Spectrophotometric Study of Equilibrium

A. Reaction

1. $M + I_2 \leftrightarrow M{\bullet}I_2$ (*charge-transfer complexation*)

2. *Equilibrium*: $K = \dfrac{[M \bullet I_2]}{[M]\,[I_2]} \equiv \dfrac{x}{([M]_0 - x)([I_2]_0 - x)}$

3. *Conditions*: $K \approx 1\ M^{-1}$, so all species present at equilibrium. (Note that $K\,[M] = [M{\bullet}I_2]/[I_2]$, so I_2 is 50:50 complexed when l.h.s. = 1.)

B. Spectrophotometry

1. $I/I_0 = 10^{-A} \equiv$ *transmittance*; A (*absorbance*) $= \varepsilon\ c\ \ell$
   (molar absorptivity × concentration × path length)

2. *Additivity*: $A = A_M + A_{I_2} + A_x + A_{solv}$

3. Choose λ where only A_x significant: $A \approx A_x = \varepsilon_x\ x\ \ell$

4. *Analysis*: Use $[\mathrm{M}]_0 >> [\mathrm{I}_2]_0$, so $[\mathrm{M}] \approx [\mathrm{M}]_0$

$$\Rightarrow \quad \frac{[\mathrm{I}_2]_0 \ell}{A_x} = \frac{1}{\varepsilon_x K [\mathrm{M}]_0} + \frac{1}{\varepsilon_x}$$

[$y = bx + a$, *i.e.*, straight line with intercept ε_x^{-1} and slope $(\varepsilon_x K)^{-1}$; define fit parameters as ε_x and $K \Rightarrow$ get uncertainties directly.]

C. Thermodynamics

1. $\Delta G° = -RT \ln K°$ [*conventional Gibbs energy change*]

2. *van't Hoff*: $\dfrac{\partial \ln K°}{\partial(1/T)} = \dfrac{-\Delta H°}{R} \Rightarrow \ln(K_2/K_1) = (\Delta H°/R)(1/T_1 - 1/T_2)$

   [NOTE: This is our third encounter with this relation.]

3. $\Delta G° = \Delta H° - T\Delta S°$ [The previous equation assumes that $\Delta H°$ and $\Delta S°$ are independent of T; with that assumption this equation yields identical $\Delta H°$ (hence $\Delta S°$) from K at two Ts.]

In all such thermodynamic applications, T is in K.

D. Spectral Results