CHEM 5200 - Final Exam - December 14, 2017

INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

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

1 L-atm = 101 J	1 L-bar = 100 J
1 kPa-L = 1 J	1 bar = 100 kPa
1 atm = 760 torr	1 bar = 750 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

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

Fluorence 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):

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

Light Energy/Wavelength Relation: $E_{ph} = h\nu = \frac{hc}{\lambda(m)} = \frac{1.99x10^{-25}\, J\cdot m}{\lambda(m)}$

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.

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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 ^oC 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 ^oC and volume 30 L. The gas has a constant volume molar heat capacity, $C_{V,m}$ = 26.0 J/mol-K. The gas undergoes a **reversible, adiabatic** compression to a final volume of 10 L (corresponding to a final temperature of 400 ^oC)

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 ^oC. 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 ^oC and 1 bar pressure?

   (A) +12.3 kJ (B) -8.8 kJ (C) -2.9 kJ (D) +8.8 kJ

6. What is the internal energy change, ΔU, when 3 moles of benzene gas are condensed to the liquid at 80 ^oC and 1 bar pressure?

(A) -25.2 kJ (B) -93.2 kJ (C) -102.0 kJ (D) -110.8 kJ

7. What is the entropy change of the **system** when 3 moles of benzene gas are condensed to the liquid at 80 ^oC and 1 bar pressure?

(A) +289 J/K (B) -96.3 J/K (C) +72.4 J/K (D) -289 J/K

8. The normal melting point of toluene is -95 ^oC. The Enthalpy of Fusion of toluene is 6.6 kJ/mol. What is the entropy change of the surroundings, ΔS_{surr}, when **one(1)** mole of liquid toluene crystallizes to solid toluene at -95 ^oC?

(A) -37 J/mol-K (B) -48.3 J/mol-K (C) +69 J/mol-K (D) +37 J/mol-K

For #9 - #11: Consider the gas phase equilibrium, $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$. For this reaction, the equilibrium constant is K = 1.3×10^{-4} at 400 ^oC. The enthalpy change for this reaction is $\Delta_r H^o$ = -92.0 kJ (independent of temperature)

9. What is the entropy change, ΔS^o, for this reaction (independent of temperature).

(A) +62.4 J/K (B) +211 J/K (C) -211 J/K (D) -62.4 J/K

10. What is ΔG for this reaction at 400 ^oC when $P_{N2} = P_{H2}$ = 3.0 bar and P_{NH3} = 0.2 bar?

(A) -42.6 kJ (B) +7.5 kJ (C) +24.7 kJ (D) +92.6 kJ

11. What is the value of the equilibrium constant, K, at 150 ^oC?

(A) 2.2 (B) 8.4×10^{-3} (C) 1.7×10^{4} (D) 7.9×10^{-9}

12. Consider the gas phase equilibrium, $A(g) \overset{K}{\rightleftharpoons} 2\,B(g)$. When the pressures of A and B are each 0.20 bar at 100 ^oC, the Gibbs Energy change for the reaction is -10.0 kJ. What is the approximate value of the equilibrium constant?

(A) 5,.0 (B) 45. (C) 0.3 (D) 12.7

13. Consider the gas phase equilibrium, 2A $\rightleftarrows$ B. If one starts with 3 moles of A and 3 moles of B in a vessel, and the reaction goes to equilibrium, the mixture contains 1.4 moles of A at a total pressure of 4 bar. Therefore, the value of the equilibrium constant, K, is approximately:

(A) 10.1 (B) 1.9 (C) 2.5 (D) 0.5

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 M, r_0= 0.120 M s^{-1}. When $[A]_0$= 0.5 M, r_0= 0.418 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 M^{-2} s^{-1} (B) 4.7 $M^{-5/2}$ s^{-1} (C) 1.7 $M^{-3/2}$ s^{-1} (D) 8.0 M^{-32} 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 $M^{-2}s^{-1}$, 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 $[A_o]$= 0.6 M, the half-life of the reaction is 48. s. When $[A]_o$= 0.2 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:

$$A_2 \underset{}{\overset{K}{\rightleftarrows}} 2A$$ Fast Pre-Equilibrium, characterized by K

$$A + B \xrightarrow{k} P$$ Slow RDS, characterized by k

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

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

20. In a photochemical reaction, A $\rightarrow$ B + 3C, the reaction quantum yield for the decomposition of A is Φ_R = 0.30 . When A is irradiated with light at the absorption wavelength,* 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) $1.0x10^{24}$ (B) $3.0x10^{24}$ (C) $1.0x10^{23}$ (D) $9.0x10^{24}$

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,

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

$$pV = nRT + \frac{A}{V}$$, where A 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**, $\Delta \mathbf{S_{sys}}$, when one (1) mole of liquid Iodine freezes irreversibly to the solid at 94 ^{o}C.

Information: The normal melting (freezing) point of Iodine is 114 ^{o}C
The Enthalpy of Fusion is 13.5 kJ/mol at 114 ^{o}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 NO(g) + O_2(g) $\rightarrow$ 2 NO_2(g), has the following mechanism:

$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_3$ followed by $NO_3 + NO \xrightarrow{k_2} 2\,NO_2$

NO_3 is an intermediate present in steady-state concentration.
Use the steady-state approximation on [NO_3] to develop an expression for the rate of the reaction, Rate = ½ d[NO_2]/dt , as a function of [NO], [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 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 $M^{-1}s^{-1}$.