

$$E^{\circ}(*\text{Cr}(\text{diammac})^{3+}/\text{Cr}(\text{diammac})^{2+}) = E_{00}(\text{Cr}^{3+}/\text{Cr}^{2+}) + E_{00}(*\text{Cr}^{3+}/\text{Cr}^{2+})$$

where  $E_{00}(*\text{Cr}^{3+}/\text{Cr}^{2+})$  is the one-electron potential corresponding to the spectroscopic energy of the excited state (ca. 1.8 eV). The temperature-independent region for diammac extends to 200 K compared with 170 K for sar complexes.<sup>11</sup> The higher ligand field of diammac compared to sar leads to a relatively high-lying quartet excited state. This would be less easily populated from the  ${}^2E_g$  excited state should deactivation occur through a mechanism of thermally induced back intersystem crossing. Alternative mechanisms may be considered, as detailed elsewhere.<sup>26</sup> Lifetimes at 77 K for  $\text{CrN}_6^{3+}$  ions in nondeuterated samples are extended considerably in the deuterated samples (Table IV).<sup>11,41</sup> The dramatic increase in the lifetime in the cold, temperature-independent region upon deuteration is in accordance with many other systems. This further substantiates the theory that the N–H stretching modes are responsible for radiationless deactivation.<sup>42</sup>

(41) Comba, P.; Mau, A. H. W.; Sargeson, A. M. *J. Phys. Chem.* **1985**, *89*, 394.

(42) Kuhn, K.; Wasgestian, F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665.

In parallel with the behavior around octahedral  $d^6$  cobalt(III), the diammac sexidentate amine ligand leads to a “compressed” chromium(III)  $d^3$  complex with physical properties reflecting this. Molecular mechanics calculations indicate that shortened bond lengths are a result of ligand demands,<sup>15,43</sup> so that “compression” should be generally observed with metal ions. This has now been seen for a range of octahedral metal ions.<sup>15,16,22,35</sup> Modest variations in physical properties of complexes of diammac appear generally, and may be turned to advantage in some applications.

**Acknowledgment.** Support of this work by the Australian Research Council is gratefully acknowledged, as is support by the Swiss National Science Foundation (Grant 20-5597-88). Assistance of Dr. E. Krausz and access to facilities at the Research School of Chemistry, The Australian National University, for photophysical studies is gratefully appreciated.

**Supplementary Material Available:** Tables of crystal data, thermal parameters, and hydrogen atom parameters and a unit cell diagram for  $[\text{Cr}(\text{diammac})](\text{ClO}_4)_3$  (6 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

(43) Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2496.

Contribution from the Department of Chemistry,  
University of Florida, Gainesville, Florida 32611

## Thermochemical Interpretation of Electrode Potentials for Transition-Metal Complexes

David E. Richardson<sup>†</sup>

Received November 27, 1989

Experimental and theoretical thermochemical quantities are interrelated to show how bond energies, solvation energies, and entropy changes lead to  $E^{\circ}$  values for several common transition-metal complex redox couples. Relevant conventions are described to demonstrate the relationship between gas-phase and solution thermochemistry of electron attachment reactions. Values of absolute electrode potentials for common reversible redox couples are estimated, and gas-phase electron attachment energies (experimental or theoretically estimated) are used to complete thermochemical cycles that lead to bond energy and solvation energy contributions to observed electrode potentials. A few common  $\text{M}^{\text{III}}\text{L}_x/\text{M}^{\text{II}}\text{L}_x$  couples ( $\text{L} = \text{NH}_3$ , bipyridine, cyclopentadienyl,  $\text{CN}^-$ , acetylacetonate) are used to illustrate why the  $E^{\circ}$  values for couples involving widely varying ligand sets are usually within a range of  $\sim 2$  V for a given metal despite the wide range ( $\sim 20$  V) of gas-phase electron attachment energies for the unsolvated complexes.

### Introduction

Little experimental or theoretical attention has been given to detailed thermochemical interpretations of observed electrode potentials for oxidation–reduction couples involving transition-metal centers in coordination complexes, metalloproteins, and organometallic compounds. Typical textbook discussions<sup>1</sup> describe trends in  $E^{\circ}$  values as a function of the metal for a given ligand environment (e.g., the  $[\text{M}(\text{H}_2\text{O})_6]^{3+/2+}$  series) and indicate the phenomenological dependence of  $E^{\circ}$  on the type of ligand. These treatments do little to relate compiled electrode potentials to general thermochemical concepts that might illuminate the reasons that a given redox couple has a particular  $E^{\circ}$  value. More advanced discussions<sup>2</sup> consider the thermochemical components of redox potentials and, for transition-metal couples, consider the role of ligand field effects in trends; however, these approaches are usually based on interpretation of relative variations of electrode potentials as the metal is changed rather than absolute values of the potentials. Some progress toward quantifying the role of bond energies and solvation in the determination of absolute electrode potentials can be made by using estimates based on rather simple models.<sup>2f</sup> Such analyses have clearly been limited by the absence of necessary gas-phase data for metal complexes, but this type of data has recently become more accessible through experimental studies.<sup>3,4</sup> The purpose of this article is to interrelate certain relevant thermochemical quantities for gas-phase and

condensed-phase complexes to show how bond energies, entropy changes, and solvation energies lead to an  $E^{\circ}$  value for a given redox couple. The emphasis here is on redox couples for transition-metal complexes in which oxidized and reduced forms retain the same ligand coordination.

Some important conventions are discussed first to demonstrate the relationship between gas-phase and solution redox thermo-

- (1) For example: (a) Porterfield, W. W. *Inorganic Chemistry*; Addison-Wesley: Reading, MA, 1984; pp 415–420. (b) Douglas, B.; McDaniel, D. H.; Alexander, J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1983; pp 495–503. (c) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 579–587. (d) Butler, I. S.; Harrod, J. F. *Inorganic Chemistry Principles and Applications*; Benjamin/Cummings: Redwood City, CA, 1989; pp 413–415.
- (2) For example: (a) Burgess, J. *Metal Ions in Solution*; Ellis Horwood: Chichester, U.K., 1978; Chapter 8. (b) Van Gaal, H. L. M.; van der Linden, J. G. M. *Coord. Chem. Rev.* **1982**, *47*, 41. (c) Burgess, J. *Ions in Solution: Basic Principles of Chemical Interactions*; Ellis Horwood: Chichester, U.K., 1988; Chapter 7. (d) Figgis, G. N. *Introduction to Ligand Fields*; Wiley Interscience: New York, 1966; p 98. (e) Lintvedt, R. L.; Fenton, D. E. *Inorg. Chem.* **1980**, *19*, 571. (f) Buckingham, D. A.; Sargeson, A. M. In *Chelating Agents and Metal Chelates*; Dwyer, F. P., Mellor, P. D., Eds.; Academic Press: New York, 1964; pp 237–282.
- (3) (a) Sharpe, P.; Eyley, J. R.; Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 2779. (b) Richardson, D. E.; Chirst, C. S.; Sharpe, P.; Ryan, M.; Eyley, J. In *Bond Energies and the Thermodynamics of Organometallic Reactions*; Marks, T. J., Ed.; ACS Symposium 428; American Chemical Society: Washington, D.C., 1990; Chapter 5. (c) Ryan, M.; Richardson, D. E. Unpublished results.
- (4) Meot-ner (Mautner), M. *J. Am. Chem. Soc.* **1989**, *111*, 2830.

<sup>†</sup> A. P. Sloan Foundation Research Fellow, 1988–1990.

chemistry. Following descriptions of experimental approaches for obtaining gas-phase electron attachment energies for metal complexes, thermodynamic cycles are presented that provide a breakdown of observed  $E^\circ$  values for some common redox couples into thermochemical components.

### Thermochemical Conventions for Oxidation–Reduction Processes

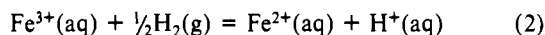
The thermodynamics of condensed-phase oxidation–reduction processes are usually presented by using the convention of the standard electrode potential,<sup>5</sup> which is defined as the Gibbs free energy per electron for an electrochemical cell reaction involving reduction by dihydrogen to produce the aqueous proton with all reactants at standard conditions ( $E^\circ = -\Delta G^\circ/nF$ , where  $n$  is the number of electrons and  $F$  is the Faraday constant). With the normal hydrogen electrode (NHE) taken as the reference ( $\text{H}^+(\text{aq}, \text{unit activity}) + \text{e}^- = 1/2\text{H}_2(\text{g}, 1 \text{ atm}), E^\circ = 0 \text{ V}$ ), half-cell reactions can be readily combined to obtain the thermodynamics of balanced redox processes ( $E_{\text{cell}}^\circ$  values). This approach offers computational ease and eliminates the need for defining the electrode processes on an energy scale that contains the energy of an electron in some reference state. Conceptually, this is a different approach from that normally taken with thermodynamic quantities related to chemical change in electron number involving gas-phase molecules and ions. For example, ionization potentials and electron affinities are referenced to the electrostatic zero potential energy of the infinitely separated electron in a field-free vacuum.<sup>6</sup> To relate condensed-phase and gas-phase redox thermochemistry directly, a common convention must be adopted.

### Single-Electrode Potentials

*Single-electrode potentials* refer to the thermodynamics of half-cell reactions without reference to the NHE convention.<sup>7</sup> Although single-electrode potentials can be estimated for a large number of half-cells, it is useful to take up the NHE first. We begin by considering the meaning of the “e<sup>-</sup>” symbol appearing in half-cell equations. In standard electrode potential half-cells, “e<sup>-</sup>” is an abbreviation for  $1/2\text{H}_2(\text{g}) - \text{H}^+(\text{aq})$ . For example, the half-cell

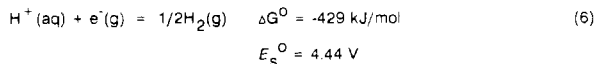
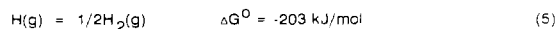
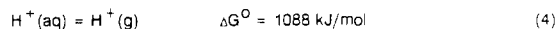
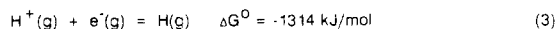


actually refers to the reaction



for which the standard free energy change  $\Delta G^\circ = -74.3 \text{ kJ/mol}$  at 298 K when all aqueous species are at unit activity and  $\text{H}_2$  is at 1 atm. Although the entropy of  $\text{H}^+(\text{aq})$  is not precisely known, the estimated thermodynamic parameters for eq 2 are  $\Delta S^\circ = 93 \text{ J/(mol K)}$  and  $\Delta H^\circ = -47 \text{ kJ/mol}$ .<sup>8</sup>

The single-electrode potential (or absolute thermodynamic potential) ( $E_s^\circ$ ) can be defined as the potential for a half-cell in which the e<sup>-</sup> is a gas-phase electron.<sup>9</sup> For the NHE,  $E_s^\circ$  is estimated by summing the Gibbs energies of the following equations:<sup>9,10</sup>



- (5) Bard, A. J.; Parsons, R.; Jordan, J., Eds. *Standard Electrode Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.  
 (6) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G., Eds. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988.  
 (7) Trasatti, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 313.  
 (8) Using  $S^\circ(\text{H}^+) - S^\circ(1/2\text{H}_2) = (-22 - 65.2) = -87 \text{ J/(mol K)}$  and data in Table I.  
 (9) Parsons, R. In ref 5, Chapter 2.

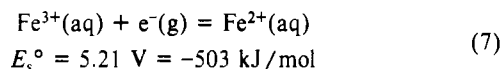
**Table I.** Single-Electrode Potential Data for Aqueous Half-Cells O + e<sup>-</sup> = R

| O/R <sup>a</sup>                     | V                      |             | kJ/mol             |                                    |                    |
|--------------------------------------|------------------------|-------------|--------------------|------------------------------------|--------------------|
|                                      | $E^\circ$ <sup>b</sup> | $E_s^\circ$ | $\Delta G_s^\circ$ | $298\Delta S_s^\circ$ <sup>c</sup> | $\Delta H_s^\circ$ |
| $\text{Fe}^{3+/2+}$                  | 0.77                   | 5.21        | -500               | 54                                 | -450               |
| $[\text{Fe}(\text{bpy})_3]^{3+/2+}$  | 1.12                   | 5.56        | -536               | 4                                  | -530               |
| $[\text{Fe}(\text{CN})_6]^{3-/4-}$   | 0.35                   | 4.79        | -460               | -52                                | -515               |
| $\text{Cp}_2\text{Fe}^{+0}$          | 0.37                   | 4.81        | -460               | -6                                 | -470               |
| $\text{Ru}^{3+/2+}$                  | 0.23                   | 4.67        | -450               | 45                                 | -410               |
| $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ | 0.070                  | 4.51        | -440               | 23                                 | -410               |
| $[\text{Ru}(\text{bpy})_3]^{3+/2+}$  | 1.29                   | 5.73        | -553               | 1                                  | -550               |
| $[\text{Ru}(\text{CN})_6]^{3-/4-}$   | 0.94                   | 5.38        | -520               |                                    |                    |
| $[\text{Ru}(\text{acac})_3]^{0/-}$   | -0.275                 | 4.16        | -401               |                                    |                    |
| $\text{Co}^{3+/2+}$                  | 1.88                   | 6.32        | -610               | ~75                                | -540               |
| $[\text{Co}(\text{en})_3]^{3+/2+}$   | -0.21                  | 4.23        | -410               | 46                                 | -460               |
| $[\text{Co}(\text{bpy})_3]^{3+/2+}$  | 0.31                   | 4.75        | -460               | 27                                 | -430               |

<sup>a</sup> Abbreviations: bpy, 2,2'-bipyridine; Cp, cyclopentadienyl; acac, acetylacetonate; en, ethylenediamine. <sup>b</sup> Values compiled from refs 12, 13, and 21–23. <sup>c</sup> Experimental values from refs 12 and 13.

The largest error in the value of  $E_s^\circ$  (NHE) estimated via this type of cycle arises from the single ion solvation free energy of the proton (eq 4), which cannot be measured directly. The value of  $\Delta G^\circ$  (eq 4) used here is derived from accurate electrochemical experiments but is based on a reference state for the electron in which the electron is near the surface of the liquid phase rather than at infinite separation.<sup>11</sup>

Since all standard electrode potentials are referenced to the NHE, the values of  $E_s^\circ$  for other half-cells can be obtained immediately. For example, the value for eq 7 is 5.21 V. Single-electrode potentials for other couples are given in Table I.



### Entropy Contributions to Electrode Potentials

It is of interest to consider the contribution of entropy changes to  $E^\circ$  and  $E_s^\circ$  values ( $E_s^\circ = -\Delta G_s^\circ/nF = (-\Delta H_s^\circ + T\Delta S_s^\circ)/nF$ ). The value of  $\Delta S^\circ$  for electrode processes can be estimated from the temperature dependence of the observed  $E_{1/2}$  for a couple.<sup>12,13</sup> The reader is referred to the literature for extensive discussion of the experimental procedures.<sup>12</sup> For the reduction of  $\text{Fe}^{3+}(\text{aq})$  to  $\text{Fe}^{2+}(\text{aq})$ , the estimated  $\Delta S^\circ = 180 \text{ J/(mol K)}$ ,<sup>13</sup> and the  $\Delta H_s^\circ$  for eq 7 is then estimated as  $-450 \text{ kJ/mol}$ . The strongly positive entropy change arises primarily from the much decreased solvent ordering tendency of the ferrous ion relative to the ferric ion.<sup>12,13</sup> In the absence of this entropy change involving the iron species, the  $E^\circ$  (vs NHE) for eq 1 would be much different (0.22 V). Experimental  $T\Delta S_s^\circ$  values at 298 K and estimated  $\Delta H_s^\circ$  values for electron attachment to transition-metal ions in solution are given in Table I. It is clear that entropy changes in these redox couples vary widely for different metal and ligand combinations, and observed electrode potentials can differ by several hundred millivolts from what would be found if  $\Delta S_s^\circ$  were zero for the examples given.

- (10) The free energy change for eq 3 can be calculated in the “ion convention”, which assumes that the free electron has no heat capacity and contributes no translational or electronic entropy to the products. Of course, this a convention rather than a statement of fact. However, an accurate calculation of the thermodynamic properties of an electron gas is not available, and treating the electron as an ideal gas (the “thermal electron convention”) is not universally meaningful under all conditions. It is important, however, that the chosen convention be used consistently when thermochemical data for electron attachment involving gas-phase and condensed-phase reactants are combined. In the case of free energies of electron attachment at 298 K, the difference between the two conventions happens to be negligible (<0.1 kJ/mol) (Sharpe, P.; Richardson, D. E. Submitted for publication), but a difference of 6.2 kJ/mol appears in enthalpies of formation.<sup>6</sup>  
 (11) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955.  
 (12) (a) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (b) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155.  
 (13) (a) Yee, E. L.; Weaver, M. J. *Inorg. Chem.* **1980**, *19*, 1077. (b) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1981**, *23*, 3639.

Table II. Selected Gas-Phase Electron Attachment Free Energies<sup>a</sup>

| O/R                                                          | $\Delta G_a^\circ$ ,<br>kJ/mol | method <sup>b</sup> | O/R                                     | $\Delta G_a^\circ$ ,<br>kJ/mol | method <sup>b</sup>  |
|--------------------------------------------------------------|--------------------------------|---------------------|-----------------------------------------|--------------------------------|----------------------|
| Fe <sup>3+/2+</sup>                                          | -2960                          | spec <sup>c</sup>   | [Ru(acac) <sub>3</sub> ] <sup>0/-</sup> | -163                           | FT-MS <sup>e</sup>   |
| Co <sup>3+/2+</sup>                                          | -3230                          | spec <sup>c</sup>   | [Co(acac) <sub>3</sub> ] <sup>0/-</sup> | -196                           | FT-MS <sup>e</sup>   |
| Ru <sup>3+/2+</sup>                                          | -2740                          | spec <sup>c</sup>   | Cp <sub>2</sub> Ni <sup>0/-</sup>       | -82                            | FT-MS <sup>e</sup>   |
| SO <sub>2</sub> <sup>0/-</sup>                               | -103                           | PE <sup>d</sup>     | Cp <sub>2</sub> Fe <sup>+0</sup>        | -646                           | FT-MS <sup>e,f</sup> |
| C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> <sup>0/-</sup> | -97                            | PHP-MS <sup>d</sup> | Cp <sub>2</sub> Ru <sup>+0</sup>        | -692                           | FT-MS <sup>e</sup>   |
| [Fe(acac) <sub>3</sub> ] <sup>0/-</sup>                      | -180                           | FT-MS <sup>e</sup>  |                                         |                                |                      |

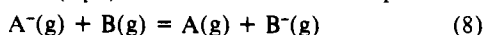
<sup>a</sup> For reactions O(g) + e<sup>-</sup>(g) = R(g) at 298 K. <sup>b</sup> Abbreviations: spec, spectroscopy and statistical mechanics (spin-orbit coupling ignored); PE, photoelectron spectroscopy and statistical mechanics; PHP-MS, pulsed high-pressure mass spectrometry; FT-MS, Fourier transform mass spectrometry. <sup>c</sup> Reference 24. <sup>d</sup> Reference 14a. <sup>e</sup> Reference 3. Note that these values assume negligible values for  $\Delta S_a$ , which is likely valid for all couples except Co(acac)<sub>3</sub><sup>0/-</sup>. <sup>f</sup> Reference 4 suggests a value of -670 kJ/mol for ferrocene by PHP-MS.

### Experimental Gas-Phase Electron Attachment Thermodynamics

Ionization potentials (IP) and electron affinities (EA) of molecules most generally refer to energies of the same type of process: the energy difference between a molecule (or ion) and the same molecule (or ion) with an electron removed to field-free space. Ionization is the successive removal of electrons beginning with the neutral molecule, while electron affinity refers to the attachment of an electron to a neutral species.<sup>6</sup> Both quantities refer to the energy change for the corresponding process at 0 K only, since by definition they do not include differences in heat capacities for the two molecular species involved. *Electron attachment* for a molecule (neutral or ion) refers to the gas-phase process M<sup>n</sup>(g) + e<sup>-</sup> = M<sup>n-1</sup>(g), where *n* is the molecular charge. The thermochemical quantities describing the thermodynamics of electron attachment at any temperature are given in this article by  $\Delta G_a^\circ$ ,  $\Delta H_a^\circ$ , and  $\Delta S_a^\circ$ . Given the international convention for writing electrode potential equations as electron attachments (eq 1, for example), electron attachment reactions will be used in referring to gas-phase processes involving a free electron for any charge *n* on the molecule and at any experimental temperature. This avoids the inconvenience and confusion of switching between the terms *ionization energy* and *electron affinity* depending on the charge of the reactant molecule and recognizes the temperature dependence of the thermodynamics of electron attachment.

In this section we will mention some experimental methods for determining  $\Delta X_a^\circ$  (*X* = *G*, *H*, and *S*) values for gas-phase molecules. Until relatively recently,  $\Delta X_a^\circ$  values for neutral and cationic species were scarce except for some of the elements in the atomic state. With modern instrumental methods, however, it has become possible to determine  $\Delta X_a^\circ$  values for many neutral molecules and monocations.<sup>4,6,14</sup> Most molecules studied have been benzene derivatives, quinones, and other aromatic species, but we and others have recently added a number of transition-metal coordination complexes to the growing list.<sup>3,4</sup> A few representative experimental  $\Delta G_a^\circ$  values are given in Table II.

Two mass spectrometric methods have been used to produce most of the known  $\Delta X_a^\circ$  (*X* = *G*, *H*, and *S*) values for neutral compounds: pulsed high-pressure mass spectrometry (PHP-MS)<sup>14</sup> and ion cyclotron resonance mass spectrometry (ICR-MS and, with Fourier transform methods, FTICR-MS).<sup>15,16</sup> To determine  $\Delta G_a^\circ$  values, two compounds (e.g., A and B) are introduced into the source (PHP-MS) or ion trap (ICR-MS) at known pressures and subjected to an electron beam. Following electron attachment to the neutral molecules, electron transfer occurs to produce a thermal equilibrium (eq 9). The establishment of equilibrium



$$K_{eq} = \exp(-\Delta G_{reacn}^\circ / RT) \quad (9)$$

(14) (a) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513. (b) Lias, S. G.; Jackson, J. A.; Argentar, H.; Liebmann, J. F. *J. Org. Chem.* **1985**, *50*, 333.

(15) Sharpe, P.; Richardson, D. E. *Coord. Chem. Rev.* **1989**, *93*, 59.

(16) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

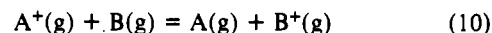
Table III. Estimated Solvation Free Energies for Transition-Metal-Complex Ions in Aqueous Solution

| ion                                                   | $\bar{A}$ |                  | $\Delta \Delta G_{solv}^\circ$ , kJ/mol <sup>a</sup> |
|-------------------------------------------------------|-----------|------------------|------------------------------------------------------|
|                                                       | $r_{max}$ | $r_{eff}$        |                                                      |
| [Ru(acac) <sub>3</sub> ] <sup>0/-</sup>               | 5.9       | 2.9 <sup>b</sup> | -240 ± 20 <sup>b</sup>                               |
| Cp <sub>2</sub> Fe <sup>+0</sup>                      | 3.8       | 3.8 <sup>b</sup> | 190 ± 20 <sup>b</sup>                                |
| [Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+/2+</sup> | 3.5       | 4.0 <sup>c</sup> | 860                                                  |
| [M(CN) <sub>6</sub> ] <sup>3-/4-</sup>                | 4.6       | 4.6              | -1040                                                |
| [M(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+/2+</sup>  | 3.4       | 4.0 <sup>c</sup> | 860                                                  |
| [M(bpy) <sub>3</sub> ] <sup>3+/2+</sup>               | 7.0       | 4.5 <sup>d</sup> | 760                                                  |

<sup>a</sup> Estimates using eq 12 and  $r_{eff}$  values except where noted. <sup>b</sup> Determined by the thermochemical cycle (see text). <sup>c</sup> Radius increased to account for dielectric saturation.<sup>19</sup> <sup>d</sup> Radius decreased to account for solvent interpenetration between chelate rings.<sup>19</sup>

in the source or ion trap can be followed, and a value of  $\Delta G_{reacn}^\circ$  for eq 8 can be extracted. Values of  $\Delta H_{reacn}^\circ$  and  $\Delta S_{reacn}^\circ$  are obtained from the temperature dependence of  $K_{eq}$ . If the absolute values of  $\Delta X_a^\circ$  are known for, e.g. B, then the values for A are readily obtained. The ladder of  $\Delta X_a^\circ$  values is typically anchored to a spectroscopically determined value for one molecule (e.g., SO<sub>2</sub><sup>0/-</sup>). Values of  $\Delta G_a^\circ$  determined by both PHP-MS and ICR-MS are generally in good agreement.

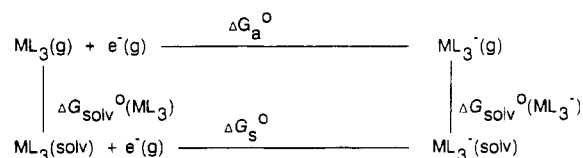
Electron attachment to monocations can also be studied by the above methods. In this case, one is determining the characteristics of equilibria such as eq 10. Again, if the value of the  $\Delta G_a^\circ$  for



B<sup>+</sup> is known, then the value for A<sup>+</sup> can be estimated if the reaction comes to measurable equilibrium in the source or trap. Values of  $\Delta G_a^\circ$  obtained in this way for ferrocenium and ruthenocenium ions are given in Table II.

### Solvation Free Energies

For cases where both gas-phase  $\Delta G_a^\circ$  and solution-phase  $\Delta G_s^\circ$  values are known, the *differential solvation free energy* for the oxidized and reduced species is readily estimated. For example, the couple ML<sub>3</sub>/ML<sub>3</sub><sup>-</sup> can be analyzed via the following cycle at 298 K:



From this cycle, the differential solvation enthalpy  $\Delta \Delta G_{solv}^\circ = \Delta G_{solv}^\circ(\text{ML}_3^-) - \Delta G_{solv}^\circ(\text{ML}_3) = \Delta G_s^\circ - \Delta G_a^\circ$ . Usually, if the reduction product, here ML<sub>3</sub><sup>-</sup>, has a greater charge than the oxidized form, the differential solvation free energy will be negative. If one of the component solvation free energies is known independently, the other is immediately obtained. Typical values of  $\Delta \Delta G_{solv}^\circ$  obtained via these types of cycles are given in Table III for Ru(acac)<sub>3</sub> and ferrocene.

Gas-phase  $\Delta G_a^\circ$  values are not available for highly charged transition-metal complexes. Therefore, to complete solvation energy cycles for such complexes, one must resort to estimation of the solvation free energies in order to estimate the gas-phase  $\Delta G_a^\circ$  value for the oxidized form. Many discussions concerning the estimation of solvation free energies for charged species have appeared.<sup>2f,17,18</sup> Most of the estimates are based on the Born equation (eq 11) and refer to the solvation of bare cations or small

$$\Delta G_{el} = -z^2 / 2r(1 - 1/\epsilon) \quad (11)$$

polyatomic anions (such as ClO<sub>4</sub><sup>-</sup>) that have ionic radii (*r*) of ~1–3 Å. From the Born equation, electrostatic solvation free energies are derived for a conducting sphere of radius *r* and charge *z* in a dielectric continuum with dielectric constant  $\epsilon$ . This equation occasionally has been misinterpreted in the literature as predicting

(17) Noyes, R. *J. Am. Chem. Soc.* **1962**, *84*, 513.

(18) Millen, W. A.; Watts, D. W. *J. Am. Chem. Soc.* **1967**, *89*, 6051 and references therein.

$\Delta G_{\text{solv}}$  values, e.g., for the process  $A^+(g) = A^+(\text{soln})$ . The proper definition for  $\Delta G_{\text{el}}$  is the electrostatic free energy change when a charge from a conducting sphere in a vacuum is transferred to a sphere of equal radius in the dielectric medium. Thus, for example, for couples of the type  $ML_x^{0/-}$ ,  $\Delta\Delta G_{\text{solv}}$  as defined above is approximately equal to  $\Delta G_{\text{el}}$ , since the effective radii of  $ML_x$  and  $ML_x^-$  are not too different. For water at 298 K, eq 11 yields eq 12. In eq 12,  $r_{\text{eff}}$  is the "effective" radius of the ion in angstroms

$$\Delta G_{\text{el}}^\circ = -686z^2/r_{\text{eff}} \quad (12)$$

that reproduces the experimentally derived value for  $\Delta G_{\text{el}}^\circ$ .

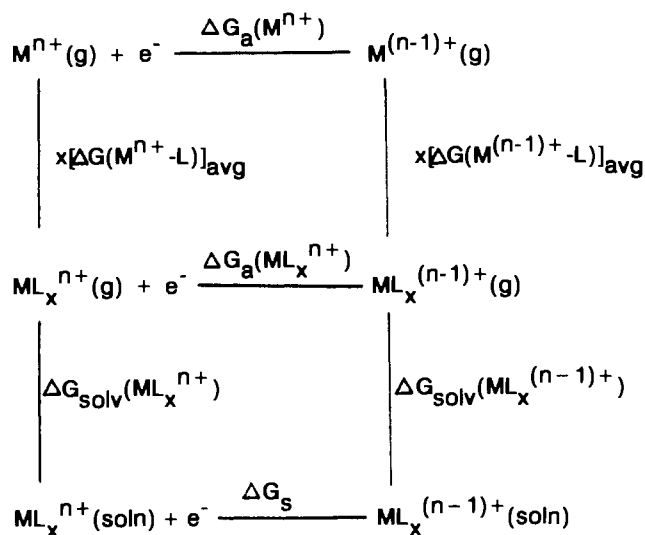
We are particularly interested in the solvation free energies for metal complexes where the solvent does not enter the inner coordination sphere of the metal. In other words, we must estimate the  $\Delta\Delta G_{\text{solv}}^\circ$  values for a metal ion with its inner coordination sphere filled with ligands. It is interesting to compare experimentally derived  $\Delta\Delta G_{\text{solv}}^\circ$  values to those predicted by the Born equation for metal complexes.  $Ru(\text{acac})_3^{0/-}$  is suitable for this analysis since the electrochemical behavior of this complex is reversible (Table I).  $E_s^\circ$  is given by  $4.44 - 0.27 = 4.17 \text{ eV} = -400 \text{ kJ/mol}$ . The FTICR-MS method predicts a  $\Delta G_a^\circ$  value for  $Ru(\text{acac})_3(g)$  of  $-160 \pm 10 \text{ kJ/mol}^3$  near room temperature. The differential solvation free energy  $\Delta\Delta G_{\text{solv}}^\circ$  is given by  $\Delta G_s^\circ - \Delta G_a^\circ = -240 \pm 20 \text{ kJ/mol}$ . From eq 12, the "thermochemical" radius  $r_{\text{eff}}$  of  $Ru(\text{acac})_3^-$  based on the estimated free energy of solvation is  $\sim 2.9 \text{ \AA}$ , while the maximum radius from crystal structures ( $M$ -methyl H) is  $\sim 6 \text{ \AA}$ . For the acac complexes, the smaller thermochemical radius compared to the crystallographic radius suggests significant solvent interpenetration between the essentially planar ligands and/or other specific interactions between the solvent and complex.

By use of a procedure similar to that above, the  $\Delta\Delta G_{\text{solv}}^\circ$  value for  $Cp_2Fe^{+/0}$  is estimated as  $190 \pm 20 \text{ kJ/mol}$ , which is quite close to the value predicted by eq 12 for this roughly spherical ion with an average radius of  $\sim 3.8 \text{ \AA}$ . That the Born equation works well for ferrocene/ferrocenium is not too surprising, given the lack of strong specific interaction of the Cp rings with solvent and the compact structure of metallocenes. The characteristics of a Born charged sphere are evidently closely approximated by the metallocenium ions.<sup>3b</sup>

Data obtained for mixed-valence complexes and ion pairs can be used to estimate  $r_{\text{eff}}$  values for highly charged complexes. Theoretical models used to fit solvation energetics to observed intervalence-transfer band energies are commonly based on the dielectric continuum model for the solvent.<sup>19</sup> To obtain satisfactory fits to the experimental energies for some complexes, the effective radii of the complexes must be adjusted to account for effects such as solvent interpenetration between planar ligands (for 2,2'-bipyridine complexes) or dielectric saturation due to specific interactions between the inner coordination sphere and the first solvation sphere.<sup>19</sup> For complexes with small ligands such as  $NH_3$ ,  $H_2O$ , and  $CN^-$ , the crystallographic radius would at first appear to give a reasonable estimate for use with eq 12, but H-bonding between ligands and solvating molecules can lead to dielectric saturation and thus a somewhat larger effective radius (fits of intervalence bands suggest that the corrections are particularly necessary for aquo and ammine complexes<sup>19</sup>). With the use of eq 12 and the suggested  $r_{\text{eff}}$  values from the mixed-valence model studies, estimates for  $\Delta\Delta G_{\text{solv}}^\circ$  for several metal complexes are collected in Table III. In comparison to the experimentally derived values discussed earlier, these values should be regarded only as very crude estimates for the semiquantitative discussion that follows.

### Illustrating Bonding and Solvation Contributions to Electrode Potentials of Transition-Metal Complexes

With the data collected in Tables I–III, we can now consider energy cycles of the type illustrated in the traditional manner in Figure 1. Experimental values and semiempirical estimates for the various components of the cycles shown are available to show



**Figure 1.** Traditional energy cycle for thermochemistry of metal ions and their complexes in the gas phase and solution. Symbols are defined in the text. If the ligand has a  $-1$  charge, the charges on the complexes are  $(n-x)^+$  and  $(n-1-x)^+$ .

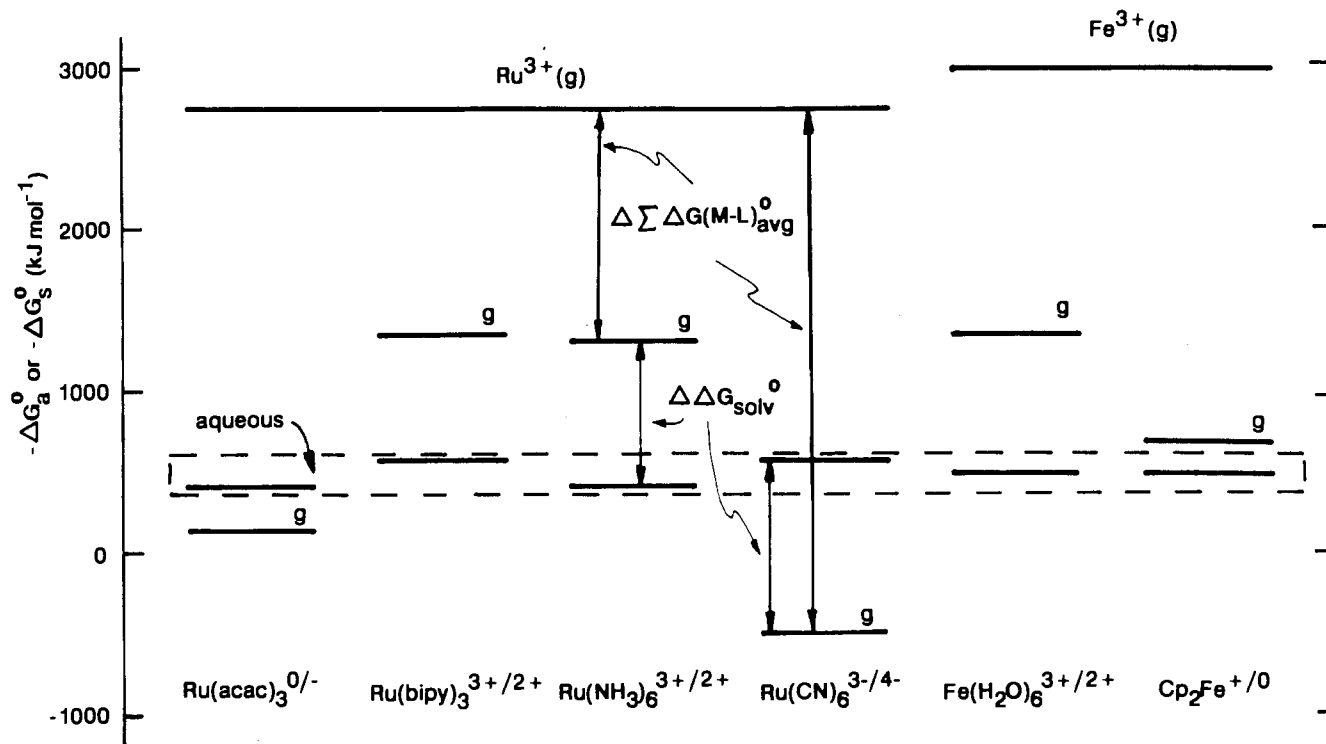
how complexation of a gas-phase free metal ion changes the electron attachment energy. Further, the role of the differential solvation energy in determination of the aqueous electrode potential (related by  $\Delta G_s^\circ$ ) is deduced. By a comparison of Tables I and II, it is seen that in general  $-\Delta G_a^\circ(M^{n+}(g)) > -\Delta G_a^\circ([ML_x]^{n+}(g))$ , since any ligand will stabilize the higher charged metal ion relative to the lower. This is equivalent to saying that the bond free energy,  $-\Delta G(M-L)^\circ$ , is always larger for the metal in the higher oxidation state. The relative values of  $\Delta G_s^\circ$  and  $\Delta G_a^\circ([ML_x]^{n+}(g))$  will depend on whether the value of  $\Delta\Delta G_{\text{solv}}$  is positive or negative (Table III).

A more striking illustration of the separate roles of complexation and solvation in determination of  $\Delta G_s^\circ$  (and therefore  $E^\circ$ ) for these types of couples is shown in Figure 2. Here the  $\Delta G_a^\circ$  values for free metal ions and gas-phase complexes are plotted on the same scale as  $\Delta G_s^\circ$  values for the solvated complexes (taken from Table I). The difference between the  $\Delta G_a^\circ$  values for a metal ion and a given complex of that ion ( $\Delta\sum\Delta G(M-L)$  in Figure 2) is a measure of the relative stabilization of the two oxidation states by complexation. The difference between the  $-\Delta G_a^\circ$  value and  $-\Delta G_s^\circ$  for a given complex is the differential solvation free energy,  $\Delta\Delta G_{\text{solv}}^\circ$ , which reflects the relative free energies of solvation for the two oxidation states.

Several interesting points concerning the nature of redox potentials for soluble transition-metal-complex couples can be made on the basis of diagrams such as Figure 2. First, it is impressive how much complexation and solvation reduce the electron attachment energy values from those of free ions, and it is clear that both effects are substantial. A second observation concerns how the nature of the ligands affects the gas-phase  $\Delta G_a^\circ$  values for metal complexes. The cationic complexes of small ligands such as  $NH_3$  and  $H_2O$  are estimated to have strongly negative  $\Delta G_a^\circ$  values, although the bipyridine complexes are roughly comparable (the differential solvation free energies of bpy and ammine complexes are much closer than expected on the basis of maximum radii as a result of the dielectric saturation and solvent interpenetration effects). When the ligands are anionic, the attenuation of  $-\Delta G_a^\circ$  is quite large (e.g., for  $Ru^{3+}$  to  $[Ru(\text{acac})_3]$  to  $[Ru(\text{CN})_6]^{3-}$ ), and this effect results from an increasing difference in the average heterolytic bond energies between the two oxidation states for the complexes with anionic ligands. When the complex is overall negative, as in the case of  $[M(\text{CN})_6]^{3-}$ , gas-phase electron attachment is expected to be highly endothermic in the cases shown (some anionic molecules such as  $CrF_6^-$  may have positive EA values, however<sup>20</sup>). Finally, solvation leads to a substantial

(19) Brunschwig, B.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.

(20) Sakai, Y.; Miyoshi, E. *J. Chem. Phys.* **1987**, *87*, 2885.



**Figure 2.** Diagram illustrating electron attachment free energies and single-electrode free energies on one graph. The lines at the top are the  $-\Delta G_a^0$  values for  $Ru^{3+}$  and  $Fe^{3+}$  ions. The horizontal lines indicate the values of the aqueous  $-\Delta G_s^0$  values (in the dashed box) and the estimated or experimental (for  $Ru(acac)_3^{0/-}$  and  $Cp_2Fe^{+/0}$ ) gas-phase  $-\Delta G_a^0$  values, indicated by "g", for the complexes shown at the bottom.  $\Delta \Sigma \Delta G(M-L)^0$  is the difference in the sum of the average heterolytic bond free energies for the  $M(3+)$  and  $M(2+)$  complexes, while  $\Delta \Delta G_{solv}^0$  is the differential solvation free energy for the oxidized and reduced complexes. These two quantities are indicated for the  $[Ru(NH_3)_6]^{3+/2+}$  and  $[Ru(CN)_6]^{3-/4-}$  couples.

reorganization of the electron attachment free energies for the complexes when going from gas phase to solution. Small, highly charged cationic complexes such as  $[Ru(NH_3)_6]^{3+/2+}$  have relatively large values of  $\Delta \Delta G_{solv}^0$  because of the  $z^2/r$  dependence of solvation energy. Larger ligands attenuate the  $\Delta \Delta G_{solv}^0$  value because of larger  $r$  values, but this attenuation is not as great as might be expected because of solvent penetration between larger ligands such as bipyridine.

It is clear from Figure 2 that *gas-phase electron attachment free energy values for complexes show substantial variations for differently sized and charged ligands, but the electrode potentials (as measured by  $-\Delta G_s^0$ ) are remarkably close to one another when viewed on a common energy scale with gas-phase  $\Delta G_a^0$  values.* Thus, the complexation and solvation phenomena total to be energetically roughly constant (i.e.,  $\Delta \Delta G_{solv}^0 + \Delta \Sigma \Delta G(M-L)^0 \approx \text{constant}$ ), and most single-electrode potentials for common transition-metal couples of the  $M(III)/M(II)$  type considered here are as a result around 3–6 V (or, on the NHE scale, about  $0 \pm 1.5$  V). In contrast, from Figure 2 the gas-phase  $\Delta G_a^0$  values for such complexes will cover a range of  $\sim 20$  V.

In closing this discussion, it is worth issuing a warning concerning the overinterpretation of relative electrode potential values for metal complexes. As demonstrated above, the ultimate value of  $E^0$  is determined by entropy, bonding, and solvation considerations, and it is important not to interpret a change in  $E^0$  when ligands are altered entirely in terms of bonding effects. A good example is the case of  $[Ru(NH_3)_6]^{3+/2+}$  and  $[Ru(bpy)_3]^{3+/2+}$ . In solution, the bpy complex is the stronger oxidizing agent by  $>1$  V. This might be interpreted as arising from  $\pi$ -back-bonding from Ru(II) to the  $\pi^*$  levels of bipyridine, which stabilizes the Ru(II) state relative to Ru(III) in the bpy complex. Note, however, in Figure 2 that the  $\Delta G_a^0$  of  $[Ru(NH_3)_6]^{3+}(g)$  is estimated to be

roughly equivalent to that of  $[Ru(bpy)_3]^{3+}(g)$ . In the absence of back-bonding, the bipyridine complex would be an even weaker gas-phase oxidant, possibly even inverting the solution order for the two complexes. Therefore, the relative  $E^0$  values of those two complexes arise not only from electronic structural factors, which clearly include  $\pi$ -bonding, but also from the solvation effects and entropic differences (Table I). Such considerations become even more dramatic when comparing couples of different charge type, where  $\Delta \Delta G_{solv}^0$  values can be vastly different (e.g.,  $[Ru(NH_3)_6]^{3+/2+}$  vs  $[Ru(CN)_6]^{3-/4-}$ ). Thus the effect of altering the ligand environment of a metal on the electrode potential should not be attributed to bonding effects alone unless entropic and solvation contributions are understood.

The overall importance of considering complexation and solvation separately can be readily appreciated from the type of plot shown in Figure 2. This approach to electrode potentials can clearly be extended to many other similar cases involving both main-group and transition elements, especially as gas-phase electron attachment data become more widely available.

**Acknowledgment.** Research in the area of gas-phase thermochemistry of metal compounds and ions is supported in the author's laboratories by the National Science Foundation (Grant CHE 8700765). Support for early work at the University of Florida was also provided by the Research Corp., the University of Florida, and the donors of Petroleum Research Fund, administered by the American Chemical Society. I wish to thank these agencies and am grateful for helpful discussions with N. Sutin, P. Sharpe, C. Christ, M. Ryan, and J. Eyler.

**Registry No.** Fe, 7439-89-6;  $[Fe(bpy)_3]^{3+}$ , 18661-69-3;  $[Fe(bpy)_3]^{2+}$ , 15025-74-8;  $[Fe(CN)_6]^{3-}$ , 13408-62-3;  $[Fe(CN)_6]^{4-}$ , 13408-63-4;  $Cp_2Fe$ , 102-54-5;  $Cp_2Fe^+$ , 12125-80-3; Ru, 7440-18-8;  $[Ru(NH_3)_6]^{3+}$ , 18943-33-4;  $[Ru(NH_3)_6]^{2+}$ , 19052-44-9;  $[Ru(bpy)_3]^{3+}$ , 18955-01-6;  $[Ru(bpy)_3]^{2+}$ , 15158-62-0;  $[Ru(CN)_6]^{3-}$ , 54692-27-2;  $[Ru(CN)_6]^{4-}$ , 21029-33-4;  $[Ru(acac)_3]$ , 14284-93-6;  $[Ru(acac)_3]^-$ , 66560-52-9; Co, 7440-48-4;  $[Co(en)_3]^{3+}$ , 14878-41-2;  $[Co(en)_3]^{2+}$ , 23523-25-3;  $[Co(bpy)_3]^{3+}$ , 19052-39-2;  $[Co(bpy)_3]^{2+}$ , 15878-95-2;  $SO_2$ , 7446-09-5;  $SO_2^-$ , 12143-17-8;  $C_6H_5NO_2$ , 98-95-3;  $C_6H_5NO_2^-$ , 12169-65-2;  $[Fe(acac)_3]$ , 14024-18-1;  $[Fe(acac)_3]^-$ , 21534-23-6;  $[Co(acac)_3]$ , 21679-46-9;  $[Co(acac)_3]^-$ , 47177-25-3;  $Cp_2Ni$ , 1271-28-9;  $Cp_2Ni^+$ , 64658-53-3;  $Cp_2Ru^+$ , 54538-51-1;  $Cp_2Ru$ , 1287-13-4.

- (21) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.
- (22) Endo, A.; Watanabe, M.; Hayashi, S.; Shimizu, K.; Sato, G. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 800.
- (23) Gritzner, G.; Murauer, H.; Gutman, V. J. *Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 177.
- (24) Moore, C. E. National Standard Reference Data Series 34; U.S. Government Printing Office: Washington, DC, 1970.