

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

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Name _____

(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 $k_2 = 20 \text{ s}^{-1}$.

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

- (A) $60. \text{ s}^{-1}$ (B) $6.7. \text{ s}^{-1}$ (C) $80. \text{ s}^{-1}$ (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 $-4810. \text{ K}$, respectively. What is the approximate Entropy of Activation, ΔS^\ddagger , for this reaction?

- (A) -40 kJ/mol (B) $+40 \text{ J/mol-K}$ (C) $+43.7 \text{ J/mol-K}$ (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 $E_0 = 80 \text{ kJ/mol}$, then at $1200 \text{ }^\circ\text{C}$, 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 M $\text{AgNO}_3(\text{aq})$ 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.

- (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:

$$E_{cell}^0 = a - \frac{b}{T}, \text{ where } a = 0.12 \text{ V and } b = +15 \text{ V}\cdot\text{K}$$

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.

(17) 3. Consider a reaction, $A \rightarrow \text{Products}$, 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

(11) (a) Calculate the rate constant for this reaction. **SHOW UNITS**

(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.

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

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

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