LIZARDI BHI 2009-10	Topics:	Marks
Batxilergoko 2. maila	Thermochemistry	
1st term	Chemical Equilibrium	
2009-11-16		

EXERCISE #1

Last century, the use of a tool called "carbide lamp" was very common. Inside that lamp a two-step process happened. First, calcium carbide was produced, according to the following reaction:

$$CaC_2\ (s) + 2\,H_2O\ (l) \rightarrow C_2H_2\ (g) + Ca(OH)_2\ (s) \qquad \Delta H = -270\ kJ$$

and, finally, acetylene (**C_2H_2**) was burned and the result was a very bright light.

a) Write the formation enthalpy of acetylene and determine the formation entahlpy change of acetylene.

b) Write the combustion equation of acetylene. Determine its combustion enthalpy change and draw the corresponding enthalpy diagram.

DATA:	$Ca(OH)_2\ (s)$	$H_2O\ (l)$	$CaC_2\ (s)$	$CO_2\ (g)$
ΔH_f^0 (kJ/mol)	-986	-286	+83	-395

a) Enthalpy formation of acetylene: $2\,C\ (s) + H_2\ (g) \rightarrow C_2H_2\ (g)$

Appling Hess' law we get:

$$CaC_2\ (s) + 2\,H_2O\ (l) \rightarrow C_2H_2\ (g) + Ca(OH)_2\ (s) \qquad \Delta H = -270\ kJ$$

$$Ca\ (s) + 2\,C\ (s) \rightarrow CaC_2\ (s) \qquad \Delta H = +83\ kJ$$

$$2\,H_2\ (g) + O_2\ (g) \rightarrow 2\,H_2O\ (l) \qquad \Delta H = -572\ kJ$$

$$Ca(OH)_2\ (s) \rightarrow Ca\ (s) + O_2\ (g) + H_2\ (g) \qquad \Delta H = +986\ kJ$$

$$2\,C\ (s) + H_2\ (g) \rightarrow C_2H_2\ (g) \qquad \Delta H = +227\ kJ$$

b) The combustion reaction of acetylene:

$$C_2H_2\ (g) + 5/2\ O_2\ (g) \rightarrow 2\,CO_2\ (g) + H_2O\ (l)$$

The enthalpy change of the combustion of acetylene:

$$C_2H_2\ (g) \rightarrow 2\,C\ (s) + H_2\ (g) \qquad \Delta H = -227\ kJ$$

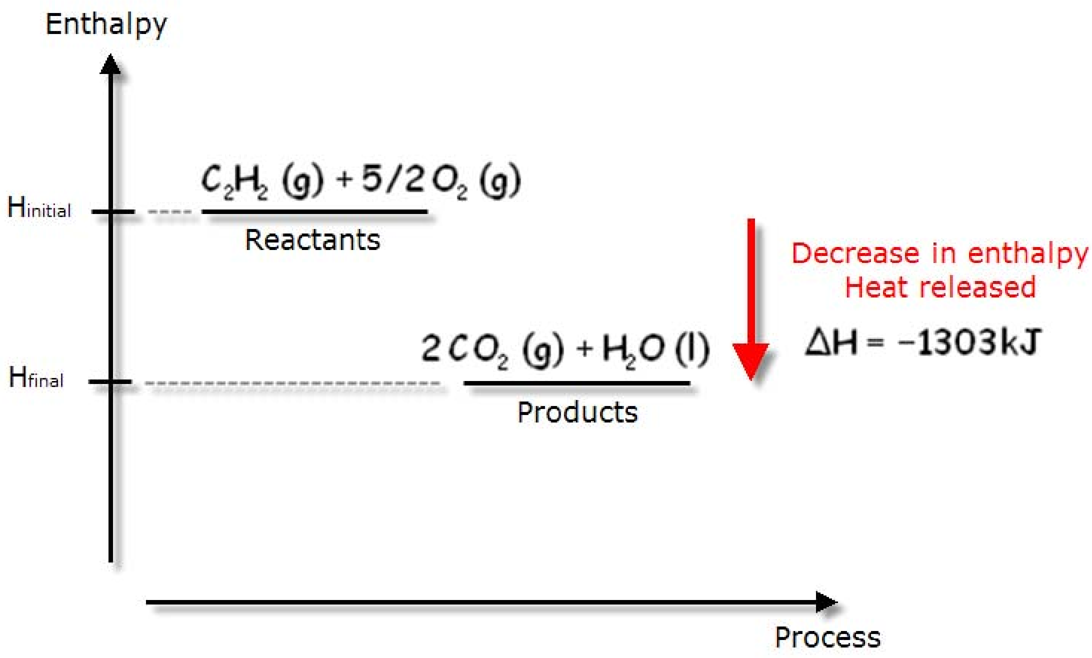
$$2\,C\ (s) + 2\,O_2\ (g) \rightarrow 2\,CO_2\ (g) \qquad \Delta H = -790\ kJ$$

$$H_2\ (g) + 1/2\ O_2\ (g) \rightarrow H_2O\ (l) \qquad \Delta H = -286\ kJ$$

$$C_2H_2\ (g) + 5/2\ O_2\ (g) \rightarrow 2\,CO_2\ (g) + H_2O\ (l) \qquad \Delta H = -1303\ kJ$$

The enthalpy of combustion of acetylene is: $\Delta H = -1303\ kJ/mol$

The enthalpy diagram:



EXERCISE #2

Here you have the formation equation of water at standerd conditions (298K and 1 atm):

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H=-241{,}8\ kJ \text{ and } \Delta S=-44{,}4\frac{J}{K}$$

Determine and reason:

a) If the reaction is endothermic or exotermic.
b) Why the entropy change is negative.
c) If the reaction is spontaneous or not at these standard conditions.
d) Study the spontaneity of the reaction (the T interval at which it will be spontaneous). Suppose that ΔH and ΔS remain constant. Build a ΔG-T diagram.

a) The enthalpy change is negative; therefore, the reaction is exothermic.

b) The entropy change is negative because the system is more ordered: the molecules have more atoms at the end of the process.

c) In order to know if the process is spontaneous or not we need to evalueate the sign of the change in Gibbs energy: if it is negative the process will be spontaneous.

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

$$\Delta G = (-241\ 800\ J) - (298\ K) * (-44.4\ J/K) = -228\ 569\ J$$

$$\Delta G < 0 \ \ldots \text{ Spontaneous process}$$

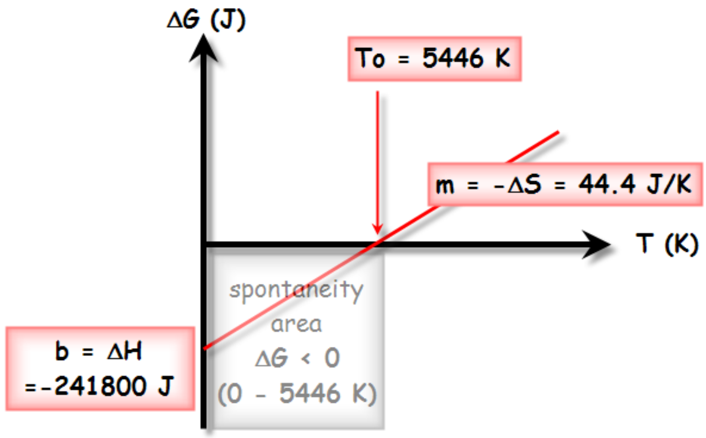
d) Study of spontaneity

First, we will calculate the temperature at which $\Delta G = 0$.

$$\Delta G = (-241\ 800\ J) - T * (-44.4\ J/K) = 0$$

$$T = -\frac{2418\ 00\ J}{44.4\ J/K} = 5\ 446\ K$$

The process wil be spontaneous between T (0 – 5446 K). Diagram:



EXERCISE #3
At 400 °C ammonia is 40% dissociated when 4 moles are initially introduced. The total pressure at equilibrium is 710 mmHg.
$2\,NH_3\,(g) \rightleftarrows N_2\,(g) + 3\,H_2\,(g)$
Determine:
a) The molar fraction and partial pressure (in atmospheres) of each component at equilibrium
b) Kp
c) Knowing that the formation enthalpy of ammonia is exothermic, determine how the reaction shifts if the equilibrium is disturbed by: • adding more ammonia • decreasing the pressure • increasing the temperature

a) Molar fractions and partial pressures are

	$2\,NH_3\,(g)$	$\rightleftarrows N_2\,(g)$	$+ 3\,H_2\,(g)$
n initial	4 mol	0	0
Δn	-1,6 mol	0,8 mol	2,4 mol
n equlibrium	2,4 mol	0,8 mol	2,4 mol

$$x\,(NH_3) = \frac{2.4\text{ mol}}{5.6\text{ mol}} = 0.43 \ldots P(NH_3) = 0.43 * \frac{710}{760}\text{ atm} = 0.40\text{ atm}$$

$$x\,(N_2) = \frac{0.8\text{ mol}}{5.6\text{ mol}} = 0.14 \ldots P(N_2) = 0.14 * \frac{710}{760}\text{ atm} = 0.13\text{ atm}$$

$$x\,(H_2) = \frac{2.4\text{ mol}}{5.6\text{ mol}} = 0.43 \ldots P(H_2) = 0.43 * \frac{710}{760}\text{ atm} = 0.40\text{ atm}$$

b) Kp

$$Kp = \frac{P_{N_2} * P_{H_2}{}^3}{P_{NH_3}{}^2} = \frac{(0.13\text{ atm}) * (0.40\text{ atm})^3}{(0.40\text{ atm})^2} = 0.052\text{ atm}^2$$

c) According to Le Châtelier:

Disturbance...	The system reacts and the reaction shifts ...
ammonia ↑	ammonia ↓ ... the reaction shift → more product
pressure ↓	pressure ↑ ... n ↑ ... the reaction shifts → more product
T ↑	T↓ ... Q ↓ ... the reaction shifts ← more reactant

EXERCISE #4

A 10 L-vessel is charged with, 0.61 mol CO_2 and 0.39 mol H_2. The equilibrium is reached at 1250°C:

$$CO_2\,(g) + H_2\,(g) \rightleftarrows CO\,(g) + H_2O\,(g)$$

At equilibrium 0.35 mol CO_2 is found. Determine:

a) Kc.
b) The concentrations at equilibrium.
c) The equilibrium is disturbed by adding 0.22 mol H_2. Determine the concentrations at the new equilibrium.

a) Kc

	$CO_2\,(g)$ +	$H_2\,(g)$ $\rightleftarrows$	$CO\,(g)$ +	$H_2O\,(g)$
n initial	0.61	0.39	-	-
Δn	-x	-x	x	x
n equilibrium	0.61-x	0.39-x	x	x

From "x" we will know all we need:

0.61 mol - x = 0.35 mol → x = 0.61 mol - 0.35 mol = 0.26 mol

$$Kc = \frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{(0.26/10)^2}{(0.35/10)\,(0.13/10)} = 1.49$$

b) The concentrations at equilibrium

$$[CO] = [H_2O] = \frac{x}{10\ L} = \frac{0.26\ mol}{10\ L} = 0.026\ M;\ \ [CO_2] = \frac{0.35\ mol}{10\ L} = 0.035\ M$$

$$[H_2] = \frac{0.39\ mol - x}{10\ L} = \frac{0.13\ mol}{10\ L} = 0.013\ M$$

c) The new concentrations

	$CO_2\,(g)$ +	$H_2\,(g)$ $\rightleftarrows$	$CO\,(g)$ +	$H_2O\,(g)$
n initial	0.35	0.35	0.26	0.26
Δn	-x	-x	x	x
n equilibrium	0.35-x	0.35-x	0.26+x	0.26+x

From Kc "x" can be known. Cancelling out the volume:

$$Kc = 1.49 = \frac{(0.26+x)^2}{(0.35-x)^2} \rightarrow \sqrt{1.49} = \frac{0.26+x}{0.35-x} \rightarrow 1.22 = \frac{0.26+x}{0.35-x}$$

x = 0.075 mol

$$[CO] = [H_2O] = \frac{0.26+x}{10\ L} = 0.0335\ M;\ [CO_2] = [H_2] = \frac{0.35 - x}{10\ L} = 0.0275\ M$$

EXERCISE #5

A 1 L vessel is charged with 0.1 mol HI. At 350°C equilibrium is reached according to this equation:

$$2\,HI\,(g) \rightleftarrows H_2\,(g) + I_2\,(g)$$

At that temperature, the value of Kc is 0.019. Determine:

a) The dissociation percent of HI.

b) The concentrations at equilibrium.

c) The equilibrium constant Kc for the following equation $HI\,(g) \rightleftarrows \frac{1}{2} H_2\,(g) + \frac{1}{2} I_2\,(g)$ at the same temperature.

a) The dissociation percent

	$2\,HI\,(g)$ $\rightleftarrows$	$H_2\,(g)$ +	$I_2\,(g)$
n initial	0.1	-	-
Δn	$-0.1\,\alpha$	$0.05\,\alpha$	$0.05\,\alpha$
n equilibrium	$0.1\,(1-\alpha)$	$0.05\,\alpha$	$0.05\,\alpha$

Simplifying the volume:

$$Kc = 0.019 = \frac{(0.05\,\alpha)^2}{\left[0.1\,(1-\alpha)\right]^2} \rightarrow \sqrt{0.019} = \frac{0.05\,\alpha}{0.1\,(1-\alpha)}$$

$$\frac{\alpha}{1-\alpha} = 0.276 \rightarrow \alpha = \frac{0.276}{1.276} = 0.216$$

b) The concentrations at equilibrium:

$$[HI] = \frac{0.1\,(1-\alpha)}{V} = 0.0784\ M$$

$$[H_2] = [I_2] = \frac{0.05\,\alpha}{V} = 0.0108\ M$$

c) Kc for the second equation (Kc_2)

$$Kc_1 = \frac{[I_2]\,[H_2]}{[HI]^2} = 0.019 \rightarrow Kc_2 = \frac{[I_2]^{1/2}\,[H_2]^{1/2}}{[HI]} = \sqrt{0.019} = 0.138$$