Chem 130A Final Exam. May 17, 2003

Q1. (20 Points)

(A) Consider a reaction in which 1 mole of a reactant, R, is converted to 1 mole of a product, P:

$R \rightarrow P$

The initial concentration of R is 0.5 M. Assume that the reaction follows first order kinetics. If the half-life of the reaction is 20 minutes, what is the rate constant? (5 points)

For first order reaction: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

$$k = \frac{\ln 2}{20\,min}$$

$$= 0.035\ min^{-1}$$

(B) Consider another reaction in which reactant R' is converted into product P':

$R' \rightarrow P'$.

In this case, when the initial concentration of R' is 0.5 M, the half life of the reaction is 20 minutes. When the initial concentration is increased to 1.3 M, the half life decreases to 7.69 minutes. What is the order of the reaction? (5 points)

n = order

$[A_0]$ = initial concentration.

P = constant

$$t_{\frac{1}{2}} \propto \frac{1}{[A_0]^{n-1}}$$

$$\therefore\ 20 = P \times \frac{1}{[0.5]^{n-1}}$$

$$7.69 = P \times \frac{1}{[1.3]^{n-1}}$$

$$\frac{20}{7.69} = \frac{(1.3)^{n-1}}{(0.5)^{n-1}}$$

$$\frac{20}{7.69} = 2.6 = \left(\frac{1.3}{0.5}\right)^{n-1} = (2.6)^{n-1}$$

$\therefore$ $n-1=1$ $\therefore$ $n=2$

2nd order.

Q1, cont. (C) What is the rate constant of the reaction in B? (Show units). (5 points)

For 2^{nd} order:

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]} \quad \therefore \quad k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A_0]}\right)$$

For $[A_0] = 0.5$, $t_{\frac{1}{2}} = 20\text{min}$ & $[A] = 0.25$

$$\therefore \left(\frac{1}{0.25} - \frac{1}{0.5}\right)\frac{1}{20} = k = (4-2)\cdot\frac{1}{20}$$

$k = 0.1\ M^{-1}s^{-1}$

(D) What is a likely molecular explanation for the difference in the order of the reactions in (A) and (B)? (5 points)

For B, it is 2^{nd} order, so 2 molecules of reactant collide and form the transition state, then product. In A the reaction is 1^{st} order. The reactants spontaneously produce products. No collissions required.

Q2. (20 points)
Two molecules, A and B, can undergo chemical reactions with different outcomes:

	E_A	A
(i) $A + B \rightarrow C + D$ (rate constant = k_1)	$60\,000\ \mathrm{J\,mol^{-1}}$	A_1
(ii) $A + B \rightarrow E + F$ (rate constant = k_2)	$75\,000\ \mathrm{J\,mol^{-1}}$	A_2

The activation energy for the first reaction is 60 kJ/mole and that for the second reaction is 75 kJ/mole. Both reactions obey Arrhenius kinetics, but the pre-exponential terms in the Arrhenius equation are different for the two reactions. Assume that the pre-exponential terms are temperature independent.

(A)At 300K, the rate constant k_1 for the first reaction is twice that of the second reaction (i.e., $k_1 = 2k_2$). Calculate the temperature at which the rate constants k_1 and k_2 will be equal (15 points).

$$k = A e^{-Ea/RT}$$

$$\frac{k_1}{k_2} = \frac{A_1 e^{-Ea_1/RT}}{A_2 e^{-Ea_2/RT}} = \frac{A_1}{A_2} e^{(Ea_2 - Ea_1)/RT}$$

At $T = 300\mathrm{K}$, $k_1 = 2k_2$

$$\therefore \quad 2 = \frac{A_1}{A_2} e^{(Ea_2 - Ea_1)/RT}$$

$$\frac{A_1}{A_2} = 2 e^{(Ea_1 - Ea_2)/RT} = 2 e^{(60000 - 75000)/8.314 \times 300}$$

$$= 0.00496$$

When $k_1 = k_2$ $\quad \frac{k_1}{k_2} = 1 = \frac{A_1}{A_2} e^{(Ea_2 - Ea_1)/RT}$

$$\ln\left(\frac{A_2}{A_1}\right) = \frac{Ea_2 - Ea_1}{R.T} \qquad T = \frac{Ea_2 - Ea_1}{R \ln\left(\frac{A_2}{A_1}\right)} = 340\mathrm{K}.$$

Q2. Cont. (B) For both reactions, the reactants are the same molecular species. Discuss possible explanations for why the pre-exponential terms in the two reactions could be different (5 points).

The 2 reactants are the same. However to react by the 2 different pathways, the A values are different. Eg, one reaction mechanism may require collision with a specific geometry. If the geometry of the transition state is more restrictive, this could give a lower A value.

Q3 (20 points)

Consider an electrode at the which the following reaction occurs:

$Cd^{2+} + 2e^- \rightarrow Cd$ ($E^\circ = -0.403$ V)

(A) How much cadmium would be deposited on the electrode if the reaction were driven in the forward direction by applying an appropriate voltage and the passage of 2 Faradays of current? (10 points)

2 Faradays of current $\Rightarrow$ 2 moles of electrons

$\Rightarrow$ 1 mole of Cd^{2+} is converted to Cd.

Atomic weight of Cd = 112.4

$\Rightarrow$ 112.4 g of Cd will be deposited.

Q3. cont. (B) What is the standard free energy change for the half reaction? State units used.

$$\Delta_r G = -\nu F E$$

$$= -2(96500)(-0.403)$$

Coulombs/mole ↖ volts

$$= 77{,}779 \text{ J/mole} \quad (1\text{C} \times 1\text{V} = 1\text{J})$$

$$= 77.779 \text{ kJ/mole}$$

Q4. Copper and zinc undergo the following electrode reactions:

$Cu^{2+} + 2e^- \rightarrow Cu$ ($E^\circ = +0.342$ V)

$Zn^{2+} + 2e^- \rightarrow Zn$ ($E^\circ = -0.762$ V)

(A) Write down the coupled reaction, showing the direction of spontaneous change, under standard conditions (5 points).

$$Cu^{2+}_{(aq)} + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

Q. 4. cont. (B) An electrochemical cell is constructed as follows: one electrode consists of a piece of zinc metal immersed in a solution containing Zn^{2+} ions at a concentration of 3.0 M. The other electrode consists of a piece of copper metal immersed in a solution containing 0.01 M Cu^{2+} ions. What will the EMF at 300K of this cell be when the electrodes are connected? (8 points)

Use the Nernst Equation:

$$E = E^0 - \frac{RT}{\nu F} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \qquad (a = \text{activity})$$

For the reaction: $Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$,

$E^0 = +0.342 - (-0.762) = 1.104\,V$ (We can add the E^0 values since the stochiometry of electrons is the same)

$\nu = 2 \qquad F = 96\,500\ C\ Mole^{-1}$

Activities of solid Cu and Zn = 1.0, so ignore. Use activity = concentration for others.

$[Zn^{2+}] = 3.0\,M \qquad [Cu^{2+}] = 0.01\,M \qquad T = 300\,K$

$$\text{So } E = 1.104 - \frac{8.314 \times 300}{2 \times 96500} \ln \left(\frac{[3.0]}{[0.01]}\right)$$

$$= 1.104 - 0.0129 \times 5.703$$

$$= 1.104 - 0.0736$$

$$\boxed{E = 1.0304\ V}$$

(C) Write down the coupled chemical reaction, showing the spontaneous direction in which the reaction proceeds when the electrodes described in (B) are connected. This reaction is very strongly driven in this direction. How low would the initial concentration of Cu^{2+} have to be for the reaction to run in the reverse direction? The zinc concentration is 3.0 M and the temperature is 300K. Estimate the initial Cu^{2+} concentration within an order of magnitude (i.e., within a factor of 10), using the fact that:
$\ln 10^{-n} = -n \ln 10 = -2.3 \times n$ (otherwise your calculator may have trouble with the very small numbers).
(7 points)

Spontaneous direction ⇒

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

When $E = 0V$ the reaction stops, and when $E < 0$ V, the reaction will reverse

When $E = 0V$, the Nernst Eqn becomes:

$$0 = E^\circ - \frac{RT}{\nu F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Rightarrow \frac{\nu F E^\circ}{RT} = \ln [Zn^{2+}] - \ln [Cu^{2+}]$$

$$\Rightarrow \ln [Cu^{2+}] = \ln [Zn^{2+}] - \frac{\nu F E^\circ}{RT} = 1099 - \frac{2 \times 96500 \times 1.104}{8.314 \times 300}$$

$$= 1.099 - 85.42$$

$$\Rightarrow \ln [Cu^{2+}] = -84.32$$ (5 POINTS)

Since $\ln 10^{-n} = -n \times 2.3$, set $-n \times 2.3 = -84.32$
$\Rightarrow n = 36.7$

$$\Rightarrow [Cu^{2+}] = 10^{-36.7} \approx 10^{-40} \text{ M}$$ (2 points)

Thus, the copper concentration has to be almost zero before the reaction runs backwards.

Q5. (25 Points)
A drug works by inhibiting a target protein found in blood. The dissociation constant, K_d, for the drug-target interaction is 10^{-12} M. Unwanted side-effects occur if the drug binds significantly (>10% occupancy) to another protein, for which the dissociation constant is $K_d=10^{-9}$ M.

(A) What is the minimal concentration of the drug in the blood such that side-effects are avoided? (13 points)

(B) What is the fractional occupancy of the drug bound to the desired target at this concentration? (12 points)

Assume that the concentrations of the proteins are very low compared to drug concentrations.

The fractional occupancy, Y, of a receptor is related to the ligand concentration by:

$1/Y = 1 + K_d/[L]$

(A) For avoiding side effects, fractional occupancy of decoy protein should be 10% or less ($K_D = 10^{-9}$ M)

For decoy protein,

$$\frac{1}{Y} = 1 + K_D/[L] \Rightarrow \frac{1}{0.1} = 1 + \frac{10^{-9}}{[L]}$$

$$\Rightarrow [L] = 10^{-9}/9 = 1.1 \times 10^{-10} \text{ M}$$

(B) At a ligand concentration of 1.1×10^{-8} M, the fractional occupancy of the desired target is:

$$\frac{1}{Y} = 1 + K_D/[L] = 1 + \frac{10^{-12}}{1.1 \times 10^{-8}}$$

] OK if you get to this stage and approximate the 2nd term as 0

$$= 1 + 0.91 \times 10^{-4}$$

$$\Rightarrow Y = \text{[illegible]}$$

0.991

Q 6. (20 points)
Consider 3 chemical reactions for which the standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) are temperature independent. Calculate the standard enthalpy changes for the two cases below, given the following information. When the temperature is increased from 300K to 320K,
(A) for reaction 1, the value of the equilibrium "constant", K_{eq}, increases by 50% (7 points)
(B) for reaction 2, the value of K_{eq} decreases by 30% (7 points)

$$K_{eq} = e^{-\Delta G^\circ/RT} = e^{-\Delta H^\circ/RT}\, e^{+\cancel{T}\Delta S^\circ/R\cancel{T}}$$

Let the equilibrium constant at 320K be K_{eq}^{320}
Let the equilibrium constant at 300K be K_{eq}^{300}

For (A) $\dfrac{K_{eq}^{320}}{K_{eq}^{300}} = 1.5$ For (B) $\dfrac{K_{eq}^{320}}{K_{eq}^{300}} = 0.6667$

For (A) $\ln K_{eq}^{320} - \ln K_{eq}^{300} = 0.405$
For B $\ln K_{eq}^{320} - \ln K_{eq}^{300} = -0.405$

$$\ln K_{eq}^{320} = \frac{-\Delta H^\circ}{8.314 \times 320} + \frac{\Delta S^\circ}{8.314} \qquad \ln K_{eq}^{300} = \frac{-\Delta H^\circ}{8.314 \times 300} + \frac{\Delta S^\circ}{8.314}$$

$$\ln K_{eq}^{320} - \ln K_{eq}^{300} = -\Delta H^\circ \left(\frac{1}{8.314 \times 320} - \frac{1}{8.314 \times 300} \right) \text{ J Mole}^{-1}$$

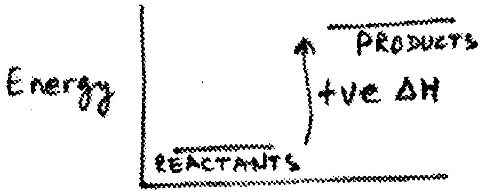
$$= -\Delta H^\circ (-0.0000250) \text{ J mole}^{-1}$$

For (A) $\Delta H^0 = \dfrac{+0.405}{+0.0000250} = 16200 \text{ J mole}^{-1} = +16.2 \text{ KJ/mole}$

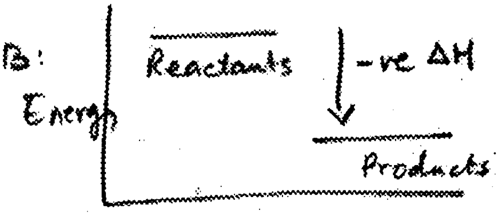
For (B) $\Delta H^0 = \dfrac{-0.405}{+0.0000250} = -16200 \text{ J mole}^{-1} = -16.2 \text{ kJ/mole}$

(C) Rationalize the sign of ΔH° that you obtained for the two cases above in terms of the Boltzmann probability distribution. (6 points)

For A :



For B:



As the temperature is increased, the Boltzmann distribution favors increasing the population of the higher energy states. For (A) this means more products are formed, and Keq increases. For (B) this means that more reactants are formed, and Keq decreases.

Q7. (25 points)
There are devices, such as components of mass spectrometers, that are able to accelerate molecules to precisely defined velocities. Suppose such a device injects Xenon atoms at a speed of 6.0×10^4 cm/sec into a thermally isolated chamber of volume 1 cm^3. After the injection is complete the molecules come to equilibrium by colliding with each other.

(A) Assume that the xenon atoms do not interact with each other, and that there is no heat exchange with the container. What is the final temperature of the system? (15 points)

The average kinetic energy of the gas molecules will be the same as the initial kinetic energy of each molecule

Average kinetic energy = $\frac{1}{2} m v^2 = \frac{3}{2} k_B T$

Multiply both sides of the equation by N_A (Avogadro's #)

$\Rightarrow \frac{1}{2} M v^2 = \frac{3}{2} RT$ where M is the molar mass

From the definition of units on page 19 we see that to calculate energy in J we should use units of kg for mass and $m\,sec^{-1}$ for speed.

For Xe $M = 131.3\text{ g} = 0.1313\text{ kg}$

Speed $= 6.0 \times 10^4\text{ cm/sec} = 6.0 \times 10^2\text{ m/sec}$

$$T = \frac{Mv^2}{3R} = \frac{0.1313 \times (6.0 \times 10^2)^2}{3 \times 8.314} = 0.1895 \times 10^4 = 1895 K$$

(B) Suppose that the device injects water molecules instead of Xenon atoms into the chamber. Would it be reasonable to calculate the temperature in the way that you did for part (A)? If not, give at least one property of water molecules that would make such a calculation unreliable, and state whether the calculated temperature would be lower or higher than the actual temperature as a consequence of this effect. (10 points)

This question can be argued many ways.

(1) You could argue that the temperature is so high that water molecules behave ideally and so the temperature calculation is correct.

(2) You could argue that water molecules form clusters when injected, which have higher kinetic energy (because mass is greater) and so the temperature would be higher.

Any physically meaningful statement will be accepted.

Q8

~~Q9~~. (25 points)

(A) Calculate the change in entropy in heating 5 moles of an ideal gas from 100K to 300K at constant pressure. Specify the units you use. (15 points)

[Assume that For this ideal gas $\overline{C}_p = \overline{C}_V + R = \frac{7}{2}R + R = \frac{9}{2}R = 37.41 JK^{-1}M^{-1}$]

iven
on board

$$\Delta S = n\overline{C}_p \ln T_2/T_1$$

$$= 5 \times 37.4 JK^{-1}M^{-1} \ln\left(\frac{300}{100}\right)$$

$$= 187 \times 1.099 = 205.4\ JK^{-1}M^{-1}$$

(B) A fundamental equation in thermodynamics is the relationship between free energy changes in solution and the natural logarithms of the concentrations of the reactants and products. Describe, conceptually, how the ideal gas calculation in (A) is connected to this fundamental free energy relationship for reactions or changes in solution (10 points). You don't need to provide the precise mathematical relationships that underlie this connection – just explain the connection.

We assume that for reactions in Solution the gaseous and Solution components are in Equilibrium. Thus their chemical potentials are equal. We further assume that the Gaseous, or vapor phase, components behave ideally, which leads to relationships between free energy changes and partial pressures, which are related to solution concentrations through Henry's Law or Raoult's Law

Q10 (25 points)
This question concerns calculating entropy changes using simple lattice models. Consider a container with 2 chambers, separated by an impermeable barrier. There are 10^7 grid points on each side of the barrier. Consider 2 states of the system:
State 1: There are 500 molecules of type X on the left, and none on the right. There are 500 molecules of type Y on the right, and none on the left.
State 2: There are 300 molecules of type X on the left and 200 on the right. There are 500 molecules of type Y on the right, and none on the left.

(A) What is the change in entropy on going from State 1 to State 2? Is this in the direction of spontaneous change? (15 points)
The entropy of the system is given by $S = k_b \ln W$, where W is the multiplicity of the system.

Use $\ln N! = N \ln N - N \simeq N \ln N$
also $\ln(a+b) \simeq \ln a$ when $a >> b$

1: $W_{LEFT} = \frac{10^7!}{500!(10^7-500)!}$

$\ln W_{LEFT} = 10^7 \ln 10^7 - 500 \ln 500 - (10^7-500)\ln(10^7) = 4951.74$

$W_{RIGHT} = W_{LEFT}$; $S = k_B \ln W_{LEFT} + k_B \ln W_{RIGHT}$

$S_1 = 9903.5\, k_B$

2: $W_L = \frac{10^7!}{300!(10^7-300)!}$ $\quad W_R = \frac{10^7}{200!\,500!\,(10^7-700)!}$

$\ln W_L = 10^7 \ln 10^7 - 300 \ln 300 - (10^7-300)\ln 10^7 = 3124.3$

$\ln W_R = 10^7 \ln 10^7 - 200 \ln 200 - 500 \ln 500 - (10^7-700)\ln 10^7 = 7115.7$

$S_2 = 10240\, k_B$

$\Delta S = 336.5\, k_B$ Slightly positive so spontaneous

(B) Describe briefly how this problem relates to the phenomenon of osmotic pressure in solutions. (10 points)

(B) This problem is conceptually similar to that of osmotic pressure because the barrier does not allow type Y molecules to pass. However, the situation given here corresponds to a very dilute solution, so dilute that the osmotic pressure is negligible

-END OF EXAM-