CHEM 130A SEC2 SECOND MIDTERM
11/16/88 WEMMER

NAME Key

1. For the reactions below at pH 7 and 25°C the standard half cell voltages are:

$2H^+ + 1/2\ O_2 + 2e^- \rightarrow H_2O$ $E^{0\prime} = 0.820$ V and

$2H^+ + \text{cystine} + 2e^- \rightarrow 2\ \text{cysteine}$ $E^{0\prime} = -0.340$ V.

a) Write the balanced reaction which will be spontaneous when these half cells are connected. If the second half cell is made with 0.01 M cystine and 0.01M cysteine both present, what will be cell the potential and ΔG for the overall reaction under these conditions?

reverse 2nd rxn

$2\ \text{cysteine} + \frac{1}{2} O_2 \rightarrow \text{cystine} + H_2O$

$E^\circ = 1.160$ V

$E = E_0 - \frac{0.0591}{2} \log \frac{[\text{cysteine}]^2 P_{O_2}}{[\text{cystine}]}$

$= 1.160 + 0.0591$

$= 1.219$ V

b) The cell voltage was also measured at 45°C, and the cell potential was found to have decreased relative to 25°C by 0.0121V. What are the values of ΔH and ΔS for the reactions in the cell?

$\Delta S = 96{,}485 \cdot 2 \cdot \frac{\Delta E}{\Delta T} = 96{,}485 \cdot 2 \cdot \frac{-0.0121}{20} = -117\ J/mol\ K$

$\Delta H = 96{,}485 \cdot 2 \left(-1.219 + 298 \left(\frac{-0.0121}{20}\right)\right) = -27\ kJ/mol$

c) If the pH in both half cells was decreased by two units would the cell potential increase or decrease (why)? If the pH in just the cystine/cysteine half cell were decreased what would happen?

Since the rxn is $2H^+$ on both sides, as long as concs on both sides are equal they cancel in Q. If H^+ on the Cys side were decreased the voltage would increase since the spont. direction produces H^+, removing product making the rxn more favorable.

2. Ribonuclease is a protein with molecular weight 14,000 g/mol. A sample was made up in water solution at pH=3 with 7 mg of protein. A calorimetric scan was done and it was found that a peak in the heat capacity occurred at 50°C in which 199mJ of heat was absorbed. The difference in heat capacity above and below this transition was determined to be .3x77 J/g/°C. $0.377\ J/g \Rightarrow 5.28 \times 10^3\ J/mol$

a) Assume this transition corresponds to unfolding of the protein. What are the values of ΔG, ΔH and ΔS for this transition at 50°C?

at 50° $\Delta H = \frac{199 \times 10^{-3}\ J}{0.5 \times 10^{-6}\ mol} = 398\ \frac{kJ}{mol}$ $\frac{7 \times 10^{-3}\ g}{14 \times 10^{3}\ g/mol} = 0.5 \times 10^{-6}\ mol$

$\Delta G = 0$ unimolecular $K_{eq} = 1$

$\Delta S = \frac{\Delta H}{T_m} = \frac{398\ kJ/mol}{323\ K} = 1.23\ kJ/mol\ K$

b) What is the equilibrium constant for the reaction unfolded → folded for the protein at 20°C?

$C_p \Delta T + \Delta H_1 - C_p \Delta T$

$C_p \ln \frac{50}{20} + \Delta S_1 + C_p \ln \frac{20}{50}$

unfolding $\Delta G = \Delta H_{50} - 293 \cdot \Delta S_{50}$

$+ \Delta C_p \left(293 - 323 - 293 \ln\left(\frac{293}{323}\right)\right)$

$= +398\ kJ/mol - 293\ K \cdot 1.23\ kJ/mol\ K + 5.28\ kJ/mol \left(-30 - 293 \ln \frac{293}{323}\right)$

$= +398\ kJ/mol - 360.9\ kJ/mol - 7.595\ kJ/mol$

$= 30\ kJ/mol$

so for folding $\Delta G = -30\ kJ/mol$

$K = e^{-\frac{\Delta G}{RT}} = 1.2 \times 10^5$

3. A galvanic cell is made at 25°C with 1M solutions of Fe^{+3} and Fe^{+2} with a platinum electrode on one side, and a saturated solution of AgCl with a Ag electrode on the other side. AgCl has a solubility product of 1.8×10^{-10} at 25°C.

a) Use the data above and that in Table 4.5 to calculate the cell voltage which would be measured.

$Fe^{+3} + e^- \rightarrow Fe^{+2}$ $+ 0.771\ V\ E^\circ_{\frac{1}{2}\ cell}$ satd soln

$Ag^+ + e^- \rightarrow Ag^\circ$ $+ 0.799\ E^\circ_{\frac{1}{2}\ cell}$

$[Ag^+] = [Cl^-] = x$

$x^2 = 1.8 \times 10^{-10}$

$x = 1.34 \times 10^{-5}\ M$

$E = E^\circ - 0.0591 \ln\left(\frac{1}{1.34 \times 10^{-5}}\right) = 0.136\ V$

full cell would be $0.771 - 0.136 = 0.635\ V$

b) If 0.01 M $NaClO_4$ is added to the silver side (assume Na and Ag ClO_4 are soluble and that perchlorate is nonreactive), what will be the change in the cell potential?

cell will change a little because activity coeff changes $I = 0.01\ M$ $\log \gamma_\pm = -0.509 \cdot 1^2 \cdot \sqrt{0.01}$

$= -0.0509$

$a_{Ag^+} = \gamma \cdot [Ag^+]$ $\gamma_\pm = 0.95$

this would change above by $-0.0591 \ln \frac{1}{\gamma} = -0.003\ V$

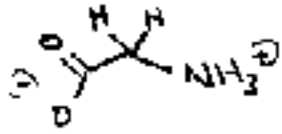
c) When NH_3 is added to AgCl it dissolves to form $Ag(NH_3)_2^+$. If NH_3 is added to the silver half cell in which direction would you expect the cell voltage to change if at all (explain your answer)?

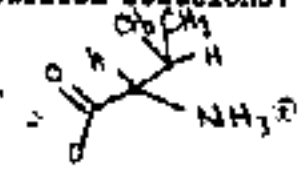
Since the AgCl dissolves the activity of Ag^+ in the equilibrium with $Ag(NH_3)_2^+$ must be less than in equil with AgCl so free $[Ag^+]$ is lower, which makes the silver half cell more negative, overall potential is then larger.

4. The solubility limit for some amino acids has been determined at 25°C:

	in water	ΔG° kJ/mol	in ethanol	ΔG°
glycine	3.09 M	−2.79	4.04×10^{-4} M	+19.36
valine	0.60 M	+1.27	1.32×10^{-3} M	+16.42

These represent the concentrations present in saturated solutions.

GLYCINE- 

VALINE- 

a) What is the ΔG for transfer of 1 mole of glycine from the crystaline form to a saturated water solution?

$Gly(solid) \rightarrow Gly(soln)$ $\quad K_{eq} = [Gly]/1 = 3.09$

$\Delta G^\circ = -RT \ln K_{eq} = -2.79$ for formation of 1M soln

Since rxn stops at satn

$\Delta G = 0$

b) What is the free energy change for transfer of 1 mole of glycine from ethanol to water saturated solutions?

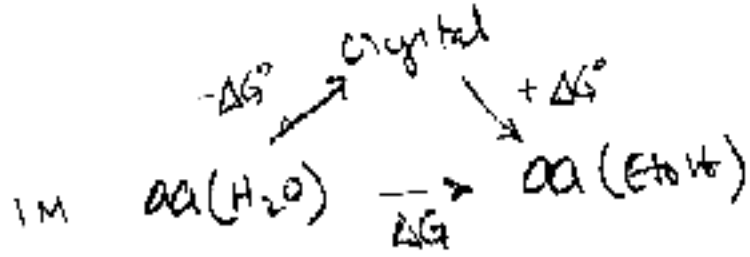
$Gly(cryst) \xrightarrow{\Delta G = 0} Gly(H_2O\ sat'd)$

$Gly(cryst) \xrightarrow{\Delta G = 0} Gly(EtOH, sat'd)$

$Gly(H_2O\ sat'd) \xrightarrow{\Delta G = 0} Gly(EtOH, sat'd)$

STILL

c) If we assume that the effects of the backbone and sidechain are simply additive (glycine functionally has no sidechain), then what is the free energy of transfer 1 mole of the valine sidechain alone from water to ethanol?



$\Delta G = -\Delta G^\circ(H_2O) + \Delta G^\circ(EtOH)$

at any fixed concentration

for Gly $\Delta G = 22.15$ kJ/mol

Val $\Delta G = 15.16$ kJ/mol

$\Delta\Delta G$ sidechain $= \Delta G(Val) - \Delta G(Gly) = -7$ kJ/mol

d) If we say that ethanol mimics the interior of a protein, by what factor will the equilibrium constant for folding of a protein be changed by a mutation of glycine to valine at an interior position of a protein?

should be $\approx e^{-\frac{\Delta\Delta G}{RT}} \approx 17$

Assumes just the transfer free energy is relevant - probably not really true.