University of Science & Technology
Faculty of Engineering
First year – Batch 31

General Chemistry

Thermochemistry

Lecture4

By

Dr. Nahla Mubarak Mahmoud

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Objectives

Thermodynamics:

Deals with energy changes in chemical or physical processes.

Thermochemistry:

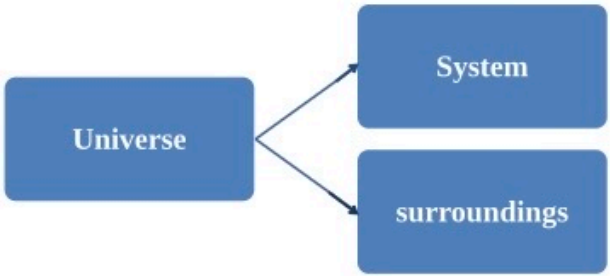
Is the study of heat changes during chemical reactions.

The system and the surroundings:

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.

* **The universe is divided into:**

  the system and the surroundings.


Universe
System
surroundings

Types of the system :

The systems are classified according to the movements of matter and energy in or out of the system.

- **Open system.**
- **Closed system.**
- **Isolated system.**


Open


Closed


Isolated

Open system:

There is exchange of energy and matter between system and surroundings.

Closed system:

There is no exchange of matter , but exchange of energy is possible between the system and surroundings.

Isolated system:

There is no exchange of energy or matter between the system and the surroundings.

The internal energy, E or U:

A quantity which represents the total energy of the system.

Sum of various type of energy related with a system

U = P.E + K.E + ……..

It may change when:

Heat passes into or out of the system.

Work is done on or by the system

Matter enters or leaves the system.

The first law of thermodynamics:

The first law of thermodynamics is often called the law of conservation of energy.

Energy can neither be created nor destroyed but only changed from one form to another.

The energy of the universe is constant.

Let work done on the system = W

Heat absorbed by the system = q

Then $\Delta E = q + W$, ΔE = change in internal energy

Enthalpy:

- **The term enthalpy, H , it is heat contained in the system measured at constant pressure.**

$$H = U + PV$$

- **It is impossible to determine absolute value of enthalpy so we determine change in enthalpy for a process (ΔH).**

$$\Delta H = H_{final} - H_{initial}$$

The thermochemical reaction:

The balanced chemical reaction indicates the physical state of all reactants and products and also indicates the heat change.

- **The thermochemical reaction is of two types:**

❖ **Endothermic reaction.**

❖ **Exothermic reaction:**

Endothermic reaction:

Those thermochemical reactions in which heat is absorbed. Change in enthalpy for this reaction is positive.

Exothermic reaction:

Those thermochemical reactions in which the heat or energy is evolved during the reaction. Change in enthalpy for this reaction is negative.

Bond Energies:

- **When chemical change takes place :**
  - **Bonds have to break and energy is taken in(endothermic).**
  - **New bonds form and energy is given out(exothermic).**
- **Bond energy is the energy needed to break one mole of a bond in the gaseous state.**
- **When measured under standard conditions the bond energy may be referred to as the bond enthalpy.**

Energy change = the bond energies for all the bonds in the reactants
minus
the bond energies for all the bonds in the products

★**Energy change or enthalpy change, ΔH.**

Example :

Hydrogen and chlorine react to form hydrogen chloride gas:

H—H + Cl—Cl ⟶ 2 ×(H−Cl).Calculate enthalpy change?

Bond energy(kJ/mol)	Bond
436	H−H
243	Cl−Cl
432	H−Cl

Solution:

Energy change = the bond energies for all the bonds in the reactants
enthalpy change minus(−)
the bond energies for all the bonds in the products

- **The bond energies for all the bonds in the reactants =**
  436 +243 679kJ/ mol =

the energy absorbed when the bonds of the reactants break.

- **The bond energies for all the bonds in the products =**
  2× 432 = 864 kJ/ mol =

the energy released when the bonds of the products form.

- **Energy change = 679- 864 = −185 kJ/ mol**

− ve sign due to the fact that the energy released by the bonds formed is greater than the energy absorbed by the bonds broken.

Bond	Bond enthalpy / kJ mol^{-1}
C— H	410
C— C	350
Cl — Cl	242
Br — Br	193
Cl — H	431

Some bond enthalpies

The heat of reaction or enthalpy of reaction:

- **The amount of heat change when moles of reactant present in the thermochemical reaction has completely reacted.**
- **Some commonly used enthalpy changes are given names:**

  The enthalpy change of formation

  The enthalpy change of combustion

Enthalpy of combustion:

The amount of heat evolved by the complete combustion of one mole of a compound.

$C_4H_{10}(g) + 13/2\ O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(L);$

$\Delta H^{o}_{c} = -2658.0$ **kJ mol^{-1}**

Enthalpy of formation:

The amount of heat evolved or absorbed when one mole of a compound is formed from its constituents elements which are in their stable standard or stable state.

- **The standard heat of formation of all the stable and free elements is taken to be zero.**

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(l) \longrightarrow HBr(g);\ \Delta H^\circ_f = -36.4\ kJ\ mol^{-1}$$

Substance	kJ mol^{-1}
$CH_4(g)$	-74.81
$CH_3OH(l)$	-238.86
$C_6H_6(l)$	+49.0
$H_2O(l)$	-285.83
NaCl(s)	-411.15

Standard molar enthalpies of formation ($\Delta H°_f$) at 298K of a few selected substances

Standard Conditions:

There are the standard conditions for measuring enthalpy changes.

Pressure of 101kPa……..?

Temperature of 298K……..?

When an enthalpy change is measured under standard conditions it is written as ΔH_{298} usually simplified ΔH°

Standard Enthalpy of formation (ΔH_f°):

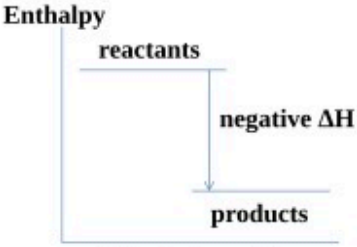
The enthalpy change accompanying the formation of one mole of the compound from its elements under standard conditions and all substances being in their standard states.

Standard Enthalpy of combustion (ΔH_c°):

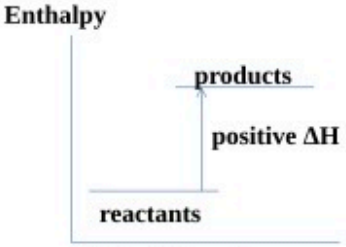
The amount of heat change when one mole of the substance is completely burnt in excess of oxygen under standard conditions.

Enthalpy level diagrams:

Enthalpy level diagrams are used to represent enthalpy changes.



Enthalpy diagram for an exothermic reaction

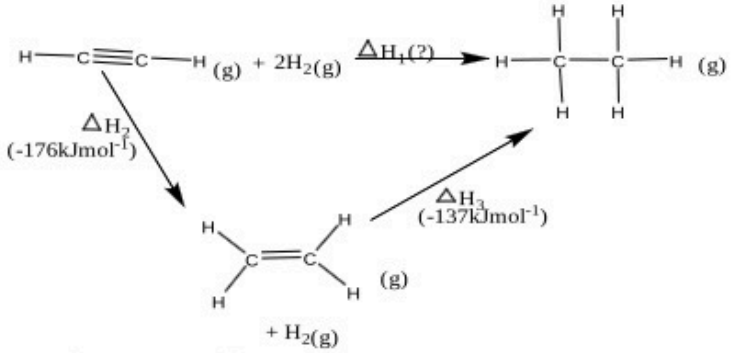


Enthalpy diagram for an endothermic reaction

- **The enthalpy changes for some reactions cannot be measured directly . To find these you use an indirect approach.**
- **It is often easy to measure enthalpies of combustion. To do this we use Hess law.**

Hess's law of constant heat summation:

In physical or chemical processes heat of reaction/ enthalpy of reaction remains the same whether it takes place in one step or multistep.



Hess's law means that :$\Delta H_1 = \Delta H_2 + \Delta H_3$

ΔH_2 = -176 kJmol^{-1}

ΔH_3 = -137 kJmol^{-1}

So ΔH_1 = (-176) + (-137) = -313 kJmol^{-1}

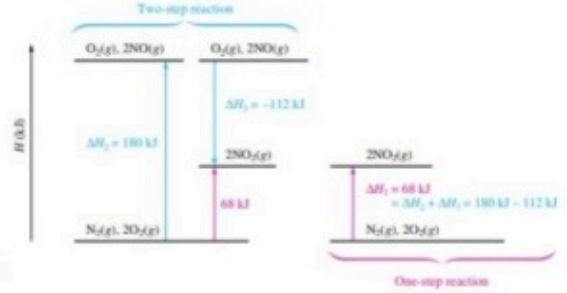
- **Many ΔH_f° are calculated from ΔH_C° via energy cycles using Hess's Law.**

1- $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$; $\Delta H = 68 kJ\ mol^{-1}$

$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$; $\Delta H = -68 kJ$

2- $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$; $\Delta H = 68 kJ\ mol^{-1}$

$2N_2(g) + 4O_2(g) \longrightarrow 4NO_2(g)$; $\Delta H = 136 kJ\ mol^{-1}$



3- $N_2(g) + O_2(g) \longrightarrow 2NO(g)$; $\Delta H_2 = 180kJ$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; $\Delta H_3 = -112kJ$

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$; $\Delta H_2 + \Delta H_3 = 68kJ$

Assessment 4

1- Standard state conditions are ……. ℃ and ……. atm.

2- Enthalpy of …….. is always negative.

3- Substance under observation during an experiment is……..

(surrounding or system)

4- An endothermic reaction is one in which heat is…….from surrounding.

5- $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H^\circ_r = -92.4$ kJ mol^{-1}

The standard enthalpy of formation of $NH_3(g)$ **is equal to……..**

6- For the reaction:

$H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O\ (l)$ $\Delta H^\circ_r = -285.83$ kJ mol^{-1} **; The enthalpy of formation of water is equal to…….**

Thank You