CHEM 5200 - Final Exam - December 15, 2016

Name Solutions

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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 °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 J/mol-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

6. What is the internal energy change, ΔU, when 3 moles of benzene gas are condensed to the liquid at 80 °C 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 °C 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 °C. 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 °C?

(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 $K = 1.3\times10^{-4}$ at 400 °C. 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 °C 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 °C?

(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 °C, 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:

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

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

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 $\Phi_R = 0.30$. 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) 1.0×10^{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.

$C_{v,m} = C_{p,m} - R = a - \frac{b}{T} - 8.31 = a' - \frac{b}{T}$ $a' = 40 - 8.31 = 31.69$ J/mol

(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 = 8.0x10³ J/mol.

$T_1 = 750K$
$T_2 = 300K$

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

$$\Delta U = \int_{T_1}^{T_2} n C_{v,m}\, dT = \int_{T_1}^{T_2} n\left(a' - \frac{b}{T}\right) dT = na'(T_2 - T_1) - nb \ln\left(\frac{T_2}{T_1}\right)$$

$$= (2\,mol)(31.69\ J/mol\text{-}K)(300K - 750K) - (2\,mol)(8\times10^3\ J/mol)\ln\left(\frac{300}{750}\right)$$

$$= -28{,}520\ J + 14{,}660\ J$$

$$= -13{,}860\ J = \boxed{-13.9\ kJ}$$

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

$$\Delta S = \int_{T_1}^{T_2} \frac{n C_{v,m}}{T}\, dT = \int_{T_1}^{T_2} \frac{n(a' - b/T)}{T}\, dT = \int_{T_1}^{T_2} na' \frac{dT}{T} - \int_{T_1}^{T_2} \frac{nb}{T^2}\, dT$$

$$= na' \left[\ln T\right]_{T_1}^{T_2} - nb\left[-\frac{1}{T}\right]_{T_1}^{T_2} = na' \ln\left(\frac{T_2}{T_1}\right) + nb\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= 2\,mol(31.69\ J/mol\text{-}K)\ln\left(\frac{300}{750}\right) + (2\,mol)(8\times10^3\ J/mol)\left[\frac{1}{300K} - \frac{1}{750K}\right]$$

$$= -58.1\ J/K + 32\ J/K$$

$$= -26.1\ J/K = \boxed{-26\ J/K}$$

$P = \frac{nRT}{V} + \frac{A}{V^2} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} - \frac{2A}{V^3}$

(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

Prelim: $dA = -SdT - pdV$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$

$\int_{V_1}^{V_2} \frac{dV}{V^2} = \left[-\frac{1}{V}\right]_{V_1}^{V_2} = \frac{1}{V_1} - \frac{1}{V_2}$

ΔH: $dH = TdS + VdP \rightarrow \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$

$= T\left(\frac{nR}{V}\right) + V\left[-\frac{nRT}{V^2} - \frac{2A}{V^3}\right] = -\frac{2A}{V^2}$

$\Delta H = \int_{V_1}^{V_2} -\frac{2A}{V^2} dV = -2A\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$

ΔG: $dG = -S\cancel{dT} + VdP \rightarrow \left(\frac{\partial G}{\partial V}\right)_T = 0 + V\left(\frac{\partial P}{\partial V}\right)_T$

$\left(\frac{\partial G}{\partial V}\right)_T = V\left[-\frac{nRT}{V^2} - \frac{2A}{V^3}\right] = -\frac{nRT}{V} - \frac{2A}{V^2}$

$\Delta G = \int_{V_1}^{V_2} -\frac{nRT}{V} dV - 2A\int_{V_1}^{V_2} \frac{dV}{V^2}$

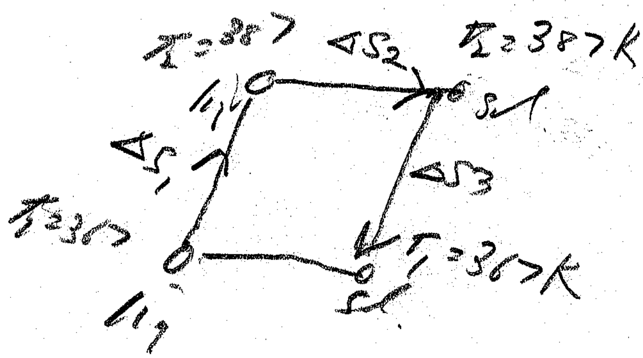
$= -nRT\ln\left(\frac{V_2}{V_1}\right) - 2A\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$

$T_1 = 94^\circ C = 367\,K$ $\quad$ $\Delta H_{frz}(T_2) = -\Delta H_{fus}(T_2) = -13.5\ kJ/mol$

$T_2 = 114^\circ C = 387\,K$ $\quad$ 387 K

(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.



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = C_{pm}(liq)\ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{frz}}{T_2} + C_p(sol)\ln\left(\frac{T_1}{T_2}\right)$$

$$= 81\ \frac{J}{mol\text{-}K}\ln\left(\frac{387}{367}\right) + \frac{-13.5\times10^3\ J/mol}{387\ K} + 54\ \frac{J}{mol\text{-}K}\ln\left(\frac{367}{387}\right)$$

$$= 4.30\ J/mol\text{-}K - 34.88\ J/mol\text{-}K + (-2.87\ J/mol\text{-}K)$$

$$= \boxed{-33.45\ J/mol\text{-}K}$$

(08) 4. The reaction, $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$, has the following mechanism:

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

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.

SS on $[NO_3]$

$$\frac{d[NO_3]}{dt} = 0 = k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO_3][NO]$$

$$0 = k_1[NO][O_2] - [NO_3](k_{-1} + k_2[NO])$$

$$\therefore \quad [NO_3] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$R = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2} \times 2\,k_2[NO_3][NO]$$

$$= k_2\left(\frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}\right)[NO]$$

$$= \frac{k_1 k_2 [NO]^2[O_2]}{k_{-1} + k_2[NO]}$$

No pts if forget the ½

$$\Phi_R = \frac{n_R}{n_{ph}(abs)} = \frac{0.12}{n_{ph}(abs)}$$

(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 .

$$E_{tot} = 120\ J/s \times \frac{60\ s}{1\ min} \times 30\ min = 2.16 \times 10^{5}\ J$$

$$E_{ph} = \frac{hc}{\lambda} = \frac{1.99 \times 10^{-25}\ J/m}{280 \times 10^{-9}\ m} = 7.11 \times 10^{-19}\ J$$

$$N_{ph} = \frac{E_{tot}}{E_{ph}} = \frac{2.16 \times 10^{5}\ J}{7.11 \times 10^{-19}\ J/ph} = 3.04 \times 10^{23}\ ph$$

$$n_{ph} = \frac{3.04 \times 10^{23}\ ph}{6.02 \times 10^{23}\ ph/mol} = 0.505\ mol$$ [now need $n_{ph}(abs)$]

$$f_{abs} = 1 - f_{tran} = 1 - 0.35 = 0.65$$

$\therefore$ $n_{ph}(abs) = 0.505\ mol \times 0.65 = 0.328\ mol$

$$\Phi_R = \frac{n_R}{n_{ph}(abs)} = \frac{0.12}{0.328} = 0.365$$

≈ 0.37

(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 $M^{-1}s^{-1}$.

$$\frac{\Phi_{f_0}}{\Phi_f} = \frac{k_f/k_0}{k_f/(k_0+k_Q[Q])} = \frac{k_0+k_Q[Q]}{k_0} = 1+\frac{k_Q}{k_0}[Q]$$

$$= 1+k_Q\tau_0[Q]$$

$\Phi_{f_0} = 0.42$

$\Phi_f = 0.18$

$[Q] = 0.02\,M$

$\tau_0 = 45\,ns \times \frac{10^{-9}s}{1\,ns} = 4.5\times10^{-8}s$

$$k_Q\tau_0[Q] = \frac{\Phi_{f_0}}{\Phi_f} - 1 = \frac{0.42}{0.18} - 1 = 1.333$$

$$k_Q = \frac{1.333}{\tau_0[Q]} = \frac{1.333}{(4.5\times10^{-8}s)(0.02M)}$$

$$k_Q = 1.48\times10^{9}\,M^{-1}s^{-1}$$

$$\approx \boxed{1.5\times10^{9}\,M^{-1}s^{-1}}$$