LIZARDI BHI 2010-11	Topics:	Marks
Batxilergoko 2. maila	Thermochemistry	
1st term	Kinetics	
2010-11-12	Chemical Equilibrium	

EXERCISE #1

When 5.6 g of CS_2 combine with oxygen (see the equation below) 79 kJ of heat are released:

$$CS_2\ (l) + 3\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ SO_2\ (g)$$

The formation enthalpy changes of carbon dioxide and sulfur dioxide are:

$$\Delta H_f^0\ (CO_{2(g)}) = -395.5\ kJ/mol;\ \ \Delta H_f^0\ (SO_{2(g)}) = -296.4\ kJ/mol$$

a) determine the enthalpy change of formation of CS_2 (l)
b) determine the volume of SO_2 (g) at 25 °C and 1 atm formed when 6000 kJ have been released in the reaction above.
c) Determine the efficiency of the process if 2110 kJ are released when 2.4 moles of CS_2 react

Atomic weights: S=32; C=12; O=16

First, we calculate the molar mass of CS_2:

$$Mm\ (CS_2) = (1 \times 12) + (2 \times 32) = 76\ g/mol$$

$$\Delta H_R = -\frac{79\ kJ}{5.6\ g\ CS_2} \times \frac{76\ g\ CS_2}{1\ mol\ CS_2} \times 1\ mol\ CS_2 = -1072\ kJ$$

By combining equations (Hess's Law) we get the enthalpy change of formation:

$$CO_2\ (g) + 2\ SO_2\ (g) \longrightarrow CS_2\ (l) + 3\ O_2\ (g) \quad \Delta H_1 = +1072\ kJ$$

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g) \quad \Delta H_2 = -395.5\ kJ$$

$$2\ S(s) + 2 O_2\ (g) \rightarrow 2\ SO_2\ (g) \quad \Delta H_3 = -592.8\ kJ$$

$$\downarrow$$

$$C\ (s) + 2\ S\ (s) \rightarrow CS_2\ (l) \quad \Delta H = +83.7\ kJ$$

$$\Delta H_f^0\ (CS_2\ (l)) = +83.7\ kJ/mol$$

The volume of SO_2 is calculated by using the general expression of a gas, PV=nRT:

$$n(SO_2) = (-6000\ kJ) \times \left(\frac{2\ mol\ SO_2}{-1072\ kJ}\right) = 11.19\ mol\ SO_2$$

$$V = \frac{nRT}{P} = \frac{11.19\ mol \times 0.082\ atm.L/K.mol \times 298\ K}{1\ atm}$$

$$V = 273.4\ L\ SO_2$$

To finish, the efficiency is the relationship between the theoretical value of heat and the real value:

$$Q_t = 2.4\ mol\ CS_2 \times \left(\frac{-1072\ kJ}{1\ mol\ CS_2}\right) = -2572.8\ kJ$$

$$r = 100 \times \left(\frac{-2110\ kJ}{-2572.8\ kJ}\right) = 82.01\ \%$$

EXERCISE #2

In this reaction

$$CH_3\text{-}CH_2OH\ (l) + O_2\ (g) \rightarrow CH_3\text{-}COOH\ (l) + H_2O\ (l)$$

determine

a) enthalpy change of reaction
b) entropy change of reaction
c) the equation of ΔG and the ΔG-T graphic
d) the interval of temperature in which the reaction is spontaneous

DATA

Formation enthalpy changes (kJ/mol)

CH_3-CH_2OH	CH_3-$COOH$	H_2O
-227.6	-487	-285.8

Entropy (J/mol.K)

CH_3-CH_2OH	CH_3-$COOH$	H_2O	O_2
160.7	159.9	70	205

First, we calculate the enthalpy change of reaction:

$$CH_3-CH_2OH \longrightarrow 2C + 3H_2 + \tfrac{1}{2}O_2 \qquad \Delta H_1 = +227.6\ kJ$$

$$2C + 2H_2 + O_2 \rightarrow CH_3-COOH \qquad \Delta H_2 = -487\ kJ$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H_3 = -285.8\ kJ$$

$$\downarrow$$

$$CH_3-CH_2OH + O_2 \rightarrow CH_3-COOH + H_2O$$

$$\Delta H_R = -545.2\ kJ$$

Next, the entropy change is calculated:

$$\Delta S_R = \left[\left(1\,mol \times 159.9\,\frac{J}{mol\,K}\right) + \left(1\,mol \times 70\,\frac{J}{mol\,K}\right)\right] -$$

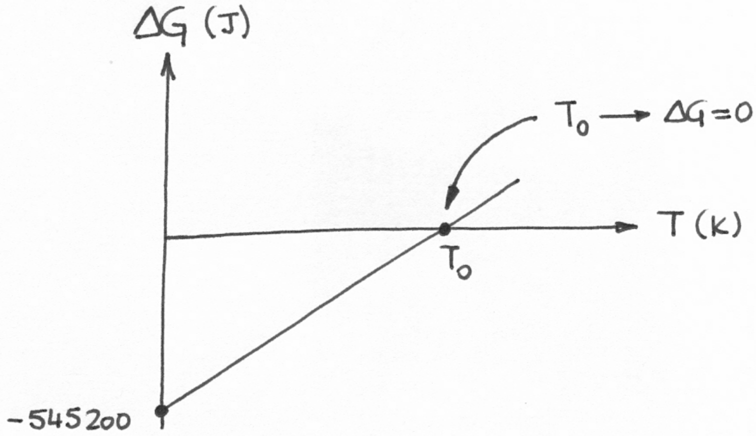
$$- \left[\left(1\,mol \times 160.7\,\frac{J}{mol \cdot K}\right) + \left(1\,mol \times 205\,\frac{J}{mol\,K}\right)\right] =$$

$$= -135.8\,\frac{J}{K}$$

Free energy is used to evaluate the spontaneity of reaction:

(c) (d)

$$\Delta G = -545200\,J + 135.8\,\frac{J}{K} \times T$$



$$T_0 \rightarrow \Delta G = 0 \rightarrow T_0 = \frac{545200\,J}{135.8\,J/K}$$

$$T_0 = 4015\,K$$

$$\Delta G < 0 \rightarrow T\ (0, 4015\,K)$$

EXERCISE #3

A 25 L-container is charged with 2 moles of H_2, 1 mol of N_2, and 3.2 moles of NH_3. At 400 °C, when the equilibrium is reached, the number of moles of ammonia has decreased to 1.8 mol. Given this equation

$$3\,H_2\,(g) + N_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \qquad \Delta H < 0$$

determine:

a) the number of moles of nitrogen and hydrogen at equilibrium
b) the values of Kc and Kp
c) the total and partial pressures at equilibrium
d) the shift of the reaction if the equilibrium is disturbed by increasing the pressure (by decreasing the volume)
e) the shitf of the reaction if the equilibrium is distubed by lowering the temperature
f) if the change in entropy is positive or negative. Give the reasons.

R = 0.082 atm.L/K.mol

From the equlibrium table we get the composition and both constants:

	$3\,H_2\,(g)$ +	$N_2\,(g)$ $\rightleftharpoons$	$2\,NH_3\,(g)$
n_0	2	1	3.2
Δn	$3x$	x	$-2x$
n_{eq}	$2+3x$	$1+x$	$3.2-2x$

$$3.2 - 2x = 1.8 \;\rightarrow\; x = \frac{3.2\text{ mol} - 1.8\text{ mol}}{2} = 0.7\text{ mol}$$

$$n_{eq}(N_2) = 1 + x = 1.7\text{ mol } N_2$$

$$n_{eq}(H_2) = 2 + 3x = 4.1\text{ mol } H_2$$

$$K_c = \frac{[NH_3]^2}{[H_2]^3\,[N_2]} = \frac{(1.8/25)^2}{(4.1/25)^3\,(1.7/25)} = 17.28$$

$$K_p = K_c \cdot (RT)^{-2} = \frac{K_c}{(RT)^2} \;\rightarrow\; K_p = 5.67 \times 10^{-3}$$

The equation of gases allows the calculation of total and partial pressures (using molar fractions):

$$P_T = \frac{n_T RT}{V} = \frac{7.6\,mol \times 0.082\,atm.L/K.mol \times 673K}{25\,L}$$

$$P_T = 16.78\,atm$$

$$P(NH_3) = \frac{1.8}{7.6} \times 16.78\,atm = 3.97\,atm$$

$$P(N_2) = \frac{1.7}{7.6} \times 16.78\,atm = 3.75\,atm$$

$$P(H_2) = \frac{4.1}{7.6} \times 16.78\,atm = 9.05\,atm$$

Le Châtelier's principle is used to determine the shift of reaction. The entropy change is negative; the system becomes more ordered because we have less gas molecules at the side of products.

ⓓ ⓔ

	①	②	③
d)	P ↑	P ↓	→
e)	T ↓	T ↑ Q ↑	→

ⓕ $\Delta S_R < 0$

EXERCISE #4

A 10 L-container is charged with 0.2 moles of N_2O_4 and heated to 35 °C in order to react as follows:

$$N_2O_4\ (g) \leftrightarrow 2\,NO_2\ (g)$$

At equilibrium, 57% of reactant is dissociated.

a) Determine the composition at equilibrium (# of moles)
b) The total pressure at equilibrium
c) The values of Kc and Kp
d) Determine the shift of the reaction if the volume of the container is reduced.

R = 0.082 atm.L/K.mol

From the table we get the composition:

	$N_2O_4\ (g)$ $\rightleftarrows$	$2\ NO_2\ (g)$
n_0	0.2	—
Δn	$-x$	$2x$
n_{eq}	$0.2 - x$	$2x$

$$x = \frac{57}{100} \times 0.2\ \text{mol} = 0.114\ \text{mol}$$

ⓐ

$$n_{eq}(N_2O_4) = 0.2 - x = 0.086\ \text{mol}\ N_2O_4$$

$$n_{eq}(NO_2) = 2x = 0.228\ \text{mol}\ NO_2$$

Gas equation is used to determine total pressure. The equilibrium constant Kc is calculated first (we know concentrations) and Kp later by using the relationship between both constants:

(b)

$$P_T = \frac{n_T RT}{V} = \frac{0.314\ mol \times 0.082\ atm \cdot L/K \cdot mol \times 308\ K}{10\ L}$$

$$P_T = 0.79\ atm$$

(c)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.228/10)^2}{(0.086/10)} = 0.06$$

$$K_p = K_c\,(RT) = 0.06 \times 0.082 \times 308 = 1.51$$

Le Châtelier's principle is used to determine the shift when the equilibrium is disturbed:

(d)

(1)	(2)	(3)
$V\downarrow\ P\uparrow$	$P\downarrow$	$\leftarrow$