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Thermodynamic Clarification of the Curious Ferric/Potassium Ion Exchange Accompanying the Electrochromic Redox Reactions of Prussian Blue, Iron(III) Hexacyanoferrate(II)

David R. Rosseinsky,[†] Leslie Glasser,[§] and H. Donald Brooke Jenkins*[†]

Contribution from the Department of Chemistry, University of Warwick, Coventry, CV4 7AL, West Midlands, U.K.; School of Chemistry, University of Exeter, Exeter EX4 4QD, U.K.; and Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, GPO Box U1987, Perth WA, 6845, Australia

Received February 17, 2004; E-mail: Don.Jenkins@warwick.ac.uk

Abstract: The recent Glasser–Jenkins method for lattice-energy prediction, applied to an examination of the solid-state thermodynamics of the cation exchanges that occur in electrochromic reactions of Prussian Blue, provides incisive thermodynamic clarification of an ill-understood ion exchange that accompanies particularly the early electrochromic cycles. A volume of $0.246 \pm 0.017 \text{ nm}^3 \text{ formula unit}^{-1}$ for the ferrocyanide ion, $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ is first established and then used, together with other formula unit–volume data, to evaluate the changes of standard enthalpy, entropy, and Gibbs energy in those ion-exchange reactions. The results impressively show by how much the exchange of interstitial Fe^{3+} ions by alkali metal ions, usually exemplified by K^+ , is thermodynamically favored.

Introduction

Electrochemically induced changes of valence that result in striking color changes constitute the process of *electrochromism*,¹ a modern evolving technology in which final “best formulations” are yet being sought. The optical change is effected by applying a small dc potential (maximally a few volts) which causes darkening of an appropriate conductive-glass “sandwich”, described below. Manifold applications include antidazzle car mirrors (several million now in use), architectural windows,² optical shutters, memory devices, and the like.¹ Thermal robustness exceeds that of liquid crystal devices. Reversible and visible changes in transmittance and/or reflectance take place in an enforced redox reaction within a galvanic cell commonly comprising conductive-glass electrodes as support for the thin-film colorants.

WO_3 , coloring intensely on partial reduction, is probably the leading choice of solid-state electrode material, but an equally satisfactory companion electrode, needed to complete the electrochromic cell, is still lacking. The neglect in application of the widely studied candidate Prussian Blue is perhaps ascribable to hitherto inexplicable aspects of its behavior described below, but mechanisms for the observations have now been adduced,^{3a} partly resolving the problems and establishing

the ideal deposition protocol. However, an understanding of the underlying thermodynamics of the processes is prerequisite to clarification and future development, hence the importance of the present study in tackling this requirement.

Until very recently, methods for estimating the thermodynamic parameters required for reactions involving such archetypal materials as Prussian Blue have proved elusive. Aside from a theoretically based paper on the detailed thermodynamics of electrochemical reactions, for which only ball-park estimates were possible for the Madelung component,^{4a} and some electrochemical studies of other solid metal hexacyanometalates,^{4b–g} the literature contains no quantitative lattice energy estimates for these materials. After recent developments made by the present authors, however, it is now possible to estimate, for the first time, component lattice energies and entropies and, hence, Gibbs energy changes for some of the key reactions involved. The predictions that emerge from the present studies closely mirror the experimental observations, which confers confidence on extending these techniques to explain the thermochemistry of further known systems, and wider applications that can supply feasibility assessments for new processes can readily be envisaged.

To preserve the electroneutrality of a *solid* electrochrome, as in WO_3 or Prussian Blue, ion uptake or loss must accompany the color-transforming electron transfer. In Prussian Blue (iron(III)hexacyanoferrate(II) or “PB”),^{3–5} the chromophore is the

[†] University of Warwick.

[‡] University of Exeter.

[§] Curtin University of Technology.

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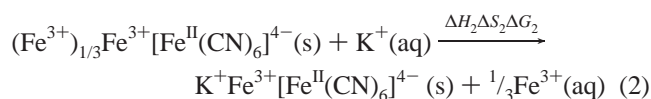
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Fe³⁺[Fe^{II}(CN)₆]⁴⁻ unit. The coloration results from an intervalence optical charge transfer, but this can be avoided if the Fe³⁺ is reduced to Fe²⁺ so leaving a clear or “bleached” product Prussian White, as in reaction 1 where only the chromophore is depicted. Color is restored on reoxidation.

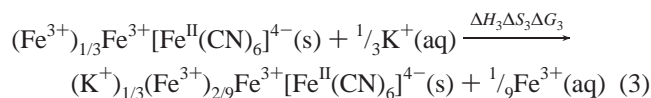


The initial PB, deposited onto conducting glass by electroreduction of a solution containing Fe³⁺[Fe^{III}(CN)₆]³⁻(aq), is virtually always the “insoluble” (non-peptisable) form Fe³⁺_{1/3}Fe³⁺-[Fe^{II}(CN)₆]⁴⁻, “iPB”, regardless of any alkali metal cations M⁺ in the electrodeposition solution.^{3,4,6} The “supernumerary” Fe³⁺_{1/3}, so-called because it largely simply preserves electro-neutrality, is interstitial⁷ as is any supernumerary cation in the cubic lattice. On subsequent cyclovoltammetric (CV) cycling (see below) in M⁺-containing solution,^{3,4,7} the monocation M⁺ replaces much of the supernumerary Fe³⁺, the best-incorporated replacement being K⁺ which, if sole supernumerary, gives^{3,4,6} the so-called “soluble” PB or “sPB”, K⁺Fe³⁺[Fe^{II}(CN)₆]⁴⁻.

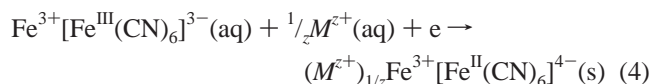
Thus, the reactions of interest, focusing on the chromophore unit as “core” species separate from the extra charge-neutralizing cation, are



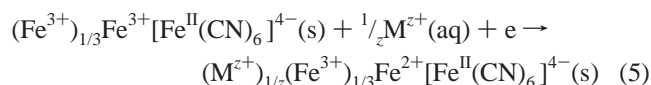
with, here, total replacement of the supernumerary. With only partial replacement (as explained below in eq 7 and text)



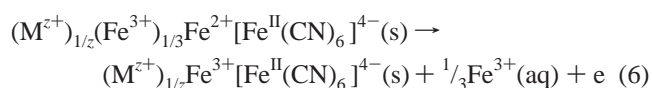
The well-rehearsed^{1,3,4,6,7} insertion electrochemistry of M⁺ supernumeraries, still largely lacking in explanation, follows the electrode reactions below (the chromophore being written intact, i.e., free of fractions or multiples). For PB electrodeposition in M^{z+} solution



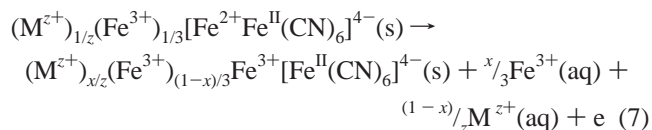
where the precursor aquo-ion is brown and the solid product deposited is blue. [The change in font to M^{z+} distinguishes the specific initial supernumerary Fe³⁺ from any other supernumeraries.] The subsequent bleaching reduction of the initial PB deposit, with its invariable supernumerary Fe³⁺, is carried out in a different solution (as would be the case in a working electrochromic cell), e.g., slightly acidified excess KCl in which K⁺ is the 1/2M^{z+}:



giving the clear “Prussian White”. On reversal, the new PB product, now differing in composition from the initial with M^{z+} replacing M^{z+}, is produced in the recolorizing oxidation:



Analytical results^{3,4,8} however show that not all supernumerary Fe³⁺ is replaced in the first cycle (reaction 4), but only a fraction *x* of about a third or more, hence,



In this study we deal largely with K⁺ as the M^{z+} ion, for which the net replacement reaction is thus reaction 2 or 3, and for these the thermodynamic parameters will be established. Reactions 2 and 3, which are both ion-exchange in nature, are in effect catalyzed by the electrochromic (bleaching + recoloration) redox reactions 4 to 7.

The mechanism proposed³ for the ion-exchange lacks any assessment of the driving energetics. Recent advances⁹ have vastly simplified the treatment of the thermodynamics of complex solid systems; when applied to the ferrocyanide lattices, these allow, for the first time, the quantification of the standard enthalpy, entropy, and Gibbs energy changes in and, hence, the equilibrium constants for, the ion-exchange reactions of interest.

Lattice-Energy Strategy. The Glasser–Jenkins predictive methods⁹ are based on using the formula unit volumes of the species involved, thus task (i) is to establish the volume of the ferrocyanide anion, [Fe(CN)₆]⁴⁻. Thereafter (in task (ii)), the enthalpy changes, Δ*H*₂ and Δ*H*₃, can be established using thermochemical cycles involving lattice enthalpy steps. We then (in task (iii)) estimate Δ*S*₂ and Δ*S*₃ using our new entropy–volume equation^{9e,g} relating absolute entropy of solids, *S*⁰₂₉₈, to the molecular (formula unit) volume, *V*_m. Finally, in task (iv), we combine enthalpy and entropy changes to estimate overall values of Δ*G*₂ and Δ*G*₃ and, hence, the equilibrium constants *K*₂ and *K*₃, for the reactions 2 and 3.

Ferrocyanide Ion Volume and Lattice Energies. The ICSD database¹⁰ contains structural information for a number of anhydrous A^{*p*+}_{*x*}B^{*q*+}_{*y*}[Fe(CN)₆]_{*z*} and hydrated A^{*p*+}_{*x*}B^{*q*+}_{*y*}[Fe(CN)₆]_{*z*}*n*H₂O ferrocyanide salts. Hydrated salts, being only partially ionic materials, are *not* immediately susceptible to

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Table 1. Estimation of Lattice Energies, U_{POT} , of Anhydrous Parent Ferrocyanides and of the Average Ion Volume, $V\{\text{Fe}(\text{CN})_6^{4-}\}/\text{nm}^3$, for the Ferrocyanide Ion, $[\text{Fe}(\text{CN})_6]^{4-}$

ferrocyanide parent	V_m {parent} nm ³	I^a	U_{POT} {parent} kJ mol ⁻¹	$V\{A^{p+}\}$, $V\{B^{q+}\}$, nm ³	$V\{[\text{Fe}(\text{CN})_6]^{4-}\}$ nm ³
Cs ₂ Mg[Fe(CN) ₆]	0.284 97	11	5686	0.018 82 0.001 99	0.2453
Cs ₂ Zn[Fe(CN) ₆]	0.277 88	11	5734	0.018 82 0.002 40	0.2378
K ₂ Cu ₃ [Fe(CN) ₆] ₂	0.4955	23	12642	0.009 86 0.001 56	0.2355
Li ₂ Cu[Fe(CN) ₆]	0.249 51	11	5943	0.001 99 0.001 56	0.2440
Na ₂ Cu[Fe(CN) ₆]	0.251 50	11	5927	0.003 94 0.001 56	0.2421
K ₂ Cu[Fe(CN) ₆]	0.249 25	11	5945	0.009 86 0.001 56	0.2280
Rb ₂ Cu[Fe(CN) ₆]	0.248 50	11	5951	0.013 86 0.001 56	0.2192
K ₂ Ni[Fe(CN) ₆]	0.247 01	11	5963	0.009 86 0.001 99	0.2253
K ₂ Co[Fe(CN) ₆]	0.256 05	11	5892	0.009 86 0.002 31	0.2340
Co ₂ [Fe(CN) ₆]	0.259 11	12	6591	0.002 31	0.2545
Ni ₂ [Fe(CN) ₆]	0.250 00	12	6670	0.001 99	0.2460
Cu ₂ [Fe(CN) ₆]	0.248 50	12	6683	0.001 56	0.2454
					av 0.2381

^a Ionic strength factor as defined by eq 10.

treatment using our simple equations for lattice energies.⁹ Rather, hydrated salts have necessitated a separate study^{9d} in order to derive a methodology for estimating their energetics. Considering first the *anhydrous (parent)* salt and adding a correction term derived from the thermodynamic difference rule^{9d} allow us to evaluate lattice energies of the hydrates.⁹ Thus, in the present paper, hydrated ferrocyanides are considered separately from their anhydrous counterparts.

Tables 1 and 2 consider data for a series of anhydrous and hydrated ferrocyanides, respectively. The volumes of the anhydrous parent, $V_m\{\text{parent}\}$, and hydrate, $V_m\{\text{hydrate}\}$ are derived from V_{cell}/Z , where V_{cell} is the unit cell volume listed in the crystal structure database¹⁰ and Z is the number of formula units per unit cell. In Table 1, the anhydrous salt volumes are

derived directly from the crystal structure data, while, in Table 2, the hydrate volumes, $V\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z \cdot n\text{H}_2\text{O}\}$, are first converted to *anhydrous* salt volumes, using the equation:

$$V_m\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z\} \equiv V_m\{\text{parent}\} = V_m\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z \cdot n\text{H}_2\text{O}\} - nV_m\{\text{H}_2\text{O}\} \quad (8)$$

where $V_m(\text{H}_2\text{O})/\text{nm}^3 = 0.0245$.^{9d} The lattice energies of the anhydrous ferrocyanides can then be estimated (column 6, Table 2) using the equation:^{9a}

$$U_{\text{POT}}\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z\}/\text{kJ mol}^{-1} = AI(2I/V_m\{\text{parent}\})^{1/3} \quad (9)$$

where $V_m\{\text{parent}\}$ is in nm³, $A = 121.39 \text{ kJ mol}^{-1} \text{ nm}$, and I is the lattice ionic strength factor:^{9f}

$$I = \sum n_i z_i^2 \quad (10)$$

where n_i is the number of ions of charge z_i in the lattice, and the summation is made over the formula unit.

The volume of the ferrocyanide anion, $V\{[\text{Fe}(\text{CN})_6]^{4-}\}$, is next estimated in Tables 1 and 2 using the relation:

$$V\{[\text{Fe}(\text{CN})_6]^{4-}\} = [V\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z \cdot n\text{H}_2\text{O}\} - xV\{A^{p+}\} - yV\{B^{q+}\} - nV\{\text{H}_2\text{O}\}]/z \quad (11)$$

where $n = 0$ for anhydrous salts. $V\{A^{p+}\}$ and $V\{B^{q+}\}$ are taken as $4\pi r_G^3/3$ where r_G is the Goldschmidt radius of the ion. The results are displayed in column 6 in Table 1 and in column 8 in Table 2, and the overall average value for $V\{[\text{Fe}(\text{CN})_6]^{4-}\}$ across the two tables is found to be

$$V\{[\text{Fe}(\text{CN})_6]^{4-}\}/\text{nm}^3 = 0.246(\pm 0.017) \quad (12)$$

thus completing task (i).

With this value now established, we are able to estimate, by summation of individual ion volumes, the values $V\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z\}$ (and thereby the lattice energies) of ferro-

Table 2. Estimation of Lattice Energies, U_{POT} , of Hydrated Ferrocyanides and of the Average Ion Volume, $V\{[\text{Fe}(\text{CN})_6]^{4-}\}/\text{nm}^3$, for the Ferrocyanide Ion, $[\text{Fe}(\text{CN})_6]^{4-}$

ferrocyanide hydrate	V_m^a {hyd} nm ³	I^b	ferrocyanide parent	V_m {par} ^c nm ³	U_{pot} {par} ^d kJ mol ⁻¹	$V\{A^{p+}\}$, $V\{B^{q+}\}$ nm ³	$V_m\{[\text{Fe}(\text{CN})_6]^{4-}\}^e$ nm ³	U_{pot} {par} ^d kJ mol ⁻¹
Fe ₄ [Fe(CN) ₆] ₃ ·14H ₂ O	1.050 63	42	Fe ₄ [Fe(CN) ₆] ₃	0.7076	25 057	0.001 26	0.2342	25 817
Fe ₄ [Fe(CN) ₆] ₃ ·14H ₂ O	1.047 22	42	Fe ₄ [Fe(CN) ₆] ₃	0.7042	25 097	0.001 26	0.2331	25 857
Cs ₂ BaFe(CN) ₆ ·2H ₂ O	0.378 13	11	Cs ₂ BaFe(CN) ₆	0.3291	5419	0.012 25	0.2792	5528
						0.018 82		
Na ₄ Fe(CN) ₆ ·10H ₂ O	0.501 94	10	Na ₄ Fe(CN) ₆	0.2569	5183	0.003 94	0.2412	5726
Na ₄ Fe(CN) ₆ ·10H ₂ O	0.491 92	10	Na ₄ Fe(CN) ₆	0.2469	5252	0.003 94	0.2312	5795
Na ₄ Fe(CN) ₆ ·10H ₂ O	0.498 44	10	Na ₄ Fe(CN) ₆	0.2534	5207	0.003 94	0.2377	5750
K ₄ Fe(CN) ₆ ·3H ₂ O	0.367 92	10	K ₄ Fe(CN) ₆	0.2944	4953	0.009 86	0.2550	5116
K ₄ Fe(CN) ₆ ·3H ₂ O	0.372 79	10	K ₄ Fe(CN) ₆	0.2962	4942	0.009 86	0.2568	5106
K ₄ Fe(CN) ₆ ·3H ₂ O	0.284 97	10	K ₄ Fe(CN) ₆	0.2993	4926	0.009 86	0.2599	5089
Na ₂ Zn ₃ [Fe(CN) ₆] ₂ ·9H ₂ O	0.738 76	23	Na ₂ Zn ₃ [Fe(CN) ₆] ₂	0.5183	12 454	0.003 94	0.2516	12 943
						0.002 40		
K ₂ Zn ₃ [Fe(CN) ₆] ₂ ·5H ₂ O	0.731 27	23	K ₂ Zn ₃ [Fe(CN) ₆] ₂	0.6088	11 804	0.009 86	0.2909	12 075
						0.002 40		
							av 0.2519	

^a $V_m\{\text{hydrate}\} = V_{\text{cell}}/Z$. ^b Ionic strength factor as defined by eq 10. ^c $V_m\{\text{parent}\} = V_m\{\text{hydrate}\} - nV_m\{\text{H}_2\text{O}\}$, where $V_m\{\text{H}_2\text{O}\}/\text{nm}^3 = 0.0245$; see ref 9d. ^d $U_{\text{POT}}\{\text{parent}\} = AI(2I/V_m\{\text{parent}\})^{1/3}$; see ref 9a. ^e $V_m\{[\text{Fe}(\text{CN})_6]^{4-}\} = V_m\{\text{hydrate}\} - xV\{A^{p+}\} - yV\{B^{q+}\} - nV_m\{\text{H}_2\text{O}\}$ based on ion volume additivity. ^f $U_{\text{POT}}\{\text{hydrate}\} = U_{\text{POT}}\{\text{parent}\} + n\theta_U\{\text{H}_2\text{O}\}$, where $\theta_U\{\text{H}_2\text{O}\} = 54.3 \text{ kJ mol}^{-1}$; see ref 9d.

Table 3. Lattice Energies of Anhydrous Salts per Ferrocyanide Ion, Estimated from Crystal Structure Data for Parents or Hydrates and from Individual Ion Volume Sums Based on $V\{[\text{Fe}(\text{CN})_6]^{4-}\}/\text{nm}^3 = 0.2458(\pm 0.017)$

ferrocyanide salt	lattice energy based on crystal structure data U_{POT} kJ mol ⁻¹ (Table 1)	lattice energy estimated from eq 13 U_{POT} kJ mol ⁻¹	% error of estimated values from ion volume summation
Fe _{4/3} [Fe(CN) ₆]	8352	8190	-1.9
Fe _{4/3} [Fe(CN) ₆]	8366	8190	-2.1
K _{1/4} Fe _{5/4} [Fe(CN) ₆]	5560	5672	-2.0
Na ₄ [Fe(CN) ₆]	5183	5153	0.6
Na ₄ [Fe(CN) ₆]	5252	5153	1.9
Na ₄ [Fe(CN) ₆]	5207	5153	1.0
K ₄ [Fe(CN) ₆]	4953	5006	1.1
K ₄ [Fe(CN) ₆]	4942	5006	1.3
K ₄ [Fe(CN) ₆]	4926	5006	1.6
NaZn _{3/2} [Fe(CN) ₆]	6227	6274	0.8
KZn _{3/2} [Fe(CN) ₆]	5902	6226	5.5
KCu _{3/2} [Fe(CN) ₆]	6321	6236	1.3
Cs ₂ Mg[Fe(CN) ₆]	5686	5683	0.1
BaCs ₂ [Fe(CN) ₆]	5419	5616	3.6
Cs ₂ Zn[Fe(CN) ₆]	5734	5680	0.9
Li ₂ Cu[Fe(CN) ₆]	5943	5929	0.2
Na ₂ Cu[Fe(CN) ₆]	5927	5898	0.5
K ₂ Cu[Fe(CN) ₆]	5945	5810	2.3
Rb ₂ Cu[Fe(CN) ₆]	5951	5753	3.3
Na ₂ Fe[Fe(CN) ₆]	5823	5901	-1.3
K ₂ Co[Fe(CN) ₆]	5892	5804	1.5
K ₂ Ni[Fe(CN) ₆]	5963	5807	2.6
Ni ₂ [Fe(CN) ₆]	5231	5232	0.0
Cu ₂ [Fe(CN) ₆]	6683	6679	0.1
Co ₂ [Fe(CN) ₆]	6591	6666	-1.1

cyanides for which crystal structures are unavailable, using the equation:^{9a}

$$U_{\text{POT}}\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z\} / \text{kJ mol}^{-1} = AI[2I/(xV\{A^{p+}\} + yV\{B^{q+}\} + zV\{[\text{Fe}(\text{CN})_6]^{4-}\})]^{1/3} \quad (13)$$

A similar procedure has recently been applied to the apatites¹¹ and gave agreement between predicted and thermochemical-cycle based values of U_{POT} of between 0.05% and 2.08% for ionic lattices, with an (expected) increased error for more covalent lattices (up to 7.4%).

In Table 2, we further estimate the *hydrate* lattice energy using eq 23 of ref 9d. This amounts to adding a correction term ($= n\theta_{\text{U}}\{\text{H}_2\text{O}\}$) equal to 54.3 kJ mol⁻¹ per hydrated water molecule to the corresponding estimate for the anhydrous ferrocyanide lattice energy.

Table 3 (column 3) compares the error involved in estimating the lattice energy of an anhydrous ferrocyanide by summing the individual ion volumes (eq 13) with that derived directly from the crystal structure volumes (column 2).

With errors ranging from -2.1 to +5.5%, the agreement is acceptably good, which means that the lattice energies may be predicted with reasonable confidence for ionic ferrocyanides of which no crystal structure data has yet been acquired.

Simple Lattice Energy Sum Rule. Simultaneously, Glasser and Jenkins¹² and Yoder and Flora¹³ have observed that the lattice energies of certain double (and even more complex) ionic

salts can be compounded by summation from the lattice energies of their individual components, provided that the enthalpy of the implied reaction is zero or adequately small. Applied to typical ferrocyanide salts, this means that

$$U_{\text{POT}}\{A^{p+}_x B^{q+}_y [\text{Fe}(\text{CN})_6]_z\} = zU_{\text{POT}}\{A^{p+}_{x/z} B^{q+}_{y/z} [\text{Fe}(\text{CN})_6]\} \approx z[(xp/4z)U_{\text{POT}}\{A^{p+}_{4/p} [\text{Fe}(\text{CN})_6]\} + (yq/4z)U_{\text{POT}}\{B^{q+}_{4/q} [\text{Fe}(\text{CN})_6]\}] \quad (14)$$

giving rise to the specific relationships given in footnotes c, e, f, g, and j of Table 4.

Of course, this result can also be extended to hydrates of differing n by suitable subtraction/addition of water molecule contributions (see footnote g, Table 4).

In the final column of Table 4, we test the applicability of this simple sum rule to the ferrocyanide salts and compare its results in a number of cases to estimates made by individual ion volume addition. The values from the lattice energy sum rule and from simple volume summation are usually satisfactorily close. Although the volume of the double salt will be *approximately* that of the volume sum of the counterparts (see discussion of isomegetic rule¹⁴), this *cannot be the reason* why these lattice energies combine additively, simply because U_{POT} displays an inverse cube root dependence⁹ on the volume (see eq 13). The success of eq 14 probably lies in the fact that the interaction terms contributing to the lattice energy terms involved in the separate dissociations of two separate salt lattices are not dissimilar to those involved in the disruption of the double salt (i.e., the cross intralattice terms are small). We shall use both methods of estimation in this work whenever possible.

Thermochemical Cycles and Thermodynamics. These appear as Figures 1 and 2 in the Supporting Information to this paper.

Thermodynamic Difference Quantities for the Fe³⁺/K⁺ Ion-Exchange Reactions. The enthalpy changes, ΔH_2 and ΔH_3 , can now be evaluated by substituting the lattice energy terms into eqs S1 and S2 [where prefix S refers to equations included in the Supporting Information to this paper], which leads us directly to the values:

$$\Delta H_2 / \text{kJ mol}^{-1} = 8366 - 7499 - 1153.6 = -287 \quad (15)$$

and

$$\Delta H_3 / \text{kJ mol}^{-1} = 8366 - 8068 - 384.3 = -86 \quad (16)$$

We have recently shown that standard entropies, S°_{298} , for a range of condensed phase inorganic materials can be estimated directly from their rectilinear dependence^{9e,g} on molecular (formula unit) volume, V_m :

$$S^\circ_{298} / \text{J K}^{-1} \text{ mol}^{-1} \approx kV_m + c \quad (17)$$

where, for ionic salts, $k = 1360 \text{ J K}^{-1} \text{ mol}^{-1} \text{ nm}^{-3}$ and $c = 15 \text{ J K}^{-1} \text{ mol}^{-1}$. Accordingly, eqs S7 and S8 can be written and,

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Table 4. Comparison of Lattice Energies Estimated Using Equations 13 and 14

ferrocyanide	I^a	lattice energy based on crystal structure data U_{pot} (Table 1)	lattice energy estimated from eq 13 U_{pot} kJ mol ⁻¹ (% error)	lattice energy estimated from eq 14 U_{pot} kJ mol ⁻¹ (% error)
Li ₄ Fe(CN) ₆	10	no crystal structure	5205	
Li ₂ CuFe(CN) ₆	11	5943 ^b	5929 (0.2%)	5944 ^d (0.0%)
Cs ₄ Fe(CN) ₆	10	no crystal structure	4812	
Cs ₄ [Fe(CN) ₆]·5H ₂ O	10	no crystal structure	5083 ^{e,i}	
Mg ₂ Fe(CN) ₆	12	no crystal structure	6672	
Cs ₂ MgFe(CN) ₆	11	5686 ^b	5683 (0.1%)	5742 ^f (0.9%)
Zn ₂ Fe(CN) ₆	12	no crystal structure	6665	
Cs ₂ ZnFe(CN) ₆	11	5734 ^b	5680 (0.9%)	5738 ^g (0.1%)
Na ₂ Zn ₃ [Fe(CN) ₆] ₂ ·9H ₂ O	23	12943 ^b	12548 ^{h,i} (0.8%)	13093 ^h (1.1%)
Rb ₄ Fe(CN) ₆	10	no crystal structure	4915	
Cu ₂ Fe(CN) ₆	12	6683	6679 (0.1%)	
Rb ₂ CuFe(CN) ₆	11	5951	5753 (3.3%)	5797 ^j (2.6%)

^a Ionic strength factor defined by eq 10. ^b Taken from Table 1. ^c Taken from Table 3. ^d $U_{\text{pot}}\{\text{Li}_2\text{CuFe(CN)}_6\} \approx 1/2 U_{\text{pot}}\{\text{Li}_4\text{Fe(CN)}_6\} + 1/2 U_{\text{pot}}\{\text{Cu}_2\text{Fe(CN)}_6\}$. ^e Derived from parent value above using difference rule: $U_{\text{pot}}\{\text{Cs}_4\text{Fe(CN)}_6 \cdot 5\text{H}_2\text{O}\} = U_{\text{pot}}\{\text{Cs}_4\text{Fe(CN)}_6\} + 5\theta_{\text{U}}\{\text{H}_2\text{O}\}$. ^f $U_{\text{pot}}\{\text{Cs}_2\text{MgFe(CN)}_6\} \approx 1/2 U_{\text{pot}}\{\text{Cs}_4\text{Fe(CN)}_6\} + 1/2 U_{\text{pot}}\{\text{Mg}_2\text{Fe(CN)}_6\}$. ^g $U_{\text{pot}}\{\text{Cs}_2\text{ZnFe(CN)}_6\} \approx 1/2 U_{\text{pot}}\{\text{Cs}_4\text{Fe(CN)}_6\} + 1/2 U_{\text{pot}}\{\text{Zn}_2\text{Fe(CN)}_6\}$. ^h $U_{\text{pot}}\{\text{Na}_2\text{Zn}_3[\text{Fe(CN)}_6]_2 \cdot 9\text{H}_2\text{O}\} \approx 1/2 U_{\text{pot}}\{\text{Na}_4\text{Fe(CN)}_6\}^h + 3/2 U_{\text{pot}}\{\text{Zn}_2\text{Fe(CN)}_6\} + 9\theta_{\text{U}}\{\text{H}_2\text{O}\}$. ⁱ Note that equation $U_{\text{pot}} = A/(2I/V_m)^{1/3}$ cannot be employed when V_m is an estimated hydrate volume. ^j $U_{\text{pot}}\{\text{Rb}_2\text{CuFe(CN)}_6\} \approx 1/2 U_{\text{pot}}\{\text{Rb}_4\text{Fe(CN)}_6\} + 1/2 U_{\text{pot}}\{\text{Cu}_2\text{Fe(CN)}_6\}$.

using the data from eqs S9, S14, and S17,

$$\begin{aligned} \Delta S_2 / \text{J K}^{-1} \text{ mol}^{-1} & \\ & \approx 1360[V_m\{\text{K}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\ & \quad V_m\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - 207.8 \\ & \approx 1360[0.2423 - 0.2347] - 207.8 \\ & \approx 10 - 207.8 = -198 \end{aligned} \quad (18)$$

and

$$\begin{aligned} \Delta S_3 / \text{J K}^{-1} \text{ mol}^{-1} & \\ & \approx 1360[V_m\{(\text{K}^+)_{1/3}(\text{Fe}^{3+})_{2/9}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\ & \quad V_m\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - 69.3 \\ & \approx 1360[0.2377 - 0.2347] - 69.3 \\ & \approx 4 - 69.3 = -65 \end{aligned} \quad (19)$$

We can make an important observation at this point that since both

$$\begin{aligned} S_{298}^\circ\{\text{K}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} & \approx \\ & S_{298}^\circ\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} \end{aligned} \quad (20)$$

and

$$\begin{aligned} S_{298}^\circ\{(\text{K}^+)_{1/3}(\text{Fe}^{3+})_{2/9}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} & \approx \\ & S_{298}^\circ\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} \end{aligned} \quad (21)$$

then ΔS_2 and ΔS_3 have values which are largely dependent on the appropriately weighted differences of the entropies of formation of the aqueous ions (e.g., $1/3\Delta H_f^\circ\{\text{Fe}^{3+}, \text{aq}\} - \Delta H_f^\circ\{\text{K}^+, \text{aq}\}$) and not on the differences between the standard entropies of the ferrocyanides involved (which are less than 10 J K⁻¹ mol⁻¹).

A combination of enthalpy and entropy terms ($\Delta G = \Delta H - T\Delta S$) at 298 K leads us to the values

$$\Delta G_2 / \text{kJ mol}^{-1} = -287 + 59 = -228 \quad (22)$$

and

$$\Delta G_3 / \text{kJ mol}^{-1} = -86 + 19 = -67 \quad (23)$$

demonstrating that both reactions 2 and 3 are thermodynamically favored and that the equilibrium constants (at 298 K) take the values

$$K_2 = 9.3 \times 10^{39} \quad (24)$$

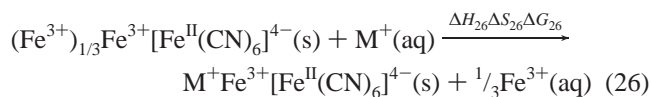
and

$$K_3 = 5.6 \times 10^{11} \quad (25)$$

Discussion

The system preference for initial deposition in the PB of the Fe³⁺ rather than the M⁺ as supernumerary, clearly contrasting with any prediction from the thermodynamics presented here, is necessarily a mechanistic problem regarding the initial deposition, which is given consideration elsewhere.³

Process 2 for various alkali metal ions M⁺ is



We can consider whether the selection of M⁺ can radically influence the thermodynamics of the reaction.

$$\begin{aligned} \Delta H_{26} & = U_{\text{pot}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\ & \quad U_{\text{pot}}\{\text{M}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} + 1/3RT \\ & \quad + \Delta H_f^\circ\{\text{M}^+, \text{g}\} - 1/3\Delta H_f^\circ\{\text{Fe}^{3+}, \text{g}\} + \\ & \quad 1/3\Delta H_f^\circ\{\text{Fe}^{3+}, \text{aq}\} - \Delta H_f^\circ\{\text{M}^+, \text{aq}\} \\ & = U_{\text{pot}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\ & \quad U_{\text{pot}}\{\text{M}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} \\ & \quad + 1/3RT - \Delta H_{\text{hyd}}^\circ\{\text{M}^+, \text{g}\} + \\ & \quad 1/3\Delta H_{\text{hyd}}^\circ\{\text{Fe}^{3+}, \text{g}\} \end{aligned} \quad (27)$$

which, by virtue of eq S16, can be written as

$$\begin{aligned}
\Delta H_{26}/\text{kJ mol}^{-1} &= U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\
&\quad \frac{1}{4}U_{\text{POT}}\{\text{M}^+4[\text{Fe}^{\text{II}}(\text{CN})_6]\} \\
&- \left(\frac{3}{4}U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}\right) \\
&+ \frac{1}{3}RT - \Delta H_{\text{hyd}}^\circ\{\text{M}^+, \text{g}\} + \frac{1}{3}\Delta H_{\text{hyd}}^\circ\{\text{Fe}^{3+}, \text{g}\} \\
&= \frac{1}{4}[U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\
&\quad U_{\text{POT}}\{\text{M}^+4[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}] \\
&- \Delta_{\text{hyd}}H^\circ\{\text{M}^+, \text{g}\} - 1486 \quad (28)
\end{aligned}$$

Also from eq 18

$$\begin{aligned}
\Delta S_{26}/\text{J K}^{-1} \text{ mol}^{-1} &\approx 1360 [V_{\text{m}}\{\text{M}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\
&\quad V_{\text{m}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}] \\
&+ \frac{1}{3}S_{298}^\circ\{\text{Fe}^{3+}, \text{aq}\} - S_{298}^\circ\{\text{M}^+, \text{aq}\} \\
&\approx 1360[V_{\text{m}}\{\text{M}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - 0.2359] \\
&+ \frac{1}{3}S_{298}^\circ\{\text{Fe}^{3+}, \text{aq}\} - S_{298}^\circ\{\text{M}^+, \text{aq}\} \\
&\approx 1360 [V_{\text{m}}\{\text{M}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - \\
&\quad S_{298}^\circ\{\text{M}^+, \text{aq}\} - 448 \quad (29)
\end{aligned}$$

using the data generated^{15–17} for $U_{\text{POT}}\{\text{M}^+4[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}/\text{kJ mol}^{-1}$ [i.e., 5205 (M = Li, Table 4); 5214 (M = Na, Table 3); 4940 (M = K, Table 3); 4915 (M = Rb, Table 4), and 4812 (M = Cs, Table 4)] and using the value $U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} = 8352 \text{ kJ mol}^{-1}$. Reaction 26 is enthalpy-driven

- (15) (a) “RT terms” are calculated using an extension of eq 4 of ref 9b. (b) $\Delta H_f^\circ\{\text{K}^+, \text{g}\} = 514.26 \text{ kJ mol}^{-1}$; $\Delta H_f^\circ\{\text{K}^+, \text{aq}\} = -252.38 \text{ kJ mol}^{-1}$; $\Delta H_f^\circ\{\text{Fe}^{3+}, \text{g}\} = 5712.3 \text{ kJ mol}^{-1}$; $\Delta H_f^\circ\{\text{Fe}^{3+}, \text{aq}\} = -48.5 \text{ kJ mol}^{-1}$; $RT = 2.5 \text{ kJ mol}^{-1}$; $S_{298}^\circ\{\text{Li}^+, \text{aq}\} = -8.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $S_{298}^\circ\{\text{Na}^+, \text{aq}\} = 36.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $S_{298}^\circ\{\text{K}^+, \text{aq}\} = 80.3 \text{ J K}^{-1} \text{ mol}^{-1}$; $S_{298}^\circ\{\text{Rb}^+, \text{aq}\} = 99.3 \text{ J K}^{-1} \text{ mol}^{-1}$; $S_{298}^\circ\{\text{Cs}^+, \text{aq}\} = 111.3 \text{ J K}^{-1} \text{ mol}^{-1}$; $S_{298}^\circ\{\text{Fe}^{3+}, \text{aq}\} = -382.5 \text{ J K}^{-1} \text{ mol}^{-1}$ (standard entropies from ref 19e).
- (16) Very little thermochemical data is established for ferrocyanide salts. The thermodynamic “difference rule”^{9d} can be utilized to validate and select thermodynamic data. For example, $\Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6, \text{s}\}/\text{kJ mol}^{-1}$ is listed to be -594.1 (ref 19a) or -523.4 (ref 18b), whilst $\Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}, \text{s}\}/\text{kJ mol}^{-1}$ is listed as -1466.5 (ref 19a) or -1412.1 (ref 19c,d). According to our “difference rule”, the difference $[\Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}, \text{s}\} - \Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6, \text{s}\}]/\text{kJ mol}^{-1}$ should equal^{9d} $3\theta_{\text{H}}(\text{H}_2\text{O}) = -896 \text{ kJ mol}^{-1}$, thus suggesting that the pair of values $\Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}, \text{s}\}/\text{kJ mol}^{-1} = -1412.1$ and $\Delta H_f^\circ\{\text{K}_4\text{Fe}(\text{CN})_6, \text{s}\}/\text{kJ mol}^{-1} = -523.4$ (difference = -889 kJ mol^{-1}) are preferred and consistent with expectation.
- (17) (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. (b) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, 1952. (c) Karapet'yants, M. Kh. Ph.D. Thesis, MKhTI im. D. I. Mendeleev, 1957. (d) Karapet'yants, M. Kh.; Karapet'yants, M. L. *Thermodynamic Constants of Inorganic and Organic Compounds*; Schmorak, J. Transl.; Humphrey Science Publishers: Ann Arbor, London, 1970. (e) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.
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Table 5. Influence on Reaction 2 of Changing the Alkali Metal Cation

	A	Li	Na	K	Rb	Cs
$U_{\text{POT}}/\text{kJ mol}^{-1}$						
$U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}$		8352 ^a	8352 ^a	8352 ^a	8352 ^a	8352 ^a
$U_{\text{POT}}\{\text{A}^+4[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}$		5205 ^b	5214 ^a	4940 ^a	4915 ^b	4812 ^b
$[U_{\text{POT}}\{(\text{Fe}^{3+})_{1/3}\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - U_{\text{POT}}\{\text{A}^+4[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}]/4$		786.75	784.5	853	859.25	885
$-\Delta_{\text{hyd}}H^\circ(\text{A}^+, \text{g})$		531	416	334	308	283
$\Delta H/\text{kJ mol}^{-1}$		-168	-286	-299	-319	-318
$V_{\text{m}}\{\text{A}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}$		0.2344 ^c	0.2364 ^c	0.2423	0.2463 ^c	0.2513 ^c
$1360 [V_{\text{m}}\{\text{A}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\}]^d$		319	322	329	335	342
$S_{298}^\circ\{\text{A}^+, \text{aq}\}^e$		-8.8	36.8	80.3	99.3	111.3
$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$		-120	-163	-199	-212	-218
$\Delta G/\text{kJ mol}^{-1}$		-132	-237	-240	-255	-253

^a Table 3 (average value). ^b Table 4. ^c Estimated from $V_{\text{m}}\{\text{K}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} - V\{\text{K}^+\} + V\{\text{A}^+\}$ (ion additivity). ^d From ref 9e. ^e $S_{298}^\circ\{\text{A}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} = 1360V_{\text{m}}\{\text{A}^+\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\} + 15$ (see ref 9e).

for all alkali metal (M⁺) species (see Table 5), and ΔG is twice as negative for Cs⁺ as it is for Li⁺. It has been argued³ from spectroscopic and mass-change data that K⁺ forms the most stable PB (except for the egregiously stable Cs⁺-containing PB of slightly different cubic structure (ref 18)). Thus, for the series of ΔG for Na⁺ to Cs⁺, the position of only Rb⁺ is incorrectly predicted from the adduced thermodynamics, which is an appreciable achievement; the Rb⁺ anomaly (PB predicted stability close to Cs⁺, experimentally³ only near Na⁺) may arise from a variable considered in ref 3, the precise amount of water accompanying the M⁺ into the lattice. Nice analytical results could confirm this supposition.

Our main conclusion is that the new thermodynamic results provide substantial clarification of a longstanding problem in an important electrochrome, providing distinctions even between different M⁺ that are largely borne out in practice.

Estimate of Errors. Our procedures for lattice energy determination have errors estimated^{9a} to be less than 7%, generally considerably less, while the error contribution to ΔG from entropy estimation^{9d} may be about 1%. In the present work, however, we consider related materials where the errors are likely to accumulate in similar fashion so that we anticipate relative error to be much reduced, leading to credible results. Indeed, the agreement among the independent procedures used to obtain quantitative results (cf. the discussion following eq S9) rather firmly support this conclusion. This study is unique, and we are unable to make a more definitive statement in the absence of any comparable studies.

Acknowledgment. The authors thank Jenny Shields (Warwick) for checking the completed calculations.

Supporting Information Available: The Born–Fajans–Haber cycles (Figures 1 and 2), their associated equations, and further details of the calculations reported in the main text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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