

CHAPTER V

THERMODYNAMICS OF ELECTRODE POTENTIAL

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Abstract: Various thermodynamic quantities such as, metal ionization potential, metal-ligand complexation energy and solvation energy, controlling the trends of E_{298}° values of metal-centered electron transfer reactions are considered in this chapter. An attempt is made to assess the relative importance of spherical and non-spherical parts of the crystal fields. Among complexes of the same metal ion, it is possible to express the shift of E_{298}° in terms of the crystal field splitting parameter. The shift of E_{298}° between iron and cobalt couples is controlled by metal ionization potential and nearly equally important spherical and non-spherical crystal field contributions. The energy of the ligand field band in copper(II) complexes linearly correlates with E_{298}° .

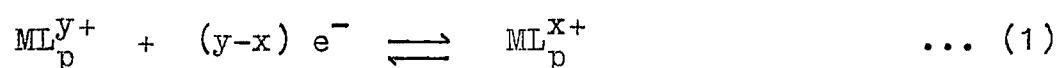
V.1 INTRODUCTION

In preceding chapters (II-IV), we have considered the sensitivity of the metal-centered redox potentials to subtle variations in the triazene 1-oxide ligand substituents, for pure as well as mixed ligand complexes of iron(III), cobalt(III) and copper(II). To gain further insight, the various thermodynamic quantities such as, metal ionization potential, metal-ligand complexation energy and solvation energy, controlling the trends of E_{298}^0 values of metal-centered electron transfer reactions are considered in this chapter. By systematically changing the complex and solvent such quantities can be ascertained at least in principle¹⁻⁵. A particular attempt is made to assess the crystal field contributions.

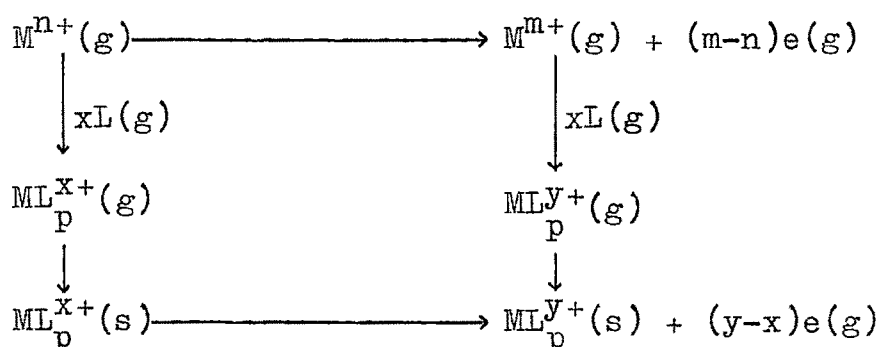
V.2 RESULTS AND DISCUSSION

A. General Considerations

The redox half cell (1) corresponds to the



Born-Haber Cycle³



where $(m-n) = (y-x)$

A similar cycle can be written for the reference half cell. The free energy change (ΔG°) for the reaction (2) (T = triazene 1-oxide) is of interest to us.



This free energy change can be written according to the cycle mentioned above as

$$-\Delta G^{\circ} = FE^{\circ} = I_p - \Delta G_F^{\circ} - \Delta G_S^{\circ} + C \quad \dots (3)$$

where I_p is the p-th ionization potential of M, ΔG_F° is the difference between the free energies of formation of $\text{MT}_p^-(g)$ and $\text{MT}_p(g)$ [in the sense, $\{\text{MT}_p^-(g) - \text{MT}_p(g)\}$], ΔG_S° is the difference between the solvational free energies of $\text{MT}_p^-(g)$ and $\text{MT}_p(g)$ and C is a constant contributed by the reference half cell. Our interest lies in the variation of E_{298}° , in going from one couple to another. In the most general case where metal, ligand and solvent varies, we have from eq (3)

$$F \Delta E^{\circ} = \Delta I_p - \Delta (\Delta G_F^{\circ}) - \Delta (\Delta G_S^{\circ}) \quad \dots (4)$$

B. Crystal Field Effects

A particularly simple situation arises if the comparison is limited among a series of complexes of the same metal ion with varying X (substituents) in a given solvent. Here we have, $\Delta I_p = 0$ and

$$\Delta (\Delta G_S^{\circ}) \sim 0 \quad \dots (5)$$

Again,

$$\Delta G_F^{\circ} = \Delta H_F^{\circ} - T \Delta S_F^{\circ} \quad \dots (6)$$

where H_f^0 and S_f^0 are symbols for enthalpy and entropy respectively. The entropy term is the sum⁵ of a solvent reorganization entropy, ΔS_s^0 and an internal reorganization entropy, ΔS_i^0 , i.e.,

$$\Delta S_f^0 = \Delta S_s^0 - \Delta S_i^0 \quad \dots (7)$$

Many of the complexes considered by us are nearly reversible, indicating that ligand rearrangements, if any, are of marginal nature. Hence, ΔS_i^0 term is likely to be small. The ΔS_s^0 term is also believed to be small. In our complexes which have bulky ligands the net charge in the electrode reaction is $0 \rightarrow -1$. Model calculations⁶⁻⁸ yield small values of S_s^0 in such a case. Thus we write

$$T \Delta (\Delta S_f^0) \sim 0 \quad \dots (8)$$

Eq (4) then becomes

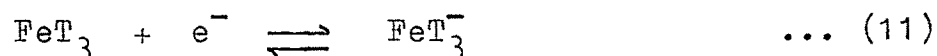
$$F \Delta E^0 = - \Delta (\Delta H_f^0) \quad \dots (9)$$

In eq (9), the variation in each quantity is measured in the sense $\{ (X=X) - (X=H) \}$. The difference between the heats of the complex formation for the two ions, $\Delta (\Delta H_f^0)$ can be further split into two terms, the ligand field stabilization energy difference $\Delta (\Delta H_{LF}^0)$ and $\Delta (\Delta H_f^{0'})$, the enthalpy change if no ligand field effect is present, i.e., the spherical part of the crystal field⁹. We thus have

$$\Delta (\Delta H_f^0) = \Delta (\Delta H_{LF}^0) + \Delta (\Delta H_f^{0'}) \quad \dots (10)$$

C. The Case of FeT₃

The redox couple is



Here, the iron(III) species is high-spin¹⁰. The ligand field strength of the triazene 1-oxides¹¹ is close to that of water. The aquo complex of iron(II) is high-spin⁴, so it is reasonable to assume that the iron(II) species in the FeT₃⁻ is also high-spin. So, here both the iron(III) and iron(II) species are high-spin and consequently³

$$\Delta H_{LF}^0 = -4 Dq^{II} - 0 = -4 Dq^{II} \quad \dots (12)$$

where Dq^{II} refers to the iron(II) state.

From eq(9) and (10) we have

$$F \Delta E^0 = 4 \Delta Dq^{II} - \Delta (\Delta H_f^{0'}) \quad \dots (13)$$

The value of $\Delta (\Delta H_f^{0'})$ is not readily ascertained. We may, however, proceed in the following manner within the frame work of the ionic crystal field model. We try to express $\Delta (\Delta H_f^{0'})$ in terms of ΔDq^{II} .

The potential (V_t) in an octahedral complex can be written as¹²

$$V_t = V_s + V_o \quad \dots (14)$$

where V_s and V_o are respectively the spherical and octahedral components. In the ionic model, the matrix elements of V_s and V_o are respectively proportional to¹²

$$ce/a$$

and

$$ce(\bar{r}^4/a^5)$$

the latter quantity being proportional to Dq . In the above expressions c is the charge on each ligand, a is the metal-ligand distance and \bar{r}^4 is the mean fourth power radius of the metal ion. In the situation where the metal ion radius and the metal-ligand distance remain invariant, it is readily seen that the matrix elements of both V_s and V_o are proportional to Dq . We assume that in the case where only a remote substituent (X) varies, these conditions (invariant a and \bar{r}^4) are fulfilled. We then write

$$\begin{aligned} \Delta H_f^{0'} &= [\text{II}] - [\text{III}] \\ &= k_{\text{II}} Dq^{\text{II}} - k_{\text{III}} Dq^{\text{III}} \quad \dots (15) \end{aligned}$$

where $[\text{II}]$ and $[\text{III}]$ are the heats of formation of FeT_3^- and FeT_3 respectively (vide eq (3)) and k_{II} and k_{III} are proportionality constants. In a closely related group of complexes, it would be appropriate to assume that Dq^{II} is a constant fraction of Dq^{III} .

We thus have the useful result

$$\Delta H_f^{O'} = k Dq^{II} \quad \dots (16)$$

whence

$$\Delta (\Delta H_f^{O'}) = k \Delta Dq^{II} \quad \dots (17)$$

where k is a proportionality constant.

Combining eq (13) and (17) we now write

$$\begin{aligned} F \Delta E^O &= 4 \Delta Dq^{II} - k \Delta Dq^{II} \\ &= (4-k) \Delta Dq^{II} \quad \dots (18) \end{aligned}$$

or equivalently,

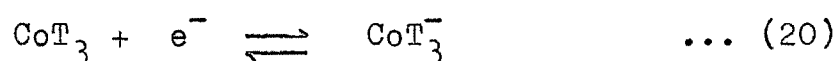
$$F \Delta E^O = \{(4-k)/k\} \{ \Delta (\Delta H_f^{O'}) \} \quad \dots (19)$$

Since $(\Delta H_f^{O'}) \gg Dq$, we have, $\Delta (\Delta H_f^{O'}) \gg (\Delta Dq)$. The observed sign of ΔE_{298}^O is systematically negative (Chapter II). Hence, the spherical contribution is dominant. There have been some recent discussions^{4,5} regarding the relative importance of ligand field and spherical contributions to ΔE^O . The present analysis though admittedly oversimplified, brings out an important point at least for high spin iron couples. For a group of closely related ligands differing only in substituents, Dq and hence the position of ligand field bands need not necessarily vary much, even when E^O is found to change significantly [Eq (18); small ΔDq but large k]. On the other hand,

if Δ, Dq is large enough to be conveniently measurable from ligand field spectra, a correlation between E^0 and Dq should obtain.

D. The Case of CoT_3

In the case of cobalt, the electrode reaction is



Here CoT_3 is low-spin¹³ and CoT_3^- like cobalt(II) complexes⁴ of ammonia, ethylenediamine, ethylenediamine tetraacetate ion, 1,10-phenanthroline and water is believed to be high-spin. Hence, we write⁴

$$\Delta H_{LF}^0 = -7 Dq^{II} - (-24 Dq^{III} + 2P) \quad \dots (21)$$

whence

$$\Delta (\Delta H_{LF}^0) = 24 (\Delta Dq^{III}) - 7(\Delta Dq^{II}) \quad \dots (22)$$

where P is the pairing energy in cobalt(III) (assumed to remain constant in going from one complex to another). Assuming that $Dq^{III} \sim 2Dq^{II}$, a treatment similar to the case of iron can follow. The important difference is that, here both the spherical and nonspherical terms act together to make ΔE^0 negative.

E. Potential Shift between Cobalt and Iron

In order to compare a cobalt couple with an iron couple under conditions of invariant ligand stereochemistry and solvent, we have from eq (4)-(6)

$$F \Delta E^{\circ} = \Delta I_3 - \Delta (\Delta H_f^{\circ}) \quad \dots (23)$$

Here, the variation in each quantity corresponds to {(iron)-(cobalt)}. The eq (23) should apply for comparison of one cobalt-iron pair with another, even when different pairs are studied in different solvents. The experimental ΔE_{298}° values and corresponding $\Delta(\Delta H_f^{\circ})$ values calculated with the help of eq (23) for selected couples^{4,14} are in Table V.1. In each case, the cobalt(III) complex is low-spin while cobalt(II), iron(III) and iron(II) complexes are high-spin. All ΔE_{298}° values are negative, showing that ΔI_p is controlling. Barring the case of the aquo complex, the variation in ΔE_{298}° values and hence $\Delta(\Delta H_f^{\circ})$ values are relatively small. For a more closely related group of ligands, one may expect ΔE_{298}° to remain virtually constant. This happens, for example, in the FeT_3-CoT_3 pairs with variable X. The ρ values of iron and cobalt lines (R=Et) are virtually equal ($0.16 \pm 0.01V$) (Chapter II, Table II.8).

Table V.1^a

Comparison of Iron and Cobalt Couples

Ligand ^b	Solvent	ΔE_{298}°	$\Delta(\Delta H_f^{\circ})$	$\Delta(\Delta H_{LF}^{\circ})$	$\Delta(\Delta H_f^{\circ'})$
H ₂ O	H ₂ O	-1.04 ^c	-42.0	-22.3	-19.7
C ₂ O ₄ ²⁻	H ₂ O	-0.58 ^c	-52.6	-20.8	-31.8
edta ⁴⁻	H ₂ O	-0.48 ^c	-55.9	-29.9	-26.0
acac ⁻	acetone	-0.33 ^d	-58.4	-22.3	-36.1
T ⁻	acetonitrile	-0.19 ^e	-61.6	-22.3	-39.3

^a Meaning of symbols are as in text; units are E_{298}°, V ;

$\Delta(\Delta H_f^{\circ}), \text{kcal/mol.}$

^b edta⁴⁻ = ethylenediamine tetraacetate anion, acac⁻ = acetylacetonate anion, T⁻ = 1-ethyl-3-phenyltriazene 1-oxide anion.

^c value from : reference (4)

^d value from : reference (14)

^e This work.

Using eq (10), (12) and (21), values of $\Delta(\Delta H_{LF}^O)$ can be computed using experimental Dq values (Table V.1). The value of $\Delta(\Delta H_f^O)$ were then calculated from eq (10) since $\Delta(\Delta H_f^O)$ is known (vide supra). The pairing energy⁴ P for cobalt(III) is 48.0 kcal. The Dq values⁴ in kK of H₂O, C₂O₄²⁻ and edta⁴⁻ used for the calculation of $\Delta(\Delta H_{LF}^O)$ are given below

Ligand	high-spin iron(II)	low-spin cobalt(III)	high-spin cobalt(II)
H ₂ O	10.4	18.2	9.3
C ₂ O ₄ ²⁻	10.0	18.0	9.1
edta ⁴⁻	9.7	19.7	10.2

Acetylaceton¹⁵ and triazene 1-oxide¹¹ were taken to have the same Dq as that of water. The value of ΔI_3 is -66 kcal³. The entries in the last two columns of Table V.1 are meant to be only rough estimates. The results, however, clearly bring out the interesting qualitative trend that spherical and non-spherical enthalpy contributions are nearly equally important in deciding ΔE_{298}^O values in cobalt-iron pairs.

F. Spectral Correlations in Copper Complexes

Since the CuT_2 complexes are planar, more than one ligand field integral is needed to describe the splitting⁹. It is, however, clear that the gross situation will remain qualitatively similar to the iron and cobalt cases. One may expect, ΔE^0 to be roughly proportional to both ligand field splitting and $\Delta(\Delta H_f^0)$. The ligand field band maxima (λ_{max}) of the CuT_2 species taken in BZ as well as in DMF shows significant shifts on changing X (Chapter III). The electronic spectral data are in Table III.5 (Chapter III). A linear correlation exists between E_{298}^0 and ν_{max} (Fig. V.1). Such correlations were occasionally observed¹⁶⁻¹⁸. The serial number of the complexes are those in Chapter III. Considering the approximation in the model discussed in this chapter and the relative broadness of the band, the observed $E_{298}^0 - \nu_{\text{max}}$ correlation can be considered as satisfactorily linear.

G. Conclusions

1. The various thermodynamic quantities controlling the trends of E_{298}^0 values of metal-centered electron transfer reactions are considered.
2. A particular attempt is made to assess the crystal field contributions.

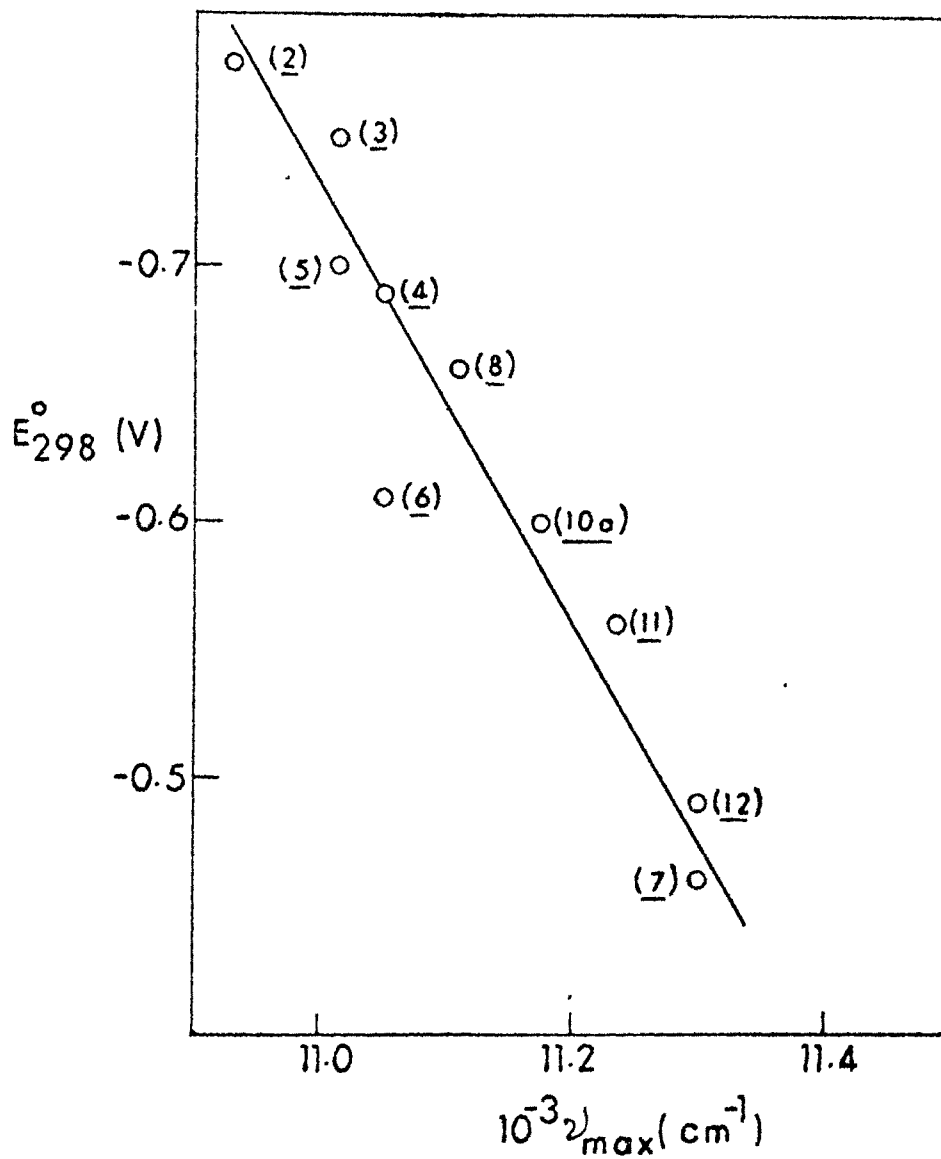


FIG. VI. LINEAR LEAST SQUARE FIT OF E_{298}° VERSUS ν_{\max} (BAND MAXIMUM) FOR CuT_2

3. Among complexes of the same metal ion, the shift of E_{298}^0 is possible to express in terms of the crystal field splitting parameter.
4. The shift of E_{298}^0 between iron and cobalt couples is controlled by metal ionization potential and nearly equally important spherical and nonspherical crystal field contributions.
5. The energy of the ligand field band in copper(II) complexes linearly correlates with E_{298}^0 .

V.3 EXPERIMENTAL SECTION

The preparation of ligands and complexes, electrochemical and electronic spectral measurements are described in Chapters - II and III.

REFERENCES

1. P. George and D.S. McClure, *Prog. Inorg. Chem.*, 1, 381 (1959).
2. A.A. Vlček, *ibid.*, 5, 211 (1963).
3. D.A. Buckingham and A.M. Sargeson in "Chelating Agents and Metal Chelates", F.P. Dwyer and D.P. Mellor, Eds., Academic Press: New York, 1964, pp.237-82.
4. P.A. Rock, *Inorg. Chem.*, 7, 837 (1968).
5. R.L. Lintvedt and D.E. Fenton, *Inorg. Chem.*, 19, 569 (1980).
6. K.J. Laidler, *Can. J. Chem.*, 34, 1107 (1956); R. M. Noyes, *J. Am. Chem. Soc.*, 84, 513 (1962).
7. G.I.H. Hanania, D.H. Irvine, W.A. Eaton and P. George, *J. Phys. Chem.*, 71, 2022 (1967).
8. E.L. Yee, R.J. Cave, K.L. Guyer, P.D. Tyma and M.J. Weaver, *J. Am. Chem. Soc.*, 101, 1131 (1979).
9. C.J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill Book Company, INC., 1962.
10. B. Behera, *Ind. J. Chem.*, 10, 555 (1972).
11. B. Behera and A. Chakravorty, *J. Inorg. Nucl. Chem.*, 31, 1791 (1969).

12. M. Gerloch and R.C. Slade, "Ligand Field Parameters", Cambridge University Press, 1973.
13. A. Chakravorty, B. Behera and P.S. Zacharias, *Inorg. Chim. Acta*, 2, 85 (1968).
14. A.M. Bond, R.L. Martin and A.F. Masters, *Inorg. Chem.*, 14, 1432 (1975).
15. Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, 29, 311 (1956).
16. A.A. Vlček, *Disc. Faraday Soc.*, 26, 164 (1958).
17. A.A. Vlček, *Electrochimica Acta*, 13, 1063 (1968).
18. J.A. Streeky, D.G. Pillsbury and D.H. Busch, *Inorg. Chem.*, 19, 3148 (1980).