CHEM 5200 - Exam 4 - November 29, 2018

INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

F = 96,500 C/mol

1 C-Volt = 1 J

R = 8.31 J/mol-K = 0.00831 kJ/mol-K

R = 8.31 C-V/mol-K = 8.31 kPa-L/mol-K

1 L-atm = 101 J

1 L-bar = 100 J

1 kPa-L = 1 J

1 bar = 100 kPa

1 bar = 750 torr

1 atm = 760 torr

The Nernst Equation: $E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log(Q) = E^{o}_{cell} - \frac{RT}{nF}\ln(Q)$

CHEM 5200 - Exam 4 - November 29, 2018

Name_____________________________

(33 points) MULTIPLE CHOICEn (3 pts. per question)

1. Consider the gas phase equilibrium, $2\,POBr_3(g) \rightleftharpoons 2\,PBr_3(g) + O_2(g)$. The enthalpy change for this reaction is +120 kJ

   For the above reaction, if the temperature is **decreased**,

   (A) the equilibrium will move to the left and K will decrease

   (B) the equilibrium will move to the right and K will increase

   (C) the equilibrium will move to the left and K will remain constant

   (D) the equilibrium will move to the right and K will remain constant

2. Consider an electrochemical concentration cell with 0.30 M $Mg(NO_3)_2$(aq) in the reference compartment (cathode) and an unknown concentration (X M) of $Mg(NO_3)_2$(aq) in the sample compartment (anode). In standard electrochemical notation, this cell would be denoted: Mg(s)|Mg^{2+}(X M)||Mg^{2+}(0.30 M)|Mg(s).

   The voltage in this concentration cell (at 25 ^oC) is +0.160 Volts. The $Mg(NO_3)_2$(aq) concentration in the sample compartment is approximately:

   (A) $3.9x10^{-6}$ M (B) $2.4x10^{-8}$ M (C) $1.2x10^{-6}$ M (D) 5.9x10

For #3 - #4: The reduction potential of Al^{3+} is -1.66 V and the reduction potential of Mn^{2+} is -1.18 V.

3. What is the equilibrium constant, K, for the electrochemical reaction given by Mn|Mn^{2+}||Al^{3+}|Al (at 25 ^oC) ?

   A) $4.7x10^{-25}$ (B) $2.2x10^{-49}$ (C) $4.5x10^{+48}$ (D) $7.8x10^{-9}$

4. What is the approximate cell potential at 25 ^oC for the reaction, Mn(s)|Mn^{2+}($2.0x10^{-5}$ M)||Al^{3+}(2.0 M)|Al(s) where the concentrations of the aqueous species are given in parentheses?

   (A) -0..63 V (B) +0.33 V (C) +0.63 V (D) -0.33 V

5. Consider a second order reaction: $\frac{d[A]}{dt} = -k[A]^2$. When the initial concentration is $[A]_o$ = 0.60 M, the concentration decreases to 0.15 M 25 seconds after the start of the reaction. Therefore the rate constant is approximately:

   (A) 0.10 $M^{-1}s^{-1}$ (B) 0.17 $M^{-1}s^{-1}$ (C) 0.20 $M^{-1}s^{-1}$ (D) 0.08 $M^{-1}s^{-1}$

For #6 - #7: Consider the reaction, A $\rightarrow$ P, which is a zeroth order reaction; i.e. $\frac{d[A]}{dt} = -k$. The rate constant for this reaction is k= 0.02 Ms^{-1}, and the initial concentration of A is 0.90 M.

6. The half-life of this reaction is approximately

   (A) 16 s (B) 23 s (C) 56 s (D) 35 s

7. The concentration of [A] 30 s after the start of the reaction is approximately

   (A) 0.49 M (B) 0.62 M (C) 0.18 M (D) 0.30 M

For #8 - #9: The reaction, A $\rightarrow$ P, is of order "x"; therefore, the initial rate is $r_0=k[A]_0^x$. When $[A]_0$= 0.2 M, r_0= 0.0100 M s^{-1}. When $[A]_0$= 0.5 M, r_0= 0.156 M s^{-1}.

8. What is the order of this reaction, x ?

   (A) 3.0 (B) 2.5 (C) 2.0 (D) 4.0

9. What is the approximate value of the rate constant, k, for this reaction?

   (A) 0.25 M^{-1} s^{-1} (B) 6.25 M^{-3} s^{-1} (C) 1.25 M^{-2} s^{-1} (D) 0.56 $M^{-3/2}$ s^{-1}

10. The reaction, A $\rightarrow$ Products, is of order "x"; i.e. rate = $k[A]^x$. When $[A_o]$= 0.1 M, the half-life of the reaction is 300 s. When $[A]_o$= 0.3 M, the half life of the reaction is 173 s. The order of the reaction, x, is

    (A) -1/2 (B) 2 (C) 1/2 (D) 3/2

11. Consider the competitive first order reactions, $A \xrightarrow{k_1} B$ *and* $A \xrightarrow{k_2} C$

    It is known that the ratio of the two first order rate constants for a pair of competitive reactions is: $k_2/k_1 = 1.50$. When a kinetics experiment is performed with the initial concentration, $[A]_o$ = 0.80 M, the approximate concentration of B at the conclusion of the reaction, (i.e. $[B]_\infty$), will be:

    (A) 0.40 M (B) 0.32 M (C) 0.53 M (D) 0.48 M

Four (4) problems follow: NOTE: You Must show your work to receive credit.

(16) 1. Consider the hypothetical gas phase equilibrium reaction: $A(g) \underset{}{\overset{K}{\rightleftarrows}} B(g) + C(g)$.
The equilibrium constant, K, for this reaction is 2.5 at 300 ^{o}C and 140. at 600 ^{o}C

Calculate the Enthalpy Change for this reaction, $\Delta_r H^o$, in kJ/mol, and the Entropy Change, $\Delta_r S^o$, in J/mol-K.

(14) 2. An electrochemical cell is prepared with 0.10 M $AgNO_3(aq)$ in the reference compartment (cathode) and a saturated solution of silver arsenate, $Ag_3AsO_4(aq)$, in the sample compartment (anode). In standard electrochemical notation, this cell would be denoted: $Ag(s)|Ag^+(xx\ M)||Ag^+(0.10\ M)|Ag(s)$.

The measured cell voltage is +0.26 V.

Calculate the Solubility Product, K_{sp}, of Ag_3AsO_4.

(16) 3. A hypothetical electrochemical reaction, $3\ A(s) + 2\ B^{3+}(s) \rightarrow 3\ A^{2+}(aq) + 2\ B(s)$, has a standard electrochemical cell potential that is temperature dependent and given by: $E^0_{cell} = a + bT^{1/2}$ where a = +0.026 V and b = $5.1\text{x}10^{-3}$ V/$K^{1/2}$

(T is temperature in Kelvin)

(8) (a) Calculate the equilibrium constant, K, for this reaction at 25 ^{o}C

(8) (b) Calculate the Enthalpy change, $\Delta_r H^o$ (in kJ), for this reaction at 25 ^{o}C.

(21) 4. Consider a reaction, A $\rightarrow$ Products, which is of fourth order with respect to [A];

i.e. $Rate = -\frac{d[A]}{dt} = k\left[A\right]^4$

(12) (a) When the initial concentration is $[A]_o$ = 0.60 M, the half-life of the reaction is 45 s

Calculate the rate constant for this reaction. **SHOW UNITS**

4. Continued.

Note: For parts (b) and (c), If you don't like your answer to part (a), use k = 0.20 $M^{-3}s^{-1}$

(5) (b) If one starts the reaction with $[A]_o$ = 0.60 M, what is the concentration, [A], 150 s after the start of the reaction.

(4) (c) What is the half-life of the reaction when $[A]_o$ = 0.40 M?