CHEM 5200 - Exam 3 - November 7, 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 bar = 750 torr

1 atm = 760 torr

1 kPa = 7.50 torr

Molar Masses $C_{10}H_8$ - 128. C_6H_6 - 78. $C_{12}H_{22}O_{11}$ - 342.
$C_6H_5CH_3$ - 92.

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Name Solutions

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

1. When 0.90 moles of $Cl_2(g)$ are mixed with 0.40 moles of $O_2(g)$ at 150 °C, the Gibbs Energy of mixing, ΔG_{mix}, is approximately:

   (A) -1.6 kJ (B) -2.1 kJ (C) -2.2 kJ (D) -2.8 kJ

2. Consider a mixture of two liquids, A and B. When 6.0 moles of A and 4.0 moles of B are mixed together, the volume of the solution is 700 cm^3. The Partial Molar Volume of A is 80. cm^3/mol. Therefore, the Partial Molar Volume of B is approximately:

   (A) 55 cm^3/mol (B) 220 cm^3/mol (C) 63 cm^3/mol

   (D) Cannot be determined without the density of the solution

3. When 90 grams of napthalene, $C_{10}H_8$, is dissolved in 200 grams of benzene, C_6H_6 ($T_b°$=80 °C, K_b=2.5 °C/m), the boiling point of the solution is

   (A) 88.8 °C (B) 71.2 °C (C) 81.8 °C (D) 108.8 °C

4. When 20 grams of an unknown compound is dissolved in 150 grams of water (K_f = 1.86 °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) 124 g/mol (C) 71. g/mol (D) 45 g/mol

5. When a sample of sucrose ($C_{12}H_{22}O_{11}$) is dissolved in 12.0 L of aqueous solution at 40 °C, the osmotic pressure of the solution is 80. torr. Aproximately how many grams of sucrose are dissolved in the solution?

   (A) 0.12 g (B) 16.8 g (C) 1.4 g (D) 52.3 g

For #6 - #9: Consider the equilibrium, $2\ PCl_3(g) + O_2(g) \rightleftharpoons 2\ POCl_3(g)$.

The enthalpy change for this reaction is -510 kJ.

The value of the equilibrium constant at 100 °C is 0.04 .

6. For the above reaction, if the temperature is **decreased**, then

   (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

7. For the above reaction, if $N_2(g)$ is added at constant total pressure, then

   (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

8. What is the approximate value of ΔG for the above reaction at 100 °C when $P_{PCl3} = P_{O2} = 2.0$ bar and $P_{POCl3} = 0.2$ bar?

   (A) -6.4 kJ (B) +10.0 kJ (C) -26.4 kJ (D) +16.4 kJ

9. What is the approximate value of the equilibrium constant for the above reaction at 120 °C?

   (A) 2.3×10^{3} (B) 170 (C) 2.3×10^{-4} (D) 9.2×10^{-6}

10. Consider the gas phase equilibrium, $A(g) \overset{K}{\rightleftharpoons} 2\,B(g)$. When the pressures of A and B are each 0.10 bar at 100 °C, the Gibbs Energy change for the reaction is -5.0 kJ. What is the approximate value of the equilibrium constant?

    (A) 0.5 (B) 2.0 (C) 5.0 (D) 0.2

FIVE (5) problems follow: NOTE: You Must show all of your work to receive credit.

$T_1 = 373\ K$ $\quad T_2 = ?$

$P_1 = 50\ torr$ $\quad P_2 = 1\ bar \times \frac{750\ torr}{bar} = 750\ torr$ [If you use 1 atm = 760 torr, that's ok too]

(12) 1. The Enthalpy of Vaporization, $\Delta_{vap}H$, of decane is 51. kJ/mol, and the vapor pressure of liquid decane is 50 torr at 100 °C.

Calculate the normal boiling point of decane, in **°C**

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\frac{-R\ln(P_2/P_1)}{\Delta H_{vap}} = \frac{1}{T_2} - \frac{1}{T_1}$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta H_{vap}}\ln\left(\frac{P_2}{P_1}\right) = \frac{1}{373K} - \frac{0.008314\ kJ/mol\,K}{51\ kJ/mol}\ln\left(\frac{750}{50}\right)$$

$$= 2.681\times10^{-3}\ K^{-1} - 4.413\times10^{-4}\ K^{-1} = 2.240\times10^{-3}\ K^{-1}$$

$$T_2 = \frac{1}{2.240\times10^{-3}\ K^{-1}} = 446K - 273 = \boxed{173^{\circ}C}$$

(15) 2. The vapor pressure of liquid toluene, $C_6H_5CH_3(l)$, is 85.5. torr at 40 °C A sample of solid napthalene, $C_{10}H_8(s)$, is added to 800 grams of liquid toluene. The vapor pressure of the mixture is 80.0 torr at 30 °C.

How many grams of napthalene are contained in the mixture.

$P_{tol} = \chi_{tol} P^0_{tol} \rightarrow \chi_{tol} = \frac{P_{tol}}{P^0_{tol}} = \frac{80}{85.5} = 0.936$

$n_{tol} = 800g \times \frac{1 mol}{92g} = 8.696 mol.$

$\chi_{tol} = \frac{n_{tol}}{n_{tol} + n_{nap}}$ ← Solve for n_{nap}

$n_{tol}\chi_{tol} + n_{nap}\chi_{tol} = n_{tol}$

$n_{nap}\chi_{tol} = n_{tol}(1 - \chi_{tol})$

$0.936\, n_{nap} = 8.696(1 - 0.936) = 0.556$

$n_{nap} = 0.595 mol.$

$mass = 0.595 mol \times 128 g/mol.$

$= \boxed{76.1 g\ nap}$

(12) 3. Consider the gas-phase equilibrium, $3A \overset{K}{\rightleftharpoons} 2B + 2C$

If one starts with 4 moles of A and 3 moles of C (no B) in a vessel, and the reaction is allowed to come to equilibrium, the mixture contains 1.3 mol of A at a total pressure of 4.0 bar.

Calculate the equilibrium constant, K, for this reaction.

Calc. X

$4 - 3X = 1.3$

$3X = 2.7$

$X = 0.9$

$3A \rightleftharpoons 2B + 2C$

n_i	$4 - 3X$	$0 + 2X$	$3 + 2X$
n_i	1.3	1.8	4.8
$\frac{n_i}{n_{tot}} = x_i$	0.165	0.228	0.608
$x_i P_{tot} = P_i$	0.660 bar	0.912 bar	2.432 bar

$n_{tot} = 1.3 + 1.8 + 4.8 = 7.9$ mol

$4.0\, x_i =$

$$K = \frac{P_B^2 P_C^2}{P_A^3} = \frac{(0.912)^2 (2.432)^2}{(0.660)^3}$$

$= 16.7$

(14) 4. Consider the gas-phase dissociation equilibrium, $A(g) \overset{K}{\rightleftarrows} 2B(g) + 2C(g)$
The equilibrium constant for this dissociation is 5.0×10^{-8}.

Calculate the fraction dissociation, α, at a total pressure of 5. bar.

Note: You may assume that $\alpha << 1$

$A \rightleftarrows 2B + 2C$

$n_i \quad n_0(1-\alpha) \quad 2\alpha n_0 \quad 2\alpha n_0$

$n_{tot} = n_0(1-\alpha) + 2\alpha n_0 + 2\alpha n_0$

$= n_0(1+3\alpha)$

$\frac{n_i}{n_{tot}} = x_i$	$\frac{1-\alpha}{1+3\alpha}$	$\frac{2\alpha}{1+3\alpha}$	$\frac{2\alpha}{1+3\alpha}$
$\approx x_i$ (eqn)	1	2α	2α
$x_i \cdot P_{tot} = P_i$	5.0	10α	10α

$x_i \cdot 5 =$

$K = 5 \times 10^{-8} = \frac{P_B^2 P_C^2}{P_A} = \frac{(10\alpha)^2 (10\alpha)^2}{5} = 2.0 \times 10^3 \alpha^4$

$\alpha^4 = \frac{5 \times 10^{-8}}{2 \times 10^3} = 2.5 \times 10^{-11}$

$\alpha = \sqrt[4]{2.5 \times 10^{-11}}$

$= 0.0022$

$\approx \boxed{0.002}$

(17) 5. Consider the gas phase equilibrium reaction: $PCl_3(g)+Cl_2(g)\rightleftarrows PCl_5(g)$.
The equilibrium constant for this reaction is K = 100. at 150 °C.
The Enthalpy Change for this reaction is $\Delta_r H^o$ = -88 kJ/mol at 150 °C

(8) (a) Calculate the $\Delta_r S^o$ at 150 °C , in J/mol-K.

$\Delta G^\circ = -RT\ln K = -8.31(423)\ln(100)$

$= -16{,}190\ J/mol$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta S^\circ = \dfrac{\Delta H^\circ - \Delta G^\circ}{T}$

$= \dfrac{-88{,}000\ J - (-16{,}190\ J)}{423}$

$= -170\ J/K$

$K_1 = 100 \quad T_1 = 423\ K$

$K_2 = ? \quad T_2 = 573\ K$

5. **(Cont'd)**

Consider the gas phase equilibrium reaction: $PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$.
The equilibrium constant for this reaction is K = 100. at 150 °C.

(9) (b) The Enthalpy change for this reaction is temperature dependent, and is given by

$\Delta_r H^\circ = a + b/T$, where a = -272 kJ/mol, b = $+7.8 \times 10^4$ kJ-K/mol.

Calculate the value of the equilibrium constant, K, at 300 °C

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\int_{K_1}^{K_2} d \ln K = \int_{T_1}^{T_2} \frac{a + b/T}{RT^2} dT$$

$$\ln(K_2/K_1) = \frac{a}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} + \frac{b}{R} \int_{T_1}^{T_2} \frac{dT}{T^3}$$

$$= \frac{a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] + \frac{b}{2R}\left[\frac{1}{T_1^2} - \frac{1}{T_2^2}\right]$$

$$= \frac{-272}{.00831}\left[\frac{1}{423} - \frac{1}{573}\right] + \frac{7.8 \times 10^4}{2(.00831)}\left[\frac{1}{423^2} - \frac{1}{573^2}\right]$$

$$\ln(K_2/K_1) = +20.26 + 11.94 = -8.72$$

$$\frac{K_2}{100} = e^{-8.72} = 1.63 \times 10^{-4}$$

$K_2 = 0.016$

$$\int_{T_1}^{T_2} \frac{dT}{T^2} = \int_{T_1}^{T_2} T^{-2} dT$$

$$= \left[\frac{-1}{T}\right]_{T_1}^{T_2}$$

$$= \frac{1}{T_1} - \frac{1}{T_2}$$

$$\int_{T_1}^{T_2} \frac{dT}{T^3} = \int_{T_1}^{T_2} T^{-3} dT$$

$$\left[\frac{1}{-3+1} T^{-3+1}\right]_{T_1}^{T_2}$$

$$\left[-\frac{1}{2} \frac{1}{T^2}\right]_{T_1}^{T_2}$$

$$= \frac{1}{2}\left[\frac{1}{T_1^2} - \frac{1}{T_2^2}\right]$$