

CHEM 5200 - Exam 4 - November 30, 2017

INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

$$F = 96,500 \text{ C/mol}$$

$$1 \text{ C-Volt} = 1 \text{ J}$$

$$R = 8.31 \text{ J/mol-K} = 0.00831 \text{ kJ/mol-K}$$

$$R = 8.31 \text{ C-V/mol-K} = 8.31 \text{ kPa-L/mol-K}$$

$$1 \text{ L-atm} = 101 \text{ J}$$

$$1 \text{ L-bar} = 100 \text{ J}$$

$$1 \text{ kPa-L} = 1 \text{ J}$$

$$1 \text{ bar} = 100 \text{ kPa}$$

$$1 \text{ bar} = 750 \text{ torr}$$

$$1 \text{ atm} = 760 \text{ torr}$$

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

The TST Equation:
$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta H^{\ddagger}}{RT}}$$
 R, N_A and h are universal constants:

where:
$$\frac{R}{N_A h} = \frac{8.31}{(6.02 \times 10^{23})(6.63 \times 10^{-34})} = 2.1 \times 10^{10}$$

CHEM 5200 - Exam 4 - November 30, 2017

Name Solutions

(36 points) MULTIPLE CHOICE

FOUR (4) points per question (Circle the ONE correct answer)

1. Consider an electrochemical concentration cell with 3.00×10^{-5} M $\text{Au}(\text{NO}_3)_3(\text{aq})$ in the sample compartment (anode) and 0.50 M $\text{Au}(\text{NO}_3)_3(\text{aq})$ in the reference compartment (cathode). In standard electrochemical notation, this cell would be denoted: $\text{Au}(\text{s})|\text{Au}^{3+}(3.00 \times 10^{-5} \text{ M})||\text{Au}^{3+}(0.50 \text{ M})|\text{Au}(\text{s})$.

The voltage in this concentration cell (at 25 °C) is approximately:

- (A) -0.12 V (B) +0.08 V (C) +0.25 V (D) -0.08 V

For #2 - #3: The reduction potential of Cr^{3+} is -0.74 V and the reduction potential of Cu^+ is +0.34 V.

2. What is the equilibrium constant, K, for the electrochemical reaction given by $\text{Cu}|\text{Cu}^+||\text{Cr}^{3+}|\text{Cr}$?

- (A) 1.9×10^{-55} (B) $1.8 \times 10^{+18}$ (C) 5.7×10^{-19} (D) 5.4×10^{-18}

3. What is the approximate cell potential for the reaction, $\text{Cu}(\text{s})|\text{Cu}^+(2.50 \text{ M})||\text{Cr}^{3+}(1.0 \times 10^{-4} \text{ M})|\text{Cr}(\text{s})$, where the concentrations of the aqueous species are given in parentheses?

- (A) +0.98 V (B) -0.50 V (C) -0.98 V (D) -1.18 V

4. The reaction, $\text{A} \rightarrow \text{P}$, is of order "x"; the initial rate is given by $r_0 = k[\text{A}]_0^x$. When the initial concentration is $[\text{A}]_0 = 0.50 \text{ M}$, $r_0 = 50.0 \text{ M/min}$. When $[\text{A}]_0 = 0.30 \text{ M}$, $r_0 = 64.5 \text{ M/min}$. Therefore, the reaction order, x, is:

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

5. The reaction, $\text{A} \rightarrow \text{Products}$, is of order "3/2"; i.e. $\text{rate} = k[\text{A}]^{3/2}$. When $[\text{A}]_0 = 0.10 \text{ M}$, the half-life of the reaction is 500 s. When $[\text{A}]_0 = 0.15 \text{ M}$, the half life of the reaction is approximately:

- (A) 920 s (B) 410 s (C) 610 s (D) 270 s

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

In a kinetics experiment, it was found that, when $[A]_0 = 0.60$ M, then at the completion of the reaction, the final concentration of C (as $t \rightarrow \infty$) is $[C]_\infty = 0.15$ M. In a separate experiment, it was determined that the **second** rate constant is $k_2 = 20$ s⁻¹.

What is the approximate value of the **first** rate constant, k_1 ?

- (A) 60. s⁻¹ (B) 6.7. s⁻¹ (C) 80. s⁻¹ (D) 5.0 s⁻¹

7. When a Transition State Theory Analysis was carried out on temperature dependent rate constant data, it was determined that the intercept and slope of the plot of $\ln(k/T)$ vs. $1/T$ were +19.5 and -4810. K, respectively. What is the approximate Entropy of Activation, ΔS^\ddagger , for this reaction?

- (A) -40 kJ/mol (B) +40 J/mol-K (C) +43.7 J/mol-K (D) -35.5 kJ/mol

For #8 - #9: In the collision theory of bimolecular gas phase reactions, the rate constant, k , is of the form: $k = C\sqrt{T}e^{-\frac{E_0}{RT}}$, where C is a constant and E_0 is the "Threshold Energy".

8. If one has rate constants, k s, as a function of temperature, T , what would one plot in order to obtain a straight line using this theory?

- (A) $\ln(k)$ vs. $1/T$ (B) $\ln(k \cdot \sqrt{T})$ vs. $1/T$
(C) $\ln\left(\frac{k}{\sqrt{T}}\right)$ vs. $1/T$ (D) $\ln\left(\frac{k}{T^{3/2}}\right)$ vs. $1/T$

9. If a given reaction is of the form given above, and you are told that the "Threshold Energy" is $E_0 = 80$ kJ/mol, then at 1200 °C, the Arrhenius Activation Energy, E_a is approximately:

- (A) 92.2 kJ/mol (B) 86.1 kJ/mol (C) 73.9 kJ/mol (D) 67.8 kJ/mol

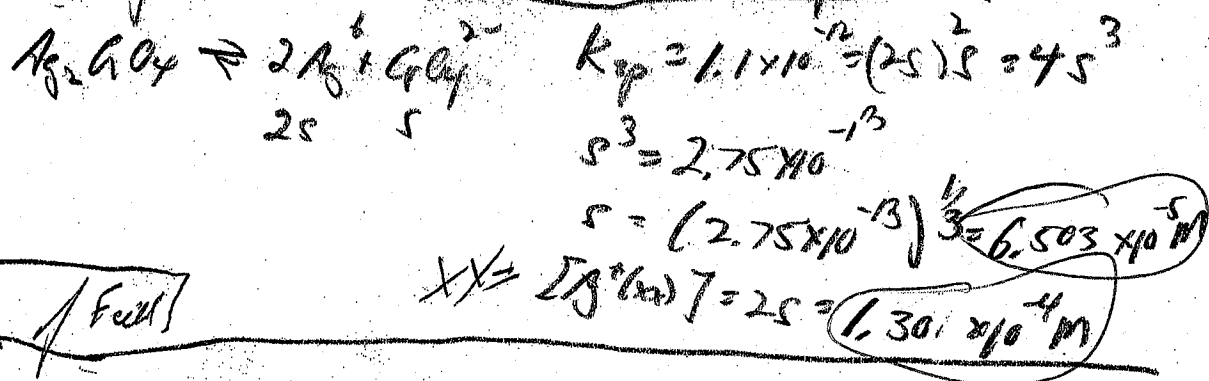
Four (4) problems follow: NOTE: You Must show all of your work to receive credit.

(14) 1. The solubility product of silver chromate, Ag_2CrO_4 , is 1.1×10^{-12} .

An electrochemical cell is prepared with $0.60 \text{ M AgNO}_3(\text{aq})$ in the reference compartment (cathode) and a saturated solution of silver chromate, $\text{Ag}_2\text{CrO}_4(\text{aq})$, in the sample compartment (anode). In standard electrochemical notation, this cell would be denoted: $\text{Ag}(\text{s})|\text{Ag}^+(\text{xx M})||\text{Ag}^+(0.60 \text{ M})|\text{Ag}(\text{s})$.

Calculate the voltage in the electrochemical cell.

1 - Calc. of $\text{Ag}^+(\text{xx})$: Ag^+ conc. in Sample Compartment



2 - Calc. of E_{cell}

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log \left(\frac{\text{xx}}{0.60} \right) \quad n=1$$

$$E_{\text{cell}} = 0 - \frac{0.0592}{1} \log \left(\frac{1.301 \times 10^{-4}}{0.60} \right)$$

$$= +0.217 = \boxed{+0.22 \text{ V}}$$

$$n = 3$$

- (18) 2. A hypothetical electrochemical reaction, $A(s) + 3 B^+(aq) \rightarrow A^{3+}(aq) + 3 B(s)$, has a standard electrochemical cell potential that is temperature dependent and given by:

$$T = 30^\circ\text{C} \quad E_{\text{cell}}^{\circ} = a - \frac{b}{T}, \text{ where } a = 0.12 \text{ V and } b = +15 \text{ V}\cdot\text{K}$$

= 303 K For this reaction, calculate $\Delta_r G^{\circ}$ (in kJ), $\Delta_r H^{\circ}$ (in kJ), and $\Delta_r S^{\circ}$ (in J/K), at 30 °C.

$$E_{\text{cell}}^{\circ} = 0.12 \text{ V} - \frac{15 \text{ V}\cdot\text{K}}{303 \text{ K}} = +0.0705 \text{ V}$$

$$\begin{aligned} \Delta G^{\circ} &= -n F E_{\text{cell}}^{\circ} = -3 \text{ mol} (96,500 \text{ C/mol}) (+0.0705 \text{ V}) \\ &= -2.041 \text{ C}\cdot\text{V} \times \frac{1 \text{ J}}{1 \text{ C}\cdot\text{V}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = -20.41 \text{ kJ} \end{aligned}$$

$$\frac{dE_{\text{cell}}^{\circ}}{dT} = 0 + \frac{b}{T^2} = \frac{15 \text{ V}\cdot\text{K}}{(303 \text{ K})^2} = 1.63 \times 10^{-4} \text{ V/K}$$

$= -20.4 \text{ kJ}$
 ΔG°

$$\begin{aligned} \Delta S^{\circ} &= n F \frac{dE_{\text{cell}}^{\circ}}{dT} = (3 \text{ mol}) (96,500 \text{ C/mol}) (1.63 \times 10^{-4} \text{ V/K}) \\ &= 47.19 \text{ C}\cdot\text{V/K} = 47.2 \text{ J/K} \Delta S^{\circ} \end{aligned}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\begin{aligned} \Delta H^{\circ} &= \Delta G^{\circ} + T \Delta S^{\circ} = -20.4 \text{ kJ} + (303 \text{ K}) (47.2 \text{ J/K}) \times \frac{1 \text{ kJ}}{10^3 \text{ J}} \\ &= -20.4 \text{ kJ} + 14.3 \text{ kJ} \\ &= -6.1 \text{ kJ} \Delta H^{\circ} \end{aligned}$$

$$\int \frac{d[A]}{[A]^{3/2}} = \int [A]^{-3/2} d[A] = \frac{1}{-3/2+1} [A]^{-3/2+1} = -2[A]^{-1/2}$$

(17) 3. Consider a reaction, $A \rightarrow$ Products, which is 3/2 order with respect to $[A]$,

i.e. $\text{Rate} = -\frac{d[A]}{dt} = k[A]^{3/2}$

When the initial concentration is $[A]_0 = 0.70 \text{ M}$, it takes 80 seconds from the start of the reaction for the concentration of A to decrease to 0.45 M

(a) Calculate the rate constant for this reaction.

$$\begin{aligned} [A]_0 &= 0.70 \text{ M} \\ t &= 0 \\ [A] &= 0.45 \text{ M} \\ t &= 80 \text{ s} \end{aligned}$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^{3/2}} = \int_0^t -k dt \rightarrow \left[\frac{-2}{-1/2} [A]^{-1/2} \right]_{[A]_0}^{[A]} = -kt$$

$$\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} = \frac{kt}{2}$$

$$k = \frac{2}{t} \left[\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}} \right] = \frac{2}{80 \text{ s}} \left[\frac{1}{(0.45 \text{ M})^{1/2}} - \frac{1}{(0.70 \text{ M})^{1/2}} \right]$$

$$= 0.00739 \text{ M}^{-1/2} \text{ s}^{-1} = \boxed{0.0074 \text{ M}^{-1/2} \text{ s}^{-1}}$$

(6) (b) If one starts the reaction with $[A]_0 = 0.70 \text{ M}$, what is the approximate concentration, $[A]$, 120 s after the start of the reaction.

$$\begin{aligned} k &= 0.0074 \text{ M}^{-1/2} \text{ s}^{-1} \\ [A]_0 &= 0.70 \text{ M} \\ t &= 120 \text{ s} \\ [A] &= ? \end{aligned}$$

Note: If you don't like your answer to part (a), use $k = 0.009 \text{ M}^{-1/2} \text{ s}^{-1}$

$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_0^{1/2}} + \frac{kt}{2} = \frac{1}{(0.70 \text{ M})^{1/2}} + \frac{(0.0074 \text{ M}^{-1/2} \text{ s}^{-1})(120 \text{ s})}{2}$$

$$= 1.64 \text{ M}^{-1/2}$$

$$[A]^{1/2} = \frac{1}{1.64 \text{ M}^{-1/2}} = 0.61 \text{ M}^{1/2}$$

$$[A] = (0.61 \text{ M}^{1/2})^2 = \boxed{0.37 \text{ M}}$$

$$(t_{1/2})_1 = 0.45 \text{ s} \quad (t_{1/2})_2 = 0.08 \text{ s}$$

$$T_1 = 60^\circ\text{C} = 333 \text{ K} \quad T_2 = 100^\circ\text{C} = 373 \text{ K}$$

- (15) 4. Consider a first order reaction for which the half-life is $t_{1/2} = 0.45 \text{ s}$ at 60°C and $t_{1/2} = 0.08 \text{ s}$ at 100°C .

Calculate the Arrhenius parameters, A (in s^{-1}) and E_a (in kJ/mol) for this reaction.

$$\frac{k_2}{k_1} = \frac{0.693/(t_{1/2})_2}{0.693/(t_{1/2})_1} = \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{0.45}{0.08}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$E_a = -\frac{R \ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{(-8.31 \text{ J/mol}\cdot\text{K}) \left(\ln\left(\frac{0.45}{0.08}\right) \right)}{\frac{1}{373 \text{ K}} - \frac{1}{333 \text{ K}}}$$

$$= 4.46 \times 10^4 \text{ J/mol} = \frac{1 \text{ kJ}}{10^3} = \boxed{44.6 \text{ kJ/mol}}$$

$$T_1 = 333 \text{ K}$$

$$k_1 = \frac{0.693}{(t_{1/2})_1} = \frac{0.693}{0.45 \text{ s}} = 1.54 \text{ s}^{-1}$$

$$\ln k_1 = \ln A - \frac{E_a}{R T_1}$$

$$\ln A = \ln k_1 + \frac{E_a}{R T_1} = \ln(1.54) + \frac{4.46 \times 10^4}{(8.31)(333)}$$

$$A = e^{16.55} = \boxed{1.54 \times 10^7 \text{ s}^{-1}} \quad (8.31)(333) = 16.55$$

Notes: $T_2 \neq (t_{1/2})_2$ gets same

answer.