

Marcus (86), Hush (87), and Henry & Slichter (83) to include the effect of pressure (88):

$$E_{th} = h\nu_{\max} - \frac{1}{16 \ln 2} \frac{(\Delta\nu_{1/2})^2}{kT} \left(\frac{\omega'}{\omega} \right)^2 \quad 2.$$

Here E_{th} is the difference in thermal energy of the two states, $\nu_{\max}$ the optical absorption frequency, $\Delta\nu_{1/2}$ the peak half-width, and ω and ω' the force constants for the ground and excited state potential wells. The relationship assumes a Gaussian shape for the optical absorption peak. Using experimental data for the $\pi \rightarrow \pi^*$ transition in phenanthroline complexes one obtains the results of the Table 1, assuming $\omega' \simeq \omega$. The calculation is approximate, but the change of sign for E_{th} occurs in the pressure region where the low spin to high spin transition initiates, and thus where significant thermal occupation of the π^* orbital would be expected.

An analogous calculation applies to the reduction process. For the acetyl-acetonates, the charge transfer peaks observed in the spectrum are definitely not assigned to the ligand to metal $\pi \rightarrow t_{2g}$ transition responsible for the reduction. A series of compounds where the charge transfer peak may have such an assignment are the ferric hydroxamates: tris(acetohydroxamato) iron(III)(AHA); tris(benzohydroxamato) iron(III)(BHA); tris(salicylhydroxamato) iron(III)(SHA); and the related biological hydroxamate ferrichrome A (FA) (89). Table 2 shows the calculated thermal energies based on Equation 2.

TABLE 1. Thermal vs optical transitions $\pi - \gamma^*$ for phenanthroline

Pressure (kbar)	$h\nu_{\max}$ (eV)	$\Delta E_{1/2}$ (eV)	E_{th} (eV)
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	-0.40
150	4.20	1.20	-0.98

TABLE 2. Optical versus thermal transitions: ferric hydroxamates and ferrichrome A for 10% reduction of Fe(III)

Compound	Pressure (kbar)	$h\nu_{\max}$ (eV)	$\Delta E_{1/2}$ (eV)	E_{th} (eV)
AHA	125	2.80	0.90	-0.11
BHA	105	2.70	0.875	-0.06
SHA	70	2.54	0.84	-0.02
FA	37	2.65	0.835	+0.11

Both the peak location and width affect the amount of reduction, and the reduction appears to initiate approximately where the calculated value of E_{th} changes sign.

These transformations in iron typically do not go to completion at a fixed pressure. In fact, the conversion may not be complete at any pressure; there can actually be a maximum in the pressure-conversion curve. Slichter & Drickamer (90) have accounted for this behavior with a thermodynamic treatment which has analogies in regular solution theory and molecular field theory of magnetism. As noted earlier, metastability may be a serious limitation on a thermodynamic treatment of solid state chemistry, but the analysis predicts all of the essential features observed. The free energy of the mixture is written

$$G = N_0[(1 - C)G_0(P, T) + CG_1(P, T) + \Gamma(P, T)C(1 - C)] - T\sigma_{mix} \quad 3.$$

where

$$\sigma_{mix} = k[N_0 \ln N_0 - N_0 C \ln N_0 C - N_0(1 - C) \ln N_0(1 - C)] \quad 4.$$

is the usual entropy contribution due to the variety of ways of choosing converted sites. G_0 and G_1 are the free energies of the pure components and Γ is a term which measures interaction among sites. A little manipulation gives:

$$\ln K = -\frac{1}{kT} [\Delta G + \Gamma(P, T)(1 - 2C)] \quad 5.$$

where

$$\Delta G = G_1 - G_0$$

Three cases were considered: 1. noninteracting sites ($\Gamma = 0$) with linear elastic behavior; 2. noninteracting sites with nonlinear elastic behavior; and 3. interacting sites. The first of these treatments involves only a balancing of volume and compressibility effects; we shall not elaborate on it here.

In the nonlinear theory the Helmholtz free energy is expressed in the form

$$F = \sum_m \frac{A_m}{V^m} \quad 6.$$

where the coefficients A_m depend on temperature but not on volume. One can use this expression to evaluate other thermodynamic properties. In the first order one can describe the physics of the situation with three terms involving $m = 1/3$, $5/3$, and $9/3$, corresponding to electrostatic, covalent, and repulsive interactions. With the use of the Murnaghan equation of state:

$$\frac{V_0}{V} = \left(1 + \frac{nP}{B}\right)^{1/n} \quad 7.$$