

Instructions: Use whatever format you would like to work on this assignment, but include in the filename the number of this quiz (i.e., 01) and your last name.

Thermodynamics

- 1) The article that you read in preparation for this discussion section (available here: <https://pubs.rsc.org/en/content/articlelanding/1977/f1/f19777300011>) described a so-called Förster cube. What are some of the approximations and/or shortcomings in such a diagram?
- 2) Pyranine is a hydroxyarene molecule with measured pK_a and pK_a^* values of ~ 7.3 and ~ 1 , respectively. Assuming that you have an aqueous solution of pyranine at pH 4 at thermal and (electro)chemical equilibrium (i.e. in the dark), and all activity coefficients equal 1, what is the relative ordering of the concentrations of all four species in the Förster cycle proton-transfer square scheme? Then assume that a constant source of light is introduced and the species are perturbed from equilibrium to a steady-state condition. Assuming that the electronic excited-state lifetimes are the same for the protonated and deprotonated forms of pyranine and are sufficiently long to enable excited-state proton-transfer chemistry to occur, what is the relative ordering of the ability of each species to perform useful non- $p_{\text{system}}dV_{\text{system}}$ work, i.e. the change in (electro)chemical potential of each species? Explain your answers to each question.
- 3) While we know that a system at (electro)chemical equilibrium has $\Delta G = 0$, how else can we write (electro)chemical equilibrium in terms of mass action rate equations and can we derive the equation for ΔG° using them? Do this for the reaction $2A + B \rightleftharpoons C$, and assume it to be spontaneous under standard-state conditions, i.e. exergonic/exoergic.
- 4) Considering that matter has properties of both particles and waves, use the plane wave equation, $\Psi = Ae^{ik_x x} e^{ik_y y} e^{ik_z z} e^{-i\omega t} = Ae^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$, to derive the operators for energy and momentum used in quantum mechanics.