

LIZARDI BHI	2008-09	<b>Topics:</b> Thermochemistry Kinetics Equilibrium	<b>Marks:</b>
Batxilergoko 2. maila			
1. term exam			
2008 - XII - 16			
<b>NAME:</b>			

### Exercise #1

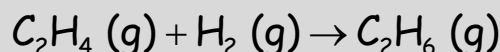
When 22 grams of ethane are burned the energy released is 1100 kJ.

a) Determine

- the combustion enthalpy of ethane
- the formation enthalpy of ethane

b) Determine the formation enthalpy of ethene

c) Determine whether the hydrogenation process of ethene is endothermic or exothermic. The process is:



Atomic weights: H=1; C=12

Enthalpies of formation of carbon dioxide and water are -394 kJ/mol and -286 kJ/mol, respectively

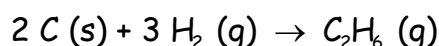
The combustion enthalpy of ethene is -1386 kJ/mol

a) The combustion enthalpy is given in heat (at constant pressure) per mole. Therefore, we have to calculate the molar mass and convert the heat given in heat per mole

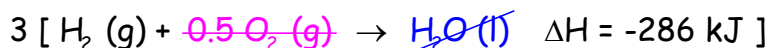
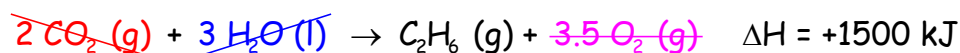
$$M (\text{ethane}) = (2 \cdot 12) + (6 \cdot 1) = 30 \text{ g/mol}$$

$$\Delta H_c^0 = 30 \frac{\text{g}}{\text{mol}} \cdot \frac{(-1100 \text{ kJ})}{22 \text{ g}} = -1500 \frac{\text{kJ}}{\text{mol}}$$

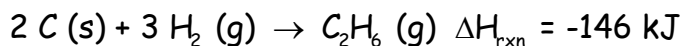
In order to get the formation enthalpy of ethane we need to combine some equations. The equation we are looking for is:



The only equation we have related to ethane is its combustion. Therefore, we will start with the combustion of ethane and then complete with the equations needed to get the formation equation (that is, the formations of carbon dioxide and water):

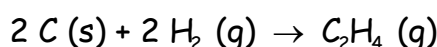


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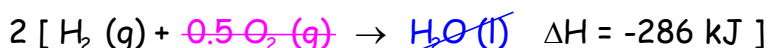
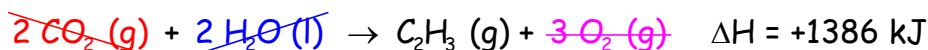


$$\Delta H_f^\circ = -146 \frac{\text{kJ}}{\text{mol}}$$

b) To determine the enthalpy of formation of ethene we need to combine equations to get this:



We can start with the reverse of the combustion of ethene:

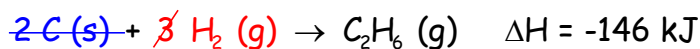


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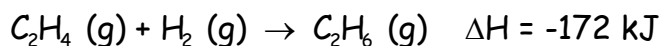


$$\Delta H_f^\circ = 26 \frac{\text{kJ}}{\text{mol}}$$

c) The hydrogenation process can be calculated by combining formation equations:



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$$\Delta H_{\text{hydrog}} = -172 \frac{\text{kJ}}{\text{mol}}$$

### Exercise #2

Graphite (C) reacts with water vapor to yield carbon monoxide and hydrogen, both in gas phase. Write the corresponding chemical equation and determine:

- $\Delta G^\circ$  for this reaction at 25 °C and whether the reaction is spontaneous or not.
- Provided that  $\Delta H$  and  $\Delta S$  do not change with temperature, study the spontaneity for this reaction (the range of temperatures in which it is spontaneous, building a  $\Delta G - T$  graphic)
- If the activation energy is  $E_a = 220$  kJ/mol, draw the corresponding enthalpy diagram. What is the meaning of activation energy?

Data	C	H <sub>2</sub> O	CO	H <sub>2</sub>
$\Delta H_f^\circ$ (kJ/mol)	0	-241.82	-110.52	0
$S^\circ$ (J/mol.K)	5.74	188.82	197.67	130.68

a) In order to determine  $\Delta G^\circ$  we will calculate the change in enthalpy  $\Delta H$  and the change in entropy  $\Delta S$ :

The enthalpy change of the reaction:

$$\Delta H_{\text{rxn}}^\circ = \sum n * \Delta H_f^\circ (\text{products}) - \sum n * \Delta H_f^\circ (\text{reactants})$$
$$\Delta H_{\text{rxn}}^\circ = -110.52 \text{ kJ} - (-241.82 \text{ kJ}) = +131.3 \text{ kJ}$$

The entropy change is:

$$\Delta S_{\text{rxn}}^\circ = \sum n * S^\circ (\text{products}) - \sum n * S^\circ (\text{reactants})$$
$$\Delta S_{\text{rxn}}^\circ = (197.67 \frac{\text{J}}{\text{K}} + 130.68 \frac{\text{J}}{\text{K}}) - (5.74 \frac{\text{J}}{\text{K}} + 188.82 \frac{\text{J}}{\text{K}}) = 133.79 \frac{\text{J}}{\text{K}}$$

The Gibbs energy at 25 °C is:

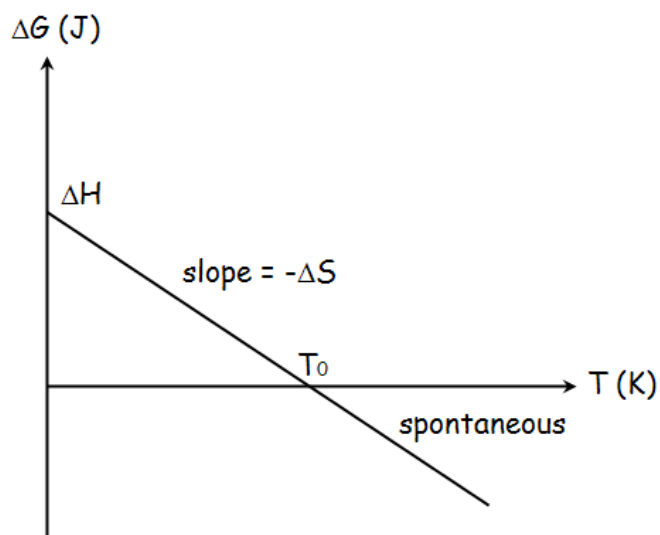
$$\Delta G^\circ = +131\,300 \text{ J} - (298 \text{ K}) * (133.79 \text{ J/K}) > 0$$

Non-spontaneous at 25 °C

b) The Gibbs energy as a function of temperature can be represented by this expression:

$$\Delta G = +131\,300\text{ J} - T * (133.79\text{ J/K})$$

The graphic that corresponds to the expression is:

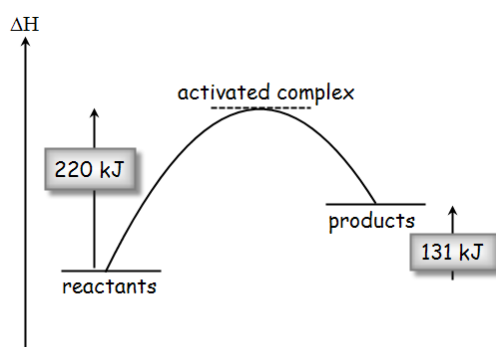


The process will be spontaneous at any temperature higher than  $T_0$ . This value can be calculated:

$$\Delta G = +131\,300\text{ J} - T_0 * (133.79\text{ J/K}) = 0$$

$$T_0 = \frac{131\,300\text{ J}}{133.79\text{ J/K}} = 981\text{ K}$$

c) The activation energy is the energetic barrier needed to overcome to form an activated complex and yield products.



**Exercise #3**

A 10 L-vessel is charged 2.5 mol of  $\text{PCl}_5$  and heated to 270 °C. Due to its dissociation, the pressure increases to 15.68 atm. The reaction is exothermic. Determine:

- the value of  $K_c$
- the composition (# of moles) at equilibrium
- apply Le Chatelier principle to establish a relationship between the changes in pressure and temperature and the shifting of the reaction.



The equilibrium can be represented as a table:

	$\text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g)$		
n initial	2.5 mol	-	-
n change	-x	x	x
n equilibrium	2.5 - x	x	x
[ ] equilibrium	(2.5 - x)/10	x/10	x/10

The total pressure at equilibrium is known; thus, the total number of moles can be calculated using the ideal-gas law:

$$P \cdot V = n \cdot R \cdot T \rightarrow n = \frac{P \cdot V}{R \cdot T} = \frac{15.68 \text{ atm} \cdot 10 \text{ L}}{0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \cdot (270 + 273) \text{ K}} = 3.52 \text{ mol}$$

$$n_{\text{total}} = (2.5 - x) + x + x = 2.5 + x$$

$$2.5 + x = 3.52 \text{ mol} \rightarrow x = 1.02 \text{ mol}$$

- The value of  $K_c$

$$K_c = \frac{[\text{PCl}_3] \cdot [\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(x/10)^2}{(2.5 - x)/10} = \frac{(1.02)^2}{10 \cdot 1.48} = 0.07$$

- The composition at equilibrium

$$n (\text{PCl}_3) = n (\text{Cl}_2) = 1.02 \text{ mol}$$

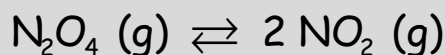
$$n (\text{PCl}_5) = 2.5 - x = 1.48 \text{ mol}$$

c) We will apply Le Chatelier in order to know how the process shifts when pressure and temperature are changed

Disturbance: change from outside	How the process shifts: How the system reacts
Pressure increases	Pressure decreases by decreasing the number of moles: Shifts to the left ... ←
Pressure decreases	Pressure increases by increasing the number of moles: Shifts to the right ... →
Temperature increases	Heat is absorbed; the system shifts towards the endothermic direction. Shifts to the left ... ←
Temperature decreases	Heat is released; the system shifts towards the exothermic direction. Shifts to the right ... →

**Exercise #4**

A 1.5 L-container is charged with 0.08 mol of dinitrogen tetroxide and heated to 35 °C. The reactant dissociates partially, according to this process:



When equilibrium is reached the pressure is 2.27 atm. Determine:

- the dissociation percent
- K<sub>p</sub> and K<sub>c</sub>

The equilibrium can be represented as a table:

	$\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2 \text{NO}_2 (\text{g})$	
n initial	0.08 mol	-
n change	-x	2x
n equilibrium	0.08 - x	2x
[ ] equilibrium	(0.08 - x)/1.5	2x/1.5

The total pressure at equilibrium is known; thus, the total number of moles can be calculated using the ideal-gas law:

$$P \cdot V = n \cdot R \cdot T \rightarrow n = \frac{P \cdot V}{R \cdot T} = \frac{2.27 \text{ atm} \cdot 1.5 \text{ L}}{0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \cdot 308 \text{ K}} = 0.135 \text{ mol}$$

$$n_{\text{total}} = (0.08 - x) + x + x = 0.08 + x$$

$$0.08 + x = 0.135 \text{ mol} \rightarrow x = 0.055 \text{ mol}$$

- The dissociation percent

$$\alpha = \frac{0.055 \text{ mol}}{0.08 \text{ mol}} \cdot 100 = 68.75 \%$$

- K<sub>c</sub> and K<sub>p</sub>

$$K_c = \frac{(2x/1.5)^2}{(0.08 - x)/1.5} = \frac{4x^2}{1.5 \cdot (0.08 - x)} = 0.323$$

$$K_p = K_c \cdot (RT)^{\Delta n} \rightarrow K_p = 0.323 \cdot 0.082 \cdot 308 = 8.16$$