CHEM 341
PHYSICAL CHEMISTRY
FINAL EXAM

Name______________________________________

Do not open this exam until told to do so. The exam consists of 6 pages, including this one. Count them to insure that they are all there.

Constants:

$R = 8.31$ J K^{-1} $mole^{-1}$

$F = 96500$ J V^{-1} $mole^{-1}$

$N_A = 6.02 \times 10^{23}$

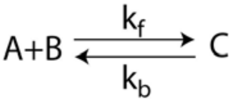
A = 0.509 for water

Do not write in the area below

Page	Score
2	/8
3	/8
4	/8
5	/8
6	/20
7	/20
8	/20
9	/8
Total	**/100**

Conceptual Problems (each problem is worth 2 points).

1) In the reaction



$$A+B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$$

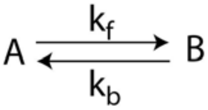
the reverse rate constant (k_b) is a

a) Zero order rate constant.
b) First order rate constant.
c) Second order rate constant.
d) Third order rate constant.

2) The units of a second order rate constant are:

a) s^{-1}
b) $J^{-1}s^{-1}$
c) $M^{-1}s^{-1}$
d) $M^{-2}s^{-1}$

3) For the reaction



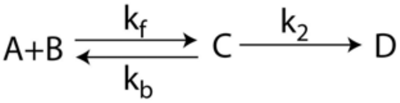
$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

a) dA/dt = 0 at equilibrium.
b) dB/dt = 0 at equilibrium.
c) The ratio of the forward and backwards rate constants are equal to the equilibrium constant.
d) All of the above

4) Which of the following is true?

a) **An increase in the activation energy of a reaction will result in a decrease in the rate constant for that reaction**.
b) An increase in the reaction free energy of a reaction will result in an increase in the rate constant for the reaction.
c) An increase in the activation energy of a reaction will result in an increase in the rate constant for that reaction.
d) An increase in the reaction free energy of a reaction will result in a decrease in the rate constant for the reaction.

5) Consider the reaction



If we assume that C achieves a steady state, this means that:

a) **dC/dt = 0**.
b) k_f and k_b are large enough so that equilibration is fast on the time scale of the overall formation of D.
c) k_f and k_b are small enough so that equilibration is slow on the time scale of the overall formation of D.
d) The concentration of C increases steadily (linearly) as a function of time.

6) The first order rate constant for the reaction A → B can be described as:

a) The inverse of the time it takes for half of A to be converted to B
b) The instantaneous probability that a molecule of A will form a molecule of B at any given time.
c) The ratio of the concentrations of A and B
d) The rate of the reaction after A decreases to half its original value.

7) In enzyme kinetics, the Michaelis constant, K_M, differs from the substrate dissociation constant, K_S, in what respect?

a) K_M is a binding constant while K_S is a dissociation constant.
b) K_M is a dissociation constant while K_S is a binding constant
c) K_M is the constant generated by using an equilibrium approximation while K_S is generated by using a steady state approximation.
d) **K_M is the constant generated by using a steady state approximation while K_S is generated by using an equilibrium approximation**.

8) The effect of an enzyme is to speed up a reaction by:

a) Decreasing the reaction free energy
b) Decreasing the activation energy of the reaction
c) Increasing the reaction free energy
d) Increasing the activation energy of the reaction

9) For a spontaneous reaction, which of the following is always true:

a) $\Delta S_{Sys} > 0$
b) $\Delta H_{Sys} < 0$
c) $\boldsymbol{\Delta S_{Tot} > 0}$
d) $\Delta G > 0$

10) In general, temperature is a measure of:

a) The internal energy of molecules.
b) The potential energy of molecules.
c) The kinetic energy of molecules.
d) The free energy of molecules.

11) At constant pressure, the change in enthalpy is the same as the

a) heat
b) work
c) internal energy change
d) free energy change

12) When a reaction comes to equilibrium it is always the case that:

a) $\Delta G^0 = 0$
b) $K_{eq} = 1$
c) $\Delta G = \Delta G^0$
d) $\boldsymbol{\Delta G = 0}$

13) At 20 C and 1 atm, which of the following is true?

a) The chemical potential of liquid water is greater than that of either ice or water vapor.
b) The chemical potential of liquid water is greater than that of ice but less than that of water vapor.
c) The chemical potential of liquid water is less than that of either ice or water vapor.
d) The chemical potential of liquid water is less than that of ice but greater than that of water vapor.

14) The cathode of an electrochemical cell is:

a) The positive electrode
b) The negative electrode
c) The electrode that takes up electrons
d) The electrode that gives off electrons

15) The overall equilibrium constant for the reaction

$$A \xrightleftharpoons{K_{eq1}} B \xrightleftharpoons{K_{eq2}} C$$

is given by:

a) The sum of the equilibrium constants for the two separate reactions
b) The ratio of the equilibrium constants for the two separate reactions
c) The product of the equilibrium constants for the two separate reactions
d) The difference between the equilibrium constants for the two separate reactions

16) The molar free energy change for transporting a positive molecule from the inside to the outside of a membrane when the concentration of this molecule is greater on the inside and the voltage across the membrane is more positive on the inside is:

a) Positive
b) Negative
c) Zero
d) Not enough information to tell

Numerical Problems (each problem is worth 10 points). ***All work must be shown for credit.***

17) ^{32}P is a radioactive element with a half life of 2 weeks (the ^{32}P decays to something else that is not radioactive or toxic). In my lab, I have generated some radioactive waste containing this material. I would like to dispose of this in the garbage, but it is not safe to do this until the concentration of the ^{32}P has decreased by a factor of a million. How long will I have to wait? (Hint, this is the same as the ^{14}C problem in your homework).

$2^N = 10^6$; N = ~20 so it will take 40 weeks

18) If the K_M (or K_S) for a simple enzyme reaction ($E + S \leftrightarrow ES \rightarrow P$) is 10^{-5} M, and the rate of product formation (dP/dt or V) is 10^{-3} moles/(liter second) when the substrate concentration is 10^{-5} M, what is the maximum velocity of the reaction (the rate of product formation when the concentration of S is very high)?

When $K_M = [S]$ then $V=0.5V_{MAX}$ so $V_{MAX} = 2 \times 10^{-3}$ moles/(liter second)

19) If the activation energy of the reaction A → B at 25.0 C is 3.00 kJ/mole and the first order rate constant for that reaction is 0.500 s^{-1} at that temperature, what will the rate constant for the reaction be at 35.0 C?

0.5 = Aexp(-3000/(Rx298)) so A = 1.68. Thus for 35C, k = 1.68 exp(-3000/(Rx308)) = 0.521

20) The molar heat capacity of a sample of liquid is 50.0 J $mole^{-1}$ K^{-1}. How much will the temperature increase when 500 J of heat is transferred into 2.00 mole of the sample?

$q = nC_P\Delta T$. $\Delta T = q/(nC_P)$ = 500J/(2 mole x 50 J/mole K) = 5 K

21) A 1 liter solution is prepared by adding 0.2 moles of sodium acetate (the conjugate weak base of acetic acid) and 0.15 moles of HCl (a strong acid) to water. The pK_A of acetic acid is 4.75. What is the pH of the solution?

$pH = pK_A + \log(Base/Acid) = 4.75 + \log(0.05/0.15) = 4.27$

22) 2 grams of ice at –20.0 C is added to 100 mls of water at 20.0 C in a container that does not allow transfer of heat to or from the surroundings. When the ice melts, what is the final temperature of the water? The molar heat capacity of ice is $37\ J\ K^{-1}\ mole^{-1}$ and the molar heat capacity of liquid water is $75.3\ J\ K^{-1}\ mole^{-1}$. The molar enthalpy of fusion of ice is $6.01\ kJ\ mole^{-1}$. The density of liquid water at these temperatures is about 1 gram/ml.

Calculate the heat needed to warm ice to 0C = 82 J
Calculate heat needed to melt ice = 668 J
Calculate heat needed to bring the 2 grams of melted ice to 20 C = 167J
The total of these must be used to cool 102 g of water.
Drops by 2.2 C to 17.8 C

23) Consider the reaction:

$2H_2 + O_2 \rightarrow 2H_2O$

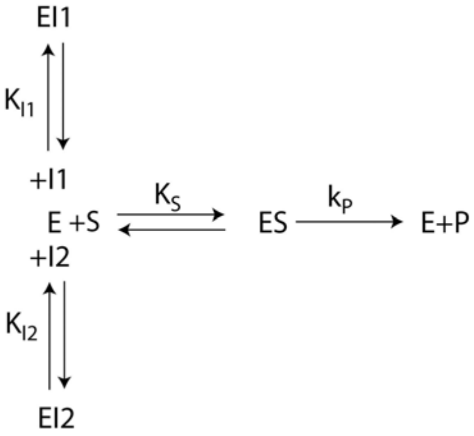
Given the half reactions:
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0 = +1.23$ V
$2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0$ V

Determine E^0 for the total reaction as well as ΔG^0 and K_{EQ} at 298K
(Note, do not be alarmed by the size of the K_{EQ} for this reaction. It is indeed a VERY spontaneous reaction.)

$E^0 = 1.23$V; $\Delta G^0 = -nFE = -(4)(96500\text{mole/C})(1.23\text{J/C}) = -475$ kJ/mole
$K_{EQ} = \exp(-\Delta G^0/RT) = 1.83 \times 10^{83}$

Quasi Real World Problem (8 points)

24) Consider an enzyme system with two different competitive inhibitors, I1 and I2. Determine the velocity of the reaction (dP/dt) in terms of the concentration of the substrate, [S], the concentration of the inhibitors, [I1] and [I2], the dissociation constants for the substrate and inhibitors, K_S, K_{I1}, K_{I2}, the total amount of enzyme, E_{tot}, and the rate constant for formation of P from the ES complex, k_P.



$$\frac{dP}{dt} = V = k_p[ES] = k_p\frac{[E][S]}{K_S}$$

$$E_{Tot} = [E] + [ES] + [EI1] + [EI2]$$

$$= [E] + \frac{[E][S]}{K_S} + \frac{[E][I1]}{K_{I1}} + \frac{[E][I2]}{K_{I2}}$$

$$[E] = \frac{E_{Tot}}{1 + \frac{[S]}{K_S} + \frac{[I1]}{K_{I1}} + \frac{[I2]}{K_{I2}}}$$

$$V = \frac{k_P E_{Tot}[S]}{\left(1 + \frac{[S]}{K_S} + \frac{[I1]}{K_{I1}} + \frac{[I2]}{K_{I2}}\right)K_S}$$