

CHEM 5200 - Final Exam - December 13, 2018

INFORMATION PAGES (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

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{R/C_{V,m}} \quad \text{or} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{C_{p,m}/C_{V,m}} = \left(\frac{V_1}{V_2} \right)^\gamma$$

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:

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

Photochemistry equations on following page.

Photochemistry

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

Fluorescence Quantum Yield (No quencher):

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

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

Fluorescence Quantum Yield (quencher, Q, present): -

NOT NEEDED THIS YEAR

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

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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

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

1. Dimanganese Decacarbonyl can be decomposed to CO(g) and Mn(s) via the reaction: $Mn_2(CO)_{10}(s) \rightarrow 2Mn(s) + 10CO(g)$

What is the work involved when a sufficient quantity of $Mn_2(CO)_{10}(s)$ is decomposed to form three(3) moles of Mn(s) at 200 °C and 1. bar pressure (in kJ)?

(A) -59.0 kJ (B) -24.9 kJ (C) +39.3 kJ (D) -39.3 kJ

2. The constant volume molar heat capacity of CO₂(g) is constant at $C_{V,m} = 28.2 \text{ J/mol-K}$. When 5. moles of CO₂(g) is cooled from 300 °C to 50 °C at a constant pressure of 1. bar, the enthalpy change and work are approximately:

(A) $\Delta H = -45.6 \text{ kJ}$ & $w = -10.4 \text{ kJ}$ (B) $\Delta H = -35.3 \text{ kJ}$ & $w = +10.4 \text{ kJ}$
(C) $\Delta H = -45.6 \text{ kJ}$ & $w = +10.4 \text{ kJ}$ (D) $\Delta H = -35.3 \text{ kJ}$ & $w = -10.4 \text{ kJ}$

For #3 - #4: Consider **four(4)** moles of a perfect gas initially at a temperature of 300 °C and volume of 20 L. The gas has a **constant volume** molar heat capacity, $C_{V,m} = 25.7 \text{ J/mol-K}$. The gas undergoes a **reversible, adiabatic** expansion to a final volume of 50 L.

3. The work, w , for this process is approximately:

(A) -11.8 kJ (B) -7.9 kJ (C) 0 kJ (D) -15.1 kJ

4. The Enthalpy change, ΔH , for this process is approximately:

(A) -15.6 kJ (B) -20.0 kJ (C) -26.4 kJ (D) -10.5 kJ

For #5 - #7: The boiling point of p-dibromobenzene is 220 °C and the Enthalpy of Vaporization is 50.0 kJ/mol. Consider the reversible condensation of **six(6)** moles of p-dibromobenzene at 220 °C and 1 bar pressure.

5. The work, w , for this process is approximately
(A) -11.0 kJ (B) +24.6 kJ (C) -24.6 kJ (D) +11.0 kJ
6. The Internal Energy change, ΔU , for this process is approximately
(A) -325 kJ (B) +325 kJ (C) -275 kJ (D) 0 kJ
7. The entropy change of the system, ΔS_{sys} , for this process is approximately
(A) -610 J/K (B) -100 J/K (C) 0 J/K (D) +610 J/K
8. The normal melting point of toluene is -95 °C. The Enthalpy of Fusion of toluene is 6.6 kJ/mol. What is the approximate entropy change of the surroundings, ΔS_{surr} , when **three(3)** moles of liquid toluene crystallize to solid toluene at -95 °C?
(A) -54 J/K (B) -111 J/K (C) +37 J/K (D) +111 J/K
9. When 20 grams of an unknown compound is dissolved in 150 grams of water ($K_f = 1.86 \text{ }^\circ\text{C/m}$), the freezing point of the solution is -3.5 °C. What is the Molar Mass of the unknown compound?
(A) 10.6 g/mol (B) 71. g/mol (C) 124.. g/mol (D) 45. g/mol

For #10 - #13: Consider the gas phase equilibrium,
 $2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_5(\text{g})$. The enthalpy change for this reaction is -170. kJ and the equilibrium constant is 2.5 at 150 °C.

10. For the above reaction, if $\text{N}_2(\text{g})$ is added at a constant total pressure of 5 bar,
(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
11. For the above reaction, if the temperature is increased,
(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

12. The Gibbs energy change, $\Delta_r G$, for the above reaction at 150 °C when $P_{N_2O_5} = 2.0$ bar and $P_{NO_2} = P_{O_2} = 0.80$ bar is approximately
- (A) -3.2 kJ (B) -7.6 kJ (C) +7.6 kJ (D) +1.2 kJ
13. The value of the equilibrium constant for the above reaction at 100 °C is approximately:
- (A) 1630. (B) 650. (C) 2.52 (D) 6.1×10^{-4}
14. Consider the gas phase equilibrium, $A(g) \rightleftharpoons 2B(g)$. When the pressures of A and B are each 0.30 bar at 100 °C, the Gibbs Energy change for the reaction is -1.50 kJ. What is the approximate value of the equilibrium constant?
- (A) 5.4 (B) 0.5 (C) 2.1 (D) 0.3
15. Radioisotope decay follows **first order** kinetics. Radioiodine (^{131}I) is used in the medical treatment of hyperthyroidism. The first order rate constant for the decays of the ^{131}I isotope is 0.087 days^{-1} . If a 50 mg sample of radioiodine is administered to a patient, how long will it take for the amount of radioiodine to decrease to 10 mg?
- (A) 26.4 days (B) 20.7 days (C) 18.5 days (D) 11.3 days

For #16 - #17: Consider the reaction, $A \rightarrow P$, which is a 3/2 order reaction; i.e. rate = $k[A]^{3/2}$. The rate constant for this reaction is $k = 0.02 \text{ M}^{-1/2}\text{s}^{-1}$, and the initial concentration of A is 0.60 M.

16. What is the half-life of this reaction?
- (A) 17 s (B) 27 s (C) 13 s (D) 53 s
17. What will be the concentration of [A] 40 s after the start of the reaction.
- (A) 0.35 M (B) 0.23 M (C) 0.12 M (D) 0.42 M
18. The reaction, $A \rightarrow P$, is of order "x"; i.e. rate = $k[A]^x$. When $[A]_0 = 0.6$ M, the half-life of the reaction is 150. s. When $[A]_0 = 0.2$ M, the half life of the reaction is 260. s. The order of the reaction, x, is
- (A) 1/2 (B) 3 (C) 3/2 (D) 5/2
19. Consider a fourth order reaction, $A \rightarrow \text{Products}$, $-\frac{d[A]}{dt} = k[A]^4$
- When the initial concentration of A is 0.15 M, the initial rate is 0.030 Ms^{-1} . The rate constant for this reaction, k, is approximately
- (A) $0.012 \text{ M}^{-3}\text{s}^{-1}$ (B) $60. \text{ M}^{-3}\text{s}^{-1}$ (C) $1.5 \times 10^{-5} \text{ M}^{-3}\text{s}^{-1}$ (D) $8.9 \text{ M}^{-3}\text{s}^{-1}$

24. In a photochemical reaction, $A \rightarrow 2 B + C$, the reaction quantum yield for the decomposition of A is $\Phi_R = 0.45$. A absorbs radiation at a rate of 5×10^{19} absorbed photons per second for a total of 90 minutes. Approximately how many moles of B have been formed by the end of the irradiation period?

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

- (A) 0.10 mol (B) 0.49 mol (C) 0.20 mol (D) 0.40 mol

For #25 - #26: In a **pulsed** laser fluorescence experiment on an organic chromophore, the fluorescence intensity 45 ns after the experiment begins is 70% of the intensity at the start of the experiment.

In a separate steady-state fluorescence experiment, it was determined that the fluorescence rate constant is: $k_F = 3.4 \times 10^6 \text{ s}^{-1}$

25. The singlet state lifetime of the chromophore, τ_0 , is approximately:
(A) 37 ns (B) 126 ns (C) 290 ns (D) 16 ns
26. The fluorescence quantum yield of the chromophore is approximately:
(A) 0.43 (B) 2.3 (C) 0.68 (D) 0.13

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

- (10) 1. A Perfect Gas has a temperature dependent **constant pressure** molar heat capacity, $C_{p,m} = a + bT^2$, with $a = 22 \text{ J/mol-K}$ and $b = 1.5 \times 10^{-5} \text{ J/mol-K}^3$. Three (3) moles of this gas, originally at 600°C and 1.5 atm is cooled reversibly at **constant volume** to 200°C . Calculate the Internal Energy change, ΔU , for this process, in kJ.

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

$$p(V - Bp^2) = nRT$$

If this gas undergoes an isothermal compression from p_1 to p_2 , develop **INTEGRATED** expressions for ΔU and ΔA in terms of n , R , T , B , p_1 and p_2 .

- (10) 3. The normal boiling point of octane is 125 °C.
The Enthalpy of Vaporization of octane is 34.4 kJ/mol at 125 °C.
The constant pressure molar heat capacity of liquid octane is 240. J/mol-K.
The constant pressure molar heat capacity of octane gas is 180 J/mol-K.

Calculate the entropy change of the **Surroundings**, ΔS_{surr} , (in J/mol-K) when one (1) mole of super heated liquid octane vaporizes irreversibly at 145 °C.

- (10) 4. Consider a first order reaction for which the the rate constant is 85. s⁻¹ at 50 °C and 3200. s⁻¹ at 150 °C.

Calculate the Arrhenius pre-exponential factor, A (in s⁻¹), for this reaction.

- (10) 5. The reaction, $2B + C \rightarrow P$ (P is the product) proceeds by the following mechanism.



“**I**” is an intermediate present in steady-state concentration. Use the steady-state approximation on [**I**] to develop an expression for the rate of formation of P as a function of [B], [C], k_1 , k_{-1} and k_2 .

- (10) 6. The fluorescence quantum yield for a given chromophore, A, has been determined to be $\Phi_F = 0.60$. A sample of A is irradiated with 260 nm radiation from a 150 W (J/s) for a period of 1 hour. The intensity of the **transmitted** light is 30% that of the incident light.

How many moles of the sample, A, have fluoresced in the 1 hour period?