± 0.3 $cm^3$ $mol^{-1}$ for the $Fe(phen)_3{}^{3+/2+}$ and +8.3 ± 0.5 $cm^3$ $mol^{-1}$ for the $Fe(bipy)_3{}^{3+/2+}$ couples.

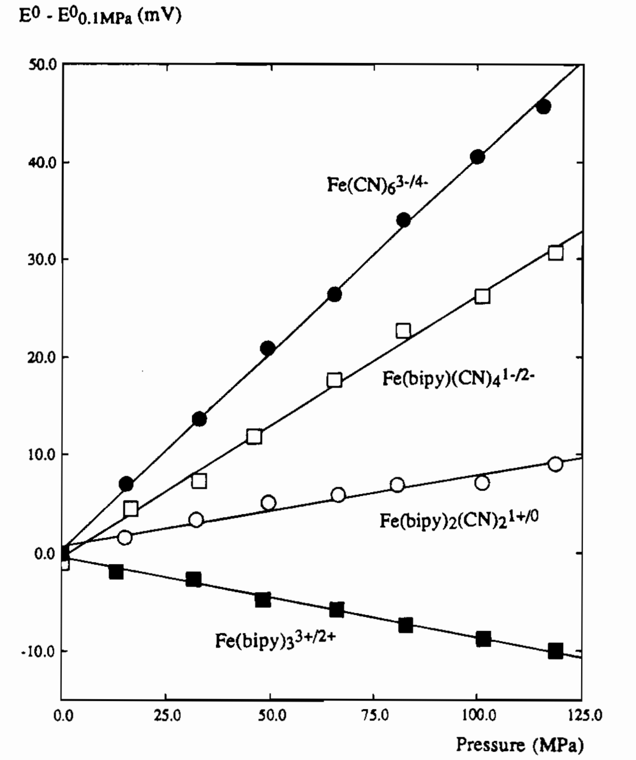

**Figure 3.** Variation of formation potential with pressure for $Fe(CN)_6{}^{3-/4-}$ (filled circles), $Fe(bipy)(CN)_4{}^{1-/2-}$ (empty squares), $Fe(bipy)_2(CN)_2{}^{1+/0}$ (empty circles), and $Fe(bipy)_3{}^{3+/2+}$ (filled squares) relative to formal potential at 0.1 MPa. Ionic strength = 1.0 M; $T = 298$ K.

To extend the study of medium effects on the reaction volume for the $Fe(CN)_6{}^{3-/4-}$ couple, a wider a range of supporting electrolyte types was used. The effects of different supporting electrolyte cations on the redox reaction volume and formal potential at 0.1 MPa for the $Fe(CN)_6{}^{3-/4-}$ couple are summarized in Table 2. For each of the systems, voltammetric conditions were held constant with a scan rate of 0.115 V $s^{-1}$; however potential limits were adjusted according to shifts in formal potentials with the different electrolytes.

## Discussion

The primary aim in this work has been to determine the effects of reactant charge on redox reaction volume for a series of Fe(III/II)−$Ag^+/Ag$ cell reactions and to use this data to resolve the half-cell volume contributions and the electrostrictive volume changes on reduction of these Fe complexes, under experimental conditions of finite concentration and ionic strength. If a reliable molar volume change associated with the reference cell can be determined for appropriate experimental conditions, the reaction volume, electrostrictive volume and intrinsic volume changes for a range of processes other than the Fe(III/II) complexes reported here may be evaluated and separated.

**Ionic Charge Effects on the Reaction Volume.** The results of our measurements for the mixed iron cyano/diimide

**Table 2.** Effects of Various Types and Concentrations of Supporting Electrolyte on Reaction Volumes and Formal Potentials at 0.1 MPa for the Reduction of 0.001 M $K_3Fe(CN)_6$ at a Gold Disk Working Electrode[a]

| electrolyte | $\mu$ (mol dm$^{-3}$) | $\Delta V°$ cell (cm$^3$ mol$^{-1}$) | $E°'$ (0.1 MPa) (mV) |
|---|---|---|---|
| $KNO_3$ | 1.00 | −38.7 (0.5) | −192 |
| | 0.33 | −41.6 (0.9) | −233 |
| | 0.10 | −42.8 (0.6) | −245 |
| | 0.03 | −42.5 (0.6) | −266 |
| | 0.01 | −39.0 (1.3) | −277 |
| $NaNO_3$ | 0.10 | −45.3 (0.7) | −254 |
| $Ba(NO_3)_2$ | 0.81 | −44.9 (1.4) | −155 |
| | 0.30 | −41.8 (0.6) | −177 |
| | 0.03 | −45.2 (1.0) | −234 |
| $Sr(NO_3)_2$ | 0.30 | −44.5 (0.8) | −174 |
| $La(NO_3)_3$ | 6.00 | −26.5 (0.7) | −47 |
| | 0.60 | −32.4 (0.4) | −114 |
| | 0.06 | −33.3 (0.5) | −146 |
| | 0.01 | −35.2 (0.5) | −172 |

[a] Scan rate 0.115 V s$^{-1}$. Reference electrode: $Ag/AgNO_3$ (0.01 M), $x$ M $KNO_3$; ionic strength identical to that of test solution.

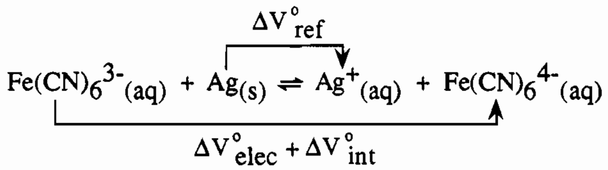

**Figure 4.** Diagrammatric representation of the molar volume contributions of two half-cells to the measured reaction volume.

Fe(III/II) couples in Table 1 show that ionic charge has a dramatic influence on the observed $\Delta V°_{cell}$. As has been outlined in eqs 2−4, and is shown schematically in Figure 4 using the hexacyano Fe(III/II) couples as an example, the observed reaction volume, $\Delta V°_{cell}$, can be conveniently considered in terms of three components: $\Delta V°_{elec}$, $\Delta V°_{int}$, and $\Delta V°_{ref}$, where $\Delta V°_{elec}$ is the electrostrictive volume change, $\Delta V°_{int}$ the intrinsic change arising from the complex ion reduction, and $\Delta V°_{ref}$ is the volume change associated with the silver oxidation in the reference half-cell.

$$\Delta V°_{cell} = \Delta V°_{elec} + \Delta V°_{int} + \Delta V°_{ref} \qquad (5)$$

Thermodynamic properties of an individual ion and hence of an electrochemical half-cell are of course not experimentally accessible and some basis for assignment is required.[13a] In resolving partial molar volume data for ionic compounds, two commonly adopted scales are (a) the assignment of $\phi_{H^+(aq)}$ as 0 cm$^3$ mol$^{-1}$ and (b) as adopted in more recent studies, a scale based on −5.4 cm$^3$ mol$^{-1}$ for $\phi_{H^+(aq)}$.[19,31,32] The use of such extrathermodynamic assumptions has provided a useful means of analyzing the factors affecting the properties of single ions. Faulkener *et al.*[5] have used such molar volume data to estimate the molar volume change for the Ag(s)/AgCl, KCl (0.1 M) reference electrode.

For the Fe(III/II) couples reported in this paper, changes in intrinsic volume contributions are expected to be minimal due to the negligible metal to ligand bond length changes between the iron complexes in the Fe(III) and Fe(II) oxidation states. Crystallographic studies of ferricyanide and ferrocyanide salts have been reported[33,34] and reviewed.[35] It has been shown that the average metal to ligand bond length changes by approximately 0.03 Å between the Fe(II) and Fe(III) oxidation states. Studies of bond length changes in solution[36] showed an even smaller change, 0.01 Å, in bond length. Studies of the Fe(II) and Fe(III) tris(phenanthroline) complexes showed no bond length difference for the two oxidation states of the complex in solution[26] in agreement with the crystallographic data.[37,38] Very little structural information is available for the mixed iron cyano/diimine complexes.[39] On the basis of the data for the hexacyano and tris(phenanthroline) complexes however, bond length differences between the Fe(II) and Fe(III) cyano/diimine complexes are expected to be negligible.

Using eq 5 and assuming the intrinsic volume contribution ($\Delta V°_{int}$) to be zero, $\Delta V°_{cell} = \Delta V°_{elec} + \Delta V°_{ref}$. This allows the trend in *electrostrictive* volume changes for the Fe complex redox couples measured under the same reference electrode conditions to be collated. The Drude−Nernst relationship[1,17] shown in eq 6, where $z$ is ionic charge, $e$ is the charge of an

$$V°_{elec} = \frac{z^2e^2}{2rD}\left(\frac{\partial \ln D}{\partial P}\right)_T = -\frac{Bz^2}{r} \qquad (6)$$

electron, $D$ is the dielectric constant of the solvent, $r$ is the ionic radius and $P$ is pressure, is widely used for predicting the electrostrictive behavior of an ion in solution. On the basis of this prediction, that the electrostrictive volume is proportional to the ion charge squared, a relationship between the electrostrictive volume change ($\Delta V°_{elec}$) for a redox reaction and the change in the square of the charge, $\Delta z^2$, where $\Delta z^2 = z^2_{ox} - z^2_{red}$, might be expected, as in eq 7. There are justified concerns

$$\Delta V_{elec} = -\frac{B}{r}(z^2_{ox} - z^2_{red}) = -\frac{B(\Delta z^2)}{r} \qquad (7)$$

that a continuum model like the Born equation (and therefore those like eq 7, derived from it) may not completely describe ion solvent interactions and that specific solvent effects may be important aspects of the process.[40,41] However, such (charge)$^2$ correlations have been observed in a number of other studies. An analogous dependence of $\Delta z^2$ on the neutralization reaction volumes for a series of differently charged complex ions in aqueous solution has been presented by Kitamura and van Eldik.[42] In that study, a linear relationship between the reaction volume and the change in the square of the complex-ion charge for 20 complexes was demonstrated. In a similar way, reaction entropies for a range of redox reactions of metal complexes, determined from the temperature dependence of formal potential, are found to correlate well with the change in the square of the charge of the complex ion.[43−45] The limitations of these empirical, but apparently sensible, correlations should

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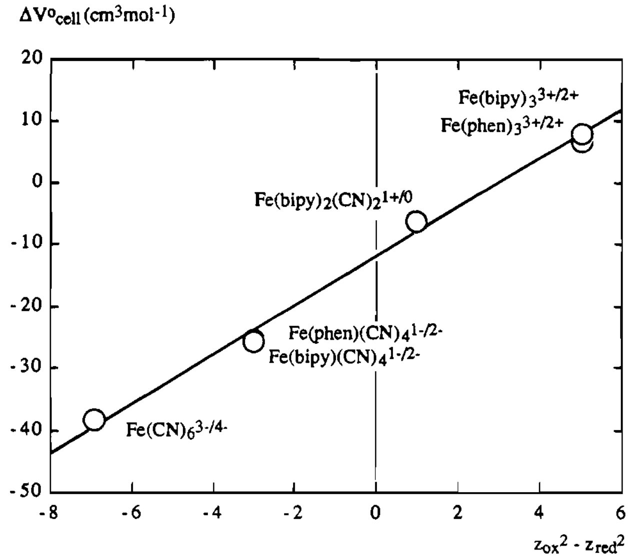

**Figure 5.** Plot of $\Delta V^\circ_{cell}$ as a function of $\Delta z^2$ for $Fe(CN)_6^{3-/4-}$, $Fe(phen)(CN)_4^{1-/2-}$, $Fe(bipy)(CN)_4^{1-/2-}$, $Fe(bipy)_2(CN)_2^{1+/0}$, $Fe(bipy)_3^{3+/2+}$, and $Fe(phen)_3^{3+/2+}$. Ionic strength = 1.0 M; $T$ = 298 K.

not be overlooked. The continuum Born model is clearly inadequate in detail. For the entropy measurements for example,[43] despite the correlation, the experimental values are not always in good quantitative agreement with those calculated from the Born equation.

The charge changes associated with the Fe(III/II) couples investigated in this study allow us to test this type of correlation for redox reaction volumes. Figure 5 shows a good linear correlation between the cell reaction volume, $\Delta V^\circ_{cell}$, and the change in the square of charge, $\Delta z^2$, for the series of iron couples. The data covers a wide range in $\Delta z^2$ and spans over 45 $cm^3\ mol^{-1}$ in reaction volume. There is excellent agreement between the phenanthroline and bipyridyl series of complexes, where both can be measured.

Changes in charge seem to dominate the measured reaction volume trends and, whether or not other factors are operating, the $\Delta z^2$ relationship can be applied very usefully. Built on this correlation, by interpolating the cell reaction volume to the point where $\Delta z^2 = 0$, the reaction volume will correspond to the volume change generated by the reference cell only (see eq 5), since at this point, both the intrinsic and electrostrictive volume changes arising from the test half-cell will be zero. This interpolation suggests a molar volume change for the reference cell of $-11.9 \pm 0.2$ $cm^3\ mol^{-1}$ for the oxidation of silver metal to silver ions in 1.0 M $KNO_3$ at 298 K.

Although the plot is linear over the $\Delta z^2$ range studied, the relationship may of course be more complex, perhaps with a radius dependent factor built into the slope, a shift in ligand–solvent interactions as the diimine ligands are substituted by cyanide, or systematic trends in supporting electrolyte association depending on the Fe-complex charge. An apparent lack of a radius dependence of the electrostrictive volume for a series of inorganic complex ions has been noted by Wherland *et al.*[14] This was explained in terms of the large size and nonspherical shape of the complexes in those cases. However, any such size or solvation dependence in the data in Figure 5 would be expected to have only a minor effect on the interpolated molar volume at $\Delta z^2 = 0$, even if the gradient or shape of the curve was found to change over a wider range of $\Delta z^2$.

This reference half-cell volume change agrees quite well with a value calculated from independent molar volume data. Using the partial molal volume of $Ag^+$ at infinite dilution ($-0.7$ $cm^3\ mol^{-1}$ from the compilation of Millero[32] or $-6.1$ $cm^3\ mol^{-1}$ on an absolute scale based on $\phi_{H^+(aq)} = -5.4$ $cm^3\ mol^{-1}$) together with the molar volume of silver metal ($+10.3$ $cm^3\ mol^{-1}$), the volume change, $\Delta V^\circ_{ref}$, is calculated as $-11.0$ or $-16.4$ $cm^3\ mol^{-1}$. Any difference between this and our result may be due to the dependence of partial molar volume on ionic strength, although based on the experimental ionic strength dependence of molar volumes of $AgNO_3$ this is not expected to be large for the singly charged silver ion.[32,46] Our measurement represents a value of the molar volume difference between Ag and $Ag^+$ obtained independently of the techniques of densitometry and dilatometry conventionally used for partial molar volume determination. The measurement makes no assumptions about the partitioning of molar volume contributions of cation and anion necessary in most measurements based on ionic salt solution properties, but is built on the observation (consistent with but not dependent on Born type behavior) that the volume changes correlate convincingly with $\Delta z^2$ and can be interpolated to $\Delta z^2 = 0$. The approach can be applied to experiments at conditions which are far from "ideal", but which are the media in which most inorganic kinetic and equilibrium measurements are made. The measurements certainly do not invalidate the data at "infinite dilution" which might be used to estimate molar volume change and in this case seem consistent with them.

**Table 3.** Electrostrictive Volume Changes for Fe(III/II) Couples of Different Charge type in 1 M $KNO_3$ Supporting Electrolyte at 298 K

| redox couple | $\Delta V^\circ_{elec}$ ($cm^3\ mol^{-1}$) | redox couple | $\Delta V^\circ_{elec}$ ($cm^3\ mol^{-1}$) |
|---|---|---|---|
| $Fe(CN)_6^{3-/4-}$ | −26.8 | $Fe(bipy)_2(CN)_2^{1+/0}$ | +5.3 |
| $Fe(phen)(CN)_4^{1-/2-}$ | −13.6 | $Fe(phen)_3^{3+/2+}$ | +18.6 |
| $Fe(bipy)(CN)_4^{1-/2-}$ | −13.8 | $Fe(bipy)_3^{3+/2+}$ | +19.9 |

The electrostrictive volume changes associated with the Fe(III/II) couples, $\Delta V^\circ_{elec}$, can now be evaluated as shown in Table 3. The data behave as would be anticipated, demonstrating decreases in molar volume associated with the increase in charge density on the ion. Indeed, the volume change of $-11.9$ $cm^3\ mol^{-1}$ determined for the oxidation of Ag to $Ag^+(aq)$ is also consistent with this, although the magnitude is somewhat greater than that determined for the $Fe(bipy)_2(CN)_2^{0/1+}$ oxidation ($-5.3$ $cm^3\ mol^{-1}$) involving a similar charge change. For Ag/$Ag^+$, first, the species have radii (144 pm for Ag and 113 pm for $Ag^+$)[47] which are only around 20% of that of the Fe complexes.[33-38] Although there may be no apparent size dependence of electrostriction for the range of Fe complexes studied, size effects may become evident for the much smaller $Ag^+$ ion. In the case of the Ag/$Ag^+$ process, the change in radius also leads to an *intrinsic* volume change of around $-3.8$ $cm^3\ mol^{-1}$, contributing to the total of $-11.9$ $cm^3\ mol^{-1}$.

Our major objective in this study was to establish an experimental basis for the separation of redox reaction volumes into oxidative and reductive components and therefore to evaluate the electrostrictive volume changes associated with ions of different charge for these Fe(III/II) systems in solution. It should be noted, however, that these components do not correspond to the formal half-cell reactions, which will also involve the electron as a reactant or product species. The difference is expected to be small; estimates of 3 $cm^3\ mol^{-1}$ have been made for the partial molar volume of the electron in a metal.[48]

**Ionic Strength Effects.** The results in Table 1 show that, for the series of iron complexes studied, small changes in the magnitude of the reaction volume occur for the $Fe(CN)_6^{3-/4-}$

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and $Fe(bipy)(CN)_4^{1-/2-}$ couples upon decreasing the solution ionic strength from 1.00 to 0.10 M. These effects are not apparent for the $Fe(bipy)_2(CN)_2^{1+/0}$ and $Fe(bipy)_3^{3+/2+}$ couples which show reaction volumes within experimental uncertainty for the two ionic strengths. This result does differ from the observations reported for the $Fe(phen)_3^{3+/2+}$ couple by Swaddle *et al.*[3] where the cell reaction volume changed from +6.2 ± 0.5 $cm^3\ mol^{-1}$ in 1.0 mol $kg^{-1}$ $KNO_3$ to +14.2 ± 0.5 $cm^3\ mol^{-1}$ in 0.25 mol $kg^{-1}$ $KNO_3$ using, in that case, a Ag/AgCl reference electrode system.

The reaction volume of −43.3 $cm^3\ mol^{-1}$ observed for the tris(oxalato)−Fe(III/II) complex at $\mu = 0.1$ M compares very well with that of the $Fe(CN)_6^{3-/4-}$ couple (−42.8 $cm^3\ mol^{-1}$, also at $\mu = 0.1$ M), which involves the same change in charge. Applying a linear interpolation to the reaction volume *vs* $\Delta z^2$ data at $\mu = 0.1$ M in Table 1 suggests a volume associated with the $Ag/Ag^+$ oxidation of around −13 $cm^3\ mol^{-1}$ at $\mu = 0.1$ M, which can be used to calculate the changes for the Fe(III/II) couples around −29.8 and −30.3 $cm^3\ mol^{-1}$ for the hexacyano and tris(oxalato) systems, respectively, at this ionic strength.

The directions of the changes in reaction volume for the $Fe(CN)_6^{3-/4-}$ and $Fe(bipy)(CN)_4^{1-/2-}$ couples with the increasing ionic strength from 0.1 to 1.0 M are consistent with a decrease in effective charge of the complex ions when a higher concentration of ion-pairing cations is present. The highly charged hexacyano couple shows the greatest dependence on supporting electrolyte concentration. An explanation for the smaller effects for the $Fe(bipy)_2(CN)_2^{1+/0}$ couple may be due to the still lower complex charge, or to the fact that for these cationic complexes, and for the $Fe(phen)_3^{3+/2+}$ and $Fe(bipy)_3^{3+/2+}$ couples, any counterion association would change mode from interactions with $K^+$ (for the anionic complexes) to interactions with weakly pairing $NO_3^-$. Although there are insufficient data at present to interpret these effects fully, it seems that the influence of secondary ion concentration is only small compared to the magnitude of the change in charge associated with the redox species.

**Effect of Supporting Electrolyte on the $Fe(CN)_6^{3-/4-}$ Reaction Volume.** Studies of ionic medium effects on the kinetics of electron exchange reactions of the $M(CN)_6^{3-/4-}$ couples, especially for Fe(III/II), have been reported often.[35,49] Wherland and Murguia[50] have reported studies of ionic strength and medium effect on redox activation volumes in non-aqueous solvents, and Swaddle and Takagi[51] recently studied the $Fe(CN)_6^{3-/4-}$ couple kinetics in aqueous solution. From the slight dependence of redox reaction volumes on ionic strength which we observe for complexes of low charge, including the silver ion discussed above, the reference cell reaction volume is expected to be only slightly affected by changes in the nature of supporting electrolyte. Any significant dependence of redox reaction volume on ionic strength would seem more likely to result from changes in the complex ion couple.

Measurements on the $Fe(CN)_6^{3-/4-}$ couple in a variety of supporting electrolytes and at different concentrations are summarized in Table 2. The results in $KNO_3$ support the form of dependence previously reported by us.[2] Changing the supporting electrolyte cation from 0.1 M $K^+$ to 0.1 M $Na^+$ has only a marginal effect on reaction volume. The value of $\Delta V^{\circ}_{cell}$ is only slightly affected by changing to a doubly charged counterion of comparable ionic strength. The reaction volumes for the $Fe(CN)_6^{3-/4-}$ couple in the presence of $K^+$, $Ba^{2+}$, and $Sr^{2+}$ at an ionic strength of 0.3 M are found to be −41.6, −41.8, and −44.5 $cm^3\ mol^{-1}$, respectively. The lack of effect of the doubly charged $Sr^{2+}$ and $Ba^{2+}$ electrolytes is surprising. Of the systems measured, only the highly charged $La^{3+}$ ions caused a major effect. There, even at the lowest ionic strength there is a significant reduction in the magnitude of the volume change, with the effect increasing at higher concentrations.

The dependence of the redox reaction volume on ionic strength and supporting electrolyte is expected to be complex. It will involve a combination of Debye−Hückel effects and, especially for the highly charged hexacyano species, ion pairing effects. At high ionic strength, significant ion pairing would be expected, with the more highly charged $Fe(CN)_6^{4-}$ affected more than the $Fe(CN)_6^{3-}$. This should produce a reduction in effective charge on the ferricyanide and ferrocyanide species and lower the change in charge squared, $\Delta z^2$, for the reaction. This is consistent with the less negative $\Delta V^{\circ}_{cell}$ observed upon increasing supporting electrolyte ionic strength, particularly for the highly charged $La^{3+}$ ion. The effect of pressure on ion association has been used by Murguia and Wherland[49] to account for the ionic strength dependence of activation volume in redox systems in a range of non-aqueous solvents. Increased ion pairing and hence a decrease in electrostrictive changes on reduction of the complex would certainly seem to be the most straightforward explanation for our observations. Insufficient data are presently available to propose any more quantitative description, but apart from the use of very highly charged ions in the reaction medium, the redox reaction volumes we have determined using high pressure voltammetry seem only marginally affected by supporting electrolyte conditions so that the values of half-cell volume changes we have derived should be able to be translated to other experiments and measurements with some confidence.

## Conclusions

High-pressure cyclic voltammetry is a versatile and convenient technique for the accurate determination of redox reaction volumes. For a series of Fe(III/II) complexes, where it can be assumed that there is no intrinsic volume contribution, the redox reaction volume is a linear function of the change in the square of the charge of the complex ion. The primary determinant of the magnitude of the reaction volumes is the change in complex charge; for these systems, effects of changes in ion radius and the nature of the ligands appear to be minor. The effects of solution ionic strength and the nature of any supporting electrolyte on the molar volume change also seem minimal. The charge dependence can be used to obtain an independent estimate of the volume change associated with the reference half-cell and the redox reaction volumes can be partitioned into the separate half-cell contributions on this basis. For the systems reported here, the metal complexes only make electrostrictive contributions to the reaction volume, and work is now proceeding on a range of metal complexes to quantify the separate effects of electrostrictive and intrinsic contributions to reaction volume.

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**Supplementary Material Available:** Listings of formal potentials, $E^{\circ\prime}$, and peak separations, $\delta E_p$, for redox couples at high pressure (7 pages). Ordering information is given on any current masthead page.

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