SELF-ASSESSMENT Chapter # 05

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **London dispersion forces are the only forces present among:**
A. molecules of water in liquid state
B. atoms of helium in gaseous state at high temperature
C. molecules of solid iodine
D. molecules of hydrogen chloride gas

(ii) **Identify equation which is used to determine the molar mass of a gas.**
A. $PV = nRT$ B. $nV = RT$ C. $pV = KT$ D. $E = mc^2$

(iii) **When water freezes at 0 °C, its density decreases due to:**
A. cubic structure of ice B. empty spaces present in the structure of ice
C. decrease in volume D. decrease in viscosity

(iv) **Which of following is the correct sequence of increasing ΔH_V values of substances mentioned?**
A. $H_2O > NH_3 > F_2$ B. $F_2 > NH_3 > H_2O$ C. $NH_3 > H_2O > F_2$ D. $H_2O > F_2 > NH_3$

(v) **Which type of intermolecular force is present in all types of molecule regardless of their polarity?**
A. Dipole-dipole forces B. Hydrogen bonds C. London dispersion forces D. Ion-dipole forces

(vi) **Which of the following is a crystalline solid?**
A. Glass B. Plastic C. Quartz D. Wax

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Why food cooking is difficult in the areas with high altitudes?
(ii) What is meant by habit of a crystal?
(iii) Discuss how hydrogen bonding is responsible for the relatively high surface tension of water.
(iv) Differentiate between crystalline and amorphous solids.
(v) One feels sense of cooling under the fan after bath.
(vi) Define vapour pressure and surface tension.
(vii) How does the heat of vaporization affect particle movement?
(viii) What are liquid crystals? Give two of their uses.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) What are London dispersion forces? Give examples, and discuss the factors affecting these forces.
(b) A sample of an unknown gas has a mass of 0.560 g. It occupies a volume of 2.87×10^{-4} m^3 at a temperature of 300 K and a pressure of 1.01×10^5 Pa. Calculate the molar mass of the gas. (Gas constant, $R = 8.31 JK^{-1}mol^{-1}$)

Chapter 06

CHEMICAL ENERGETICS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe those chemical reactions are accompanied by enthalpy changes and these changes can be exothermic (ΔH° is negative or endothermic ΔH° is positive). (Understanding)
- Interpret a reaction pathway diagram, in terms of the reaction and of the activation energy. (Understanding)
- Define terms such as standard conditions, enthalpy change, reaction, formation, combustion and neutralization. (Understanding)
- Explain that energy transfer occurs during chemical reactions because of the breaking and making of bonds. (Understanding)
- Calculate the bond energies for the enthalpy change of reaction ΔH°. (Understanding)
- Describe that some bond energies are exact and some bond energies are approximate. (Understanding)
- Calculate enthalpy changes from approximate experimental results, including the use of the relationships $q = mcdT$ and $\Delta H^\circ = -mcdT/n$. (Application)
- Define terms such as enthalpy change of atomization, lattice energy, ΔH°, first electron affinity, EA. (Knowledge)
- Use terms such as enthalpy change of atomization, lattice energy, first electron affinity. (Application)
- Construct Born Haber's Cycles for ionic solids. (Application)
- Perform calculations involving Born- Haber cycles. (Understanding)
- Explain the effect of ionic charge and ionic radius on the numerical magnitude of lattice energy. (Understanding)
- Apply enthalpy change with reference to hydration and solution. (Application)
- Construct an energy cycle involving enthalpy change of solutions and enthalpy change of hydration. (Application)
- Perform calculations involving energy cycles. (Application)
- Explain the effect of ionic charge and ionic radius on the numerical magnitude of an enthalpy change of hydration. (Understanding)
- Define the term entropy, S, as the number of possible arrangements of the particles and their energy in a given system. (Understanding)
- Explain the sign of entropy changes that occur during a change in state, temperature change and a reaction in which there is a change in the number of gaseous molecules. (Understanding)
- Calculate the entropy change for a reaction, ΔS°, given the standard entropies, S, of the reactants and the products. (Application)
- Explain the concept of heat as a form of energy. (Understanding)
- Explain the relationship between temperature and kinetic energy of particles. (Understanding)
- State that total energy is conserved in chemical reactions. (Understanding)

- Explain the concept of standard conditions and standard states in measuring energy changes. **(Understanding)**
- Explain Hess's Law. **(Understanding)**
- Apply Hess's Law to calculate enthalpy changes in a reaction carried out in multiple steps. **(Application)**
- Explain the relationship between bond formation energy and bond breaking energy. **(Understanding)**
- Explain Gibbs free energy. **(Understanding)**
- Apply the concept of Gibbs free energy to solve problems. **(Application)**
- Outline how enthalpy change relates to the calorie concept of the food we eat. **(Application)**
- Explain factors affecting the electron affinities of elements. **(Understanding)**

➲ Thermochemistry

Thermochemistry is the study of the quantity of heat energy absorbed or evolved during physical or chemical changes. That is why it is also called *energetics* and is largely based on the first law of thermodynamics. Hess's law, a special case of 1st law of *thermodynamics*, is a remarkable tool in a chemist's hand and finds numerous applications in analytical chemistry. Moreover, thermodynamics allows us to predict whether a particular reaction can occur under specified conditions i.e., it discusses the spontaneity of a reaction.

ENTHALPY CHANGE

The energy possessed by a substance due to its structure (types of bonds) and physical state is called its heat content or enthalpy denoted by H. Every substance possesses a characteristic amount of enthalpy. This is the reason that the total enthalpy of products (H_p) is never equal to that of reactants (H_R). Hence during a chemical reaction, when reactants are converted into products, there occurs a change in enthalpy denoted as ΔH. In other words, enthalpy change is the net energy, which is either evolved or absorbed in the form of heat. Mathematically,

Rack Your Mind!
1. What is a thermochemical equation?

$$\Delta H = (\text{Heat content of products, } H_p) - (\text{Heat content of reactants, } H_R)$$

➲ Exothermic Process Vs Endothermic Process

There are two cases:

i. **$H_P < H_R$:** such reactions involve a lowering of enthalpy and always take place with the evolution of heat which is equal to $H_p - H_R$ and ΔH carries negative sign.
"A chemical reaction or a physical change in which heat is evolved from the system to surroundings is called exothermic process."
For example, combustion of carbon in oxygen is an exothermic reaction.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJ mol}^{-1}$$

Rack Your Mind!
2. Which of the following is an endothermic reaction?
(A) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$
(B) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$
(C) $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$
(D) $C_2H_5OH_{(aq)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$

ii. **$H_P > H_R$:** such reactions involve an increase in enthalpy and always take place by the absorption of heat which is equal to $H_p - H_R$ and ΔH carries positive sign.
"A chemical reaction or a physical change in which heat is absorbed by the system from surroundings is known as endothermic process."
For example, The dissolution of ammonium chloride ($NH_4C\ell$) in water is an endothermic process.

$$NH_4C\ell_{(s)} \xrightarrow{H_2O_{(\ell)}} NH_4^+{}_{(aq)} + C\ell^-_{(aq)} \quad \Delta H = +16.2 \text{ kJ mol}^{-1}$$

Interesting Information!
The dissolution of ammonium chloride ($NH_4C\ell$) in water is an endothermic reaction. This reaction is used in cold packs (or ice packs) to treat internal injuries. When the pack is kneaded, water and $NH_4C\ell$ crystals mix and energy is absorbed from the surroundings, producing a cooling sensation.

Rack Your Mind!
3. Why in exothermic reactions heat is released from the system?

Following Figure shows the enthalpy diagram of exothermic and endothermic reactions.

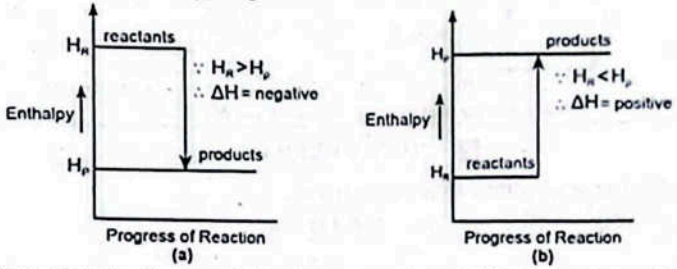
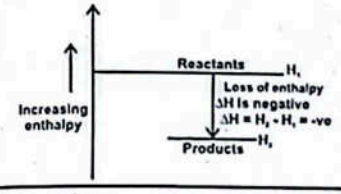
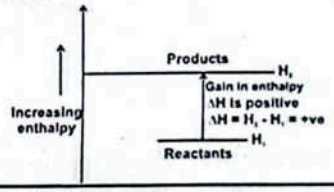


Figure: Enthalpy diagram of (a) Exothermic Reaction and (b) Endothermic Reaction

Exothermic reaction	Endothermic reaction
1. The reaction in which heat is evolved from the system is called exothermic reaction.	1. The reaction in which heat is absorbed by the system is called endothermic reaction.
2. The heat contents of product is less than that of reactants. 	2. The heat contents of products is more than that of reactants. 
3. ΔH is negative.	3. ΔH is positive.
4. The Number of bonds formed is greater than the bonds breakage during a reaction.	4. The number of bond breakage is greater than the bonds formation during a reaction.
5. The temperature of the system rises and eventually heat flows from system to surroundings.	5. The temperature of the system falls and eventually heat flows from surroundings to system.
6. The most spontaneous reactions are exothermic.	6. The most non-spontaneous reactions are endothermic.
Example: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7$ kJ mol^{-1}	Examples: $N_{2(g)} + O_{2(g)} \longrightarrow NO_{(g)}$ $\Delta H = 180$ kJ mol^{-1}

ENERGY PROFILE DIAGRAM

➲ Energy of Activation

All chemical reactions involve the breaking of bonds in the reactant molecules before the formation of new bonds. This can be achieved only if the reactant molecules collide with sufficient amount of energy to overcome an energy barrier. This minimum amount of energy required by the reactant molecules just to cross that energy barrier is called **energy of activation** denoted by E_a.

Rack Your Mind!
4. In a reaction pathway diagram, the peak represents to:
A) Reactants B) Products
C) Activation energy D) Heat released

The energy profile diagram of exothermic and endothermic reactions are given in Figure.

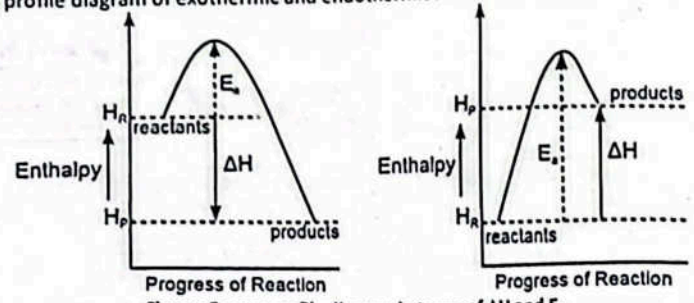


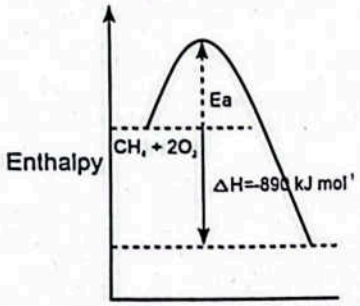
Figure: Energy profile diagram in terms of ΔH and E_a

☑ QUICK CHECK 6.1

Draw the energy profile diagrams for the following reactions:

i. $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\quad \Delta H = -890.3 \text{ kJ mol}^{-1}$

Ans.

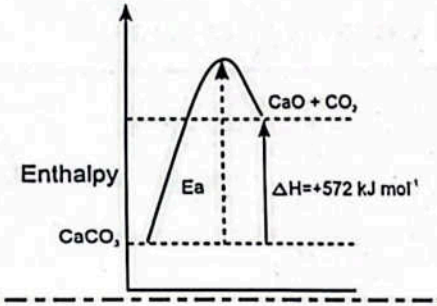


1. Reactants start at higher energy than products (exothermic)
2. Energy barrier represents activation energy
3. Vertical drop shows the large heat release (–890.3 kJ/mol)
4. Liquid water product is at lower energy than gaseous reactants

   The downward slope shows this is highly exothermic, typical of combustion reactions. The exact activation energy isn't specified here, but the diagram shows there must be some energy input to initiate the reaction.

ii. $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ $\quad \Delta H = +572 \text{ kJ mol}^{-1}$

Ans.



1. Reactants ($CaCO_3$) start at a lower energy level than products ($CaO + CO_2$).
2. Energy absorbed: The reaction requires +572 kJ/mol (endothermic), shown as an upward arrow.
3. Activation energy (E_a): Not specified, but implied by the curve's peak (not drawn here for simplicity).
   - Endothermic reactions always show products at a higher energy level than reactants.
   - The +ΔH value confirms energy is absorbed (e.g., thermal decomposition of limestone).

STANDARD ENTHALPY CHANGES

The enthalpy of a substance not only depends upon its physical state but also on the pressure and temperature. Hence, we must specify these conditions while writing an equation. Therefore, when making accurate comparisons of enthalpy changes for various reactions, ΔH is determined under certain standard conditions, which are summarized below:

a) Temperature: 25°C or 298 K
b) Pressure: 1 atm or 101 kPa

Did You Know?

The standard state of an element is its most stable form at 298 K and 1 atm pressure. For example, the standard state of C is graphite not diamond. By definition, the standard enthalpy change of formation of any element in its standard state is zero.

Rack Your Mind!

5. What is meant by atomization energy?

Enthalpy Change of Reaction (ΔH°_r)

The standard enthalpy of a reaction is the enthalpy change involved when stoichiometric amounts of reactants in their standard states react together completely to form products under standard conditions.
Example: Consider the reaction between hydrogen and oxygen gases to form 1 mole of water:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H^\circ_r = -286 \text{ kJ mol}^{-1}$$

Enthalpy Change of Combustion (ΔH°_c)

The standard enthalpy change of combustion of a substance is the enthalpy change involved when one mole of the substance is completely burnt in excess of oxygen, under standard conditions.
It is always exothermic.

Example: Standard enthalpy of combustion ΔH°_c of ethanol is $-1368 \text{ kJ mol}^{-1}$.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H^\circ_c = -1368 \text{ kJ mol}^{-1}$$

Enthalpy change of combustion is useful in calculating calorie content of foods and fuels.

Enthalpy Change of Formation (ΔH°_f)

Standard enthalpy change of formation of a compound is the enthalpy change involved when one mole of the compound is formed from its elements under standard conditions.
It can be exothermic or endothermic.

Example: ΔH°_f for methane is given below.

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^\circ_f = -74.8 \text{ kJ mol}^{-1}$$

Enthalpy Change of Atomization (ΔH°_{at})

"The standard enthalpy change of atomization of an element is the enthalpy change involved when one mole of gaseous atoms is formed from the element, under standard conditions."
Example:

$$H_{2(g)} \longrightarrow 2H_{(g)} \qquad E_{H-H} = +436 \text{ kJ mol}^{-1}$$
$$1/2H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^\circ_{at} = +218 \text{ kJ mol}^{-1}$$

Enthalpy Change of Neutralization (ΔH°_n)

The standard enthalpy change of neutralization is the enthalpy change involved when one mole of water is formed by the reaction of an acid with an alkali under standard conditions. It is always exothermic.

Example: The enthalpy of neutralization of NaOH by HCℓ is −57.1 kJ mol^{-1}.
When these solutions are mixed together during the process of neutralization, the only change that occurs is the formation of water molecules leaving Na^+ and $C\ell^-$ as free ions in solution. Thus, the enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components and the actual neutralization reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H^\circ_n = -57.1 \text{ kJ mol}^{-1}$$

For all strong acid-base reactions ΔH° is always near −57.1 kJ mol^{-1}.

Electron Affinity (ΔH°_{ea})

The first electron affinity is the enthalpy change involved when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions under standard conditions.
Example: Electron affinity of chlorine atom.

$$C\ell_{(g)} + e^- \longrightarrow C\ell^- \qquad \Delta H = -348.8 \text{ kJ mol}^{-1}$$

Since, energy is released, so first electron affinity carries negative sign.
Note: A detailed discussion of electron affinity is given in chapter 1.

Rack Your Mind!

6. Why is it necessary to mention the physical states of reactants and products in a thermo chemical reaction? Apply Hess's law to justify your answer.

QUICK CHECK 6.2

a) Write equations, including state symbols, that represent the enthalpy change of atomization of:
(i) Oxygen (ii) Barium (iii) Bromine

Ans. (i) Oxygen (O_2)

$$\frac{1}{2}O_{2(g)} \longrightarrow O_{(g)} \quad \Delta H_{at} = +249 \text{kJ/mol}$$

(ii) Barium (Ba)

$$Ba_{(s)} \longrightarrow Ba_{(g)} \quad \Delta H_{at} = +180 \text{kJ/mol}$$

(iii) Bromine (Br_2)

$$\frac{1}{2}Br_{2(\ell)} \longrightarrow Br_{(g)} \quad \Delta H_{at} = +112 \text{kJ/mol}$$

b) Classify the enthalpy change in each of the following reactions:

i) $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$

Ans. Enthalpy Change of Formation (ΔH°_f)

ii) $HC\ell_{(g)} + NH_{3(g)} \longrightarrow NH_4C\ell_{(s)}$

Ans. Enthalpy Change of Combustion (ΔH°_c)

iii) $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(\ell)}$

Ans. Enthalpy Change of Reaction (ΔH_r)

BOND ENERGY (BOND DISSOCIATION ENERGY) AND ENTHALPY CHANGES

Chemical reactions involve the breaking and making of chemical bonds. When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms; we call this, bond dissociation energy.

Bond Energy

It is defined as, "The average amount of energy required to break (dissociate) one mole of a particular bond in a substance."
It may be denoted as E. If we are determining bond energy of a particular bond in a particular substance, we call this exact bond energy.

This is to be noted that bonds between the same pair of atoms usually have different bond energy (B.E.) values, in all of their compounds. Actually, bond energy is affected by other atoms in a molecule. For example, C–C bonds usually have bond energy values of approximately 350 to 380 kJ/mol.

- In ethane: $[H_3C-CH_3]$; $E_{C-C} = 376 \text{ kJ mol}^{-1}$
- In propane: $[H_3C-CH_2-CH_3]$; $E_{C-C} = 356 \text{ kJ mol}^{-1}$
- In butane: $[H_3C-CH_2-CH_2-CH_3]$; $E_{C-C} = 352 \text{ kJ mol}^{-1}$

In these examples, E_{C-C} for ethane is exact bond energy. Similarly for propane and butane, E_{C-C} are exact bond energies. When we take average of all E_{C-C} in different molecules, we obtain average C–C bond energy. Practically, average bond energy is used instead of exact bond energies. Average bond energies of some bonds are given in Table.

Rack Your Mind!

7. Energy is absorbed when:
A) Bonds are formed
B) Bonds are broken
C) Reaction is exothermic
D) Products form

Table: Average Bond Energies of Some Important Bonds (kJ mol^{-1})

	H–	C–	C=	C≡	N–	N=	N≡	O–	O=	F–	Cℓ–	Br–	I–
H	436	413			391			463					
C	413	348	615	812	292	615	891	351	728				
N	391	292	615	891	161	418	945	222	607				
O	463	351	728		222	607		139	498				
S	339	259	477					347		327	251	213	
F	563	441			270			185		159	255		
Cℓ	432	328			200			203			243	218	209
Br	366	276										192	180
I	299	240						201					151

ENTHALPY CHANGE OF REACTION (ΔH_r) AND CHEMICAL BONDS

A chemical reaction is defined as a process during which old bonds are broken and new bonds are formed. Therefore, the enthalpy change (ΔH_r) in a chemical reaction actually comes from the breaking and forming of chemical bonds.
A chemical bond represents a form of energy known as chemical energy (which, like the others, is interconvertible into all forms of energy). Bond breaking absorbs energy (ΔH = +ve) while bond formation relèases it (ΔH = −ve) and their difference will decide the overall sign of ΔH. That is whether a reaction is exothermic or endothermic is determined by the net change.
Overall reaction is exothermic if the energy released in making of new bonds is greater than that absorbed in bond breaking. The reverse is true for an endothermic reaction.
Example:
Formation of Water:
In the formation of water, energy is needed to break the H–H bonds (of hydrogen molecules) and the O=O bonds (of oxygen molecules) while energy is released in the making of the H–O bonds (of water). However, the net reaction is exothermic because more energy is released in forming the H–O bonds than is absorbed in breaking the H–H and O=O bonds (Figure 6.5). Thus,

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)} \qquad \Delta H_r = -ve$$

Sample Problem 6.1

With the help of the following bond energy data; calculate the enthalpy change of the following reaction:

$$E_{H-H} = 436 \text{ kJ mol}^{-1};\ E_{O=O} = 495 \text{ kJ mol}^{-1} \text{ and } E_{H-O} = 463 \text{ kJ mol}^{-1}$$

$$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(g)}$$

Solution:

$$\underbrace{H-H + 1/2\,O=O}_{436 + 1/2(495)} \qquad \underset{2\times(463)}{\overset{O}{\diagup\diagdown}\ H\ H}$$

(bond breaking energy) (bond forming energy)

$$\because \Delta H^\circ = \sum E_b - \sum E_f$$

$$= [E_{H-H} + E_{O=O}] - [2E_{H-O}]$$

$$= [436 + 247.5] - [2(463)]$$

$$\Delta H^\circ = -242.5 \text{ kJ mol}$$

MEASUREMENT OF ENTHALPY CHANGE OF A REACTION

The amount of heat evolved or absorbed during a physical or chemical change can be measured by an instrument called calorimeter, which generally measures the change in temperature during the process. At its simplest, a calorimeter consists of an insulated vessel, a stirrer and a thermometer. There are various types of calorimeters but here we will describe only "Glass Calorimeter".

Rack Your Mind!

8. If $q = m\,c\,\Delta T$, what does 'c' represent?
   A) Concentration
   B) Specific heat capacity
   C) Constant
   D) Speed

Calorimetry relies on the fact that it takes 4.18 J of energy to increase temperature of 1 g of the water by 1°C. The amount of heat energy required to raise the temperature of a substance of mass 1 kg through 1 K (or 1°C) is known as specific heat capacity, c, of the liquid. So the specific heat capacity of water is 4.18 $Jg^{-1}K^{-1}$ or $(Jg^{-1}°C^{-1})$.

The energy is transferred as heat and is shown by relationship

$$q = c \times m \times \Delta T$$

Where,

q = heat transferred in Joules
m = mass of water/solution in grams
c = specific heat of water = 4.184 J/g °C

ΔT is the temperature change in °C.

Here,

$(\Delta T = T_f - T_i)$

➲ Glass Calorimotor

A glass calorimeter is suitable for measuring heat-flow for reactions in solutions.

Construction:

It consists of a beaker, a stirrer, a thermometer and a loose-fitting lid to keep the contents at atmospheric pressure as shown in Figure 6.3. The outside walls of the calorimeter (beaker) are insulated using cotton wool to minimize the exchange of heat with the surrounding air.

Process:

The reaction is carried out inside the beaker and the heat evolved or absorbed is measured by the temperature change. Since the pressure inside the calorimeter is constant, the temperature measurement makes it possible to calculate the enthalpy change ΔH during the reaction.

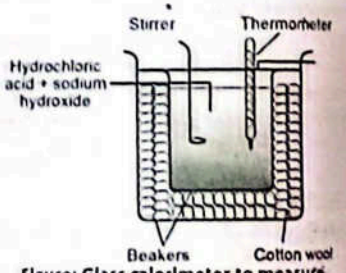


Figure: Glass calorimeter to measure enthalpy change of reactions

Calculation of ΔH:

ΔH is calculated as follows:

As all the heat evolved during the reaction remains within the calorimeter and absorbed by water, so

i) $q = m_{water} \times c_{water} \times \Delta T$

ii) Convert into kJ by dividing with 1000.

iii) Calculate ΔH for the reaction using relation.

The solutions we are using here are so dilute that almost all of their mass consists of water, therefore, we can simply use specific heat capacity of water. Such a calorimeter could be used to measure the heat of neutralization (ΔH_n°).

Limitation of glass calorimeter it cannot be used for reactions involving gases which would escape from the vessel, nor it would be appropriate for reactions in which the products reach high temperatures.

Sample Problem 6.2

Neutralization of 100 cm^3 of 0.5 mol dm^{-3} NaOH at 25°C with 100 cm^3 of 0.5 mol dm^{-3} HCl at 25°C raised the temperature of the reaction mixture to 28.5°C. Find the enthalpy of neutralization. Specific heat of water = 4.2 $Jg^{-1}K^{-1}$.

Solution:

Density of H_2O is around 1 g cm^{-3}, so total volume of solution which is 200 $cm^3 \approx 200$ g. Rise in temperature,

$$\Delta T = 28.5 - 25.0 = 3.5°C = 3.5 \text{ K}$$

∵ Amount of total heat evolved, $q = m \times c \times \Delta T$

$= 200 \times 4.2 \times 3.5 = 2940$ J

$= 2.94$ kJ

➲ Calculation of n (No. of moles of H_2O formed)

Using mole = Concentration $(mol/dm^3) \times$ Volume (dm^3)

$n_{(HCl)} = n_{(NaOH)} = 0.5 \times 100/1000 = 0.05$ mol

Using equation, Number of moles of water formed, $n_{(H_2O)} = 0.05$ mol

Heat evolved in the formation of 0.05 mole of water, $q = -2.94$ kJ

$$\Delta H_n^\circ = q/n = -2.94 \text{ kJ}/0.05 \text{ mol}$$

So, Enthalpy of neutralization, $\Delta H_n^\circ = -58.8$ kJ mol^{-1}

☑ QUICK CHECK 6.3

Calculate ΔH_n° of the reaction of 50 cm^3 of HNO_3 with 50 cm^3 of 1.5 mol/dm^3 of NaOH. The change in temperature is 4°C.

Given Data:

- **Volume of HNO_3: 50 cm^3 (0.050 dm^3)**
- **Volume of NaOH: 50 cm^3 (0.050 dm^3)**
- **Concentration of NaOH: 1.5 mol/dm^3**
- **Temperature change (ΔT): +4°C**
- **Assumptions:**
  - **HNO_3 is a strong acid (fully dissociates).**
  - **NaOH is a strong base (fully dissociates).**
  - **The density of the solution ≈ 1 g/cm^3 (so total mass = 100 g).**
  - **Specific heat capacity (c) of the solution ≈ 4.18 J/g°C (same as water).**

Step 1: Determine Limiting Reagent (Moles of H^+ and OH^-)

- **Both HNO_3 and NaOH are monoprotic, so moles of H^+ = moles of OH^-.**
- **Moles of NaOH (and thus OH^-):**

$$nNaOH = C \times V = 1.5 \text{ mol/dm}^3 \times 0.050 \text{ dm}^3 = 0.075 \text{ moles}$$

Step 2: Calculate Heat Released (q)

$$q = m \times c \times \Delta T$$

- **Total mass (m): 50 cm^3 + 50 cm^3 = 100 g**
- **c: 4.18 J/g°C**
- **ΔT: 4°C**

$$Q = 100 \text{ g} \times 4.18 \text{ J/g °C} \times 4 \text{ °C} = 1672 \text{ J} = 1.672 \text{ kJ}$$

Step 3: Calculate ΔH_n° (per mole of H_2O formed)

- Moles of H_2O formed = moles of OH^- reacted = 0.075 mol
- ΔH_n° is heat released per mole:

$$\Delta H_n^\circ = \frac{-q}{n} = \frac{-1.672\ kJ}{0.075\ mol} = 22.29\ kJ/mol$$

ENTHALPY CHANGE AND CALORIE CONTENT OF FOOD

We will discuss foods as fuels. When food is digested, the chemical energy stored in the food (also called calorie content) is released as heat energy. In other words, digestion of food releases same amount of energy as it is burned outside the body. So, the overall enthalpy of combustion is the same as the heat of combustion, which can be determined in a calorimeter (typically in a bomb calorimeter).

Calorie Content: The calorie content of food is a measure of the energy 'released' when the food is completely consumed in the body.

Unit: This energy is typically expressed in units of kilocalories (k cal) or joules (J).

➲ Relation between Enthalpy Change and Calorie Content

The enthalpy of combustion of a food (ΔH_c) is the calorie content of that food when it is translated or converted into kilocalories per gram.

Look at the energy provided from glucose.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} \quad \Delta H^\circ = -2803\ kJ\ mol^{-1}$$

The calorie content of glucose can be calculated as follows: First, we find ΔH per gram of glucose. Molar mass of glucose is 180 g mol^{-1}. Above equation shows that;

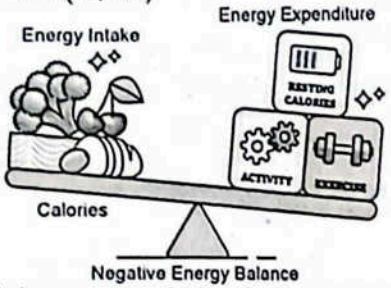
mol(180.0 g) of glucose burns to produce energy = 2803 kJ

$$1.0\ g\ of\ Glucose = \frac{2803\ kJ/g}{180\ g/mol} = 15.57\ kJ/g$$

Using the relation,

$$\Delta H(kJ/g) = -4.184 \times \text{calorie content}$$

$$\text{Calorie content} = -\frac{\Delta H(\ kJ/g)}{4.184(\ kJ/kcal)} = -\frac{15.57\ kJ/g}{4.184(\ kJ/kcal)} = -3.72\ kcal/g$$



Remember, the calorie content we take from food must be balanced by working, exercising and doing positive activities. Otherwise, our bodies will have imbalanced growth and maintenance

HESS'S LAW OF HEAT SUMMATION

Exercise LO 5

Q. State and explain Hess' law. Give its two applications.

First law of thermodynamics is actually a manifestation of law of conservation of energy, which states, "Energy can neither be created nor destroyed, but can be converted from one form to another."

Germain Henri Hess applied the law of conservation of energy to enthalpy changes. There are many reactions, for which ΔH cannot be measured directly by calorimetric method. For example, tetrachloromethane CCl_4 cannot be prepared directly by combining carbon and chlorine. Hess's Law helps us calculating the enthalpy changes for such reactions or processes.

Statement:

"The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

Explanation:

Hess's law can be illustrated by drawing enthalpy cycles, often called energy cycles or Hess cycles. Let A be converted to ' B ' directly in a single step, which is the direct route; or in a series of two or three steps designated as indirect route 1 and Indirect route 2 respectively as shown in Figure. The products formed in these routes (M, N and X, Y, Z) are called reaction intermediates.

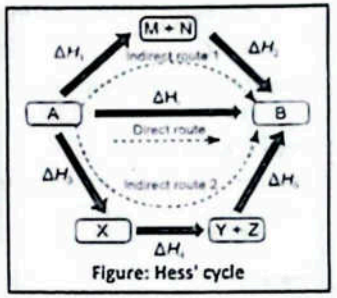


Figure: Hess' cycle

Then according to Hess' law,

For the indirect route 1, we can write: $\Delta H_r = \Delta H_1 + \Delta H_2$

For the indirect route 2, we can write: $\Delta H_r = \Delta H_3 + \Delta H_4 + \Delta H_5$

Below are few examples of it.

(i) Calculating Enthalpy of Formation (ΔH_f°) using Enthalpy of Combustion (ΔH_c°)

Sample Problem 6.3

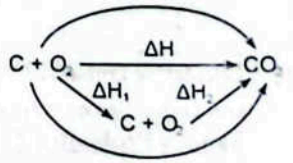
Calculate the enthalpy change of formation of CO using Hess cycle with the help of following combustion data.

Solution:

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.5\ kJ\ mol^{-1}$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_2 = -283\ kJ\ mol^{-1}$$

$$C_{(graphite)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H_1 = ?$$



Solution: Applying Hess's law, we can write

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = -393.5 - (-283)$$

$$= -110.5\ kJ\ mol^{-1}$$

(ii) Calculating Enthalpy Change of Reaction (ΔH°) using Enthalpies of formation (ΔH_f°)

Sample Problem 6.4

Calculate the enthalpy change of reaction of

$$C_2H_4 + HC\ell \longrightarrow C_2H_5C\ell + \Delta H_2$$

Using Hess cycle with the help of following combustion data.

Solution:

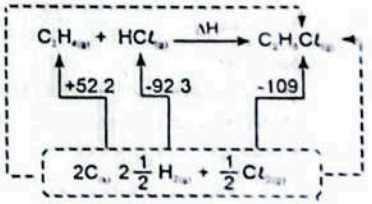
$$\Delta H_f^\circ \text{ of } C_2H_4 = +52.2\ kJ\ mol^{-1}$$

$$\Delta H_f^\circ \text{ of } HC\ell = 92.3\ kJ\ mol^{-1}$$

$$\Delta H_f^\circ \text{ of } C_2H_5C\ell = -109\ kJ\ mol^{-1}$$

$$= -109 - [+52.2 + (-92.3)]$$

$$= -68.9\ kJ\ mol^{-1}$$



☑ QUICK CHECK 6.4

Calculate the standard enthalpy change for the formation of methane (ΔH_f°):

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(\ell)} \qquad \Delta H_f^\circ = ?$$

The standard enthalpies of combustion of $C_{(s)}, H_{2(g)}$ are $-394 kJmol^{-1}, -286 kJmol^{-1}$ and enthalpy of formation of $C_6H_{6(\ell)}$ $-3267 kJmol^{-1}$ respectively.

Given Data:

Combustion reactions and enthalpies:

- $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_c^\circ = -394\ kJ\,mol^{-1}$ (per mole of C)
- $H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta H_c^\circ = -286\ kJ\ mol^{-1}$ (per mole of H_2)
- $C_6H_{6(\ell)} + 15/2 O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(\ell)}$ $\Delta H_c^\circ = -3267\ kJ\ mol^{-1}$ (per mole of C_6H_6)

Target formation reaction:

$$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)} \qquad \Delta H_f^\circ = ?$$

Step 1: Apply Hess's Law

The enthalpy of formation (ΔH_f°) of benzene can be calculated using the combustion enthalpies of the reactants and products:

$$\Delta H_f^\circ = \sum \Delta H_c^\circ (\text{reactants}) - \sum \Delta H_c^\circ (\text{products})$$

Here:

- **Reactants:** $6C_{(s)} + 3H_{2(g)}$
- **Product:** $C_6H_{6(\ell)}$

So:

$$\Delta H_f^\circ = \left[6 \times \Delta H_c^\circ(C) + 3 \times \Delta H_c^\circ(H_2)\right] - \left[1 \times \Delta H_c^\circ(C_6H_6)\right]$$

Step 2: Plug in the Values

$$\Delta H_f^\circ = \{6(-394) + 3(-286)\} - [-3267]$$
$$\Delta H_f^\circ = [-2364 - 858] + 3267$$
$$\Delta H_f^\circ = -3222 + 3267$$
$$\Delta H_f^\circ = +45\ kJ\,mol^{-1}$$

iii) Calculating Enthalpy Change of Formation of a substance (ΔH_f°) using Enthalpy of Combustion and Enthalpies of Formation of other substances

Sample Problem 6.5

Propane ($C_3H_{8(g)}$) burns in oxygen according to the equation:

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

When 14.64 g of propane is burned in an excess of oxygen in a calorimeter at 25°C and 1 atm pressure, 678.6 kJ of heat is evolved. Calculate the standard enthalpy of formation of propane. The standard enthalpies of formation of $CO_{2(g)}$ and $H_2O_{(g)}$ are $-393.51\ kJ\ mol^{-1}$ and $-241.82\ kJ\ mol^{-1}$ respectively.

Solution:

The first step is to find the enthalpy change when one mole of propane is burned.

Molar mass of propane, $C_3H_8 = 3(12.011) + 8(1.0079) = 36.033 + 8.0632 = 44.096$

No. of moles of propane $= 14.64 / 44.096 = 0.3320$ mol

So, 0.3320 mol propane evolves heat $= 678.6$ kJ

1.0 mol propane evolves heat $= 678.6 / 0.3320\ kJ\ mol^{-1} = -2044\ kJ\ mol^{-1}$

According to Hess's law:

$$\Delta H_r = \left[3 \times \Delta H_f^\circ(CO_2) + 4 \times \Delta H_f^\circ(H_2O)\right] - \left[1 \times \Delta H_c^\circ(C_3H_8) + 5 \times \Delta H_c^\circ(O_2)\right] - 2044\ kJ$$
$$= \left[3 \times (-393.51) + 4 \times (-241.82)\right] - \left[1 \times \Delta H_f^\circ(C_3H_8) + 5 \times (0)\right]$$

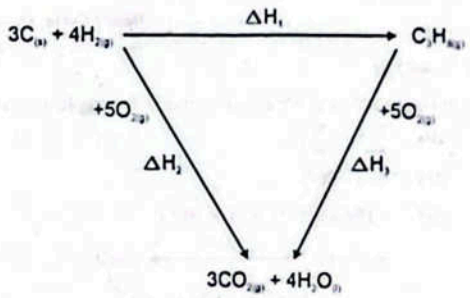
Taking the heat of combustion of $O_{2(g)}$ to be zero and solving this equation for $\Delta H_f^\circ(C_3H_8)$ gives,

$$\Delta H_f^\circ(C_3H_8) = -104\ kJ\ mol^{-1}$$

☑ QUICK CHECK 6.5

Draw enthalpy cycle of sample problem 6.5 according to Hess's law to validate above calculation.

Solution:



iv) Calculating Enthalpy Change of Reactions (ΔH_r) using Bond Energies

A special case of Hess's law involves the use of bond energies to estimate heats of reaction for gas-phase reactions.

First Step:

In the first step, the bonds in all the reactant molecules are broken to give free atoms in the gas phase. The enthalpy change for this step can be calculated by adding the bond enthalpies from Table.

Second Step:

In the second step, the product molecules are formed. The enthalpy change for this step can be estimated from the bond enthalpies of Table, which must now be taken with minus sign because the bonds are being formed instead of broken. In general, the heat of reaction for any gaseous chemical reaction can be calculated from average B.E.'s by use of the following version of Hess's law:

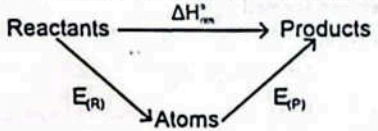


Figure: Hess Cycle; showing the relationship between B.E.'s and $\Delta H_r = \sum nE_R - \sum nE_P$

Sample problem 6.6

In the case of formation of $HC\ell_{(g)}$ from $H_{2(g)}$ and $C\ell_{2(g)}$, use B.E. data from Table 6.1 to estimate ΔH for the reaction:

$$H_{2(g)} + C\ell_{2(g)} \longrightarrow 2HC\ell_{(g)}$$

And finally calculate the heat of formation of HCl.

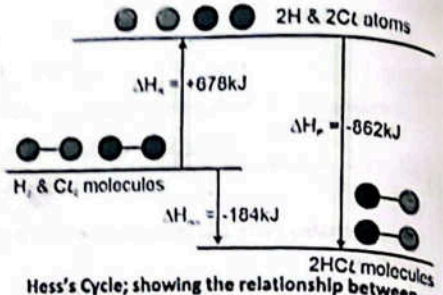
We replace this reaction by a hypothetical two-step process. The bonds in all the reactant molecules are first broken, and then the atoms are combined to make the products.

First Step:

$$H_{2(g)} + C\ell_{2(g)} \longrightarrow 2H + 2C\ell_{(g)}$$

$E_{H-H} = 436\ kJ\ mol^{-1}$; $E_{Cl-Cl} = 242\ kJ\ mol^{-1}$

$$E_R = \left(1\ mol \times 436 \frac{kJ}{mol}\right) + \left(1\ mol \times 242 \frac{kJ}{mol}\right)$$
$$= 436\ kJ + 242\ kJ$$
$$= 478\ kJ$$



Hess's Cycle; showing the relationship between B.E.'s and ΔH.

Second Step:

$$2H_{(g)} + 2C\ell_{(g)} \longrightarrow 2HC\ell_{(g)}$$

$E_{H-Cl} = 431\ kJ\ mol^{-1}$

$E_P = 2\ mol \times 431\ kJ\ mol^{-1} = 862\ kJ$

The standard enthalpy change in the reaction is obtained by the following formula:

$$\Delta H_r^\circ = \sum E_R - \sum E_P$$
$$\Delta H_r^\circ = 678 - 862$$
$$\Delta H_r^\circ = -184\ kJ\ (\text{for 2 mol of } HC\ell)$$

$$H_{2(g)} + C\ell_{2(g)} \xrightarrow{\Delta H_r^\circ} 2HC\ell_{(g)}$$
$$2H_{(g)} + 2C\ell_{(g)}$$

Enthalpy of formation of $HC\ell = -184/2\ kJ = -92\ kJ\ mol^{-1}$

QUICK CHECK 6.6

a) The reaction for the Haber process is: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

The relevant bond energies are: $E_{N\equiv N} = 945\ kJmol^{-1}$, $E_{H-H} = 436\ kJmol^{-1}$, $E_{N-H} = 391\ kJmol^{-1}$.

Calculate the enthalpy change of the above reaction.

Solution:

To calculate the enthalpy change (ΔH) for the Haber process reaction:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

We'll use bond enthalpies (bond energies) to determine the energy changes associated with breaking and forming bonds.

Step 1: Identify Bonds Broken and Formed

Bonds Broken (Endothermic, +ΔH):

- 1 N≡N triple bond (in N_2): $\Delta H = +945\ kJ\ mol^{-1}$
- 3 H-H single bonds (in H_2): $3 \times \Delta H = 3 \times (+436\ kJ\ mol^{-1}) = +1308\ kJ\ mol^{-1}$

Bonds Formed (Exothermic, −ΔH):

- 6 N-H single bonds (in $2NH_3$, since each NH_3 has 3 N-H bonds):

$$6 \times \Delta H = 6 \times (-391\ kJ\ mol^{-1}) = -2346\ kJ\ mol^{-1}$$

Step 2: Calculate Total Enthalpy Change

$\Delta H_{reaction} = \text{Energy absorbed (bonds broken)} + \text{Energy released (bonds formed)}$

$\Delta H_{reaction} = (+945 + 1308) + (-2346)$

$\Delta H_{reaction} = 2253 - 2346$

$\Delta H_{reaction} = -93\ kJ\ mol^{-1}$ (For 2 moles of NH_3) and For 1 mole $= \frac{-93\ kJ/mol}{2} = -46\ kJmol^{-1}$

b) Calculate the enthalpy change for the following reaction

$$C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$$

The bond energies of various bonds (in $kJmol^{-1}$) are given below:

$$E_{C-C} = +347,\ E_{C-H} = +410,\ E_{C-O} = +336,\ E_{O=O} = +496,\ E_{C=O} = +805,\ E_{O-H} = +465$$

Given Data:

The enthalpy change (ΔH) for the combustion of ethanol (C_2H_5OH), we use bond energies:

Step 1: Bonds Broken (Reactants)

1. C_2H_5OH (Liquid Ethanol):
   - 1 C-C: 347 kJ/mol
   - 5 C-H: 5 × 410 = 2050 kJ/mol
   - 1 C-O: 336 kJ/mol
   - 1 O-H: 465 kJ/mol

   Total for C_2H_5OH = 347 + 2050 + 336 + 465 = 3198 kJ/mol
2. 3 O_2 (Gaseous Oxygen):
   - 3 O=O: 3 × 496 = 1488 kJ/mol

Total Bonds Broken = 3198 + 1488 = 4686 kJ/mol

Step 2: Bonds Formed (Products)

1. 2 CO_2 (Gaseous):
   - 4 C=O: 4 × 805 = 3220 kJ/mol
2. 3 H_2O (Liquid):
   - 6 O-H: 6 × 465 = 2790 kJ/mol

Total Bonds Formed = 3220 + 2790 = 6010 kJ/mol

Step 3: Calculate ΔH

ΔH = Energy Absorbed (Bonds Broken) − Energy Released (Bonds Formed)

ΔH = 4686 − 6010 = −1324kJ/mol

ENERGETICS OF SOLUTION

The process of dissolving a solute in a solvent is called dissolution. It is assumed that the formation of a solution, takes place in three steps.

I. Overcoming the intermolecular forces in the solvent to make room for the solute (expanding the solvent).
II. Breaking up the solute into individual components (expanding the solute).
III. Allowing the solute and solvent to interact to form the solution

In this process heat is either given out or taken in. Standard enthalpy change of solution is used to describe it.

➢ Standard enthalpy Change of Solution (ΔH_{sol}°)

"The standard enthalpy of solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in a solvent to give an infinitely dilute solution."

It is denoted by ΔH_{sol}°. It may be exothermic or endothermic. The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

$$Na_2CO_{3(s)} + aq \longrightarrow 2Na^+_{(aq)} + CO_3^{2-}{}_{(aq)} \qquad \Delta H_{sol}^\circ = -25\ kJ\ mol^{-1}$$

$$NH_4C\ell_{(s)} + aq \longrightarrow NH_4^+{}_{(aq)} + C\ell^-_{(aq)} \qquad \Delta H_{sol}^\circ = +16.2\ kJ\ mol^{-1}$$

In Table are given values of heats of solution of different ionic solids in water at infinite dilution. The magnitude of heat of solution gives information regarding the strength of intermolecular forces of attraction between components which mix to form a solution.

An ionic compound consists of oppositely charged ions, held together by strong electrostatic forces.

➢ Factors Governing Process of Dilution:

Two factors govern the process of dissolution

Table: Heats of solution of some important ionic solids ($kJmol^{-1}$)

Substance	Heat of Solution
NaCl	4.98
KCl	17.8
KBr	19.9
KI	21.4
NH_4Cl	16.2
NH_4NO_3	26.0

I. Hydration energy (accounts for the attraction of solute ions with water molecules)
II. Lattice energy (controls the breaking of the ionic compounds)

Hydration

When ionic compounds are dissolved in water, they are dissociated into ions, which are then surrounded by water molecules. **"The process in which water molecules surround and interact with the solute ions is called hydration."** The forces are created between water molecules and the ions which are called Ion dipole forces as shown in Figure.
And as a result, all the ions in aqueous solution are said to be hydrated. The energy of attraction due to an ion-dipole force is known as enthalpy of hydration, defined as follows:

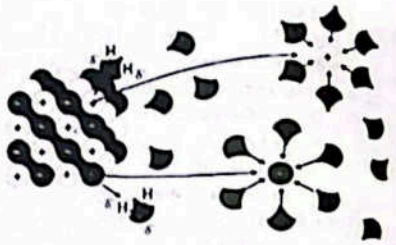


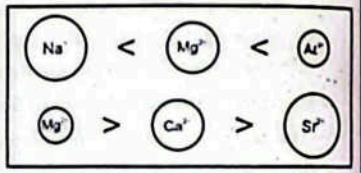
Figure: Dissolution of an ionic compound through the process of hydration.

Enthalpy of Hydration:

"The enthalpy change involved when one mole of a solute is dissolved in excess of water to make infinitely dilute solution under standard conditions is called enthalpy of hydration."
It is denoted by ΔH_{hyd}. This energy is always released as it is formation of ion-dipole bond.

Factors Affecting the magnitude of Hydration Energy

The heat of hydration depends on following factors:
I. Charge on the ion II. Size of the ion
We usually use a combined term for these two factors i.e., **"charge density"** which is defined as charge per unit area. If greater charge is present on smaller ion, the charge density is large and vice versa. And large value of charge density means that ions are strongly attracted by water molecules during the process of hydration, thereby increasing the hydration energy values. For example, enthalpies of hydration of the given ions are in the order:
On the same basis we can explain the hydration energy of anions.



(Exercise 6.4)

Q. What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

Lattice Energy (ΔH°_{latt})

"The lattice energy of an ionic crystal is the enthalpy change involved when one mole of the ionic compound is formed from gaseous ions under standard conditions."

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H^\circ_{latt} = -787 \text{ kJ mol}^{-1}$$

Factors Affecting the magnitude of Lattice Energy

The lattice energy depends on following factors:
I. Charge on the ion II. Size of the ion

Lattice energy and size of the Ions

Figure show the values of lattice energies of alkali metal halides. It is clear from the data that lattice energy decreases with the increase in the size of the cation/anion. With the increase in the size of either cations or anions, the packing of oppositely charged ions become less and less tight.

Lattice Energy and Charge on the Ions

Lattice energies is directly proportional to the charges on the ions i.e., greater the magnitude of the charge on an ion, greater is its lattice energy and vice versa.

Explanation

Let us try to understand this fact by comparing lithium fluoride, LiF, with magnesium oxide, MgO.
These compounds have the same arrangement of ions in their lattice structure and comparative sizes of cations and anions are same in both compounds.
The major physical difference between LiF and MgO is the ionic charge, which affects the lattice energy.

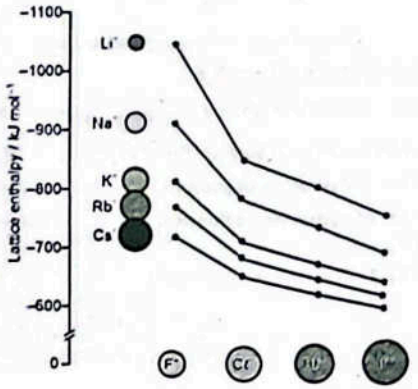


Figure: Lattice energies of alkali metal halides

Magnesium oxide $\Delta H_{latt[MgO]} = -3923 \text{ kJ mol}^{-1}$ is a greater than lithium fluoride $\Delta H_{latt[LiF]} = -1049 \text{ kJ mol}^{-1}$.

The doubly-charged Mg^{2+} and O^{2-} ions in MgO attract each other more strongly than the singly-charged ions of the same size in LiF. For ions of similar size, the greater the ionic charge, the higher the charge density. This results in stronger ionic bonds being formed.

Solubility Trends of Group II Hydroxides and Sulphates

ΔH°_{sol} depends on both lattice energy and hydration enthalpy.

- Look at the solubility trends of group II metal hydroxides. Both hydration energy and lattice enthalpy decreases down the group due to decrease in charge density of group 2 cations. But it is observed that the lattice energy decreases more rapidly in the series $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ than does the energy of hydration in ions
- Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. For this reason, the lattice energy factor dominates this solubility trend. ΔH°_{sol} becomes more exothermic so solubility increase.
- **The solubility trends of group II metal sulphates:** As the SO_4^{2+} is much larger than the OH^-, the decrease in lattice energy going through the series of sulphates from $MgSO_4$ to $BaSO_4$ is less, but the energy of hydration of the cation decreases by a greater amount. Now the energy of hydration dominates the solubility trend, and the solubility decreases from $MgSO_4$ to $BaSO_4$. ΔH°_{sol} becomes more endothermic so solubility increase.

Calculating Enthalpy Change of Solution (ΔH°_{sol})

We can calculate the enthalpy change of solution or the enthalpy change of hydration by constructing an enthalpy cycle and using Hess's law (Figure).

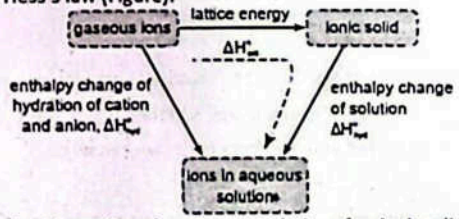


Figure: Energy cycle of formation of an aqueous solution of an ionic solid using Hess's law

We can see from this enthalpy cycle that:

$$\Delta H^\circ_{sol} + \Delta H^\circ_{(ii)} = \Delta H^\circ_{(i)}$$

We can use this energy cycle to calculate:

Sample Problem 6.6

Determine the enthalpy change of solution (ΔH°_{sol} of sodium fluoride NaF) using the following data:

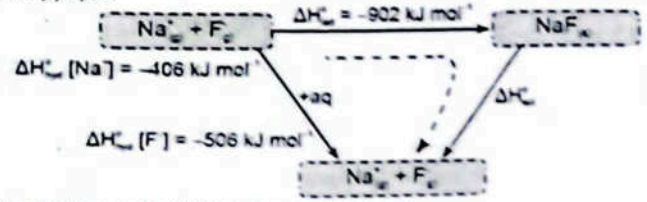
Lattice energy of sodium fluoride (NaF) = −902 kJ mol^{-1}

Heat of hydration of sodium ions (Na^+) = −406 kJ mol^{-1}

Heat of hydration of fluoride ions (F^-) = −506 kJ mol^{-1}

Solution:

Step 1: Draw the enthalpy cycle



Step 2: Rearrange the equation and substitute the values to find Δ

$$\Delta H^\circ_{sol} + \Delta H^\circ_{(ii)} = \Delta H^\circ_{(i)}$$

$$\Delta H^\circ_{sol} = (-406) + (-506) - (-902)$$

$$\Delta H^\circ_{sol}[NaF] = -10 \text{ kJ mol}^{-1}$$

BORN-HABER CYCLE

- It is impossible to determine the lattice energy of a compound by a single direct experiment.
- We can, however, calculate the value for $\Delta H^\circ_{(i)}$ using several experimental data and an energy cycle called the **Born-Haber cycle**.
- Born-Haber cycle is an application of Hess's law.

Calculation of Lattice Energy of NaCl:

Consider calculation of lattice energy of sodium Chloride using Hess's law and Born-Haber cycle.

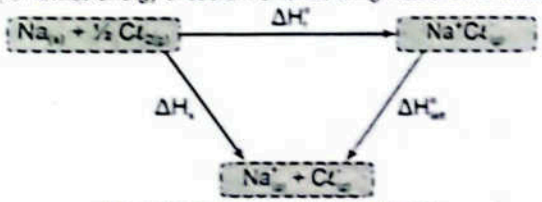


Figure: Enthalpy cycle of sodium chloride

where,

ΔH°_f : Standard enthalpy of formation of NaCl can be measured conveniently in a calorimeter.

ΔH_a : Total energy involved in changing sodium and chlorine from their standard physical states to gaseous ions. Applying Hess's law on the above energy cycle, we can write

$$\Delta H_a + \Delta H^\circ_{(i)} = \Delta H^\circ_f$$

The above energy triangle has been extended to show the various stages involved in finding ΔH_a. The complete energy cycle is called the Born-Haber cycle and it is presented in Figure.

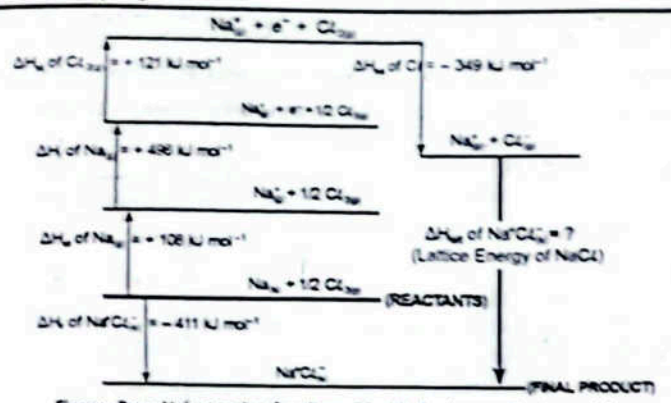


Figure: Born Haber cycle of sodium chloride (not according to scale)

Calculation of ΔH_a

From above cycle we have, $\Delta H_a = \Delta H_{a(Na)} + \Delta H_{i(Na)} + \Delta H_{a(Cl_2)} + \Delta H_{eg(Cl_2)}$

Using, $\Delta H^\circ_{(i)} = \Delta H^\circ_f - \Delta H_a$

$$\Delta H^\circ_{(i)} = -787 \text{ kJ mol}^{-1}$$

Sample Problem 6.7

Calculate the heat of formation of sodium fluoride, which crystallizes in the sodium chloride lattice. The heat of atomization of $Na_{(s)}$ is kJ / mol, half the bond energy of $F_{2(g)}$ is 79 kJ / mol, the ionization energy of sodium atoms is 494 kJ / mol, the electron affinity of fluorine atoms is −328 kJ / mol, and the lattice energy is −939 kJ / mol.

Solution: Values are given for all the quantities in the Born-Haber cycle, so we can apply Hess's law:

$$\Delta H^\circ_f = \Delta H^\circ_{sol} + \Delta H^\circ_{a(Na)} + \Delta H^\circ_{i(Na)} + \Delta H^\circ_{a(F_2)} + \Delta H^\circ_{eg(F)}$$

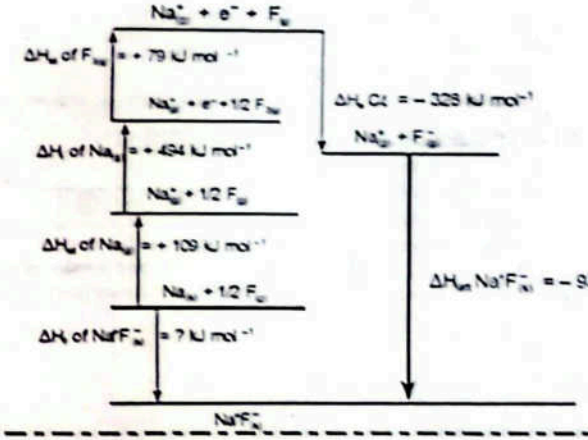
$$= (-939 + 109 + 494 + 79 - 328) \text{ kJ mol}^{-1}$$

$$\Delta = -585 \text{ kJ mol}$$

QUICK CHECK 6.7

a) Draw Born-Haber cycle for sample problem 6.7.

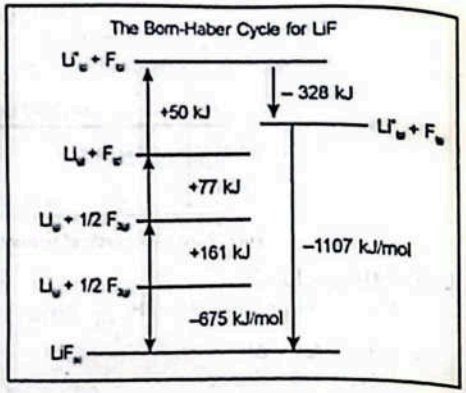
Ans.



b) Calculate the heat of formation of lithium fluoride. The heat of atomization of $Li_{(s)}$ is 161 kJ/mol, half the bond energy of $F_{2(g)}$ is 79 kJ/mol, the ionization energy of lithium atoms is 520 kJ/mol, the electron affinity of fluorine atoms is −328 kJ/mol, and the lattice energy is 1107 kJ/mol.

Ans. Given Data:

1. **Heat of atomization of Li(s):**
   $Li_{(s)} \rightarrow Li_{(g)} \quad \Delta H_{atom} = +161 kJ/mol$
2. **Half the bond energy of $F_{2(g)}$:**
   $1/2F_{2(g)} \rightarrow F_{(g)} \quad \Delta H_{B.E} = +79 kJ/mol$
   (Full bond energy of F_2 = 158 kJ/mol, but we use half since the cycle requires 1 F atom.)
3. **Ionization energy (IE) of $Li_{(g)}$:**
   $Li_{(g)} \rightarrow Li^+_{(g)} + e^- \quad IE = +520 kJ/mol$
4. **Electron affinity (EA) of $F_{(g)}$:**
   $F_{(g)} + e^- \rightarrow F^-_{(g)} \quad EA = -328 kJ/mol$
5. **Lattice energy (U) of $LiF_{(s)}$:**
   $Li^+_{(g)} + F^-_{(g)} \rightarrow LiF_{(s)} \quad \Delta H_{latt} = -1107 kJ/mol$



Enthalpy of Formation:

$Li_{(s)} + 1/2F_{2(g)} \rightarrow LiF_{(s)} \quad \Delta H_f^\circ = ?$

We know that $\Delta H^\circ_{latt} = \Delta H_f^\circ - \Delta Hx$

$\Delta H_x = \Delta H_{at_{(Li)}} + \Delta H_{I.E} + \Delta H_{at_{(F_2)}} + \Delta H_{E.A}$

$\Delta H_x = 161 + 520 + 79 - 328$

$= 432 kJmol^{-1}$

So, $\Delta H_f^\circ = \Delta H^\circ_{latt} + \Delta H_x = -1107 + 432 = -675 kJ/mol$

ENTROPY

Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature.

➢ **Important Points:**

- When the energy is distributed in more ways, a system is more stable.
- Entropy is a measure of the randomness or disorder of a system.
- The higher the randomness or disorder, the greater the entropy of the system.
- The system becomes energetically more stable when it becomes more disordered.

➲ Entropy, Diffusion and Number of Ways of Arrangement

We can show that the molecules in a vapour diffuse by chance by thinking about the probability of finding them at one place at any one time. Consider the simplified model shown in Figure below.

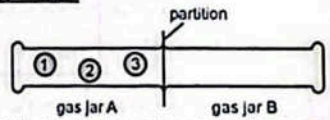


Figure: Diffusion and number of possible arrangements

There are 8 different ways for these molecules to arrange themselves in two jars by diffusion from Jar A to jar B that is:

- This is calculated as under
- Number of molecules in A = 3
- Number of Jars = 2
- Number of possible arrangements = $2^3 = 8$

Similarly, if there were 5 molecules initially in jar A, the possible ways of arrangement will be 2^5, i.e. 32. And if there were 100 molecules, the probability will be 2^{100}. A general formula x^y can be written for the calculation of probability, where x is the number of places and y is the number of particles to be arranged. Diffusion happens because there is a large number of ways of arranging the molecules. The concept of the 'number of ways' of arrangement either particles or the energy within these particles helps predict whether it can happen or not.

➲ Comparison of Entropy Values

Entropies of different substances can be compared based on the number of particles, physical properties, and state.

Small number of particles means low entropy and vice versa, for example $CaCO_3$ has higher standard entropy ($92.9 JK^{-1} mol^{-1}$) than CaO($39.7 JK^{-1} mol^{-1}$). This is because the number of possible arrangements is lower when the number of particles is smaller.

The entropy of substances having similar chemical nature is dictated by their hardness. Harder substances have lower entropy than softer ones. Diamond has lower entropy than graphite because it is much harder. Stronger forces result in limited vibrations in harder substances which decrease the probability of disorder. A substance has lower entropy in solid state than in liquid and gaseous states. The entropy of ice near its melting point is $48.0 JK^{-1} mol^{-1}$, for water, it is $69.9 JK^{-1} mol^{-1}$; whereas water vapour just above the boiling point is $188.7 JK^{-1} mol^{-1}$.

Dissolution of sugar in tea increases the entropy of both the solute and solvent

☑ QUICK CHECK 6.8

Explain the difference in the entropy of each of the following pairs of substances in terms of their states and structures.

I. $Br_{2(l)} S^\circ = 151.6 J K^{-1} mol^{-1}$ and $I_{2(s)} S^\circ = 116.8 JK^{-1} mol^{-1}$

Ans. The difference in entropy (ΔS) between $Br_2(l)$ and $I_2(s)$ can be calculated and explained as follows:

Given: $S^\circ[Br_2(l)] = 151.6 J K^{-1} mol^{-1}$

$S^\circ[I_2(s)] = 116.8 J K^{-1} mol^{-1}$

Entropy Difference Calculation:

$\Delta S = S^\circ[Br_2(l)] - S^\circ[I_2(s)]$

$= 151.6 - 116.8$

$= +34.8 J K^{-1} mol^{-1}$

Explanation of the Difference:

1. **State Effect (Major Contribution):**
   - $Br_2(l)$ is a liquid → molecules have translational and rotational freedom
   - $I_2(s)$ is a solid → molecules are fixed in a crystal lattice
   - Liquids always have higher entropy than solids for the same substance
2. **Molecular Mass Effect (Minor Contribution):**
   - I_2 (254 g/mol) is heavier than Br_2 (160 g/mol) → would normally give I_2 higher entropy
   - However, the state difference (liquid vs solid) dominates here
3. **Structural Considerations:**
   - Both are simple diatomic molecules
   - $Br_2(l)$ has weaker London dispersion forces than $I_2(s)$
   - Less energy needed to disrupt order in $Br_2(l)$

In short, The $+34.8 J K^{-1} mol^{-1}$ difference shows that $Br_2(l)$ is significantly more disordered than $I_2(s)$, primarily because liquids have greater molecular freedom than solids, outweighing iodine's greater molecular mass.

ii. $H_{2(g)}S^{o} = 130.6\,JK^{-1}\,mol^{-1}$ and $CH_{4(g)}S^{o} = 186.2\,JK^{-1}\,mol^{-1}$

Ans. The standard molar entropy (S°) values are:

- $H_2(g)$: 130.6 J K^{-1} mol^{-1}
- $CH_4(g)$: 186.2 J K^{-1} mol^{-1}

$CH_4(g)$ has higher entropy due to:

1. **Molecular Complexity**
   - $H_2(g)$:
     - Simple diatomic molecule (2 atoms).
     - Only translational and rotational motion contribute to entropy.
   - $CH_4(g)$:
     - Tetrahedral structure (5 atoms).
     - More vibrational modes and rotational freedom → higher entropy.
2. **Degrees of Freedom**
   - $H_2(g)$:
     - 3 translational + 2 rotational = 5 degrees of freedom.
   - $CH_4(g)$:
     - 3 translational + 3 rotational + 9 vibrational = 15 degrees of freedom.
3. **Mass & Size**
   - CH_4 (M = 16 g/mol) is heavier than H_2 (M = 2 g/mol), leading to more energy states and higher entropy.

Calculation of Entropy Difference

$$\Delta S^{\circ} = S^{\circ}(CH_4) - S^{\circ}(H_2) = 186.2 - 130.6 = 55.6\,J\,K^{-1}mol^{-1}$$

Conclusion

$CH_4(g)$ has higher entropy because:

- More atoms → more vibrational/rotational modes.
- Larger mass → more microstates.

iii. $Hg_{(\ell)}S^{o} = 76.00\,JK^{-1}\,mol^{-1}$ and $Na_{(s)}S^{o} = 51.20\,JK^{-1}\,mol^{-1}$

Ans. Substances:

- **Hg(l)** (liquid mercury), S° = 76.00 $J{\cdot}K^{-1}{\cdot}mol^{-1}$
- **Na(s)** (solid sodium), S° = 51.20 $J{\cdot}K^{-1}{\cdot}mol^{-1}$

Explanation:

Entropy (S°) is a measure of disorder or randomness in a system. The higher the entropy, the more disordered the system.

- Hg(l) is a liquid, meaning its atoms are more free to move and have greater positional and kinetic randomness than in a solid.
- Na(s) is a solid, where atoms are arranged in a fixed, orderly lattice with limited movement, hence lower entropy.

iv. $SO_{2(g)}S^{o} = 248.1\,JK^{-1}\,mol^{-1}$ and $SO_{3(s)}S^{o} = 95.60\,JK^{-1}\,mol^{-1}$

Given Data:

- S° of $SO_{2(g)}$ = 248.1 JK^{-1} mol^{-1}
- S° of $SO_{3(\ell)}$ = 95.60 JK^{-1} mol^{-1}

Entropy Difference (ΔS):

$\Delta S = S^{\circ}(SO_{2(g)}) - S^{\circ}(SO_{3(\ell)})$

ΔS = 248.1 J K^{-1} mol^{-1} − 95.60 J K^{-1} mol^{-1}

ΔS = +152.5 J K^{-1} mol^{-1}

Positive ΔS confirms $SO_{2(g)}$ has higher disorder than $SO_{3(\ell)}$.

Reasons:

- Gaseous SO_2 has more translational/rotational freedom than liquid SO_3.
- Liquids have stronger intermolecular forces, reducing molecular randomness.

The +152.5 J K^{-1} mol^{-1} difference quantifies the entropy loss when SO_2 condenses into liquid SO_3.

Entropy Changes In Reactions

In a chemical reaction, if we compare the entropies of the reactants and products, we can try to explain the magnitude of the entropy change and whether or not it increases or decreases.

Rules about change in Entropy of Reaction:

The following rules must be followed to know about the change in entropy of a reaction

- When a solid is converted to a liquid or a gas in the product, the entropy change is positive.
- If no. of moles in the products are more the entropy change is positive.
- If there is a change in the number of gaseous molecules in a reaction, due to high values of entropy are associated with gases.
- The more gas molecules, there are, the greater is the number of ways of arranging them and the higher the entropy.

For example:

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

There is an increase in entropy of the above system because the gas is being produced (high entropy) but the reactant, calcium carbonate, is a solid (low entropy). Such reactions are spontaneous.

Also, consider the reaction:

$$2N_2O_{(g)} \longrightarrow 4NO_{(g)} + O_{2(g)}$$

We should expect an increase of entropy of the system because there are a greater number of moles of gas molecules in the products (5 molecules) than in the reactants (2 molecules). This is also a spontaneous process.

The sign of Entropy Change and Spontaneity of a Process:

The entropy of a substance is always positive, however, when the entropy changes it may have positive or negative value.

A positive entropy change value (ΔS° = +ve) means a spontaneous process

A negative entropy change value (ΔS° = −ve) implies more ordered molecules and a decrease in disorder

For some reactions, however, the entropy change fails to tell about the spontaneity of the reaction and we need another quantity called free energy.

Calculating the Entropy Change of the System (Reaction)

In order to calculate the entropy, change of the system we use the relationship:

$$\Delta S^{\circ}_{system} = S^{\circ}_{products} - S^{\circ}_{reactants}$$

Let us calculate the entropy change of the system for the reaction:

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

The standard entropy values are:

$$S^{\circ}_{[Ca(s)]} = 41.40\ J\ K^{-1}\ mol^{-1}$$

$$S^{\circ}_{[Ca(s)]} = 41.40\ J\ K^{-1}\ mol^{-1}$$

$$S^{\circ}_{[O2(g)]} = 205.0\ J\ K^{-1}\ mol^{-1}$$

$$S_{[CaO(s)]} = 39.70\ J\ K^{-1}\ mol^{-1}$$

As

$$\Delta S^{\circ}_{system} = S^{\circ}_{products} - S^{\circ}_{reactants}$$

$$= 2\times S^{\circ}_{[CaO(s)]} - \left\{2\times S^{\circ}_{[Ca(s)]} + S^{\circ}_{[O2(g)]}\right\}$$

$$= 2\times 39.70 - \left\{(2\times 41.40) + 205.0\right\}$$

$$= 79.40 - 287.8$$

The negative value for the entropy change shows that the entropy of the system has decreased. We know, however, that calcium reacts spontaneously with oxygen. So the entropy of the surroundings must also play a part because the total entropy change must be positive for the reaction to be feasible.

➲ Total Entropy Change, $\Delta S°_{total}$

$\Delta S°_{total}$ is sum of standard entropy change of system and standard entropy change of surrounding. $\Delta S°$ for system can be found out by subtracting the standard entropies of reactants from the standard entropies of products (Similar to the way you obtained $\Delta H°$).

$$\Delta S°_{system} = \Sigma S°_{(products)} - \Sigma S°_{(reactants)}$$

Where, respective no. of moles of reactants and products in balanced chemical equation are multiplied with entropy of reactants and products.

$\Delta S°$ for surrounding is calculated using following equation:

$$\Delta S°_{surrounding} = \frac{-\Delta H°_r}{T}$$

Where,

- The value of $\Delta H°_r$ is in kJ/mol so must be multiplied with 1000. This is because entropy changes are measured in J/K mol.
- The negative sign is part of equation and not the sign of $\Delta H°_r$

$\Delta S°_{(total)}$ is calculated using following equation:

$$\Delta S°_{total} = \Delta S°_{system} + \Delta S°_{surrounding}$$

$$\Delta S°_{total} = \Sigma S°_{(products)} - \Sigma S°_{(reactants)} + \left[\frac{-\Delta H°_r}{T}\right]$$

It is useful to be able to predict about spontaneity of reaction using the sign of $\Delta S°_{(total)}$

- $\Delta S°_{total}$ is +ve ⇒ entropy increases ⇒ **reaction is spontaneous**
- $\Delta S°_{total}$ is –ve ⇒ entropy decreases ⇒ **reaction is nonspontaneous**

Sample Problem 6.8

Calculate the entropy change of the system $\Delta S°$ system for the reaction:

$$2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

The standard entropy values are: $S°_{[Ca(s)]} = 41.40\ JK^{-1}\ mol^{-1}$

$S°_{[O2(g)]} = 205.0\ JK^{-1}\ mol^{-1}$

$S°_{[CaO(s)]} = 39.70\ JK^{-1}\ mol^{-1}$

As $\Delta S°_{system} = \Sigma S°_{(products)} - \Sigma S°_{(reactants)}$

$= 2 \times S°_{[CaO(s)]} - \{2 \times S°_{[Ca(s)]} + S°_{[O2(g)]}\}$

$= 2 \times 39.70 - \{(2 \times 41.40) + 205.0\}$

$= 79.40 - 287.8$

$\Delta S°_{system} = -208.4\ JK^{-1}\ mol^{-1}$

Sample Problem 6.9

Calculate the entropy change of the surroundings $\Delta S°_{surrounding}$ for the reaction at 298K:

$$2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)} \quad \Delta H°reaction = -1270.2\ kJ\ mol^{-1}$$

Step 1: Convert the enthalpy change into J mol^{-1} by multiplying by 1000.

$-1270.2 \times 1000 = -1270\ 200\ J\ mol^{-1}$

Step 2: Apply the relationship

$$\Delta S°_{surrounding} = \frac{-\Delta H°_{reaction}}{T}$$

$$\Delta S°_{surrounding} = \frac{-1270200}{298}$$

$$= +4262.4\ JK^{-1}\ mol^{-1}$$

Sample Problem 6.10

Calculate the total entropy change $\Delta S°_{total}$ for the reaction and check its spontaneity.

$$2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

$\Delta S°_{system} = -208.4\ JK^{-1}\ mol^{-1}$

$\Delta S°_{surrounding} = +4262.4\ JK^{-1}\ mol^{-1}$

As, $\Delta S°_{total} = -208.4 + 4262.4$

$\Delta S°_{total} = +4054.0\ JK^{-1}\ mol^{-1}$

The total entropy change is positive and the reaction is feasible.

THE FREE ENERGY CHANGE, (ΔG)

In determining whether a chemical reaction is likely to be spontaneous, we use the new quantity Gibbs free energy change, ΔG. The Gibbs free energy change is given by the relationship.

$$\Delta G = -T\Delta S_{total}$$

Multiplying the $\Delta S°_{(total)}$ expression by –T, we can also get the expression without having to consider the entropy changes of the surroundings. This expression is called Gibbs equation

$$-T \times \{\Delta S°_{total} = \Delta S°_{system} + \left[\frac{\Delta H°_r}{T}\right]\}$$

$$-T\Delta S_{total} = -T\Delta S_{system} + \Delta H°_r$$

$$\Delta G° = \Delta H°_r - T\Delta S°$$

And draw the following conclusion from it:

i. If $\Delta G < 0$ (–ve), the given process may occur spontaneously.

ii. If $\Delta G > 0$ (+ve), the indicated process cannot occur spontaneously; instead, the reverse of it may occur.

iii. If $\Delta G = 0$ neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium.

Rock Your Mind!

9. What is the significance of Gibbs free energy in thermodynamics?
(A) Measures entropy change
(B) Predicts spontaneity of reactions
(C) Calculates enthalpy change
(D) Determines reaction rate

Extend your Knowledge

The unit of temperature times entropy ($T\Delta S$) is Joule. $\Delta S°$ represents $\Delta S°_{system}$.

Rock Your Mind!

10. What are the information's given by Gibbs free energy for a reaction?

➲ Calculating $\Delta G°$ for a Reaction

Sample Problem 6.11

For the Reaction:

$$CaSO_{4(s)} \longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$ at 25°C using the following data; and discuss its spontaneity.

Heat of Formation:

$$\Delta H°_f\left[CaSO_{4(s)}\right] = -1432.7\ kJ,\ \Delta H°_f\left[Ca^{2+}_{(aq)}\right] = -543.0\ kJ,\ \Delta H°_f\left[SO^{2-}_{4(aq)}\right] = -907.5\ kJ$$

Standard Entropy:

$$S°\left[CaSO_{4(s)}\right] = 106.7\ J/K,\ S°\left[Ca^{2+}_{(aq)}\right] = -55.2\ J/K,\ S°\left[SO^{2-}_{4(aq)}\right] = +17.2\ J/K$$

Solution

i. $\Delta H° = \sum\Delta H_{f(products)} - \sum\Delta H_{f(reactants)} = \left[-543.0 - 907.5\right] - \left[-1432.7\right] = -17.8\ kJ$

ii. $\Delta S° = \sum S°_{(products)} - \sum S°_{(reactants)} = \left[(-55.2 + 17.2) - (106.7)\right] J/K = -1447\ J/K$

$\Delta S° = -0.1447\ kJ/K$

iii. $\Delta G° = \Delta H° - T\Delta S° = (-17.8\ kJ) - (298\ K) \times (-0.1447\ kJ/K) = +25.3kJ$

Note that you substitute $\Delta S°$ in units of kJ/K in the formula of $\Delta G°$.

Result: We conclude that this process is nonspontaneous at standard conditions at 25°C.

Sample Problem 6.12

What is the standard free-energy, ΔG° for the following reaction (Haber's process) at 25°C? Also discuss its spontaneity.

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

Heat of Formation: $\Delta H_f^\circ\left[N_{2(g)}\right] = 0$ kJ, $\Delta H_f^\circ\left[H_{2(g)}\right] = 0$ kJ, $\Delta H_f^\circ\left[NH_{3(g)}\right] = -45.9$ kJ

Standard Entropy: $S^\circ\left[N_{2(g)}\right] = 191.5$ J/K, $S^\circ\left[H_{2(g)}\right] = 130.6$ J/K, $S^\circ\left[NH_{3(g)}\right] = +193$ J/K

Solution:

$$\Delta H^\circ = \sum \Delta H_{f(\text{products})} - \sum \Delta H_{f(\text{reactants})} = \left[2\times(-45.9)\right] - \left[0+0\right] = -91.8 \text{ kJ}$$

$$\Delta S^\circ = \sum nS^\circ_{(\text{products})} - \sum mS^\circ_{(\text{reactants})} = \left[2\times(193)\right] - \left[191.5 + 3\times 130.6\right] \text{J/K} = -197 \text{ J/K}$$

$$\Delta S^\circ = -0.197 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-91.88 \text{ kJ}) - (298 \text{ K}) \times (-0.197 \text{ kJ/K}) = -33.1 \text{kJ}$$

Result: Since ΔG° is a negative value, thus it is concluded that Haber's process is spontaneous at standard conditions, i.e. at 25°C.

➲ Spontaneity and Temperature Change

Until now we obtained the free–energy for a reaction at 25°C. How do we find ΔG° at another temperature? For this purpose, we use the same equation i.e., $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. We get the value of ΔG at any temperature by substituting values of ΔH° and ΔS° at 25°C. But in the method, we assume that ΔH° and ΔS° are essentially constant w.r.t temperature (this is only approximately true).

Remember that the superscript degree sign (°) refers to substances in standard states, which are substances at 1 atm and at the *specified temperature*. Although until now this was 25°C (298 K), we now consider other temperatures. Note that in general, ΔG depends strongly on temperature.

In Table, all of the four possible choices of signs for ΔH° and ΔS°, give different temperature behaviors for ΔG° are being discussed. In all this discussion temperature is always positive as it is taken on Kelvin scale.

Table: Effect of temperature on the spontaneity of reactions

ΔH°	ΔS°	ΔG°	Description*
–	+	–	Spontaneous at all T
+	–	+	Non-spontaneous at all T
–	–	+ or –	Spontaneous at low T; non-spontaneous at high T
+	+	+ or –	Non-spontaneous at low T; spontaneous at high T

*The term low temperature and high temperature are relative. For a particular reaction, high temperature could mean room temperature.

Sample Problem 6.13

Calculate ΔG° at 1000°C for the following reaction and discuss it spontaneity.

$$CaCO_{3(s)} \rightarrow CaCO_{(s)} + CO_2$$

Solution:

For this reaction, $\Delta H^\circ = +178.0$ kJ and $\Delta S^\circ = +160.4$ J/K = 0.1604 kJ/K

Substituting $T = 1000 + 273 = 1273$ K

$$\Delta G = \Delta H - T\Delta S = (+178.0 \text{ kJ}) - (1273 \text{ K}) \times (0.1604 \text{ kJ/K})$$
$$= +178.0 \text{ kJ} - 204.2 \text{ kJ}$$
$$= \mathbf{-26.2 \text{ kJ}}$$

We conclude that this reaction is spontaneous at 1000°C and 1 atm, since ΔG has negative sign. In other words, at 1000°C, limestone ($CaCO_3$) will decompose in an open container.

☑ QUICK CHECK 6.9

a) What do you expect about the entropy value of the following reactions, whether it would be positive or negative?

i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Ans. Entropy Change (ΔS):
- **Reactants:** 1 mol N_2 + 3 mol H_2 = 4 moles of gas
- **Products:** 2 mol NH_3 = 2 moles of gas

Conclusion:
- The total number of gas molecules decreases.
- Therefore, disorder decreases, and entropy decreases.

ii) $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

Ans. Entropy Change (ΔS): Positive or Negative?
Positive (ΔS > 0)
Reason:
- Number of gas molecules remains the same (2 moles of gas on both sides), but the products are different substances, leading to greater molecular randomness.
- The reaction results in increased disorder, as two different gas species (H_2 and I_2) are formed from a single type (HI), which increases entropy.

Conclusion:
ΔS = Positive

b) Which of the following changes are likely to be spontaneous?

i. The smell from an open bottle of aqueous ammonia diffusing throughout a room.

Ans. The smell from an open bottle of aqueous ammonia diffusing throughout a room.
Spontaneous
- Gas particles spread out to increase entropy (disorder).
- No energy input required.

ii. Water turning to ice at –10°C

Ans. Spontaneous
- Below 0 °C, freezing is thermodynamically favorable (exothermic).
- Even though it decreases entropy, the low temperature makes the process favorable.

iii. Ethanol vaporising at 20°C

Ans. Spontaneous
- Vaporization increases entropy.
- Ethanol has a low boiling point (~78 °C), and enough molecules have sufficient energy to evaporate slowly at 20 °C.

iv. Water mixing completely with salt

Ans. Spontaneous
- Dissolution increases entropy as ions disperse in water.
- No energy input needed.

v. Limestone (calcium carbonate) decomposing at room temperature

Ans. Not Spontaneous
- Endothermic reaction that requires heat input to break bonds.
- Doesn't occur naturally at room temperature.

Likely Spontaneous: i, ii, iii, iv
Not Spontaneous: v

Solution File — Rack Your Brain!

Sr.	Option	Explanation
1.	S.Q	**Thermochemical Equation:** "A balanced chemical equation which fully describes the physical states of reactants and products in the form of state symbols along with an enthalpy change during the reaction is called a thermochemical equation." **Information from thermochemical equation:** It tells us about: i. Physical states of both reactants and products. ii. Exact number of moles of reactants and products. iii. Heat evolved or absorbed during a reaction. **Example:** $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(\ell)}$ $\Delta H = -285.8\ kJ\ mol^{-1}$
2.	B	Energy is required to break the strong N ≡ N triple bond: $N_2 + O_2 \rightarrow 2NO$, ΔH = +ve (energy absorbed).
3.	S.Q	In exothermic reaction, the number of bonds formed is greater than bonds breakage during the reaction. Moreover heat content of products is less than that of reactants ($H_2 > H_1$). That is why when reactants convert into product heat is released from system to surroundings. **Example:** $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(\ell)}$ $\Delta H = -285.5\ kJ\ mol^{-1}$
4.	C	The height of the peak in a reaction pathway diagram represents the activation energy, which is the minimum energy required for the reaction to occur.
5	S.Q	**Atomization Energy:** The energy required to convert a substance in atomic state is called atomization energy. It is always endothermic in nature. $\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H°_{at} = 218\ kJ\ mol^{-1}$
6.	S.Q	It is necessary to mention the physical state of reactants and products, because enthalpy is associated with a typical phase of a substance. With a change in physical state of reactants or products, enthalpy change of the reaction will be changed. So apparently two reactions are chemically same but thermo ,chemically, they may be different from each other. **Application of Hess's Law:** Steam is produced from H_2 and O_2 by two different routes. Route I: i. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -241.5\ kJ\ mol^{-1}$ Route II: ii. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ $\Delta H_1 = -285.8\ kJ\ mol^{-1}$
7.	B	Energy is absorbed when bonds break because it requires energy to overcome the attractive forces between atoms in a molecule, allowing the bond to dissociate.
8.	B	In the equation $Q = mc\Delta T$, c represents the specific heat capacity, which is the amount of heat energy required to raise the temperature of a unit mass of a substance by 1 degree Celsius (or Kelvin).
9.	B	Gibbs free energy (ΔG) determines whether a reaction is spontaneous or not. If ΔG is negative, the reaction is spontaneous; if ΔG is positive, the reaction is non-spontaneous. This makes ΔG a crucial thermodynamic property in understanding reaction feasibility.
10.	S.Q	The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process. i. If $\Delta G < 0$(-ve), the given process may occur spontaneously ii. If $\Delta G > 0$(+ve), the indicated process cannot occur spontaneously; instead, the reverse of it may occur. iii. If $\Delta G = 0$, neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which of the following equations represents standard heat of formation of C_2H_4?

a) $2C(diamond) + 2H_{2(g)} C_2H_{4(g)}$ b) $2C(graphite) + 2H_{2(g)} C_2H_{4(g)}$

c) $C(graphite) + H_{2(g)} 1/2C_2H_{4(g)}$ d) $2C(diamond) + 4H_{(g)} C_2H_{4(g)}$

II. Which of the following equations correctly defines lattice energy of $MgC\ell_2$?

a) $Mg_{(s)} + C\ell_{2(g)} \longrightarrow MgC\ell_2$ b) $Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(g)}$

c) $Mg^{2+}_{(s)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$ d) $Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$

III. Suppose there are 100 molecules of a gas initially in jar A, which is connected to an evacuated jar B. When the stopcock is opened the possible ways of arrangement of molecules will be:

a) 100 b) 1/100 c) 2^{100} d) $1/2^{100}$

IV. For a reaction to occur spontaneously,

a) $(\Delta H - T\Delta S)$ must be negative b) $(\Delta H + T\Delta S)$ must be negative.

c) ΔH must be negative. d) ΔS must be negative.

V. The calorie content of food, often expressed in Calories (kcal), is fundamentally related to which thermodynamic quantity during its metabolism or combustion?

a) Entropy change (ΔS) b) Gibbs free energy change (ΔG)

c) Enthalpy change (ΔH) d) Specific heat capacity (c)

VI. Which of the following quantities is NOT typically determined using Hess's Law?

a) Enthalpy change of formation b) Enthalpy change of combustion

c) Activation energy d) Enthalpy change of reaction

VII. Which of the following factors would lead to a greater enthalpy change of hydration (more exothermic)?

a) A larger ionic radius and a smaller charge b) A smaller ionic radius and a smaller charge

c) A larger ionic radius and a larger charge d) A smaller ionic radius and a larger charge

VIII. The enthalpy of solution can be expressed in terms of which of the following enthalpy changes?

a) $\Delta H_{lattice} + \Delta H_{hydration}$ b) $\Delta H_{lattice} - \Delta H_{hydration}$ c) $-\Delta H_{lattice} + \Delta H_{hydration}$ d) $-\Delta H_{lattice} - \Delta H_{hydration}$

IX. Which of the following reactions has an enthalpy change that is equal to the standard enthalpy of formation of water, $\Delta H_f°[H_2O_{(\ell)}]$?

a) $2H_{(g)} + O_{(g)} \rightarrow H_2O_{(\ell)}$ b) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$

c) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(\ell)}$ d) $2H^+_{(aq)} + O^{2-}_{(aq)} \rightarrow H_2O_{(\ell)}$

X. The enthalpy change for a reaction depends on:

a) Pathway taken from reactants to products

b) Presence of a catalyst

c) Initial and final states of the reactants and products

d) Rate of the reaction

XI. Which of the following processes would typically result in an increase in entropy of the system?

a) Freezing of water

b) Condensation of steam

c) Dissolving a solid in a liquid

d) Formation of a crystal from a saturated solution

XII. **Consider a reaction with $\Delta H > 0$ and $\Delta S < 0$. This reaction will be:**

a) Spontaneous at all temperatures b) Non-spontaneous at all temperatures

c) Spontaneous only at high temperatures d) Spontaneous only at low temperatures

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	$C_{(graphite)} + H_{2(g)} \; 1/2 C_2H_{4(g)}$	**Standard heat of formation requires:** • Elements in their most stable natural states (graphite for carbon, H_2 gas for hydrogen) • Formation of exactly 1 mole of the compound • Diamond and atomic hydrogen are not standard states • Option c only forms half mole of C_2H_4
II.	d	$Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$	Lattice energy is: • The energy released when gaseous ions form 1 mole of solid ionic compound • Must start with separated gaseous ions (not elements or solid ions) • Must form solid crystalline compound
III.	c	2^{100}	• Each molecule has 2 choices (jar A or B) • For 100 independent molecules: total arrangements = $2 \times 2 \times \ldots \times 2$ (100 times) = 2^{100} • Demonstrates the statistical nature of entropy
IV.	a	$(\Delta H - T\Delta S)$ must be negative	• Gibbs free energy equation: $\Delta G = \Delta H - T\Delta S$ • For spontaneity: $\Delta G < 0$ • Thus $\Delta H - T\Delta S$ must be negative • Neither ΔH nor ΔS alone determines spontaneity
V.	c	Enthalpy change (ΔH)	• Calories measure heat released during combustion (ΔH) • 1 Calorie = 1 kcal = energy to raise 1kg water by 1°C • ΔG includes unusable energy; ΔH measures total heat
VI.	c	Activation energy	• Hess's Law calculates enthalpy changes (ΔH) only • Activation energy is kinetic parameter (energy barrier) • Can't be determined from reaction enthalpies
VII.	d	Smaller radius + larger charge	• Hydration enthalpy depends on ion-water attraction • **Smaller ions:** water molecules can approach closer • **Higher charge:** stronger electrostatic attraction • Most exothermic when ions are small and highly charged
IX.		$H_{2(g)} + 1/2 O_{2(g)} \rightarrow H_2O_{(\ell)}$	• Standard formation requires: o Elements in standard states (H_2 gas, O_2 gas) o Formation of 1 mole of product o Correct physical state (liquid water) • Other options use non-standard states or form gas
X.	c	Initial and final states	• Enthalpy (ΔH) is a state function • Depends only on initial and final states • Independent of pathway or catalyst • Rate is kinetic property, unrelated to ΔH
XI.	c	Dissolving solid	• Dissolving increases disorder (solid → dispersed solution) • Freezing/condensing/crystallization decrease entropy (more ordered states) • Entropy generally increases when particles become more dispersed

XII.	b	Non-spontaneous at all temperatures	$\Delta G = (+\Delta H) - T(-\Delta S) = \Delta H + T(\Delta S)$ Since $\Delta H > 0$ and $T\Delta S$ adds positively, $\Delta G > 0$ for all temperatures. So, ΔG is always positive → Reaction is non-spontaneous at all temperatures. When $\Delta H > 0$ and $\Delta S < 0$, no temperature can make ΔG negative.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Differentiate between exothermic and endothermic reactions.

Ans.

Property	Exothermic Reactions	Endothermic Reactions
Energy Change	Release energy (heat) to surroundings	Absorb energy (heat) from surroundings
Enthalpy (ΔH)	Negative ($\Delta H < 0$)	Positive ($\Delta H > 0$)
Temperature	Increases in the surroundings (heats up)	Decreases in the surroundings (cools down)
Example	Combustion of fuels, respiration, freezing water	Photosynthesis, melting ice, boiling water
Reaction Profile	Energy of products < energy of reactants	Energy of products > energy of reactants

b. What do you understand by the enthalpy of a system?

Ans. Enthalpy (H) of a system is the total heat content of the system at constant pressure.

It is defined as: $H = U + PV$

Where:

- H = enthalpy
- U = internal energy of the system
- P = pressure
- V = volume

c. Differentiate clearly between entropy (S) and Gibbs free energy (G).

Ans.

Property	Entropy (S)	Gibbs Free Energy (G)
Definition	Measure of **disorder or randomness** in a system	Measure of the **usable energy** available to do work
Symbol	S	G
Units	$J \cdot mol^{-1} \cdot K^{-1}$	$kJ \cdot mol^{-1}$
Nature	Tells how **dispersed energy** is in a system	Tells whether a process is **spontaneous**
Formula	No single formula (but used in ΔS)	$\Delta G = \Delta H - T\Delta S$
Interpretation	Higher S = more disorder	Negative ΔG = spontaneous process
Temperature Dependency	Affects spontaneity when multiplied by T in ΔG	Directly determines spontaneity of a reaction

d. Distinguish clearly between standard enthalpy of reaction and standard enthalpy of formation.

Ans.

Property	Standard Enthalpy of Reaction ($\Delta H^\circ_{reaction}$)	Standard Enthalpy of Formation (ΔH°_f)
Definition	Heat change during a chemical reaction under standard conditions	Heat change when 1 mole of a compound forms from its elements in their standard states

Reactants and Products	Any type of substances (elements or compounds)	Always starts from elements in standard states
Amount Involved	Varies depending on the reaction equation	Always forms exactly 1 mole of product
Symbol	ΔH°_{rxn}	ΔH°_f
Example	**Combustion of CH_4:** $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	**Formation of H_2O:** $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$

e. Define the following enthalpies and give one example of each.
(i) Standard enthalpy of solution **(ii) Standard enthalpy of hydration**
(iii) Standard enthalpy of atomization **(iv) Standard enthalpy of combustion**

Ans.

(i) Standard enthalpy Change of Solution (ΔH°_{sol})

"The standard enthalpy of solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in a solvent to give an infinitely dilute solution."

The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

$$Na_2CO_{3(s)} + aq \longrightarrow 2Na^+_{(aq)} + CO^{2-}_{3\,(aq)} \qquad \Delta H^\circ_{sol} = -25 \text{ kJ mol}^{-1}$$

$$NH_4C\ell_{(s)} + aq \longrightarrow NH^+_{4\,(aq)} + C\ell^-_{(aq)} \qquad \Delta H^\circ_{sol} = +16.2 \text{ kJ mol}^{-1}$$

(ii) Standard enthalpy of hydration

"The enthalpy change involved when one mole of a solute is dissolved in excess of water to make infinitely dilute solution under standard conditions."

(iii) Enthalpy Change of Atomization (ΔH°_{at})

"The standard enthalpy change of atomization of an element is the enthalpy change involved when one mole of gaseous atoms is formed from the element, under standard conditions."

$$H_{2(g)} \longrightarrow 2H_{(g)} \qquad E_{H-H} = +436 \text{ kJ mol}^{-1}$$

$$1/2H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^\circ_{at} = +218 \text{ kJ mol}^{-1}$$

(iv) Enthalpy Change of Combustion (ΔH°_c)

The standard enthalpy change of combustion of a substance is the enthalpy change involved when one mole of the substance is completely burnt in excess of oxygen, under standard conditions.

For example, standard enthalpy of combustion ΔH° C of ethanol is -1368 kJ mol^{-1}.

$$C_2H_5OH_{(\ell)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \qquad \Delta H^\circ_c = -1368 \text{ kJ mol}^{-1}$$

f. Explain why the lattice enthalpy of an ionic compound is typically a large negative value.

Ans. The lattice enthalpy of an ionic compound is typically a large negative value because:
It represents the energy released when gaseous ions combine to form one mole of a solid ionic crystal.
This process involves strong electrostatic attraction between oppositely charged ions. Since a large amount of energy is released during this bond formation, the lattice enthalpy is highly exothermic (negative value).

g. What factors influence the magnitude of the lattice enthalpy?

Ans. The magnitude of lattice enthalpy is mainly influenced by two key factors:

1. **Ionic Charge**
   - Greater ionic charge ⇒ Stronger electrostatic attraction between ions.
   - This leads to a more negative (larger) lattice enthalpy.

   Example:
   Lattice enthalpy of MgO (Mg^{2+} and O^{2-}) is much higher than that of NaCℓ (Na^+ and $C\ell^-$) due to higher charges.

2. **Ionic Radius (Size of Ions)**
   - Smaller ions ⇒ Ions are closer together ⇒ Stronger attraction.
   - Smaller size = more negative lattice enthalpy.

   Example:
   Lattice enthalpy of LiF is greater than that of CsF, because Li^+ is smaller than Cs^+.

h. Explain why the enthalpy of hydration is always an exothermic process for gaseous ions. What are the main interactions responsible for the release of energy during hydration?

Ans. Enthalpy of Hydration: Always an exothermic process
The enthalpy of hydration is the heat released when gaseous ions dissolve in water and become surrounded by water molecules. It is always exothermic because:
When gaseous ions dissolve, the water molecules surround and stabilize the ions, leading to a decrease in the system's energy.

Main Interactions Responsible for Energy Release:

(i) Ion-Dipole Interactions:
The polar water molecules interact with the charged ions through their partial charges (δ^- on oxygen and δ^+ on hydrogen). This creates a stable interaction between the ion and the water molecules, releasing energy.

(ii) Electrostatic Attraction:
Water molecules are strongly attracted to the ions, especially smaller, highly charged ions (like Mg^{2+} or Na^+), which increases the energy released during hydration.

i. For the reaction $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$, identify all the bonds that need to be broken and all the bonds that need to be formed to carry out a bond energy calculation of ΔH.

Ans. To carry out a bond energy calculation for the reaction:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Bonds that need to be broken (in reactants):

1. **CH_4 (Methane):**
   4 C-H bonds (broken to form C and H atoms)
2. **O_2 (Oxygen):**
   2 O=O bonds (broken to form 2 oxygen atoms)

Bonds that need to be formed (in products):

1. **CO_2 (Carbon Dioxide):**
   2 C=O bonds (formed between carbon and oxygen)
2. **H_2O (Water):**
   2 O-H bonds in each H_2O molecule (2 molecules of H_2O, so 4 O-H bonds are formed)

To calculate ΔH we would use the bond energies (bond dissociation energies) for each of these bonds and apply the formula:

$$\Delta H = \text{Bonds Broken (Energy required)} - \text{Bonds Formed (Energy released)}$$

j. For a reaction to be spontaneous, what is the required sign of the Gibbs free energy change (ΔG)? Under what conditions of enthalpy change (ΔH) and entropy change (ΔS) will a reaction always be spontaneous?

Ans. For a reaction to be **spontaneous**, the required sign of the **Gibbs free energy change (ΔG)** is:

$$\Delta G < 0$$

This means that the reaction must have a **negative Gibbs free energy change** for it to occur spontaneously under constant temperature and pressure.

In other words:

- **$\Delta G < 0$** indicates a spontaneous reaction.
- **$\Delta G > 0$** indicates a non-spontaneous reaction.
- **$\Delta G = 0$** indicates a system in equilibrium.

The Gibbs free energy change (ΔG) must be negative, i.e., $\Delta G < 0$.

The relationship between **ΔG**, **ΔH** (enthalpy change), and **ΔS** (entropy change) is given by the equation:

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

Where:

- ΔG = Gibbs free energy change
- ΔH = Enthalpy change
- T = Temperature (in Kelvin)
- ΔS = Entropy change

Conditions for Always Spontaneous Reaction:

1. **$\Delta H < 0$** (Exothermic reaction)
2. **$\Delta S > 0$** (Increase in disorder)

Explanation:

- **Exothermic ($\Delta H < 0$)** reactions release heat, making the system more stable.
- **Increase in entropy ($\Delta S > 0$)** means the system becomes more disordered, which also favours spontaneity.

These conditions ensure that **ΔG** will always be negative, regardless of the temperature. The **negative ΔH** and **positive ΔS** make both terms in the equation contribute to a negative value for **ΔG**.

k. The enthalpy of solution can be either positive or negative. Explain what a positive ΔH_{sol} and a negative ΔH_{sol} indicate about the energy changes during the dissolution process.

Ans. The enthalpy of solution (ΔH_{sol}) represents the heat change when a solute dissolves in a solvent. The sign of ΔH_{sol} gives us information about the energy changes that occur during the dissolution process.

(i) Positive ΔH_{sol} (Endothermic Dissolution):

- $\Delta H_{sol} > 0$ means the dissolution process is endothermic.
- Energy is absorbed from the surroundings to dissolve the solute.
- This occurs when the energy required to break the interactions between solute particles (like ionic or covalent bonds) is greater than the energy released when solvent particles interact with the solute.
- **Example:** When ammonium nitrate (NH_4NO_3) dissolves in water, it absorbs heat, making the solution feel cold.

(ii) Negative ΔH_{sol} (Exothermic Dissolution):

- $\Delta H_{sol} < 0$ means the dissolution process is exothermic.
- Energy is released into the surroundings as the solute dissolves.
- This occurs when the energy released during the interaction of solute particles with solvent molecules exceeds the energy needed to separate the solute particles.
- Example: When sodium hydroxide (NaOH) dissolves in water, heat is released, making the solution feel warm.

l. Consider two ions with similar charges but different sizes, or similar sizes but different charges. Explain how the concept of charge density can be used to predict which ion will have a more exothermic enthalpy of hydration and why.

Ans. The concept of charge density is essential for understanding which ion will have a more exothermic enthalpy of hydration.

- **Charge Density:**
  - Charge density is the charge of an ion divided by its size (radius).
  - Charge density = charge/radius.
- **Prediction of Enthalpy of Hydration:**
  - Higher charge density means stronger ion-dipole interactions between the ion and water molecules, leading to a more exothermic enthalpy of hydration i.e., more energy released during hydration.
- **For ions with similar charges but different sizes:**
  - Smaller ions have a higher charge density because their charge is concentrated over a smaller area.
  - Smaller ions (higher charge density) will have a more exothermic enthalpy of hydration because they create stronger interactions with water molecules.
- **For ions with similar sizes but different charges:**
  - Ions with higher charges have a higher charge density, meaning they can interact more strongly with water molecules.
  - Higher charge e.g., $Ae^{3+} > Mg^{2+} > Na^{+}$ density results in a more exothermic enthalpy of hydration.

DESCRIPTIVE QUESTIONS

Q.3 State and explain Hess's law. Give its two applications.

Ans. See Page No. (183)

Q.4 What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

Ans. See Page No. (188)

NUMERICAL PROBLEMS

Q.5 (a) When 0.400 g NaOH is dissolved in 100.0 g of water, the temperature rises from 25.00 to 26.02°C. Calculate: (i) q_{water}, (ii) ΔH for the solution process

Given Data:

Mass of NaOH (m_n) = 0.400 g
Mass of water (m) = 100.0 g
Mass of Solution = 100 g + 0.4 g
= 100.4 g
Initial temperature (T_1) = 25.00°C
Final temperature (T_2) = 26.03°C
Specific heat capacity of water (c) = 4.18 J/g°C

Step (i): Calculate of q_{water}

$$q_{water} = m \times c \times \Delta T$$

Where:

$$\Delta T = T_2 - T_1 = 26.03°C - 25.00°C = 1.03°C$$

Substitute the values:

$$q_{water} = 100.4\ g \times 4.18\ J/g°C \times 1.03\ °C = 434.33\ J$$

Step (ii): ΔH for the solution process

Mass of NaOH = 0.400 g

Molar mass of NaOH (n) = $\frac{m}{M}$

$= \frac{0.4}{40} = 0.01$ mol

0.01 moles of NaOH = 434.33 J

1 mole of NaOH = $\frac{434.33}{0.01}$ J = 43433 J = 43.433 kJ

As the temperature of solution is raised so heat of solution is Exothermic. Thus $\Delta H_{sol} = -43.433\ kJ\ mol^{-1}$

Q.6 By applying Hess's law, calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl gas. The results for the various reactions are as follows.

(i) $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H = -35.16\ kJ\ mol^{-1}$

(ii) $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H = -72.41\ kJ\ mol^{-1}$

(iii) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48\ kJ\ mol^{-1}$

Given Data:

i. $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H_1 = -35.16\ kJ\ mol^{-1}$
ii. $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H_2 = -72.41\ kJ\ mol^{-1}$
iii. $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H_3 = -51.48\ kJ\ mol^{-1}$

Required:

$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)}$ $\Delta H_f = ?$

Solution:

To get the required equation from the given data, added up equations i, ii and iii.

i. $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H_1 = -35.16$ kJ mol^{-1}

ii. $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H_2 = -72.41$ kJ mol^{-1}

iii. $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H_3 = -51.48$ kJ mol^{-1}

$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)}$ $\Delta H_4 = -159.09$ kJ mol^{-1}

Enthalpy of formation of NH_4Cl = −159.09 kJ mol^{-1}

Q.7 Calculate the heat of formation of ethyl alcohol from the following information

(i) Heat of combustion of ethyl alcohol is −1367 kJ mol^{-1}

(ii) Heat of formation of carbon dioxide is −393.7 kJ mol^{-1}

(iii) Heat of formation of water is −285.8 kJ mol^{-1}

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_2 + 3H_2O_{(l)}$ $\Delta H = -1367$kJ / mol (1)

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7$kJ / mol (2)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -285.8$kJ / mol (3)

Calculation of heat of formaiton of ethyl alcohol is i.e.

$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$ $\Delta H = ?$

Multiply eq. 2 by 2 and 3 by 3 and ivverting eq. 1 and all of then modified equation.

$2C + 2O_2 \longrightarrow 2CO_2$ $\Delta H = -787.4$kJ / mol

$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$ $\Delta H = -857.4$kJ / mol

$2CO_2 + 3H_2O \longrightarrow C_2H_5OH + 3O_2$ $\Delta H = +1367$kJ / mol

$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_2 \longrightarrow C_2H_5OH$ $\Delta H = -277.8$kJ / mol

Q.8 Using the information given in the table below, calculate the lattice energy of potassium bromide.

Reactions	ΔH / kJmol^{-1}
$K_{(s)} + 1/2Br_{2(l)} \longrightarrow K^+Br^-$	−392
$K_{(s)} \longrightarrow K_{(g)}$	+90
$K_{(s)} \longrightarrow K^+_{(g)} + e^-$	+420
$1/Br_{2(l)} \longrightarrow Br_{(g)}$	+112
$Br + e^- \longrightarrow Br^-$	−342

Given Data:

i. $K_{(s)} + \frac{1}{2}Br_{2(l)} \longrightarrow KBr_{(s)}$ $\Delta H = -392$ kJ mol^{-1}

ii. $K_{(s)} \longrightarrow K_{(g)}$ $\Delta H = +90$ kJ mol^{-1}

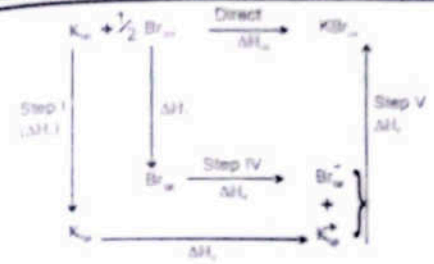
iii. $K_{(g)} \longrightarrow K^+_{(g)} + e^-$ $\Delta H = 420$ kJ mol^{-1}

iv. $\frac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)}$ $\Delta H = 112$ kJ mol^{-1}

v. $Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$ $\Delta H = -342$ kJ mol^{-1}

Required:

$K^+_{(g)} + Br^-_{(g)} \longrightarrow KBr$ $\Delta H_{lattice} = ?$



Solution:

The equation (i) shows the enthalpy of formation of potassium bromide. According to Hess's law the enthalpy of formations is equal to sum of all the enthalpies along with lattice energy.

$\Delta H_f = \Delta H_{lattice} + \Delta H_4$

$\Delta H_{lattice} = \Delta H_f - \Delta H_4$

Where ΔH_4 is equal to some of all the given enthalpies to get ΔH_4 add equations (ii), (iii), (iv) and (v).

ii. $K_{(s)} \longrightarrow K_{(g)}$ $\Delta H = +90$ kJ mol^{-1}

iii. $K_{(g)} \longrightarrow K^+_{(g)} + e^-$ $\Delta H = 420$ kJ mol^{-1}

iv. $\frac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)}$ $\Delta H = 112$ kJ mol^{-1}

v. $Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$ $\Delta H = -342$ kJ mol^{-1}

$K_{(s)} + \frac{1}{2}Br_{2(l)} \longrightarrow K^+_{(g)} + Br^-_{(g)}$ $\Delta H_4 = -280$ kJ mol^{-1}

$\Delta H_{lattice} = \Delta H_f - \Delta H_4$

$\Delta H_{lattice} = -392 - 280$

$\Delta H_{lattice} = -672$ kJ mol^{-1}

Thus the lattice energy of potassium bromide = −672 kJ mol^{-1}

Q.9 Calculate the entropy change of the surroundings $\Delta S^\circ_{surrounding}$ for the reaction at 298K:

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)} \qquad \Delta H^\circ_{reaction} = -1270.2 \text{ kJ mol}^{-1}$$

Given Data:

- $\Delta H^\circ_{reaction} = -1270.2$ kJ/mol (exothermic)
- Temperature T = 298 K

The entropy change of the surroundings (ΔH°_{surr}) is related to the heat transferred to the surroundings ($q_{surrounding}$) at constant temperature:

$$\Delta S^\circ_{surrounding} = \frac{q_{surrounding}}{T}$$

For an exothermic reaction, the system releases heat to the surroundings, so:

$$q_{surrounding} = -\Delta H^\circ_{reaction}$$

(Negative sign because the system loses heat, but the surroundings gain it.)

$$\Delta H^\circ_{reaction} = -1270.2 \text{ kJ/mol},$$

The heat absorbed by the surroundings is:

$$q_{surrounding} = -(-1270.2) = +1270.2 \text{ kJ/mol}$$

(Positive sign indicates heat is added to the surroundings.)

Now, convert $q_{surrounding}$ to joules (since entropy units are J/K mol):

$$q_{surrounding} = 1270.2 \text{ kJ/mol} \times 1000 = 1,270,200 \text{ J/mol}$$

To Calculate $\Delta S^\circ_{surrounding}$ we use the formula:

$$\Delta S^\circ_{surrounding} = \frac{q_{surrounding}}{T} = \frac{1,270,200 \text{ J/mol}}{298 \text{ K}} = 4262.4 \text{ J mol}^{-1}\text{K}^{-1}$$

$$= 4.2624 \text{ kJ mol}^{-1}\text{K}^{-1}$$