

## Thermodynamic boxes, $E_m$ s and $pK_a$ s

- 1) In Rich, P. R., and Bendall, D. S. (1979) A mechanism for the reduction of cytochromes by quinols in solution and its relevance to biological electron transfer reactions, *FEBS Lett.* 105, 189-194. FIG 4
  - a) Each place the curve changes slope is a  $pK$  for either a reactant or product. Tell me what the  $pK$  is for each species considered in the figure.
  - b) Write out the reaction for each segment and compare the proton dependence of the reaction with the slope in the figure.
  
- 2)
  - a) Draw a thermodynamic box ( $E_m$  horizontal,  $pK_a$  vertical) for the reaction connecting Q and  $QH_2$ .
  - b) If the  $pK_a$  for  $Q^-$  to  $QH$  is 4.9 and the  $E_m$  for Q to  $Q^-$  is -145 what is the free energy for the  $Q \rightarrow QH$  electron transfer reaction at pH 7? What about at pH 8?
  
- 3)
  - a) Draw a thermodynamic box for a  $pK_a$  for an Asp in solution (on top) and the protonation of Asp in the protein on the bottom.
  - b) The Asp  $pK_a$  is 4 in water. If it's 6 in the protein what's the difference in  $K_d$  of the neutral and ionized Asp?