Printed Name: YANN ANDRE

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Circle your section for bonus marks:. **Al V** or [✓ **Yann André**]

a place of mind

University of British Columbia
Chemistry 123
Physical and Organic Chemistry

Date: Monday, March 19, 2012
Time: 8:00– 09:25 h

Dr. Al Vaisius prepared this examination.
There are ten problems and six pages to this examination.
There is a data sheet at the end of this exam. Tear it off to use.
The ten problems are of equal value but not of equal difficulty.
Precisely answer all problems on this exam.

To obtain full marks:

- Clearly identify all data used in calculations.
- Clearly show your algebra by writing out equations *as used* in logically solving problems, e.g., show rearrangements of equations from the data sheet.
- Include *units* with the final answer.
- Make *sensible* use of significant figures in your final answer, e.g., 298 K is often given as an exact number.

Please, do not write below on this page.

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Problem 1)

The decomposition reaction of sulfuryl chloride, SO_2Cl_2, is: $SO_2Cl_2\ (g) \leftrightharpoons SO_2\ (g) + Cl_2\ (g)$

a) If 1 mol of SO_2Cl_2 comes to equilibrium in a 2.0 L flask at 30°C, the SO_2 concentration is 0.0239 M. Determine the amount (moles) of each gas at equilibrium.

	$SO_2Cl_2(g)$ $\rightleftharpoons$	$SO_2(g)$ +	$Cl_2(g)$
initial (mol)	1	0	0
change (mol)	$-x$	$+x$	$+x$
final (mol)	$1-x$	x	x

$[SO_2] = 0.0239M$

$x = n_{SO_2} = [SO_2] \times V$

$x = 0.0239 \times 2.0$

$x = 0.048$ mol so

$1 - x = 0.952$ mol SO_2Cl_2

$$\left(\begin{aligned} [SO_2Cl_2] &= \frac{n_{SO_2Cl_2}}{V} = \frac{0.952}{2.0} = 0.476\ mol.L^{-1} \\ [SO_2] &= [Cl_2] = 0.0239\ mol.L^{-1} \end{aligned} \right)$$

b) Calculate K_c for the reaction.

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.0239)^2}{0.476}$$

$$K_c = 1.20 \times 10^{-3}$$

Problem 2)

Determine the pH at which $Mn(OH)_2$ will begin to precipitate from a solution having an initial concentration of 0.10 M Mn^{2+} (aq). For $Mn(OH)_2$, $K_{sp} = 2.00 \times 10^{-13}$.

$$Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2\ OH^-$$

$$K_{sp} = [Mn^{2+}][OH^-]^2$$

$$K_{sp} = [Mn^{2+}] \frac{K_w^2}{[H_3O^+]^2}$$

$$K_w = [OH^-][H_3O^+]$$

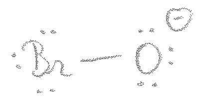
$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

$$[H_3O^+] = \sqrt{[Mn^{2+}]} \times \frac{K_w}{\sqrt{K_{sp}}} = \sqrt{0.1} \times \frac{10^{-14}}{\sqrt{2 \times 10^{-13}}} = 7.07 \times 10^{-9}$$

$$pH = -\log[H_3O^+] = 8.15$$

Problem 3)

Give the structural formula for the conjugate base of hypobromous acid, HBrO, and determine its K_b at 25°C. For hypobromous acid, HBrO, $K_a = 2.00\times10^{-9}$ at 25°C.



$$K_a = \frac{[BrO^{\ominus}][H_3O^+]}{[HBrO]} \qquad K_a K_b = K_w$$

$$K_b = \frac{[HBrO][OH^-]}{[BrO^-]} \qquad K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{2.00\times10^{-9}} = 5.00\times10^{-6}$$

K_b is 5.00×10^{-6}

Problem 4)

For the combustion of propane: $CH_3CH_2CH_3\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (g)$ $\Delta H = -2221.0\ kJ\cdot mol^{-1}$ Assuming that heat transfer is only 60% efficient, calculate the mass of propane that must be burned to provide 1.3×10^8 J of transferable heat. [$CH_3CH_2CH_3$ MM = 44.10 $g\cdot mol^{-1}$]

$$Q = \frac{60}{100}\Delta H$$

$$\Delta H = \frac{Q}{0.6} = \frac{1.3\times10^8}{0.6} = 2.2\times10^8\ J$$

$$\Delta H_{rxn} = n_{C_3H_8} \times \Delta H$$

$$n_{C_3H_8} = \frac{\Delta H_{rxn}}{\Delta H} = \frac{-2.2\times10^8\ J}{-2221.0\times10^3\ J.mol^{-1}}$$

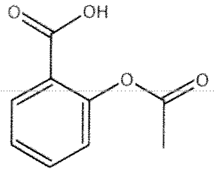
$$n_{C_3H_8} = 97.6\ mol\ C_3H_8$$

$$m_{C_3H_8} = n_{C_3H_8}\times M_{C_3H_8} = 97.6\times 44.10 = 4302\ g$$

We must burn 4.30 kg of propane.

Problem 5)

Acetylsalicylic acid (a.k.a. aspirin), $HC_9H_7O_4$, has a $K_a = 3.00\times10^{-4}$ at 25°C. Calculate the pH of a solution made by dissolving 0.65 g of $HC_9H_7O_4$ (s) into 50.00 ml of water at 25°C.
Acetylsalicylic acid, MM = 180.157 g•mol^{-1}



let AH the acetylsalicylic acid

$$n_{AH} = \frac{m_{AH}}{M_{AH}} = \frac{0.65}{180.157} = 3.61\times10^{-3}\ \text{mol}$$

$$\begin{array}{ccccccc} AH & + & H_2O & \rightleftharpoons & A^{\ominus} & + & H_3O^{\oplus} \\ 3.61\times10^{-3} & & / & & 0 & & 0 \\ 3.61\times10^{-3}-x & & / & & x & & x \end{array}$$

$$K_a = \frac{[A^-][H_3O^+]}{[AH]} = \frac{x^2/(50\times10^{-3})^{\cancel{2}}}{(3.61\times10^{-3}-x)\cancel{(50\times10^{-3})}}$$

$$-3.61\times10^{-3}K_a + K_a x + 20x^2 = 0$$

$$\Delta = b^2-4ac = K_a^2 - 4\times20\times-3.61\times10^{-3}\times K_a$$
$$= 8.673\times10^{-5}$$

$$x = \frac{-b+\sqrt{\Delta}}{2a} = \frac{-K_a+\sqrt{8.673\times10^{-5}}}{2\times20} = 9.31\cdot10^{-3}$$

I have an error.

Problem 6)

a) For the reaction at equilibrium: $H_2\,(g) + I_2\,(s) \leftrightharpoons 2HI\,(g)$ Predict with a very brief explanation whether the reaction quotient, Q, will increase, decrease, or remain the same with the addition of I_2 (s).

I_2 (s) is a solid. Q is $Q = \frac{[HI]^2}{[H_2]}$ so no effect on the equilibrium

b) When CO_2 vapour mixed in air having a P_{CO2} of 39.0 Pa at 25° C is taken into the lungs at 37°C the P_{CO2} increases to 5332.0 Pa. Predict with a very brief explanation whether the entropy of the system in the lungs will increase, decrease or remain unchanged.

$\Delta S > 0$ increase

Problems 7 & 8)

For the reaction: $4HCl_{(g)} + O_{2(g)} \leftrightharpoons 2Cl_{2(g)} + 2H_2O_{(g)}$

at 298 K	HCl (g)	H_2O (g)	O_2 (g)	Cl_2 (g)
ΔH^0_f kJ•mol^{-1}	-92.31	-241.8	0	0
S^0 J•mol^{-1}•K^{-1}	186.9	188.8	205.1	223.1

Problem 7)

For the above reaction, calculate ΔH^0_{rxn}, ΔS^0_{rxn} and ΔG^0_{rxn}.

★ $\Delta H^\circ_{rxn} = 2\times \Delta H^\circ_f(Cl_2) + 2\times \Delta H^\circ_f\, H_2O - 4\times \Delta H^\circ_f\, HCl - \Delta H^\circ_f(O_2)$

$\Delta H^\circ_{rxn} = 2\times 0 + 2\times(-241.8) - 4\times(-92.31) - 0$

$\Delta H^\circ_{rxn} = -114.36$ kJ.mol^{-1}

★ $\Delta S^\circ_{rxn} = 2\times \Delta S^\circ(Cl_2) + 2\times \Delta S^\circ(H_2O) - 4\times \Delta S^\circ(HCl) - \Delta S^\circ(O_2)$

$\Delta S^\circ_{rxn} = 2\times 223.1 + 2\times 188.8 - 4\times 186.9 - 205.1$

$\Delta S^\circ_{rxn} = -128.9$ J.mol^{-1}.K^{-1}

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

$\Delta G^\circ = -114.36\times 10^3 - 298\times(-128.9)$

$\Delta G^\circ = -75.95$ kJ.mol^{-1}

Problem 8)

For the above reaction at 480°C, ΔG_{rxn} = -59.75 kJ•mol^{-1}. Calculate K_{eq} at 480°C.

$$\Delta G = \Delta G^\circ + RT\ln K_{eq}$$

$$\ln K_{eq} = \frac{\Delta G - \Delta G^\circ}{RT}$$

$$K_{eq} = e^{\frac{\Delta G - \Delta G^\circ}{RT}}$$

$$K_{eq} = e^{\frac{-59750-(-75950)}{8.314\times(273+480)}}$$

$$K_{eq} = e^{2.587}$$

$$K_{eq} = 13.3$$

Problem 9)

a) Differentiate between $\Delta G_{reaction}$ (a.k.a. ΔG_{rxn}) and ΔG^0.

ΔG = any conditions

ΔG° = standard conditions : 1 atm and 298K (or 25°C).

b) Briefly, state the relevance of the third law of thermodynamics to absolute entropy.

The entropy of a perfect crystal at absolute zero is exactly equal to ze

But the absolute zero is only theoretical.

Problem 10)

Calculate the change in enthalpy (ΔH_{rxn}) for the auto-ionization of water as the temperature is raised from 0°C to 60°C.

At 0°C, $K_w = 1.14\times10^{-15}$ = 273 K

At 60°C, $K_w = 9.62\times10^{-14}$ = 333 K

Van't Hoff equation : $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\Delta H^\circ = \ln\left(\frac{K_2}{K_1}\right) \times R \times \frac{T_2 T_1}{T_2 - T_1}$$

$$\Delta H^\circ = \ln\left(\frac{9.62\times10^{-14}}{1.14\times10^{-15}}\right) \times 8.314 \times \left(\frac{333\times273}{333-273}\right)$$

$$\Delta H^\circ = 55.9 \text{ kJ.mol}^{-1}$$

Chemistry 123-2012
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Fundamental Constants:

Avogadro's constant	N_A	6.02214×10^{23} mol^{-1}
Gas constant	$R=N_Ak$	8.31447 J•K^{-1}•mol^{-1} 8.31447 L•kPa•K^{-1}•mol^{-1} 8.20574×10^{-2}L•atm•K^{-1}•mol^{-1} 62.3637 L•Torr•K^{-1}•mol^{-1}
Boltzmann's constant	k_B	1.381×10^{-23} J•K^{-1}

Unit Conversions:

1 atm = 760.0 Torr (exact) = 1.01325×10^5 Pa (exact) = 1.01325 bar (exact)
K = 273 + °C
1 J = 1 N m = 1 kg•m^2•s^{-2}
1 W = 1 J•s^{-1}
At 298 K, RT = 2.479 kJ•mol^{-1}

Useful Formulas:

$$[A]=[A]_0e^{-kt} \qquad \ln[A]=-kt+\ln[A]_0 \qquad \ln\frac{[A]_0}{[A]}=kt \qquad t_{\frac{1}{2}}=\frac{\ln 2}{k}$$

$$\frac{1}{[A]}=\frac{1}{[A]_0}+kt \qquad t_{\frac{1}{2}}=\frac{1}{k[A]_0} \qquad k=Ae^{-E_a/RT}$$

$$K_p=K_c(RT)^{\Delta n} \qquad pH=pK_a+\log\frac{[conjugate\,base]}{[acid]} \qquad \ln\left(\frac{k_1}{k_2}\right)=\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$C_P=\frac{\Delta H}{\Delta T} \qquad \Delta T=\frac{q}{C_p} \qquad \Delta H_{rxn}=nC_p\Delta T+H_C\Delta T$$

$$S=k_B\ln\Omega \qquad \Delta S=\frac{q_{reversible}}{T} \qquad \Delta S=S_2-S_1=C_P\ln\frac{T_2}{T_1}$$

$$\Delta S=S_2-S_1=C_V\ln\frac{T_2}{T_1}$$

$$\Delta G=RT\ln\left(\frac{Q}{K}\right) \qquad \ln\left(\frac{K_2}{K_1}\right)=\frac{\Delta H^0}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad \Delta G^0=-RT\ln K$$

$$\Delta G=\Delta G^0+RT\ln Q \qquad \Delta G=\Delta H-T\Delta S$$