6 CHEMICAL ENERGETICS

Student Learning Outcomes [C-11-A-93 to C-11-A-123]

After studying this chapter, students will be able to:

- Describe the chemical reactions that 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)**

Thermodynamics is the science of the relationships between heat and other forms of energy. It has vast applications in chemistry, engineering and throughout physics. Thermochemistry is one area of thermodynamics that is concerned with 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' law, a special case of Ist law of thermodynamics, is a remarkable tool in a chemist's hand and finds numerous applications in analytical chemistry. Moreover, thermodynamic information allows us to predict whether a particular reaction can occur under specified conditions i.e., it discusses the spontaneity of a reaction.

6.1 ENTHALPY CHANGE

The sum of all the possible, potential and kinetic energies, of a system 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,

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

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**."

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**."

Following **Figure 6.1** shows the **enthalpy diagram** of exothermic and endothermic reactions.

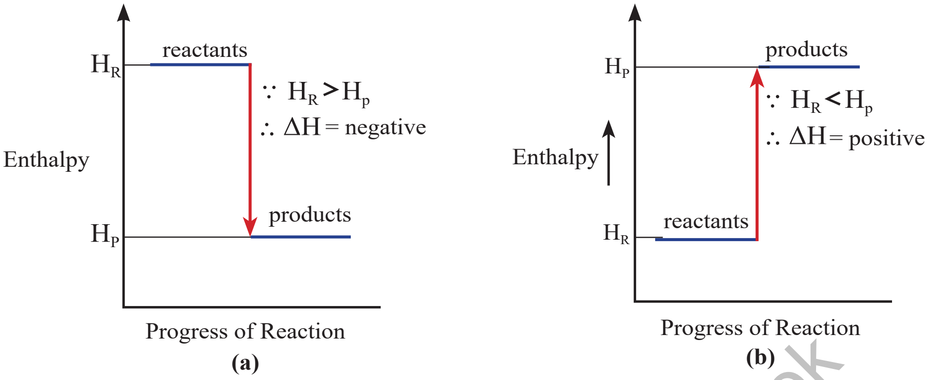


Figure 6.1: Enthalpy diagram of (a) Exothermic Reaction and (b) Endothermic Reaction

For example, combustion of carbon in oxygen is an exothermic reaction.

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

The dissolution of ammonium chloride (NH_4Cl) in water is an endothermic process.

$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH_4{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \qquad \mathbf{\Delta H} = +16.2\ \text{kJ mol}^{-1}$$

Interesting information

The dissolution of ammonium chloride (NH_4Cl) in water is an endothermic process. This reaction is used in cold packs (or ice packs) to treat internal injuries. When the pack is kneaded, water and NH_4Cl crystals mix and energy is absorbed from the surroundings, producing a cooling sensation.

6.2 ENERGY PROFILE DIAGRAM

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. The energy profile diagram of exothermic and endothermic reactions are given in **Figure 6.2**.

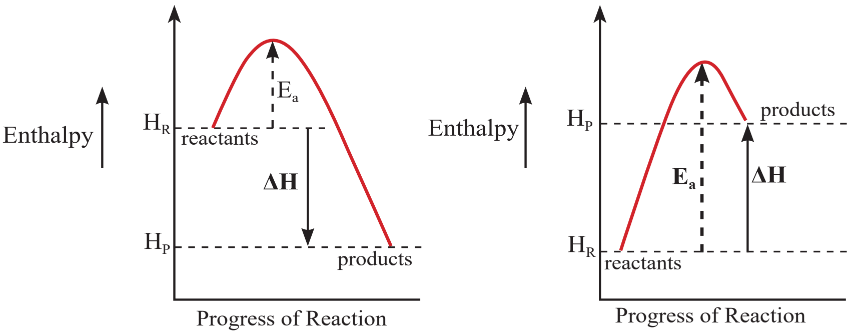


Figure 6.2 Energy profile diagram in terms of ΔH and E_a

Quick Check 6.1

Draw the energy profile diagrams for the following reactions:

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

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

6.3 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 1atm 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**.

6.3.1 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.

For example, the reaction between hydrogen and oxygen gases to form 1 mole of water:

$$H_{2(g)} + \tfrac{1}{2}\ O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad \mathbf{\Delta H^o_r} = -286\ kJ\ mol^{-1}$$

6.3.2 Enthalpy Change of Combustion (ΔH^o_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**.** For example, standard enthalpy of combustion $\mathbf{\Delta H^o_C}$ of ethanol is −1368 kJ mol^{-1}.

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

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

6.3.3 Enthalpy Change of Formation (ΔH^o_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. For instance, $\mathbf{\Delta H^\circ_f}$ for methane is given below.

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

6.3.4 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."

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

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

6.3.5 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. For 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 Cl^- as spectator 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 net neutralization reaction is:

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

For all strong acid-base reactions $\mathbf{\Delta H^o_n}$ is always near -57.1 kJ mol^{-1}.

6.3.6 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.

Electron affinity of chlorine atom.

$$Cl_{(g)} + e^- \longrightarrow Cl^- \qquad \Delta H^o_{ea} = -348.8 \text{ kJ mol}^{-1}$$

Since, energy is released, so first electron affinity carries negative sign.

Quick Check 6.2

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

b) Name the enthalpy changes that occur in each of the following reactions:

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

ii) $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$

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

6.4 BOND ENERGY (BOND DISSOCIATION ENERGY) AND ENTHALPY CHANGES

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** which 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 B.E. values, in all of their compounds. Actually, B.E. is affected by other atoms in a molecule. For example, C–C bonds usually have B.E. values of approximately 350 to 380 kJ/mol.

In ethane: $[H_3C—CH_3]$; $E_{C\text{-}C} = 376\ kJ\ mol^{-1}$

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

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

In these examples, $E_{c\text{-}c}$ for ethane is exact bond energy. Similarly for propane and butane, $E_{c\text{-}c}$ are exact bond energies. When we take average of all $E_{c\text{-}c}$ 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 6.1**.

Table 6.1. 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

6.5 ENTHALPY CHANGE OF REACTION (ΔH_r) AND CHEMICAL BONDS

A chemical bond represents a form of energy known as chemical energy, which is inter-convertible into all forms of energy. Bond breaking absorbs energy (ΔH = +ve) while bond formation releases 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.

For example, the formation of water 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. This is calculated in **Sample Problem 6.1**.

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

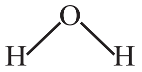
Sample Problem 6.1

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

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

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

Solution: $\underbrace{H{-}H + \tfrac{1}{2}\, O{=}O}$ $\longrightarrow$



$436 \ + \tfrac{1}{2}(495)$ $\qquad$ $2 \times (463)$

(bond breaking energy) (bond forming energy)

$$\begin{aligned} \because\ \Delta H^o_r &= \sum E_R - \sum E_P \\ &= [E_{H\text{-}H} + E_{O=O}] - [2\, E_{H\text{-}O}] \\ &= [436 + 247.5] - [2(463)] \\ \mathbf{\Delta H^o_r} &\mathbf{= -242.5 \text{ kJ mol}^{-1}} \end{aligned}$$

6.6 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**. 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".

The amount of heat energy required to raise the temperature of a substance of mass 1kg through 1K (or 1°C) is known as specific heat capacity, c, of the liquid. So the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{K}^{-1}$(or $\text{J g}^{-1}\ \mathbf{{}^\circ C}^{-1}$), which is rounded off to $4.2 \text{ J g}^{-1} \text{K}^{-1}$.

6.6.1 Glass Calorimeter

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

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.

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.

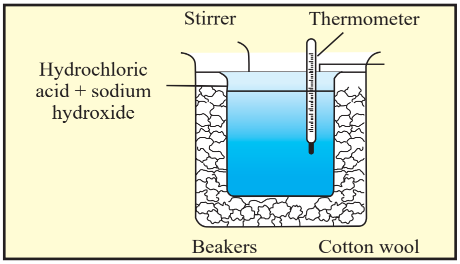


Figure 6.3 Glass calorimeter to measure enthalpy change of reactions

ΔH is calculated as follows:

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

ii) Convert into kJ by dividing with 1000.

iii) Calculate ΔH for the reaction using relation:

$$\mathbf{\Delta H} = -\frac{q}{n}\ \text{kJmol}^{-1} \text{ (for exothermic reaction)}$$

or

$$= -\frac{mc\mathbf{\Delta T}}{n}\ \text{kJ mol}^{-1} \text{ (n = no. of moles)}$$

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 (**Δ**) as explained in the following example.

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 J $g^{-1}K^{-1}$

Solution

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

Rise in temperature, ΔT = 28.5 – 25.0 = 3.5**°C** = 3.5 K

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

$= 200 \times \mathbf{4.2} \times \mathbf{3.5} = 2940$ J

$= 2.94$ kJ

Calculation of no. of moles of H_2O formed (n)

Using mole = Concentration(mol/dm^3) x Volume (dm^3)

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

Using equation, Number of moles of water formed, $n_{(H2O)} = 0.05$ mol

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

$$\Delta H^o_n = \frac{q}{n} = \frac{-2.94 \text{ kJ}}{0.05 \text{ mol}}$$

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

Quick Check 6.3

Calculate ΔH^o_n of the reaction of 50 cm^3 of 1.5 mol dm^{-3} HNO_3 with 50 cm^3 of 1.5 mol/dm^3 of NaOH. The change in temperature is 4 ºC,

6.7 ENTHALPY CHANGE AND CALORIE CONTENT OF FOOD

In this section, we will look at 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 enthalpy 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. This energy is typically expressed in units of kilocalories (k cal) or joules (J).

6.7.1 Relation between Enthalpy Change and Calorie Content

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

$$\text{Calorie content} = \frac{\Delta H^o\ (\text{kJ/g})}{4.184}$$

Look at the energy provided from glucose.

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

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

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

$$= 15.57\ \text{kJ/g}$$

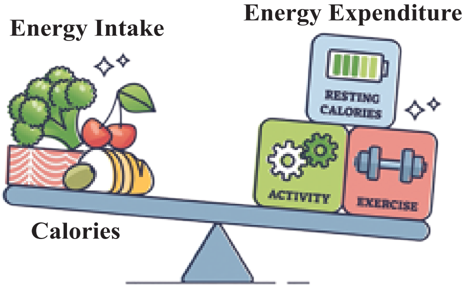
Using the relation,

ΔH (kJ/g) = – 4.184 × calorie content

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

$$= -\frac{15.57\ \text{kJ/g}}{4.184\ (\text{kJ/kcal})}$$

calorie content = – 3.72 kcal/g



Negative Energy Balance

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

6.8 HESS' LAW OF HEAT SUMMATION

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' Law helps us to calculate the enthalpy changes for such reactions or processes. It states:

"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."

Hess' 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 6.4**. The products formed in these routes (M, N and X, Y, Z) are called reaction intermediates.

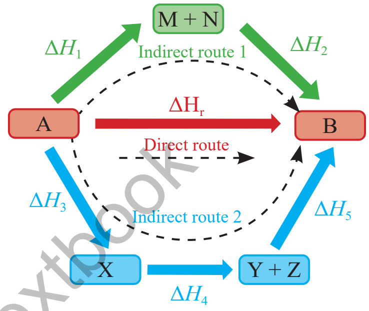


Figure 6.4 Hess' cycle

Then according to Hess' law,

For the indirect route 1, we can write: $\mathbf{\Delta H^o_r} = \Delta H_1 + \Delta H_2$

For the indirect route 2, we can write: $\mathbf{\Delta H^o_r} = \Delta H_3 + \Delta H_4 + \Delta H_5$

Below are few examples of it.

i) Calculating Enthalpy of Formation (ΔH^o_f) using Enthalpy of Combustion (ΔH^o_c)

Sample problem 6.3

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

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

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

$$C(\text{graphite}) + \tfrac{1}{2} O_{2(g)} \qquad CO_{(g)} \quad \mathbf{\Delta H_1} = ?$$

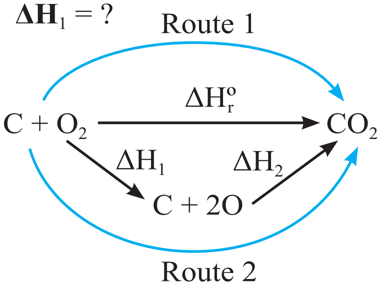
Solution: Applying Hess' law, we can write

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

$$\Delta H_1 = \Delta H - \Delta H_2$$

$$= -393.5 - (-283)$$

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



ii) Calculating Enthalpy of Reaction (ΔH^o_r) using Enthalpies of formation (ΔH^o_f)

Sample Problem 6.4 Calculate the enthalpy change of reaction of

$$C_2H_{4(g)} + HCl_{(g)} \longrightarrow C_2H_5Cl_{(g)}$$

Using Hess cycle with the help of following combustion data.

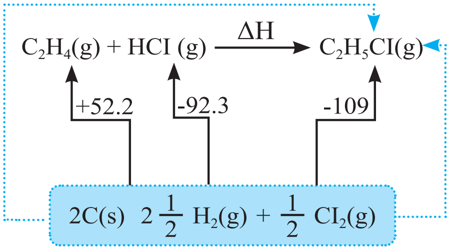
ΔH^o_f of $C_2H_4 = +52.2$ KJ mol^{-1}

ΔH^o_f of $HCl = -92.3$ KJ mol^{-1}

ΔH^o_f of $C_2H_5Cl = -109$ 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°):

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(\ell)}$$

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

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:

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

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, $C_3H_8 = 3(12.011) + 8(1.0079) = 44.096$ g mol^{-1}

$$\text{No. of moles of propane} = \frac{445}{44.096} = 0.3320 \text{ mol}$$

So, 0.3320 mol propane evolves heat = 678.6 kJ

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

According to Hess' law:

$$\Delta H_r = [3 \times \Delta H^o_f (CO_2) + 4 \times \Delta H^o_f (H_2O)] - [1 \times \Delta H^o_c (C_3H_8) + 5 \times \Delta H^o_c (O_2)]$$

$$-2044 \text{ kJ} = [3\times(-393.51) + 4 \times(-241.82)] - [1 \times \Delta H^o_f (C_3H_8) + 5 \times(0)]$$

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

$$\Delta H^o_f (C_3H_8) = -104 \text{ kJ mol}^{-1}$$

Quick Check 6.5

Draw enthalpy cycle of **Sample Problem 6.5** according to Hess' law to validate the above calculation.

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

A special case of Hess' law involves the use of bond energies to estimate heats of reaction for gas-phase reactions. 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 6.1**. In the second step, the product molecules are formed. The enthalpy change for this step can again be estimated from the bond enthalpies of **Table 6.1**, 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 bond energies by use of the following version of Hess' law:

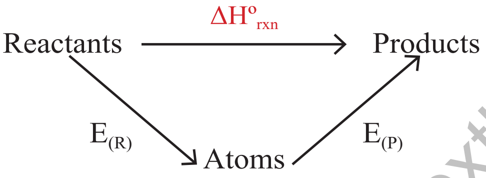


Figure 6.5 Hess Cycle; showing the relationship between bond energies and ΔH_r. $= \sum E_R - \sum E_P$

Sample problem 6.6 In the case of formation of $HCl_{(g)}$ from $H_{2(g)}$ and $Cl_{2(g)}$, use B.E. data from **Table 6.1** to estimate ΔH for the reaction:

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}$$

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

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

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

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

$= 436\ \text{kJ} + 242\ \text{kJ}$

$= 678\ \text{kJ}$

$$\begin{tikzcd} H_{2(g)} + Cl_{2(g)} \arrow[rr, "\Delta H_r^\circ"] \arrow[dr, bend right] & & 2HCl_{(g)} \\ & 2H_{(g)} + 2Cl_{(g)} \arrow[ur, bend right] & \end{tikzcd}$$

Second Step:

$$2\,H_{(g)} + 2\,Cl_{(g)} \longrightarrow 2\,HCl_{(g)}$$

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

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

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

$\Delta H_r^\circ = \sum E_R - \sum E_P$

$\Delta H_r^\circ = 678 - 862$

$\Delta H_r^\circ = -184\ \text{kJ}$ (for 2 mol of HCl)

Enthalpy of formation of HCl, $= -184/2\ \text{kJ mol}^{-1} = -92\ \text{kJ mol}^{-1}$

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:

$E_{N\equiv N} = 945$ kJ mol^{-1} , $E_{H\text{-}H} = 436$ kJ mol^{-1}, $E_{N\text{-}H} = 391$ kJ mol^{-1}.

Calculate the enthalpy change of the above reaction.

b) Calculate the enthalpy change for the following reaction

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

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

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

6.9 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^{o}_{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^{o}_{sol} and it may be exothermic or endothermic. The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

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

$$NH_4Cl_{(s)} + aq \longrightarrow NH_4^{+}{}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H^{o}_{sol} = +16.2 \text{ kJ mol}^{-1}$$

In **Table 6.2** values of heats of solution of different ionic solids in water at infinite dilution are given.

An ionic compound consists of oppositely charged ions, held together by strong electrostatic forces. Two factors govern the process of dissolution

i. Hydration energy (accounts for the attraction of solute ions with water molecules)

ii. Lattice energy (controls the breaking of the ionic compounds)

Table 6.2 Heats of solution of some important ionic solids (kJ mol^{-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

6.9.1 Hydration

“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 6.6.** 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:

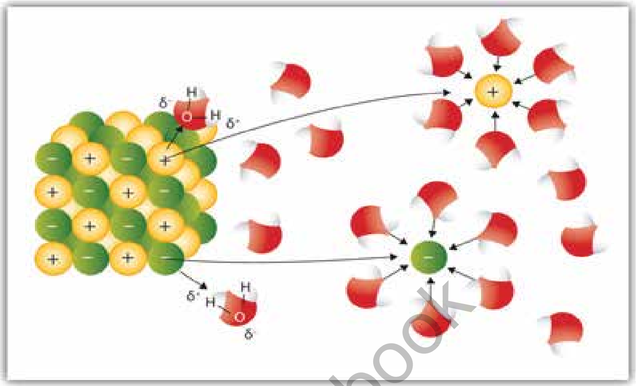


Figure 6.6 Dissolution of an ionic compound through the process of hydration.

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

It is denoted by ΔH^o_{hyd}. This energy is always released as it is formation of ion-dipole bond.

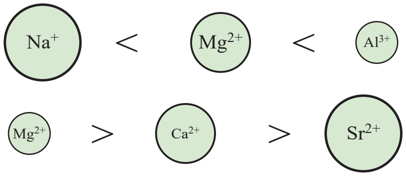
Factors affecting the magnitude of hydration energy

The heat of hydration depends on following factors:

i. Charge on the ion

ii. Size of the ion

We use a combined term for these two factors i.e., “charge density” 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 increase in the hydration energy values. For example, enthalpies of hydration of following ions are in the order:



On the same basis we can explain the hydration energy of anions.

6.9.2 Lattice Energy (ΔH^o_{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.”

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

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 6.7 shows the values of lattice energies of alkali metal halides decrease with the increase in the size of the cation/anion. With the increase in the size of either cations or anions, oppositely charged ions become less and less tightly packed.

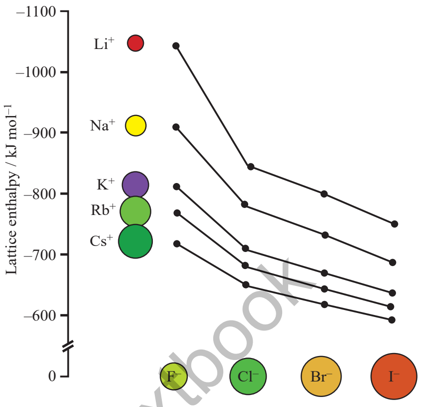


Figure 6.7 Lattice energies of alkali metal halides

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. 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.

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

Solubility trends of group 2 hydroxides and sulphates

$\mathbf{\Delta H^{\circ}_{sol}}$ 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 of ions Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. For this reason, the lattice energy factor dominates. $\mathbf{\Delta H^{\circ}_{sol}}$ becomes more exothermic, so solubility increase.

- Now look at the solubility trends of group 2 metal sulphates. Because 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 and the solubility decreases from $MgSO_4$ to $BaSO_4$. $\mathbf{\Delta H^{\circ}_{sol}}$ becomes more endothermic, thus solubility decreases.

6.9.3 Calculating Enthalpy Change of Solution (ΔH^o_{sol})

We can calculate the enthalpy change of solution or the enthalpy change of hydration by constructing an enthalpy cycle and using Hess' law **Figure 6.8.**

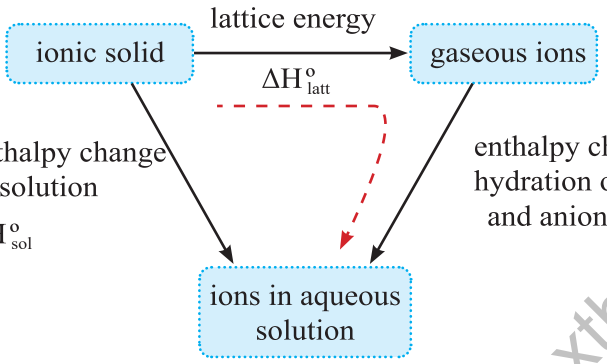


Figure 6.8 Energy cycle of formation of an aqueous solution of an ionic solid using Hess' law

We can see from this enthalpy cycle that:

$$\Delta H^o_{latt} + \Delta H^o_{sol} = \Delta H^o_{hyd}$$

We can use this energy cycle to calculate:

Sample problem 6.6

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

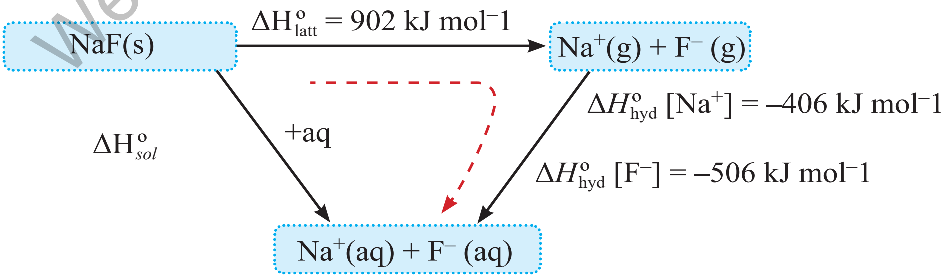
Lattice energy of sodium fluoride (NaF) = –902 kJ mol^{-1}

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

Enthalpy 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 ΔH^o_{sol} 11

$$\Delta H^o_{sol} = \Delta H^o_{latt} + \Delta H^o_{hyd}$$

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

$$\Delta H^o_{hyd}\,[NaF] = +10 \text{ kJ mol}^{-1}$$

6.10 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 ΔH^o_{latt} using several experimental data and an energy cycle called the Born–Haber cycle. Born-Haber cycle is an application of Hess' law. Let us consider the calculation of lattice energy of sodium Chloride using Hess' law and Born-Haber cycle.

$$\begin{tikzcd}
Na_{(s)} + \frac{1}{2} Cl_{2(g)} \arrow[rr, "\Delta H^o_x"] \arrow[dr, "\Delta H^o_f"'] & & Na^+Cl^-_{(g)} \arrow[dl, "\Delta H^o_{latt}"] \\
& Na^+_{(g)} + Cl^-_{(g)} &
\end{tikzcd}$$

Figure 6.9 Enthalpy cycle of sodium chloride

where,

ΔH^o_f : standard enthalpy of formation of NaCl can be measured conveniently in a calorimeter.

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

$$\Delta H^o_f = \Delta H_x + \Delta H^o_{latt}$$

The above energy triangle has been extended to show the various stages involved in finding ΔH_x. The complete energy cycle is called the Born-Haber cycle and it is presented in **Figure 6.10**.

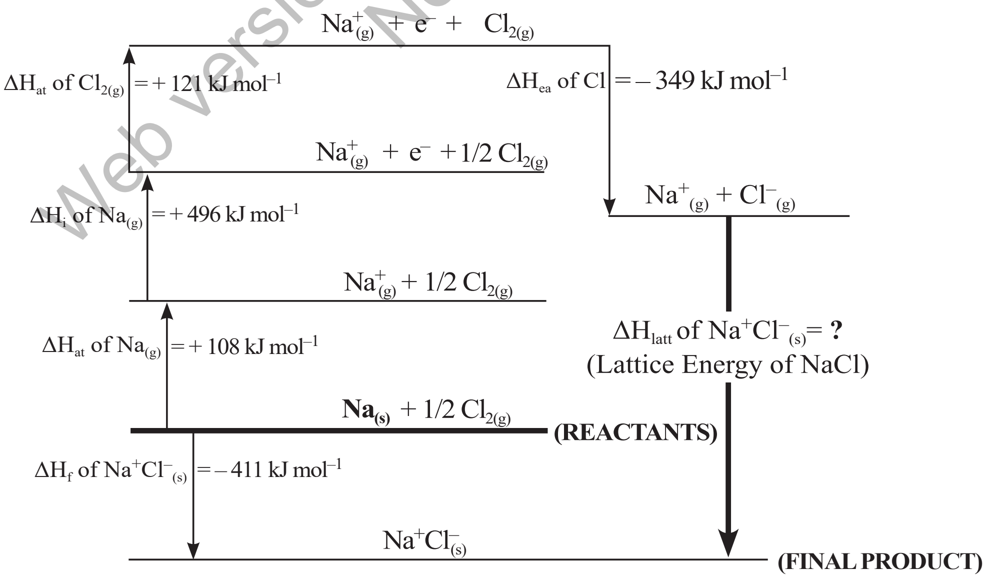


Figure 6.10 Born Haber cycle of sodium chloride (not according to scale)

Calculation of ΔH_x

From above cycle we have,

$$\Delta H_x = \Delta H_{at\ (Na)} + \Delta H_{i1\ (Na)} + \Delta H_{at\ (Cl2)} + \Delta H_{ea1\ (Cl2)}$$

$$\Delta H_x = 376\ kJ\ mol^{-1} \text{--------------(ii)}$$

Using, $\Delta H^o_{latt} = \Delta H^o_f - \Delta H_x = -411 - 376$

$$\mathbf{\Delta H^o_{latt} = -787\ kJ\ mol^{-1}}$$

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 109 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' law:

$$\mathbf{\Delta H^o_f} = \mathbf{\Delta H^o_{latt}} + \Delta H^o_{at\ (Na)} + \Delta H^o_{1i\ (Na)} + \Delta H^o_{at\ (F2)} + \Delta H^o_{1ea\ (F)}$$

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

$$\Delta = \mathbf{-585\ kJ\ mol^{-1}}$$

Quick Check 6.7

a) Draw Born-Haber cycle for Sample Problem 6.7.

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.

6.11 ENTROPY

Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature. When the energy is distributed in more ways, a system is more stable. Entropy can also be thought of as 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.

6.11.1 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 6.11** below.

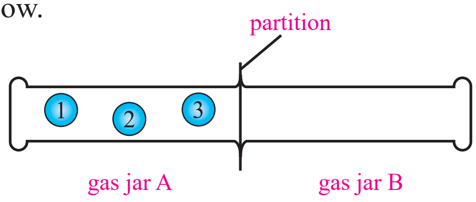


Figure 6.11 Diffusion and number of possible arrangements

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

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.

6.11.2 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.

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

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 $JK^{-1}mol^{-1}$.

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. $Br_{2(\ell)}\ S^{O} = 151.6\ J\ K^{-1}\ mol^{-1}$ and $I_{2(s)}\ S^{O} = 116.8\ J\ K^{-1}\ mol^{-1}$

ii. $H_{2(g)}\ S^{O} = 130.6\ J\ K^{-1}\ mol^{-1}$ and $CH_{4(g)}\ S^{O} = 186.2\ J\ K^{-1}\ mol^{-1}$

iii. $Hg_{(\ell)}\ S^{O} = 76.00\ J\ K^{-1}\ mol^{-1}$ and $Na_{(s)}\ S^{O} = 51.20\ J\ K^{-1}\ mol^{-1}$

iv. $SO_{2(g)}\ S^{O} = 248.1\ J\ K^{-1}\ mol^{-1}$ and $SO_{3(\ell)}\ S^{O} = 95.60\ J\ K^{-1}\ mol^{-1}$

6.11.3 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. 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:

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

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.

6.11.4 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:

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

$$S^{\circ}_{[O_{2(g)}]} = 205.0\ J\ K^{-1}\ mol^{-1}$$

$$S^{\circ}_{[CaO(s)]} = 39.70\ J\ K^{-1}\ mol^{-1},$$

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

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

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

$$= 79.40 - 287.8$$

$$\Delta S^{\circ}_{system} = -208.4\ J\ K^{-1}\ mol^{-1}$$

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.

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

$\Delta S°_{total}$ is sum of standard entropy change of system and standard entropy change of surrounding. ΔS° 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 ΔH°).

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

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

ΔS° for surrounding is calculated using following equation:

$$\Delta S°_{surrounding} = \frac{-\Delta H^{o}_{r}}{T}$$

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/Kmol.
- The negative sign is part of equation and not the sign of $\Delta H_r°$.

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

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

$$\Delta S°_{total} = \sum S°_{(products)} - \sum S°_{(reactants)} + [\frac{-\Delta H^{o}_{r}}{T}]$$

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:

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

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

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

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

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

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

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

$= 79.40 - 287.8$

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

Sample Problem 6.9 Calculate the entropy change of the surroundings $\Delta S^\circ_{surrounding}$ for the reaction at 298K:

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

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

$$-1270.2 \times 1000 = -1\ 270\ 200\ J\ mol^{-1}$$

Step 2 Apply the relationship

$$\Delta S^\circ_{surroundings} = \frac{-\Delta H^o_{reaction}}{T}$$

$$\Delta S^\circ_{surroundings} = \frac{-1270200}{298}$$

$$= +4262.4\ J\ K^{-1}\ mol^{-1}$$

Sample Problem 6.10 Calculate the total entropy change ΔS°_{total} for the reaction and check its spontaneity.

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

$$\Delta S^\circ_{system} = -208.4\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^\circ_{surrounding} = +4262.4\ J\ K^{-1}\ mol^{-1}$$

As,

$$\Delta S^\circ_{total} = -208.4 + 4262.4$$

$$\Delta S^\circ_{total} = +4054.0\ J\ K^{-1}\ mol^{-1}$$

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

6.12 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 $\Delta S^\circ_{(total)}$ 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

$$-T\ x\ \{\ \Delta S^\circ_{total} = \Delta S^\circ_{system} + [\frac{\Delta H^o_r}{T}]\}$$

$$-T\Delta S_{total} = -T\Delta S_{system} + \Delta H^o_r$$

$$\mathbf{\Delta G^\circ = \Delta H^\circ_r - T\Delta S^\circ}$$

And draw the following conclusion from it

Extend your knowledge

The unit of temperature times entropy (TΔS) is Joule. ΔS° represents $\Delta S^\circ_{system.}$

i. **If ΔG < 0 (–ve),** the given process may occur spontaneously

ii. **If ΔG > 0 (+ve),** the indicated process cannot occur spontaneously; instead, the reverse of it may occur

iii. **If ΔG = 0** neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium

6.12.1 Calculating ΔG° for a Reaction

Sample Problem 6.11 For the reaction:

$$CaSO_{4(s)} \longrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Calculate ΔH°, ΔS° and ΔG° at 25 °C using the following data; and discuss its spontaneity.

Enthalpy of Formation: $\Delta H^\circ_{f\,(CaSO4(s))} = -1432.7$ kJ, $\Delta H^\circ_{f\,(Ca^{2+}{}_{(aq)})} = -543.0$ kJ, $\Delta H^\circ_{f\,(SO4^{2-}{}_{(aq)})} = -907.5$ kJ

Standard entropy: $S^\circ_{(CaSO4(s))} = 106.7$ J/K, $S^\circ_{(Ca^{2+}{}_{(aq)})} = -55.2$ J/K , $S^\circ_{(SO4^{2-}{}_{(aq)})} = +17.2$ J/K

Solution

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

ii. $\Delta S^\circ = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)} = [(-55.2 + 17.2) - (106.7)]$ J/K = -1447 J/K $\Delta S^\circ = -0.1447$ kJ/K

iii. $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = (-17.8\ \text{kJ}) - (298\ \text{K}) \times (-0.1447\ \text{kJ/K}) = +25.3$ kJ

Note that you substitute ΔS° in units of kJ/K in the formula of ΔG°.

We conclude that this process is non-spontaneous 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.

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

Enthalpy of Formation: $\Delta H^\circ_{f\,(N2(g))} = 0$ kJ, $\Delta H^\circ_{f\,(H2(g))} = 0$ kJ, $\Delta H^\circ_{f\,(NH3(g))} = -45.9$ kJ

Standard entropy: $S^\circ_{(N2(g))} = 191.5$ J/K, $S^\circ_{(H2(g))} = 130.6$ J/K , $S^\circ_{(NH3(g))} = +193$ J/K

Solution:

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

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

$= \mathbf{-0.197\ kJ/K}$

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

ΔG° is a negative value thus it is concluded that Haber's process is spontaneous 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., ΔG° = ΔH° – T ΔS°. We get the value of ΔG at any temperature by substituting values of ΔH° and ΔS° at 25°C. But in this 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 6.3**, 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 6.3 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 its spontaneity.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_2$$

Solution:

For this reaction, ΔH° = +178.0 kJ and ΔS° = +160.4 J/K = 0.1604 kJ/K

Substituting T = 1000 + 273 = 1273 K

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

$$= +\,178.0\text{ kJ} - 204.2\text{ kJ}$$

$$= \mathbf{-26.2\ kJ}$$

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) $N_{2(g)} + 3H_{2(g)}\ 2NH_3(g)$ ii) $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

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

ii. Water turning to ice at -10 °C iii. Ethanol vaporising at 20 °C

iv. Water mixing completely with salt

v. Limestone (calcium carbonate) decomposing at room temperature

EXERCISE

MULTIPLE CHOICE QUESTIONS

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) $2C\ (\text{diamond}) + 2H_{2(g)} \longrightarrow C_2H_{4(g)}$

b) $2C\ (\text{graphite}) + 2H_{2(g)} \longrightarrow C_2H_{4(g)}$

c) $C\ (\text{graphite}) + H_{2(g)} \longrightarrow \tfrac{1}{2}\,C_2H_{4(g)}$

d) $2C\ (\text{diamond}) + 4H_{(g)} \longrightarrow C_2H_{4(g)}$

II. Which of the following equations correctly defines lattice energy of $MgCl_2$?

a) $Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_2$ b) $Mg^{2+}_{(g)} + 2Cl^-_{(g)} \longrightarrow MgCl_{2(g)}$

c) $Mg^{2+}_{(s)} + 2Cl^-_{(g)} \longrightarrow MgCl_{2(s)}$ d) $Mg^{2+}_{(g)} + 2Cl^-_{(g)} \longrightarrow MgCl_{2(s)}$

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) $\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$ b) $\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$

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

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

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

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

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

SHORT-ANSWER QUESTIONS

Q.2Attempt the following short-answer questions:

a. Differentiate between exothermic and endothermic reactions.

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

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

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

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

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

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

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?

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.

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?

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.

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.

DESCRIPTIVE QUESTIONS

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

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

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 26.03°C. Calculate: (i). q_{water} , (ii). ΔH for the solution process

Q.6 By applying Hess' 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) $NH_{3(g)} + aq \quad NH_{3(aq)} \longrightarrow \Delta H = -35.16\ kJ\ mol^{-1}$

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

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

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}

Q8 Using the information given in the table below, calculate the lattice energy of potassium bromide.

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

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

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

Q.10 For the reaction: $CaSO_{4(s)} \quad Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

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