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 Solutions

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

1. Consider the gas phase equilibrium, $2POBr_3(g) \rightleftarrows 2PBr_3(g) + O_2(g)$. 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 °C) is +0.160 Volts. The $Mg(NO_3)_2(aq)$ concentration in the sample compartment is approximately:

   (A) 3.9×10^{-6} M (B) 2.4×10^{-8} M (C) 1.2×10^{-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 °C) ?

   A) 4.7×10^{-25} (B) 2.2×10^{-49} (C) $4.5 \times 10^{+48}$ (D) 7.8×10^{-9}

4. What is the approximate cell potential at 25 °C for the reaction, $Mn(s)|Mn^{2+}(2.0 \times 10^{-5}\ M)||Al^{3+}(2.0\ M)|Al(s)$ 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, $A \to P$, 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, $A \to P$, 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, $A \to$ 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.

$k_1 = 2.5$ $\quad$ $k_2 = 140$

$T_1 = 573\,K$ $\quad$ $T_2 = 873$

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

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Delta H^0 = \frac{-R\ln(K_2/K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-8.31\ \text{J/mol-K}\ \ln\left(\frac{140}{2.5}\right)}{\frac{1}{873K} - \frac{1}{573K}}$$

$$= 55780\ \text{J/mol} = \boxed{55.8\ \text{kJ/mol}}$$

$$\Delta G_1^o = -RT_1 \ln K_1 = -8.31(573)\ln(2.5) = -4363\ \text{J/mol}$$

$$= \Delta H^0 - T\Delta S^0$$

$$\therefore \quad \Delta S^0 = \frac{\Delta H^0 - \Delta G_1^0}{T_1} = \frac{55780 - (-4363)}{573}$$

$$= \boxed{105\ \text{J/mol-K}}$$

Get same ΔS^0 if use K_2 & T_2

(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.

Calc $[Ag^+]$: $Ag^+(0.10\,m) \rightarrow Ag^+(xx\,m)$

$+0.26 = E_{cell} = 0 - \frac{.0592}{1}\log\left(\frac{xx}{0.10\,m}\right) \rightarrow \log\left(\frac{xx}{0.10}\right) = -\frac{1}{0.0592}(0.26V)$

$\log\left(\frac{xx}{0.10}\right) = -4.39 \rightarrow \frac{xx}{0.10} = 10^{-4.39} = 4.06\times10^{-5}\,M$

$[Ag^+] = 0.10\,(4.06\times10^{-5}) = 4.06\times10^{-6}\,m$

Calc K_{sp}

$Ag_3AsO_4 \rightleftharpoons 3Ag^+ + AsO_4^{3-}$
$\quad\quad\quad\quad 3s \quad\quad s$

$[AsO_4^{3-}] = \frac{1}{3}(4.06\times10^{-6}\,m) = 1.35\times10^{-6}\,m$

$K_{sp} = [Ag^+]^3[AsO_4^{3-}] = (4.06\times10^{-6})^3(1.35\times10^{-6})$

$= \boxed{9.0\times10^{-23}}$

$T = 25°C = 298 K$ $n = 6$

(16) 3. A hypothetical electrochemical reaction, 3 A(s) + 2 B^{3+} (s) → 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 = 5.1x10^{-3} V/$K^{1/2}$

(T is temperature in Kelvin)

(8) (a) Calculate the equilibrium constant, K, for this reaction at 25 °C

$E_0 = a + bT^{1/2} = +0.026V + (5.1 \times 10^{-3} V/K^{1/2})(298 K)^{1/2}$

$= 0.114V$

$E_0 = \frac{0.0592}{n} \log K \rightarrow \log K = \frac{nE^0}{.0592} = \frac{6(0.114)}{0.0592} = 11.56$

$K = 10^{11.56} = \boxed{3.6 \times 10^{11}}$

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

$\Delta G^0 = -nFE^0 = -6(96,500 C/mol)(0.114V) = -66,000 C \cdot V/mol$
$= -66,000 J/mol$

$\Delta S^0 = nF \frac{dE^0}{dT} = nF(0 + \frac{1}{2} b T^{-1/2})$

$= \frac{nFb}{2T^{1/2}} = \frac{6(96,500 C/mol)(5.1 \times 10^{-3} V/K^{1/2})}{2(298K)^{1/2}} = +85.5 J/mol \cdot K$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta H^0 = \Delta G^0 + T\Delta S^0 = -66,000 J/mol + 298K(85.5 J/mol \cdot K)$

$= -40,500 J/mol = \boxed{-40.5 kJ/mol}$

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

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

(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**

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^4} = \int_0^t -k\,dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^4} = \int_{[A]_0}^{[A]} [A]^{-4}\,d[A]$$

$$= \frac{1}{-4+1}\left\{[A]^{-3}\right\}_{[A]_0}^{[A]}$$

$$= -\frac{1}{3}\left[\frac{1}{[A]^3} - \frac{1}{[A]_0^3}\right]$$

$$-\frac{1}{3}\left[\frac{1}{[A]^3} - \frac{1}{[A]_0^3}\right] = -kt$$

$$\boxed{\frac{1}{[A]^3} - \frac{1}{[A]_0^3} = +3kt}$$

$[A]_0 = 0.60M$, $t_{\frac{1}{2}} = 45s$ → $[A] = 0.30M$ at $t = 45s$

$$k = \frac{1}{3t}\left[\frac{1}{[A]^3} - \frac{1}{[A]_0^3}\right] = \frac{1}{3(45s)}\left[\frac{1}{(0.30M)^3} - \frac{1}{0.60M^3}\right]$$

$$\boxed{k = 0.24\ M^{-3}s^{-1}}$$

$k = 0.24\ M^{-3}s^{-1}$

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.

$[A]_o = 0.60M$

$t = 150 s$

$[A] = ?$

$$\frac{1}{[A]^3} = \frac{1}{[A]_o^3} + 3kt = \frac{1}{(0.60M)^3} + 3(0.24M^{-3}s^{-1})(150s)$$

$$= 112.6\ M^{-3}$$

$$\frac{1}{[A]} = (112.6M^{-3})^{1/3} = 4.83\ M^{-1}$$

$$[A] = \frac{1}{4.83M^{-1}} = 0.21\ M$$

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

$[A]_o = 0.40M$

$[A] = \frac{1}{2}(0.40) = 0.20M$

$t = t_{1/2} = ?$

$$t = \frac{1}{3k}\left[\frac{1}{[A]^3} - \frac{1}{[A]_o^3}\right]$$

$$= \frac{1}{3(0.24M^{-3}s^{-1})}\left[\frac{1}{(0.20M)^3} - \frac{1}{(0.40M)^3}\right]$$

$$= 150\ s$$