

CHEM 5200 - Final Exam - December 14, 2017

INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

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

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

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

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

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

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

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

Relations for Adiabatic Expansions and Compressions of a Perfect Gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{R/C_{V,m}} \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^{C_{p,m}/C_{V,m}} = \left(\frac{V_1}{V_2} \right)^\gamma$$

Photochemistry

$$\text{Singlet State Lifetime: } \tau_0 = \frac{1}{k_0} = \frac{1}{k_F + k_{IC} + k_{ISC}}$$

Fluorescence Quantum Yield (No quencher):

$$\Phi_{F,0} = \frac{k_F}{k_F + k_{IC} + k_{ISC}} = \frac{k_F}{k_0}$$

Fluorescence Quantum Yield (quencher, Q, present):

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} = \frac{k_F}{k_0 + k_Q[Q]}$$

$$\text{Light Energy/Wavelength Relation: } E_{ph} = h\nu = \frac{hc}{\lambda(m)} = \frac{1.99 \times 10^{-25} \text{ J} \cdot m}{\lambda(m)}$$

CHEM 5200 - Final Exam - December 15, 2016

Name _____

If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

Four (4) digit number for posting

(60) MULTIPLE CHOICE [3 points per question] (Circle the ONE correct answer)

1. Solid Tungsten hexacarbonyl, $W(CO)_6(s)$ can be decomposed to $W(s)$ and $CO(g)$ at high temperature. What is the work involved when **two (2)** moles of $W(CO)_6(s)$ are decomposed at 150 °C and 1 bar pressure.?
- (A) +21.1 kJ (B) -42.2 kJ (C) -21.1 kJ (D) -10.5 kJ

For #2 - #3: Consider **five(5)** moles of a perfect gas initially at a temperature of 200 °C and volume 30 L. The gas has a constant volume molar heat capacity, $C_{V,m} = 26.0 \text{ J/mol}\cdot\text{K}$. The gas undergoes a **reversible, adiabatic** compression to a final volume of 10 L (corresponding to a final temperature of 400 °C)

2. The work, w , for this process is approximately:
- (A) +11, kJ (B) +5. kJ (C) +26 kJ (D) -11. kJ
3. The Enthalpy change, ΔH , for this process is approximately:
- (A) +34. kJ (B) -18. kJ (C) +14. kJ (D) +18. kJ
4. The Entropy change for this process, ΔS , is approximately:
- (A) -14.2 J/K (B) 0 J/K (C) +14.2 J/K
(D) None of the above

For #5- #7: Consider **three (3)** moles of benzene gas at its normal boiling point of 80 °C. The enthalpy of vaporization of benzene is 34.0 kJ/mol

5. What is the work involved when 3 moles of benzene gas are condensed to liquid at 80 °C and 1 bar pressure?
- (A) +12.3 kJ (B) -8.8 kJ (C) -2.9 kJ (D) +8.8 kJ

For #14 - #15: The reaction, $A \rightarrow P$, is of order "x"; therefore, the initial rate is $r_0 = k[A]_0^x$. When $[A]_0 = 0.35 \text{ M}$, $r_0 = 0.120 \text{ M s}^{-1}$. When $[A]_0 = 0.5 \text{ M}$, $r_0 = 0.418 \text{ M s}^{-1}$.

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

- (A) 5/2 (B) 3 (C) 7/2 (D) 4

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

- (A) $2.8 \text{ M}^{-2} \text{ s}^{-1}$ (B) $4.7 \text{ M}^{-5/2} \text{ s}^{-1}$ (C) $1.7 \text{ M}^{-3/2} \text{ s}^{-1}$ (D) $8.0 \text{ M}^{-3/2} \text{ s}^{-1}$

For #16 - #17: Consider the reaction, $A \rightarrow P$, which is a third order reaction; i.e. rate = $k[A]^3$. The rate constant for this reaction is $k = 0.10 \text{ M}^{-2} \text{ s}^{-1}$, and the initial concentration of A is 0.40 M .

16. What is the half-life of this reaction?

- (A) 94 s (B) 28 s (C) 6.9 s (D) 188 s

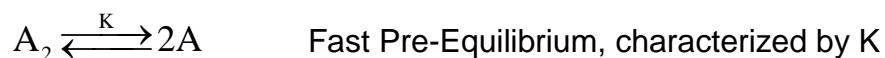
17. What will be the concentration of [A] 25 s after the start of the reaction.

- (A) 0.09 M (B) 0.26 M (C) 0.17 M (D) 0.30 M

18. The reaction, $A \rightarrow P$, is of order "x"; i.e. rate = $k[A]^x$. When $[A]_0 = 0.6 \text{ M}$, the half-life of the reaction is 48. s. When $[A]_0 = 0.2 \text{ M}$, the half life of the reaction is 250. s. The order of the reaction, x, is

- (A) 3/2 (B) 2 (C) 5/2 (D) 3

19. A reaction, $A_2 + 2B \rightarrow P$, proceeds by the following two step mechanism:



The rate law for the formation of product is of the form:

- (A) $k_{\text{eff}}[A_2]^2[B]$ (B) $k_{\text{eff}}[A_2][B]$ (C) $k_{\text{eff}}[A_2]^{1/2}[B]$ (D) $k_{\text{eff}}[A_2][B]^{1/2}$

20. In a photochemical reaction, $A \rightarrow B + 3C$, the reaction quantum yield for the decomposition of A is $\Phi_R = 0.30$. When A is irradiated with light at the absorption wavelength, λ for a period of time, it is found that 1.5 mol of C is formed. Approximately how many photons were absorbed by A in this experiment.

*The numerical value of λ is unnecessary to work the question.

- (A) 1.0×10^{24} (B) 3.0×10^{24} (C) 1.0×10^{23} (D) 9.0×10^{24}

There are six (6) problems following. You must show your work to receive credit.

(16) 1. A Perfect Gas has a temperature dependent constant pressure molar heat capacity,

$$C_{p,m} = a - \frac{b}{T}, \text{ with } a = 40 \text{ J/mol-K and } b = 8.0 \times 10^3 \text{ J/mol.}$$

Two (2) moles of this gas, originally at 750 K and 1.5 atm is cooled reversibly at **constant volume** to 300 K.

(8) (a) Calculate ΔU for this process, in kJ

(8) (b) Calculate ΔS for this process, in J/K

(14) 2. Consider a hypothetical gas that obeys the equation of state:

$$pV = nRT + \frac{A}{V}, \text{ where } A \text{ is a constant}$$

If this gas undergoes an isothermal expansion from V_1 to V_2 , develop **INTEGRATED** expressions for ΔH and ΔG in terms of n , R , T , A , V_1 and V_2

- (10) 3. Calculate the entropy change of the **system**, ΔS_{sys} , when one (1) mole of liquid iodine freezes irreversibly to the solid at 94 °C.

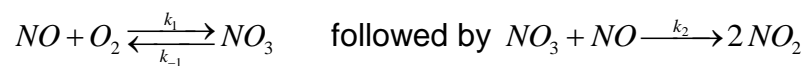
Information: The normal melting (freezing) point of Iodine is 114 °C

The Enthalpy of Fusion is 13.5 kJ/mol at 114 °C.

The constant pressure molar heat capacity of liquid Iodine is 81. J/mol-K

The constant pressure molar heat capacity of solid Iodine is 54. J/mol-K.

(08) 4. The reaction, $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$, has the following mechanism:



NO_3 is an intermediate present in steady-state concentration.

Use the steady-state approximation on $[\text{NO}_3]$ to develop an expression for the rate of the reaction, $\text{Rate} = \frac{1}{2} d[\text{NO}_2]/dt$, as a function of $[\text{NO}]$, $[\text{O}_2]$, k_1 , k_{-1} , and k_2 .

- (10) 5. In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 280 nm radiation from a 120 W (J/s) source for 30 min. The intensity of the transmitted light was 35% that of the incident light. As a result of the irradiation, 0.120 mol of the absorbing substance decomposed.

Determine the reaction quantum yield, Φ_R .

- (10) 6. The fluorescence quantum yield for a chromophore dissolved in water is 0.42. When a quencher is added to the solution, with $[Q] = 0.02 \text{ M}$, the quantum yield is reduced to 0.18. Given that the singlet state lifetime is 45 ns, calculate the quenching rate constant, k_Q , in $\text{M}^{-1}\text{s}^{-1}$.