Chem. 103 Practice problems #9

1) Criticize the statement: Provided that $\Delta G°$ is negative for a particular chemical reaction at 298K, this reaction will always be product favored under all conditions as long as the temperature is held constant at 298K. [2 pts]

2) Consider the phase change of N_2O_4 from liquid to gas. Use the following thermodynamic table to answer the questions below: [6 pts]

Species .	$\Delta H°_f$(kJ/mol) (at 298K)	$S°_f$(J/molK) (at 298K)	$\Delta G°_f$ (kJ/mol) (at 298K)
N_2O_4 (l)	-19.50	209	97.54
N_2O_4 (g)	9.16	304	97.89

a) What is the boiling point of N_2O_4 ? (show clear calculations or there will be no credit given). _____ °C

b) What is the value of K_p for this process at 25°C and the partial pressure of this gas at 25°C? K_p = _____ P_{N2O4} = _____ Bar

3) Explain how a highly reactant-favored (i.e. very nonspontaneous and endergonic) reaction can be made to form product inside a living cell. To illustrate your answer give relevant hypothetical chemical equations with their hypothetical values of $\Delta G°$. [2]

4) Consider the following given expressions: $E°_{PuO_2^{2+}/Pu^{4+}}$ = 1.000 V and $E°_{ReO_4^-/ReO_2(s)}$ = 0.510 V

a) Write down the half reactions (unbalanced) for each redox couple:

b) Verify that they are reductions. (Place the correct number of electrons in the half rxn)

c) Balance each half reaction (you can add H_2O to balance the O's and H^+ to balance the H's, assuming that the solution is acidic; check if balanced -both charge and mass)

d) Determine which half reaction needs to be reversed and write it in reversed form:

e) Add the 2 balanced half reactions such all the "free electrons" are eliminated from the resulting redox equation:

$2\ ReO_2(s) + 3PuO_2^{2+} + 4\ H^+ \rightarrow 2\ ReO_4^- + 3Pu^{4+} + 2H_2O$

f) Calculate the standard potential for this redox reaction, E°:

5) In this week's experiment, what would you expect the signs on $\Delta H°$ and $\Delta S°$ for the observed reaction, $C_{10}H_8(s) <==> C_{10}H_8$ (solution) to be? Explain your answer.

6) For the reaction 2 $KClO_3(s)$ - - - - > 2 KCl (s) + 3 $O_2(g)$:
Calculate $\Delta G°$ for this reaction at 298 K, given $\Delta H°$ for the reaction = -91.0 kJ/mol and $S°$ for $KClO_3(s)$ is 143.0 J/molK; for $O_2(g)$, 205 J/molK; for KCl(s) , 82.7 J/molK. Will the reaction occur spontaneously? What happens if the temperature is raised?

Answers:

1) Not true. Under nonstandard conditions, $\Delta G = \Delta G° + RT \ln Q$. Ultimately what determines if a reaction is product favored is ΔG, and that depends on Q.

2) a) At the boiling point, $Q = K = 1$ (since both liquid and gas have equal activities, while at the same being at equilibrium). So $\Delta G=0=\Delta G°$; Since we can write:

$\Delta G°=0= \Delta H° -T\Delta S°$, therefore, $T = \Delta H°/\Delta S°$.

Now get $\Delta H°$ and $\Delta S°$ for the phase change: $\Delta H°$ (i.e, enthalpy of vaporization, ΔH_{vap}) = $\Delta H°_f(N_2O_4 (g)) - \Delta H°_f(N_2O_4 (l)) = (9.16x10^3-(-19.50x10^3))$ J/mol=$2.866x10^3$ J/mol

$\Delta S°= S°_f(N_2O_4 (g)) - S°_f(N_2O_4 (l)) = (304-209)$ J/molK $= 95$ J/molK

$T = 2.866x10^4$ J/mol / 95 J/molK $= 302$ K or, T = 302-273 = 29°C

b) Since the T = 298, we can just use $\Delta G°$ directly from the table since that's the value at 298K): $\Delta G° = (97.89x10^3 – 97.54x10^3)$ J/mol $= 350$ J/mol

$\Delta G°= -RT\ln K_p$, or, $K_p = \exp(- (\Delta G°/RT)) = \exp(- (350$ J/mol$)/((8.314$ J/molK$)(298K))$
or, $K_p = 0.868$

and since, $K_p = P_{N2O4}/1 = P_{N2O4} = 0.868$

3) In a cellular environment, a highly $\Delta G>0$ (i.e. reactant favored) reaction can be made product-favored by *coupling* it with an even more highly $\Delta G<0$ reaction. This reaction often involves the hydrolysis of the phosphate group from ATP, which yields a $\Delta G° = - 30$ kJ/mol. If the net $\Delta G <0$, then the product is favored. The product/reactant ratio can be altered tremendously as shown in the lecture notes.

4) a) answer: $PuO_2^{2+} \rightarrow Pu^{4+}$ and $ReO_4^- \rightarrow ReO_2(s)$

b) answer: $PuO_2^{2+} + 2e^- \rightarrow Pu^{4+}$ and $ReO_4^- + 3e^- \rightarrow ReO_2(s)$
      +6,-2   +4   +7   +4,-2

c) answer: (1) $PuO_2^{2+} + 2e^- + 4H^+ \rightarrow Pu^{4+} +2H_2O$

(2) $4H^+ + ReO_4^- + 3e^- \rightarrow ReO_2(s) + 2 H_2O$

d) answer:

-(2) $ReO_2(s) + 2 H_2O \rightarrow 4H^+ + ReO_4^- + 3e^-$ (because $E_{Re}° =.510 <E_{Pu}°=1.000$)
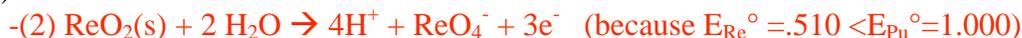
e) answer: multiply the following and then add: (1) x 3 + (-1(2))x2

Balanced equation:
      $2 ReO_2(s) + 4 H_2O + 3PuO_2^{2+} + 12H^+ \rightarrow 8H^+ + 2 ReO_4 + 3Pu^{4+} +6H_2O$
finally eliminate the redundant ones:

f) answer: $E°_1 –E°_2 = 1.000 – 0.510 = 0.490$ V

5) Since the equation is written as a "melting" process, we go from solid to liquid. that would require heat energy to disrupt the ordered structure of the solid, so endothermic (just like melting of solid ice to liquid water), $\Delta H° > 0$. Since the process changes from an ordered (solid) to a disordered structure (liquid), S would increase, or $\Delta S° >0$.

6) We recall: $\Delta G° = \Delta H° - T\Delta S°$; where $\Delta H° = - 91.0x10^3$ J/mol (given); and

$\Delta S° = 2 S°_f(KCl (s))+S°_f(O_2(g))-2 S°_f(KClO_3 (s)) = 2(82.7)+3(205)-2(143.0)$ J/molK
$\Delta S° =494$ J/molK.

Thus, $\Delta G° = - 91.0x10^3$ J/mol $– (298$ K$)(494$ J/molK$) = -238x10^3$ J/mol <0 spontaneous!
If the temperature is raised, it becomes more spontaneous.