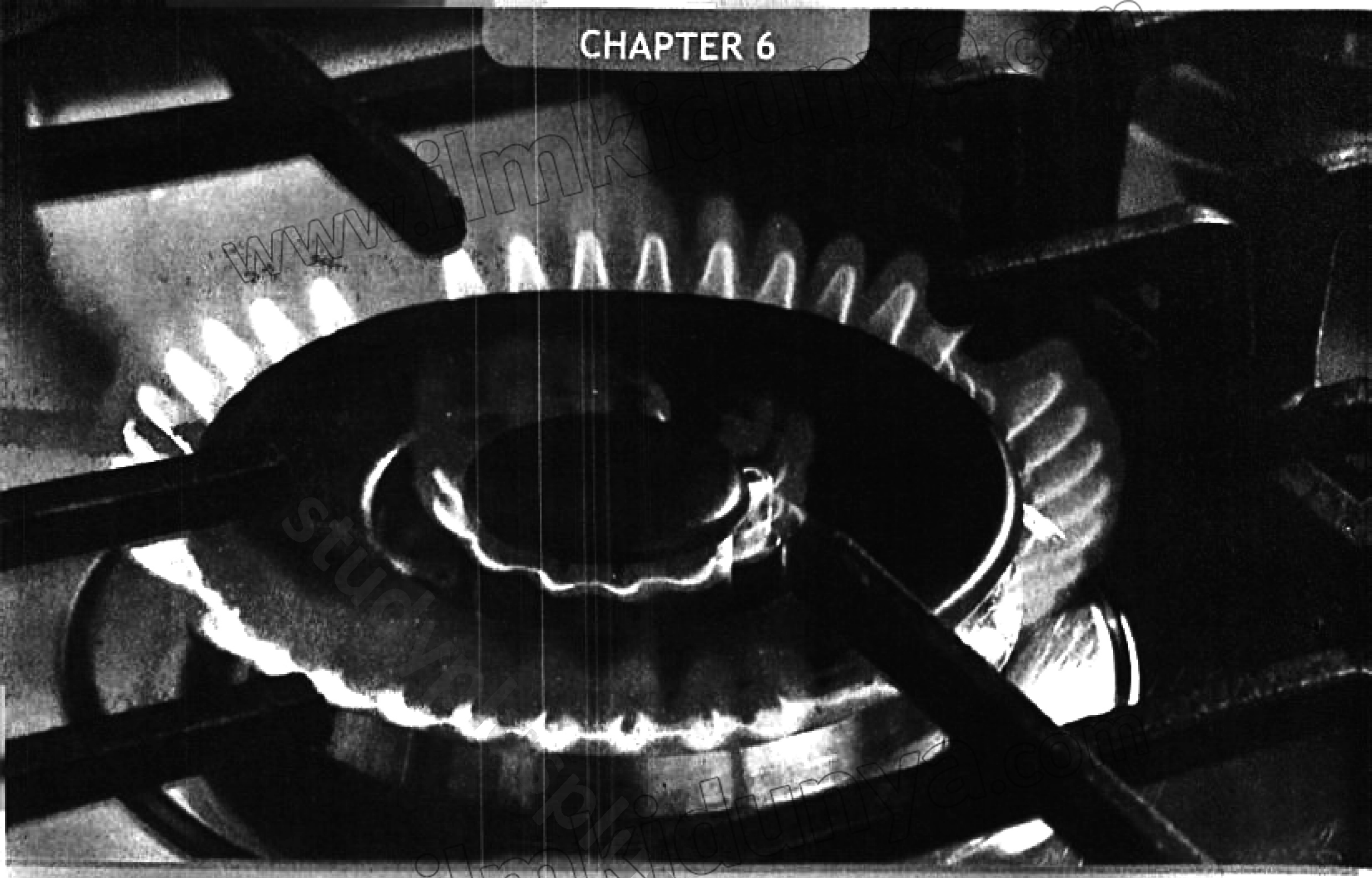

CHAPTER 6

ENERGETICS

SLOs: After completing this lesson, the student will be able to:

1. Describe that chemical reactions are accompanied by enthalpy changes and these changes can be exothermic (ΔH° is negative or endothermic ΔH° is positive).
2. Interpret a reaction pathway diagram, in terms of the reaction and of the activation energy
3. Define terms such as standard conditions, enthalpy change, reaction, formation, combustion, neutralization.
4. Explain that energy transfer occurs during chemical reactions because of the breaking and making of bonds.
5. Calculate the bond energies for the enthalpy change of reaction ΔH°
6. Describe that some bond energies are exact and some bond energies are approximate.
7. Calculate enthalpy changes from approximate experimental results, including the use of the relationships $q = mcdT$ and $\Delta H^\circ = - mcdT/n$
8. Define terms such as enthalpy change of atomization, lattice energy, ΔH°, first electron affinity, EA.
9. Use terms such as enthalpy change of atomization, lattice energy, fist electron affinity.
10. Explain factors affecting the electron affinities of elements.
11. Construct Born Haber's Cycles for ionic solids.
12. Perform calculations involving Born- Haber cycles.
13. Explain the effect of ionic charge and ionic radius on the numerical magnitude of lattice energy.
14. Apply enthalpy change with reference to hydration, and solution.
15. Construct an energy cycle involving enthalpy change of solutions, and enthalpy change of hydration.

16. Perform calculations involving energy cycles.
17. Explain the effect of ionic charge ionic radius on the numerical magnitude of an enthalpy change of hydration.
18. Define the term entropy, S, as the number of possible arrangements of the particles and their energy in a given system.
19. 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.
20. Calculate the entropy change for a reaction, ΔS°, given the standard entropies, S , of the reactants and the products.
21. Explain the concept of heat as a form of energy.
22. Explain the relationship between temperature and kinetic energy of particles.
23. State that total energy is conserved in chemical reactions.
24. Explain the concept of standard conditions and standard states in measuring energy changes.
25. Explain Hess's Law.
26. Apply Hess's Law to calculate enthalpy changes in a reaction carried out in multiple steps.
27. Explain the relationship between bond formation energy and bond breaking energy.
28. Explain Gibbs free energy.
29. Apply the concept of Gibbs free energy to solve problems.
30. Outline how enthalpy change relates to the calorie concept of the food we eat.

Every process in this universe, whether in living cells or test tubes, in the atmosphere or in water, etc., implies a change of energy. Some processes release energy, others require energy. But in all these cases, the total amount of energy in the universe remains unchanged. In this chapter, we will discuss the principles that govern energy changes. We will study the role of energy in chemical reactions. We will also discuss measuring the heat of a chemical reaction so that we can focus on the central topic of the chapter, the amount of heat released or absorbed in a reaction. The study of energy changes associated with all types of physical and chemical changes is known as energetics.

6.1 ENERGY IN CHEMICAL REACTIONS

The energy in the form of heat is either evolved or absorbed as a result of chemical reaction. This is because, in chemical reactions old bonds are broken and new bonds are formed. Bond breaking always consumes energy and bond making always releases energy. When the energy released by bond formation is greater than the energy consumed by bond breaking, there is a net transfer of chemical energy from system to the surroundings. Whereas as energy is transferred from surroundings to the system, when the energy consumed by bond breaking is greater than the energy released by bond formation. Thus, in chemical reactions energy transfer occurs between a system and the surroundings.

6.1.1 Units of Thermal Energy

Unit of heat or thermal energy used in SI system is the Joule (J). **Thermal energy** is the energy in an object or system due to the movement of its molecules and atoms.

Another common unit of heat is the calorie. It is defined as **the heat or thermal energy required to raise the temperature of one gram of water from 14.5°C to 15.5°C.**

1 Calorie = 4.18 Joules

6.1.2 Thermochemical Reactions

When a chemical change takes place, energy is exchanged between system and its surroundings. Energy has many forms such as heat, light, work etc. A chemical reaction which proceeds with the evolution or absorption of heat is called a thermochemical reaction. **A balanced chemical equation which also shows heat change of a chemical reaction is called thermochemical equation. The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.**

For example

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5kJ$$

There are two types of thermochemical reactions: -

(1) Exothermic Reactions

A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction. In an exothermic reaction the chemical system transfers energy to the surroundings as the reactants are converted to products e.g. burning of fuels is a highly exothermic reaction. The energy released can be used to heat a room, or to drive an engine or to cook food. Examples of exothermic reactions are given below:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5kJ$

(ii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)} \qquad \Delta H^\circ = -571.6kJ$

(iii) $C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H^\circ = -110.5kJ$

(2) Endothermic Reactions:

A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction. In these reactions heat is transferred from surrounding to the system. Examples of endothermic reactions are given below:

(i) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \qquad \Delta H^\circ = +53.8kJ$

(ii) $C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)} \qquad \Delta H^\circ = +131.4kJ$

(iii) $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \qquad \Delta H^\circ = +180.5kJ$

Concept Assessment Exercise 6.1

Classify the following processes as exothermic or endothermic.

(a) Freezing of water

(b) Combustion of methane

(c) Sublimation of dry ice

(d) $H_2O_{(g)} \longrightarrow H_2O_{(l)}$

(e) Decomposition of limestone.

6.1.3 Heat of Reaction

The amount of energy released or absorbed depends on the amounts of substances that react. For example, as more fuel burns, more energy is released. Thus, when we report an energy change we must also report the amounts of the chemical substances that generate the energy change. For this purpose energy changes are expressed in terms of molar quantities of reactants and products.

The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and products are same as shown in a chemical reaction is called heat of reaction.

Heat of reaction measured at 25°C (or 298K) and one atmospheric pressure is known as standard enthalpy change. It is denoted by ΔH°.

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5kJ$

DO YOU KNOW

Chemical reactions support our lives and assist us at home and at work. For instance, cellular respiration is a series of chemical reactions that releases energy from the food we eat to "Power "all the functions and activities inside our body. Combustion reactions help release energy to heat our homes and move our vehicles.

This equation shows that 1 mole of solid carbon (12g) reacts with 1 mole of oxygen gas (32g) to give 1 mole of CO_2 gas (44g) at 25°C and 1 atmospheric pressure and 393.5 KJ heat is evolved. What does the following equation show?

(ii) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \qquad \Delta H^\circ = +53.8kJ$

If a reaction is exothermic when going in one direction, it will be endothermic in the reverse direction. When a reaction is reversed, the magnitude of ΔH° remains the same but its sign changes.

Thus above two thermochemical reactions in the reverse direction would be represented as follows:

$$CO_{2(g)} \longrightarrow C_{(s)} + O_{2(g)} \qquad \Delta H^\circ = +393.5kJ$$

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)} \qquad \Delta H^\circ = -53.8KJ$$

6.1.4 Relation between Enthalpy Change and Heat of Reaction or Heat of Combustion of a Reaction

Because most chemical reactions occur at constant pressure, we can equate the heat change in these reactions to the change in enthalpy. This means we can define heat of a reaction as the change in enthalpy (ΔH), as the difference between the enthalpies of the products (final estate) and the enthalpies of the reactants (initial state).

$$\Delta H = H_{products} - H_{reactants}$$

The enthalpy change of a reaction can be positive or negative depending upon the process. For an exothermic process, in which heat is released by the system to the surrounding ΔH is negative For an endothermic process, in which heat is absorbed by the system from the surroundings ΔH is positive. Since, combustion is an exothermic process in which heat is released by the system to its surroundings, ΔH is negative.

6.1.5 Standard states and standard enthalpy changes

ΔH varies with conditions, we use standardized ΔH values. These values are calculated when all the substances are in their standard state (condition).

6.1.6 Conditions for Standard Heat of Reaction

Conditions for the standard states are as follows:

1. Standard state for a gas is 1 atm.
2. Standard state for an element or a compound is the most stable physical state at 1 atm. and 25^0C (298 K).
3. Standard state for a substance in aqueous solution is 1M concentration.

Now we will define important enthalpies.

1. Standard Enthalpy of Reaction $\left(\Delta H_r^o\right)$

The enthalpy change in a chemical reaction, when reactants and products are in their standard states and their molar quantities are same as shown by the balanced chemical equation is called standard enthalpy of reaction. Examples are given below:

(i) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\quad \Delta H_r^o = -571.6kJ$

(ii) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\quad \Delta H_r^o = -890.4kJ$

(iii) $2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2Fe_{(s)}$ $\quad \Delta H_r^o = -850kJ$

2. Standard Enthalpy of Formation $\left(\Delta H_f^o\right)$

It is defined as the enthalpy change that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. Standard enthalpies of formation of some compounds are shown in table 6.1.

For writing thermochemical equation for enthalpy of formation, write elements as reactants and 1mole of the compound as product. Show standard states of all the substances. Finally balance the atoms.

Example 6.1

Write thermochemical equation for the formation of H_2O, SO_3 and H_2O_2. Use data given in table 11.1

Solution:

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H_f^o = -285.8\ \text{kJ mole}^{-1}$

(ii) $S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$ $\Delta H_f^o = -395.7\ \text{kJ mole}^{-1}$

(iii) $H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2(l)}$ $\Delta H_f^o = -187.8\ \text{kJ mole}^{-1}$

Standard enthalpies of formation of some substances are shown in table 6.1.

Table 6.1: Standard enthalpies of formation of some compounds in kJ mole^{-1}

$H_2O_{(g)}$	-245.1	$Fe_2O_{3(s)}$	-824.2	$Na^+_{(aq)}$	-240.1
$H_2O_{(l)}$	-285.8	$Fe_2O_{3(s)}$	-824.2	$Na^+_{(aq)}$	-240.1
$H_2O_{2(l)}$	-187.8	$SiO_{2(s)}$	-910.9	$K^+_{(aq)}$	-252.4
$NH_{3(g)}$	-46.1	$CaCO_{3(s)}$	-1207	$Mg^{2+}_{(aq)}$	-466.9
$NH_{3(aq)}$	-80.3	$BaCO_{3(S)}$	-1219	$Ca^{2+}_{(aq)}$	-542.8
$N_2N_{4(l)}$	50.6	$NaOH_{(s)}$	-425.6	$Al^{3+}_{(aq)}$	-524.7
$HF_{(g)}$	-271.1	$KOH_{(s)}$	-424.8	C(s, diamond)	1.9
$HCl_{(g)}$	-92.3	$HONO_{2(l)}$	174.1	$CH_{4(g)}$	-74.8
$HCl_{(aq)}$	167.2	$HONO_{2(aq)}$	-207.4	$C_2H_{2(g)}$	226.7
$HBr_{(g)}$	-36.4	$(HO)_2SO_{2(l)}$	-814.0	$C_2H_{4(g)}$	52.3
$HI_{(g)}$	26.5	$(HO)_2SO_{2(aq)}$	-909.3	$C_2H_{6(g)}$	-84.7
$H_2S_{(g)}$	-20.6	$NH_4Cl_{(s)}$	-314.4	$C_3H_{8(g)}$	-103.9
$CO_{(g)}$	-110.5	$NaCl_{(s)}$	-411.2	$C_4H_{10(g)}$	-126.2
$CO_{2(g)}$	-393.5	$NaBr_{(s)}$	-361.1	$C_6H_{6(l)}$	49.0
$NO_{(g)}$	90.3	$NaI_{(s)}$	-287.8	$C_6H_5CH_{3(l)}$	12.1
$NO_{2(g)}$	33.2	$KCl_{(s)}$	-436.8	$C_8H_{18(l)}$	-249.9
$N_2O_{4(g)}$	9.2	$KBr_{(s)}$	-393.8	$CH_3OH_{(l)}$	-238.7
$SO_{2(g)}$	-296.8	$KI_{(s)}$	327.9	$C_2H_5OH_{(l)}$	-277.7
$SO_{3(g)}$	-395.7	$AgCl_{(s)}$	-127.1	$CH_3CHO_{(l)}$	-192.3
$MgO_{(s)}$	-601.7	$CaCl_{2(s)}$	-795.8	$CH_3COCH_{3(l)}$	-248.1
$CaO_{(s)}$	-635.1	$AlCl_{3(s)}$	-704.2	$CH_3COOH_{(l)}$	-484.5

3. Standard Enthalpy of Combustion $\left(\Delta H^o_c\right)$

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion. Standard enthalpies of combustion of some substances are shown in table 6.2.

Table 6.2: Standard enthalpies of combustion in kJ mole $^{-1}$

$H_{2(g)}$	-285.8	$CH_{4(g)}$	-890.4	$C_6H6_{(l)}$	-3268
$C_{(graphite)}$	-393.5	$C_2H_{6(g)}$	-1560	$C_2H_5OH_{(l)}$	-1367
$C_{(diamond)}$	-395.4	$C_8H_{18(l)}$	-5512	$CH_3CHO_{(l)}$	-1167
$S_{(rhombic)}$	-296.9	$C_2H_{4(g)}$	-1411	$CH_3COOH_{(l)}$	-875
$S_{(monoclinic)}$	-297.2	$C_2H_{2(g)}$	-1300	$C_6H_{12}O_{6(s)}$	-2802

For writing thermochemical equation for enthalpy of combustion, write 1mole of the element or compound and oxygen as reactant. Write oxides of the given element or oxides of elements present in the compound as products. Show standard states of all the substances. Finally, balance the atoms.

Example 6.2

Write thermochemical equation for the combustion of, C, CH_4 and H_2. Use data given in 11.2.

Solution:

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H^o_c = 393.5 \text{ kJ mole}^{-1}$

(ii) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H^o_c = -890.4 \text{ kJ mole}^{-1}$

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H^o_c = -285.8 \text{ kJ mole}^{-1}$

4. Standard Enthalpy of Atomization $\left(\Delta H^o_{at}\right)$

The enthalpy change when one mole of gaseous atoms are formed from its element under standard conditions is called standard enthalpy of atomization. e.g.,

(i) $\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H^o_{at} = +218 \text{ kJ mole}^{-1}$

(ii) $\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ $\Delta H^o_{at} = +121 \text{ kJ mole}^{-1}$

5. Standard Enthalpy of Neutralization $\left(\Delta H^o_n\right)$

It is defined as the amount of heat evolved when one mole of H⁺ ions from an acid combine with one mole of OH⁻ ions from a base to form one mole of water under standard conditions. e.g.,

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H^o_n = -\ 57.4kJ\ mole^{-1}$$

Strong acids and bases ionize completely in their aqueous solutions. Thus, when solutions of NaOH and HCl are mixed together, the only change which occurs is the formation of water. Na⁺ and Cl⁻ ions remain in solution. Thus, heat of neutralization is due to the formation of water from H⁺ and OH⁻ ions. For example,

$$Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)} \quad \Delta H^o_n = -\ 57.4kJ\ mole^{-1}$$

$$\text{or} \quad H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \quad \Delta H^o_n = -\ 57.4kJ\ mole^{-1}$$

6. Standard Enthalpy of Solution $\left(\Delta H^o_{sol}\right)$

It is the enthalpy change when one mole of a substance is dissolved in so much of solvent that further dilution results in no detectable heat change, under standard conditions. e.g.,

$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH^+_{4(aq)} + Cl^-_{(aq)} \quad \Delta H^o_{sol} = +15.1kJmole^{-1}$$

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)} \quad \Delta H^o_{sol} = -75\ kJmole^{-1}$$

Concept Assessment Exercise 6.2

1. Write thermochemical equation form the given information.
   a) Standard enthalpy of formation of benzene (l) is +49.0 kJ mole^{-1}
   b) Standard enthalpy of formation of ethanol (l) is -277.7 kJ mole^{-1}
   c) Standard enthalpy of combustion of acetic acid(l) is -876 kJ mole^{-1}
   d) (d) When ethanol is burned in air -1367 kJ mole^{-1}energy is released at 1 atm. and 25°C.
2. Which of the following equations describe a reaction for which ΔH° is equal to the enthalpy of formation of a compound, ΔH^o_f?
   a) $4\ Al_{(s)} + 2O_{2(g)} \rightarrow 2Al_2O_{3(s)}$
   b) $4\ Al_{(s)} + 3/2O_{2(g)} \rightarrow Al_2O_{3(s)}$
   c) $CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)}$

7. Standard Enthalpy of first Electron Affinity

The energy released when one mole of gaseous atoms gains an electron to form one mole of gaseous ions with a single negative charge, under standard conditions. For example;

$$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)} \quad \Delta H^o_{E.A} = -349\ kJ/mole$$

8. Lattice Energy

The energy released when one mole of an ionic compound(solid) is formed from its constituent gaseous ions is called lattice energy.

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

6.2 BOND ENERGY

When a chemical reaction occurs, old bonds are broken and new bonds are formed. Breaking bonds always requires energy, and forming a bond always releases energy. The energy required when one mole of a particular bond breaks apart to form neutral atoms is called the bond dissociation energy. The amount of energy released when one mole of neutral atoms forms bond is called bond energy. The difference between the bond dissociation energy and the bond energy determines whether the reaction absorbs or releases energy. For any chemical reaction, the enthalpy change is the sum of the bond dissociation energies of the reactants minus the sum of the bond energies of the products.

Example 6.3

We can theoretically calculate bond energy of a bond from the known bond energy data. For example, we can calculate bond energy on H-Cl as follows;

Bond dissociation energy of H_2 = 436 kJ/mol.

Bond dissociation energy of Cl_2= 243kJ/mol.

Bond energy of HCl = ?

Total energy absorbed in bond breaking = Total energy released in bond formation Bond dissociation energy of H-H + Bond dissociation nenergy of Cl-Cl = 2(Bond energy of H-Cl)

$$436 + 242 = 2\ (\text{Bond energy of H-Cl})$$

$$679 = 2(\text{Bond energy of H-Cl})$$

$$\text{Bond energy of H-Cl} = 339\ kJ/mol.$$

Thus theoretically calculated bond energy of HCl = 339kJ/mol. Experimentally determined bond energy of HCl = 431.5 kJ/mol. This is because the theoretical values are averages and do not take into account situations where the bond strength differs from the average. For example, unequal distribution of electron pairs due to differences in electronegativity values. This energy difference also appears as the enthalpy of reaction. For any chemical reaction, the enthalpy change is the sum of bond dissociation energies of the reactants minus the sum of bond energies of products.

$$\Delta H = \Sigma H_{(\text{bonds broken})} - \Sigma H_{(\text{bonds formed})}$$

For the reaction between H_2 and O_2 to produce H_2O.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \quad \Delta H = ?$$

$\Delta H^\circ = 2(\text{ B.D.E of } H_{2(g)}) + \text{B.D.E of } O_{2(g)} - 4(\text{ B.E.of O-Hbonds})$

$= 2(436\text{kJ}) + 493.6\text{kJ} - 4(460\text{ kJ})$

$= 872\text{kJ} + 493.6\text{ kJ} - 1840\text{kJ}$

$= -474.4\text{ kJ}$

Thus the reaction between hydrogen and oxygen to form water is exothermic.

Calculation of bond energy for the enthalpy of reaction

You can calculate the bond energy for the enthalpy of a reaction. For example,

You can calculate the bond energy per mole of methane gas by breaking the C-H bonds as follows:

$$CH_{4(g)} \rightarrow 4H_{(g)} + C_{(s)} \quad \Delta H^\circ = +1662\text{ kJ}$$

In this reaction 4 moles of C-H bonds are broken and 1662 kJ of energy is absorbed.

The bond dissociation energy per mole of CH_4 is +1662 kJ

As 4 mol of C-H bonds are broken.

The average bond energy per mole of C-H bond = +1662 /4

The average bond energy per mole of C-H bond = + 415.5 kJ

6.2.1 Variability in Bond Energies

Some bond energies are relatively well defined and precise, others are approximate and can vary depending on the specific molecules involved and the environment in which the bond occurs.

For simple diatomic molecules such as H_2, O_2, N_2 and Cl_2, binding energies can be considered relatively accurate. This is because these molecules are made up of identical atoms and the bond dissociation energy is the same for every bond in the molecule. For example, the binding energy of an H-H bond in H_2 is approximately 436 kJ/mol.

But in complex molecules or molecules in different environments, binding energies can be more approximate. This is because the bond strength can be affected by factors such as neighbouring atoms, molecular geometry and inductive effect of functional groups.

For example, the C-C bond energy in ethane (C H) can be considered approximate because it depends on the specific isomer (e.g., linear or branched) and the general structure of the molecule. Similarly, the binding energy of a CH bond can vary depending on the chemical environment and the molecule in question.

Some bonds have different strengths in different compounds. For example, the O-H bond is present in various compounds. The bond energy of an OH bond in methanol (CH_3OH) is different from that in water (H_2O) due to differences in molecular structure and chemical environment.

6.3 HEAT AND TEMPERATURE

Heat as a form of energy

When we boil water in a cooking utensil, the lid of the cooking utensil will jump off in the air after being heated for some time. So what causes the lid to jump off? Well, there must be some mechanical energy behind the jump. The mechanical energy that causes the cooking utensil lid to jump off is the heat energy from the burner flame. This example shows that heat is an energy that can be converted into its other forms.

The law of conservation of energy states that energy cannot be produced in any physical or chemical process, but can only be changed from one form to another. Different forms of energy include light energy, mechanical energy, chemical energy, thermal energy, nuclear energy and magnetic energy.

Heat is all the energy produced by the movement of the molecules of a substance. Heat is a form of energy. When a body absorbs heat, it becomes hotter, and when it releases heat, it becomes colder. The impact of heat on a body is indicated by its temperature. Temperature refers to the intensity of heat of a body. Heat is a form of energy and temperature is measure of that energy. So it is measured in the units of energy. SI unit of heat is Joule(J). It is also measured in calories.

Temperature is a measure of the average kinetic energy of the molecules of a substance. It describes the hotness or coldness of a substance or an object. The amount of heat absorbed by a body is directly proportional to the temperature change. SI unit of temperature is Kelvin(K). Temperature is also measured using various scales such as Fahrenheit (^{0}F) and Celsius(^{0}C).

The heat of a substance depends on factors such as particle velocity, size and number of particles. You can understand this difference from the following example. If you fill the jar and the glass completely and measure the temperature of the water in both containers. The water temperature in both containers is the same. But because there are more water molecules in the jar, the water in the jar has more heat or thermal energy.

The amount of heat absorbed (q) by a substance is proportional to the temperature change.

$$q \propto \Delta T$$

$$q = \text{Heat capacity} \times \Delta T$$

Where heat capacity is constant of proportionality.

$$\text{Heat Capacity} = \frac{\text{Heat}}{\Delta T} \qquad \text{------}(1)$$

The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity. It is expressed in Joules per Kelvin.

The amount of heat required to raise the temperature of one gram of a substance by 1Kelvin is called specific heat capacity. It is expressed in Joules per gram per Kelvin.

$$\text{Specific heat capacity (c)} = \frac{\text{Heat}}{\text{mass} \times \Delta T} \quad \text{-------------(2)}$$

$$\text{Heat} = \text{specific heat capacity (c)} \times \text{mass} \times \Delta T$$

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

Example,

Specific heat capacity of Cu = $0.387\ J.g^{-1}K^{-1}$

Molar heat Capacity of Cu = 0.387×63.54

$= 24.59\ Jmole^{-1}K^{-1}$

Knowing specific heat capacity of a substance, its mass and temperature change of substance being heated or cooled, we can determine heat absorb or released.

6.3.1 Measurement of heat of reaction

A device that measures heat flow is called calorimeter. Calorimeters measure the heat released from a system either at constant pressure or at constant volume . Thus there are two types of calorimeters.

Constant Pressure Calorimeter

In constant pressure calorimeter pressure of the system is fixed. For this purpose we need a thermally insulated container with a thermometer and stirrer. For most purposes a coffee cup calorimeter is used.

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

Where, m = mass of reactants

c = specific heat of reaction mixture

ΔT = change in temperature.

This process can be understood by the following example.

Example 6.4

When $50cm^3$ of 1.0M NaOH neutralizes $50cm^3$ of 1.0M HCl at 25°C. The temperature rises from 25°C. to 31.9°C. Calculate the heat of Neutralization. (Specific heat of water = $4.2\ Jg^{-1}K^{-1}$. Density of water=$1\ g.cm^{-3}$)

Solution

We can calculate the amount of heat evolved by the following equation.

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

Volume of NaOH = $50cm^3$

Volume of HCl = $50cm^3$

Total Volume of reaction mixture = $50cm^3 + 50cm^3 = 100cm^3$

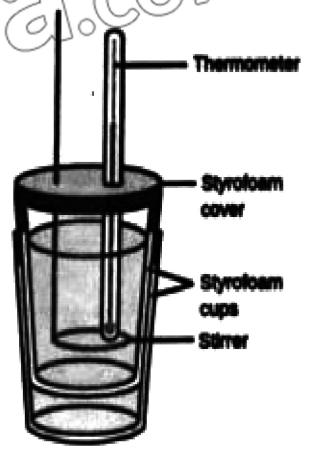

Figure 6.1: Coffee Cup calorimeter

Density of water = $1\ g.cm^{-3}$

Total mass of reaction mixture(m) = $100cm^3 \times 1g.cm^{-3} = 100g$

Raise in temperature ΔT = $31.9^\circ C - 25^\circ C$

= $6.9^\circ C$

or = $6.9K$

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

$q = 100g \times 4.2 J.g^{-1} K^{-1} \times 6.9K$

$q = 2.9 \times 10^3 J$

No. of moles of NaOH = $\frac{M \times \text{Vol of solution } cm^3}{1000}$

= $\frac{1 \times 50}{1000} = 0.05$

Similarly, No of moles of HCl = $\frac{1 \times 50}{1000} = 0.05$

Considering, chemical equation.

$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$

1 mole 1 mole 1 mole

0.05 mole 0.05 mole 0.05 mole

Thus formation of 0.05 moles of water release heat = 2.9×10^3 J

Formation of 1 mole of water will release heat = $\frac{2.9 \times 10^3}{0.05}$

= $5.8 \times 10^4 J\ mole^{-1}$

= $58.0\ kJ\ mole^{-1}$

Since heat is evolved at constant pressure,

$q_p = \Delta H^\circ_n = -58.0\ kJ\ mole^{-1}$

Concept Assessment Exercise 6.3

Experimental data shows that when $87.5\ cm^3$ of a 0.10M HCl solution is mixed with $25.0cm^3$ of 0.35M NaOH in a calorimeter, complete neutralization occurs. The temperature of the calorimeter changes from 25°C to 26.07°C. Use this data to determine heat of neutralization for the reaction. (Ans:-57.78kJ)

6.4 HESS'S LAW

Enthalpy is a state function; therefore, enthalpy change in a chemical reaction in going from some initial state to some final state is independent of the path followed by the reaction. Thus in going from a particular set of reactant to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in many steps. This principle is known as Hess's law.

G.H. Hess stated this law in 1840. **It states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.**

Mathematically $\Sigma\Delta H\ (\text{Cycle}) = 0$

Suppose a reactant A changes into the product B in one step and enthalpy change in this step is ΔH. Now suppose this change takes place in three steps, involving a change from A to C, C to D, and finally D to B as shown below:

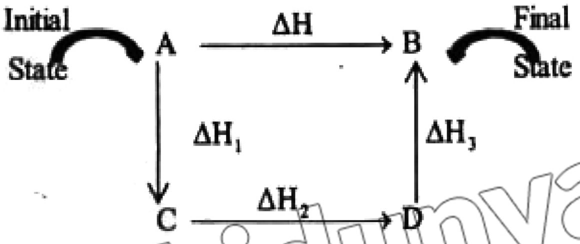

Fig. 6.3

If ΔH_1, ΔH_2 and ΔH_3 are enthalpy changes in these steps, as shown in the figure (6.3). Then according to the Hess's Law. $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Example 6.6

Combustion of C to CO_2 evolves 393.5 KJ of energy.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5\text{kJ}$$

This reaction may takes place in two steps.

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H_1^\circ = -110.52\text{kJ}$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2^\circ = -282.98\text{kJ}$$

Net reaction $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_1^\circ + \Delta H_2^\circ = -393.51\ \text{kJ}$

Thus the enthalpy change in a chemical reaction is independent of the path followed. Fig.6.4 shows energy cycle for this reaction.

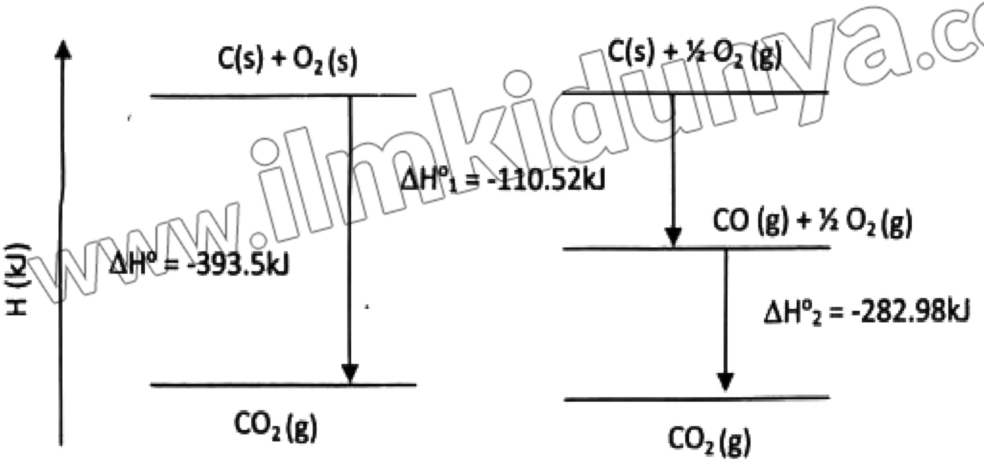

Figure 6.4: Energy cycle for the reaction between C(s) and $O_{2(g)}$ to produce CO_2 (g)

There are many compounds which cannot be prepared directly from their elements. Some of these compounds cannot be decomposed into their constituent elements. e.g. CCl_4. Some elements do not burn completely due to the formation of a protective covering on their surface. Such as, Al, B etc. Thus enthalpies of formation of CCl_4, Al_2O_3, B_2O_3 etc cannot be determined directly by a calorimeter, Hess's law is particularly useful for determining enthalpies of formation of such compounds.

Example 6.7

Enthalpy of formation of methane cannot be measured directly. By the application of Hess's law it can be determined indirectly from the enthalpies of combustion for CH_4, H_2 and C.

(i) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H^\circ = -890.4 \text{kJ mole}^{-1}$

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H^\circ = -285.5 \text{kJ mole}^{-1}$

(iii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H^\circ = -393.5 \text{kJ mole}^{-1}$

(iv) $C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$ $\Delta H^\circ = ?$

To obtain ΔH° for the required reaction we must some how combine equations i, ii, and iii to produce that reaction and add the corresponding ΔH° values. This can be done by focusing on reactants and products of the required reaction. The reactants are $C_{(s)}$ and $2H_{2(g)}$ and the product is $CH_{4(g)}$. How can we obtain the correct equation? Reaction (iii) has $C_{(s)}$ as reactant which is needed in the required equation. Thus equation (iii) will be used as such. Equation (ii) has $H_{2(g)}$ as reactant but the required equation needs $2H_{2(g)}$, thus equation (ii) will be used after multiplying by 2. Equation (i) has $CH_{4(g)}$ as reactant, but this is needed as product in the required equation. Thus reaction (i) must be reversed and the sign of ΔH°is changed accordingly. Adding the equations and deleting the species that occur on both sides we get.

$$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)} \quad \Delta H^o = +890.4\ kJ$$

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \quad \Delta H^o = -571.6\ kJ$$

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

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \quad \Delta H^o = -74.6\ kJ\ mole^{-1}$$

This gives the required equation and its enthalpy.

6.4.1 Enthalpies of Reactions from Enthalpies of Formation

It is often convenient to calculate the ΔH^o values for a reaction from values of the standard enthalpies of formation, ΔH_f^o of the reactants and products. For a given reaction:

$$\Delta H^o = \sum coeff \Delta H_f^o \text{ (products)} - \sum Coeff \Delta H_f^o \text{ (reactants)}$$

Where coeff = Coefficient

Elements in their standard states are not included in the ΔH^o reaction calculation i.e. ΔH_f^o for an element in its standard state is zero. When balanced equation for a reaction is multiplied by an integer, the value of ΔH^o for that reaction should be multiplied by the same integer.

Example 6.8

Calculate ΔH^o for the following reaction, which take place when gasoline burns in internal combustion engines. Where the values of ΔH_f^o are -269kJ, 0 kJ, -393.5 kJ and -285 kJ for $C_8H_{18(l)}$, $O_{2(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ respectively

$$2C_8H_{18(l)} + 25O_{2(g)} \longrightarrow 16CO_{2(g)} + 18H_2O_{(l)}$$

Solution:

$$\Delta H^o_{reaction} = \sum coeff_p \Delta H_f^o \text{ (products)} - \sum coeff_r \Delta H_f^o \text{ (reactants)}$$

$$= [16 \times \Delta H_f^o \text{ for } CO_{2(g)} + 18 \times \Delta H_f^o \text{ for } H_2O_{(l)}] -$$

$$[2 \times \Delta H_f^o \text{ for } C_8H_{18(l)} + 25 \times \Delta H_f^o \text{ for } O_{2(g)}]$$

$$= 16(-393.5\ kJ) + 18\ (-285.8\ kJ) - 2\ (-269\ kJ) - 25(0)$$

$$= -6296\ kJ - 5144.4\ kJ + 538\ kJ + 0$$

$$= -11440.4\ kJ + 538\ kJ$$

$$= -10902.4\ kJ$$

$$= -1.09 \times 10^4\ kJ$$

Example 6.9

Calculate $\Delta H^\circ_{reaction}$ for the following reaction. This reaction takes place in the tissues of the living organisms. Where the values of ΔH°_f are -1258.18 kJ, 0 kJ, -393.5 kJ and -285 kJ for $C_6H_{12}O_{6(s)}$, $O_{2(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ respectively

Solution:

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)} \qquad \Delta H^\circ_{reaction} = ?$$

$$\Delta H^\circ_{reaction} = \sum Coeff_p \Delta H^\circ_f (products) - \sum coeff_r (\Delta H^\circ_f (reactants)$$

$$\Delta H^\circ_{reaction} = \left[6\Delta H^\circ_f CO_{2(g)} + 6\Delta H^\circ_f (H_2O_{(l)})\right] - [\Delta H^\circ_f\ C_6H_{12}O_6 + 6\Delta H^\circ_f O_{2(g)}]$$

$$= [6(-393.5kJ)+6(-285.8kJ)] - [-1258.18kJ + 6\times 0]$$

$$= [-2361.0kJ - 1714.8kJ] - [-1258.18kJ]$$

$$= -4075.8kJ + 1258.18kJ$$

$$= -2817.62kJ$$

This means one mole (180g) of glucose provides 2818.82 kJ energy. Therefore energy provided by one gram of glucose will be $\frac{2817.62\,kJ\,mole^{-1}}{180\,g\,mole^{-1}} = 15.65\ kJ$.

6.4.2 Calculation of Enthalpy of Combustion

The enthalpy of combustion, ΔH°_c is the heat evolved when 1 mol of a substance burns completely in oxygen at standard conditions. It can be calculated be calculated by the following general formula.

$$\Delta H^\circ_c = \sum coeff_p \Delta H^\circ_f (products) - \sum coeff_r \Delta H^\circ_f (reactants)$$

Example 6.10:

Calculate the ΔH°_c for ethyne (C_2H_2). The standard enthalpies of formation of $C_2H_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(l)}$ are +226.73kJ/mol, -393.5 kJ/mol, -285.8 kJ/mol respectively.

Solution:

$$C_2H_{2(g)} + \frac{5}{2} O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$$

$$\Delta H^\circ_c = \sum coeff_p \Delta H^\circ_f (products) - \sum coeff_r \Delta H^\circ_f (reactants)$$

$$\Delta H^\circ_c = [\,2(-393.5) + 2(-285.8) - [\,(+226.73) + \tfrac{5}{2}(0)]$$

$= [-1082.8] - [+226.73]$

$= -1082.8 - 226.73$

$= -1309.53$ kJ/mol

The enthalpy of combustion of acetylene is -1309.53 kJ/mol.

6.5 BORN HABER CYCLE

This is special application of Hess's law to binary ionic compounds. It helps us to calculate lattice energies of binary ionic compounds (M^+X^-).

The change in energy that takes place when separated gaseous ions are packed together to form one mole of an ionic solid is called lattice energy.

$$M^+_{(g)} + X^-_{(g)} \longrightarrow MX_{(s)}$$

- Lattice energy cannot be determined directly. However, it can be determined indirectly by means of Born Haber cycle. Consider the case of NaCl. Its standard enthalpy of formation (ΔH^o_f) is -411kJ mole^{-1}. The formation reaction can be considered as taking place in several steps, one of which is the formation of lattice. This complete sequence of reaction is called a cycle (Fig.6.5)

Step-I: Sublimation of solid sodium. The energy of sublimation for Na(s) is 108 kJ mole^1

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H^o_s = +108 \text{ kJ/mole}$$

Step-II: Ionization of $Na_{(g)}$ atom to form $Na^+_{(g)}$ ion. This process corresponds to the first ionization energy for Na.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \qquad \Delta H^o_i = +496 \text{ kJ/mole}$$

Step-III: Dissociation of Cl_2 molecules. We need to form one mole of Cl atoms by breaking the Cl-Cl bond in $\frac{1}{2}$ mole of Cl_2 molecules. The energy required to break this bond is 121 kJ/mole and is known as enthalpy of atomization for Cl_2.

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H^o_{at} = +121 \text{ kJ/mole}$$

All these three steps are endothermic and are drawn upward in the figure (6.5).

Step-IV: Formation of $Cl^-_{(g)}$ ion. Energy is released in this step equal to the electron affinity for Cl.

$$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)} \quad \Delta H^o_{E.A} = -349 \text{ kJ/mole}$$

Step-V: Formation of solid NaCl from the gaseous Na^+ and Cl^- ions. This corresponds to the lattice energy (ΔH_l) for $NaCl_{(s)}$ which is to be calculated.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H^\circ_l = ?$$

Since the sum of these five steps gives the overall reaction and the sum of the individual energy changes give the overall energy change. Thus

$$\Delta H^\circ_f = \Delta H^\circ_s + \Delta H^\circ_{IE} + \Delta H^\circ_{at} + \Delta H^\circ_{EA} + \Delta H^\circ_l$$

$$-411kJ = +108kJ + 496kJ + 121kJ + (-349kJ) + \Delta H^\circ_l$$

$$\Delta H^\circ_l = -411kJ - (108\ kJ + 4961kJ + 121kJ - 349kJ)$$

$$\Delta H^\circ_l = -787kJ\ mole^{-1}$$

Thus lattice energy of NaCl is 787 kJ/mole.

$Na_{(s)} \longrightarrow Na_{(g)}$ 1st Step

$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^-$ 2nd Step

$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}$ 3rd Step

$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)}$ 4th Step

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$ 5th Step

$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow NaCl_{(s)}$ Net reaction

Electron affinities of atoms are usually calculated from Born-Haber cycle because it is difficult to determine electron affinities directly.

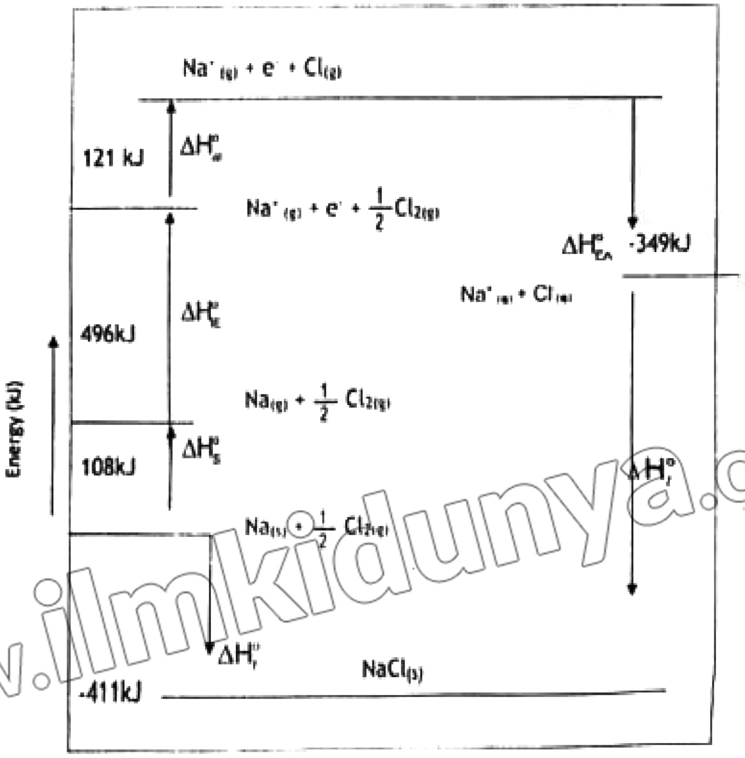

Figure 6.5: Born-Haber Cycle for the formation of NaCl (s)

Concept Assessment Exercise 6.5

Draw a complete Born Haber Cycle for the formation of $MgO_{(s)}$. Calculate the lattice energy for MgO from the following data.

Standard enthalpy of formation of MgO = –602 $kJmole^{-1}$

Standard enthalpy of sublimation of Mg = 150 $kJmole^{-1}$

Ionization energy of $Mg_{(g)}$ to form $Mg^{2+}_{(g)}$ = 2180 kJ $mole^{-1}$

Standard enthalpy of atomization of O_2 = 247 kJ $mole^{-1}$

Electron affinity of $O_{(g)}$ to form $O^{1-}_{(g)}$ = –141 kJ $mole^{-1}$

Electron affinity of $O^{1-}_{(g)}$ to form $O^{2-}_{(g)}$ = 878 kJ $mole^{-1}$

(Ans: -3916kJ)

6.5.1 Factors Affecting Lattice Energy

The magnitude of lattice energy is influenced by the charge density of an ion. The charge density is defined as the ratio of ionic charge to the ionic radius of an ion.

Charge density = Ionic charge/ ionic radius

There are two factors that have significant effect on lattice energy

1. Ionic Charge

The magnitude of the ionic charge is important in determining the lattice energy. As the magnitude of the ionic charge increases, the lattice energy also increases. The reason is that the higher charges have strong electrostatic attractions, and they release higher energy when they come together to form an ionic lattice. For example, MgO has a higher lattice than NaCl. This is because Mg^{+2} and O^{-2} ions have a larger magnitude of charge as compared to the Na^{+1} and Cl^{-1} ions.

2. Ionic Radius

Ionic radii also affect the lattice energy. As the ionic radius increases, the lattice energy decreases. The reason is, larger ions have higher electron-electron repulsions. This keeps opposite ions at a greater distance, leading to a weaker electrostatic attraction between the ions. Larger ions need less energy to separate them. This results in lower lattice energy. For example, lithium fluoride(LiF) and potassium fluoride(KF) have the same ionic charge, but different ionic radii. Li^+ ion is smaller than K^+ ion, due to this LiF has higher electrostatic attraction between its ions as compared to KF. So, LiF has higher lattice energy than KF.

Concept Assessment Exercise 6.6

Which of the following compounds is expected to have higher lattice energy? Why?

a. LiF or NaF
b. NaCl or $MgCl_2$

6.5.2 Role of Hydration in the Dissolving Process

The energy change of solution formation depends on three types of interactions between solute-solute, solvent-solvent, and solute-solvent particles. When a solution is formed, the interactions between solute particles are broken. At the same time, the solvent molecules also move apart to accommodate the solute particles. Because it takes energy to break the interaction. Therefore, both processes are endothermic. At the same time, interactions between the solute and solvent particles occur, i.e., hydration occurs. Solvent molecules surround the solute particles on all sides. Energy is released in these interactions, so it is exothermic. Thus, the strength of these two types of interactions determines whether the dissolution process is endothermic or exothermic.

Therefore, when a solute dissolves in water, the attractive force of the solute particles must be overcome to break the solute particles out of the solid lattice. A strong force must bind these separate solute particles to the water molecules in the solution. Therefore, the heat of solution measures the net flow of energy that occurs when a substance dissolves. The energy required to break the solute particles is equal to the lattice energy ($\Delta H_{lattice}$) of the solute. On the other hand, the energy released when solute particles bind to water molecules in solution is equal to the enthalpy of hydration (ΔH_{hyd}). For other solvents, this energy is called the heat of dissolution. The enthalpy of solution includes both the energy required to push the solvent molecules apart and the energy released when they surround the solvate particles. So, enthalpy of solution $\Delta H_{solutoin}$ is the difference in $\Delta H_{lattice}$ and ΔH_{hyd}.

$$\Delta H_{solutoin} = \Delta H_{lattice} - \Delta H_{hyd}$$

When $\Delta H_{solution}$ is very large, the solute is unlikely to be soluble. But if $\Delta H_{solution}$ is moderately positive, then solute dissolves. For example, when ammonium nitrate dissolves in water 25.7 kJmole^{-1}energy is absorbed and the flask becomes cold. This is because crystal binds NH_4^+ and NO_3^- ions more tightly than the solution.

$$NH_4NO_{3(s)} + xH_2O_{(l)} \longrightarrow NH^+_{4(aq)} + NO^-_{3(aq)} \qquad \Delta H_{solution} = 25.7\ kJmole^{-1}$$

On the other hand, if solvent binds solute particles more tightly than the crystal, energy is released as the solute dissolves and we have an exothermic solution process.

For example, when NaOH dissolves in water 44.5 kJmole^{-1}energy is released and the flask becomes hot

$$NaOH_{(s)} + xH_2O_{(l)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)} \qquad \Delta H_{soln} = -44.5\ kJmole^{-1}$$

Thus solution process can be endothermic or exothermic depending upon the difference in the lattice energy for solute and heat of hydration for solute particles. Other examples are given below

$$CaCl_{2(s)} + H_2O_{(l)} \longrightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \qquad \Delta H_{soln} = -83.0\ kJmole^{-1}$$

$$MgSO_{4(s)} + xH_2O_{(l)} \longrightarrow Mg^{2+}_{(aq)} + SO^{2-}_{4(aq)} \qquad \Delta H_{soln} = -91.2\ kJmole^{-1}$$

The values of standard enthalpies of solution of some ionic solids in water are given in table (6.3)

Table 6.3: Enthalpies of Solutions of some ionic solids.

Substance	Enthalpy of Solution ($kJ\ mole^{-1}$)
LiCl	-37.0
NaCl	+2.98
KCl	+17.2
KI	+20.3
NH_4NO_3	+25.7
$AlCl_3$	-321.0

6.5.3 Energy cycle involving enthalpy of solution, lattice energy and enthalpy of hydration

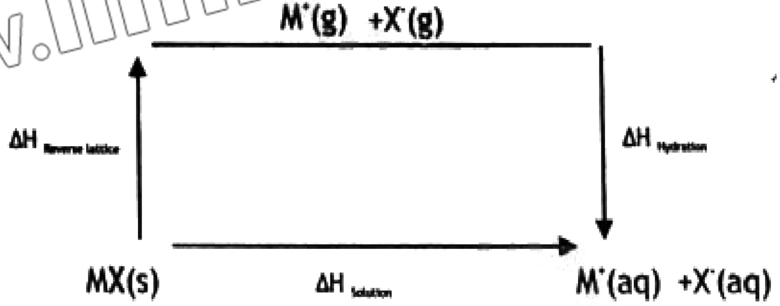

Figure 6.6: Energy cycle involving enthalpy of solution, lattice energy and enthalpy of hydration

According to Hess`s Law

$$\Delta H_{\text{Solution}} = \Delta H_{\text{Reverse lattice}} + \Delta H_{\text{Hydration}}$$

ΔH Hydration is determined by adding the ΔH Hydration of both cations and anions. Note that ΔH Reverse lattice has the same magnitude as ΔH lattice but opposite sign.

Concept Assessment Exercise 6.7

Constructan energy cycle and energy level diagram to calculate the ΔH Solution for NaCl and calculate its enthalpy of solution from the following data,

ΔH lattice = -786kJ/mol

ΔH Hydration = -783 kJ/mol

6.5.4 Factors Affecting Enthalpy of Hydration

The magnitude of enthalpy of hydration is influenced by the charge density of an ion. The charge density is defined as the ratio ionic charge to the ionic radius of an ion.

Charge density = Ionic charge/ ionic radius

Therefore, two factors affect enthalpy of hydration.

1. Ionic charge

The ionic charge of an ion affects the electrostatic interaction between the ion and water molecules. Ions with a higher charge exert stronger attractive forces on water molecules through ion-dipole interactions, resulting in a higher enthalpy of hydration. Therefore, as the ionic charge increases, the hydration enthalpy also increases and the hydration process becomes exothermic. For example, the hydration enthalpy of MgO is more exothermic than that of NaCl. These compounds are ionic compounds and consist of Mg^{2+}, O^{2-} and Na 1, Cl^{1-} ions, respectively. Both Mg^{2+} and O^{2-} have a greater charge than Na^{1+} and Cl^{1-} so the hydration enthalpy of MgO is more exothermic than NaCl.

2. 2.Ionic radius

The size of the ion also affects the enthalpy of hydration. Smaller ions have a higher charge density, exert a stronger attraction on water molecules. Therefore, more energy is released when they hydrate and the enthalpy of hydration becomes exothermic. On the other hand, larger ions spread out the charge distribution and exert a weaker attractive force on water molecules. Thus, less energy is released when they hydrate. For example, the hydration enthalpy of $MgSO_4$ is greater than that of $CaSO_4$. Sulphate ions are common in these compounds, their hydration enthalpy difference must be due to Mg^{2+} and Ca^{2+} ions. Both Mg and Ca belong to group 2 of the periodic table. Mg is in the group below Ca, so the Mg^{2+} ion is smaller than the Ca^{2+} ion. Thus, the attraction of water molecules to Mg^{2+} ions is stronger than to Ca^{2+} ions. As a result, the hydration enthalpy of $MgSO_4$ is more exothermic than that of $CaSO_4$.

6.5.5 Factors Affecting Electron Affinity

Three factors effect electron affinity.

1. Nuclear charge 2. Atomic size 3. Shielding effect

For detail see section 10.5.1.

Concept Assessment Exercise 6.8

Which has higher enthalpy of hydration? Justify your answer.

a. LiF or NaF

b. KNO_3 or $NaNO_3$

6.6 ENTROPY

Which state of matter has more disorder, random order, and minimum particle energy, solid or gas? The degree of disorder and randomness of a system is called its entropy. It is marked with the symbol "S". As a system moves from a more ordered state to a less ordered state, the entropy of the system tends to increase. Melting ice gives us a great example of entropy. In ice, the individual molecules have a fixed and ordered arrangement and minimum energy. As the ice melts, the energy of its molecules increases, they gain more freedom of movement and become more disordered. As a result, the entropy of the system increases. On the other hand, when water vapour condenses into a liquid, the molecules become more ordered and less energetic. Therefore, the entropy of the system decreases.

The entropy change of the system is denoted by ΔS.

- If the entropy of the system increases, this is represented as a positive change $\Delta S > 0$
- When the entropy of a system decreases, it is represented as a negative change $\Delta S < 0$
- In general, when the temperature of a system increases, its entropy also increases, its $\Delta S > 0$.
- As the temperature of the system decreases, its $\Delta S < 0$.

6.6.1 Calculation of The Entropy Change

The entropy change for a chemical reaction can be calculated by the following equation.

$$\Delta S^0 = \Sigma S^0_{products} - \Sigma S^0_{reactants}$$

Suppose we want to calculate ΔS^0 for the following reaction.

$$A \quad + \quad 2B \quad \rightarrow \quad C$$

S^0 (A) = 40kJ/mol.

S^0 (B) = 50kJ/mol.

S^0 (C) = 100kJ/mol.

Solution

$$\Delta S^0 = \Sigma S^0_{\text{products}} - \Sigma S^0_{\text{products}}$$

$$= [1(100)] - [1(40) + 2(50)]$$

$$= 100 - [\ 40 + 100]$$

$$= - 40\text{kJ/mol.}$$

As the number of gaseous molecules in a chemical reaction increases the entropy also increases.

Concept Assessment Exercise 6.9

For which of the following reactions ΔS^0 is positive or negative ?

a) $CO_{2(g)} \quad \rightarrow \quad CO_{2(s)}$

b) $2H_{2(g)} + O_{2(g)} \quad \rightarrow \quad 2H_2O_{(l)}$

c) $H_2O_{(l)} \quad \rightarrow \quad H_2O_{(g)}$

6.7 GIBBS FREE ENERGY

Gibbs free energy is a measure of amount of a useable energy of a system at constant temperature and pressure. It is defined as the enthalpy of a system minus the product of its temperature and entropy. Gibbs free energy is also known as "Available energy". It is denoted by symbol G, after the name of its discoverer, American scientist Josiah Willard Gibbs in 1876.

$$G = H - TS$$

Where G = Gibbs free energy

H = Enthalpy of reaction

S = Entropy

Gibbs free energy is a state function, it does not depend on the path followed by a reaction. Therefore, change in Gibbs free energy is given by;

$$\Delta G^\circ = \Delta H^\circ - \Delta(TS)$$

When the reaction is carried out at constant temperature

$$\Delta T = 0$$

Therefore

$$\Delta G^\circ = \Delta H^\circ - \Delta S^0$$

This equation is called as Gibbs-Helmholtz equation. ΔG° is particularly useful in determining the spontaneity and equilibrium state of a chemical reaction.

The sign and magnitude of ΔG° indicate whether the process is spontaneous or at equilibrium. There are three possibilities.

- If $\Delta G^\circ < 0$ or negative, the process is spontaneous in the forward direction. This also means that the system releases energy (exothermic) and tends to move to a lower energy state.
- If $\Delta G^0 >$ is positive, the process is non-spontaneous in the forward direction and requires energy (endothermic).
- If $\Delta G^0 = 0$, the system is in equilibrium. Gibbs free energy is also useful for understanding phase transitions, such as from liquid to solid or gas and vice versa. Consider, for example, the melting of ice

$$H_2O_{(s)} \longrightarrow H_2O_{(l)}$$

At the melting point, $\Delta G^0 = 0$, so the solid and liquid phases are in equilibrium. Below the melting point, ΔG^0 is negative, indicating that the solid phase is more ordered. Instead, above the melting point, ΔG^0 is positive, indicating that the liquid phase is more disordered.

Enthalpy and Calorie Contents of Food

The amount of energy in a food or drink is measured in calories. Calories in food refer to the amount of energy stored in food, which is released through the metabolic processes in our body. The enthalpy change associated with these processes corresponds to the amount of energy released or absorbed during the process of digestion and metabolism. The energy content of food is measured in Kilocalories and is often just calories. 1 Kilocalorie(kcal) is approximately equivalent to 4.184 Kilojoules(kJ). This conversion factor relates the energy released during a chemical reaction to the calorie content of food.

Key Points

- The branch of chemistry which deals with the heat or thermal energy changes in chemical reactions is called thermochemistry.
- A chemical reaction that proceeds with the evolution of heat is called an exothermic reaction.
- A chemical reaction that proceeds with the absorption of heat is called an endothermic reaction.
- The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and product are same as shown in a chemical reaction is called heat of reaction.
- The study of all types of energy changes associated with chemical and physical changes is known as thermodynamics.
- The condition of a system when various properties like temperature, pressure, volume, number of moles etc of system have definite values is called state of the system.
- The properties that are determined by the state of the system regardless of how that condition was achieved are called state functions.
- The sum of all kinds of energies of the particles of the system is called as internal energy.
- Thus, enthalpy of a substance is defined as the system's internal energy plus the product of its pressure and volume ($H = E + PV$).
- The amount of heat required to raise the temperature of given amount of a substance by 1Kelvin is called heat capacity.
- A device that measures heat flow is called calorimeter.
- Hess's Law states that the enthalpy change in a chemical reaction is same whether the reaction takes place in a single step or in several steps.

References for Further information:

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- Steven S. Zumdahl, Chemistry
- Olmsted Williams, Chemistry, The Molecular Science
- Bonder Pardue, Chemistry, An experimental Science
- Darrell D. Ebbing, R.A.D Wentworth, Introductory Chemistry.
- Raymond Chang, Essential Chemistry
- Graham Hill and John Holman, Chemistry in context

Exercise

1. Choose the Correct Answer

(i) Which of the following substances have zero value for their standard enthalpy of formation?

(a) O_3 (b) H_2O

(c) ZnO (d) None of these.

(ii) Calorie is equivalent to;

(a) 4.18J (b) 4.18kJ

(c) 0.418J (d) 0.418kJ.

(iii) Enthalpy of neutralization of all the strong acids and strong basis has the same value due to;

(a) The formation of salt and water

(b) The formation of salt

(c) The complete ionization of acids and bases

(d) The combination of H^+ and OH^- ions

(iv) Total heat content of a system is called;

(a) Enthalpy (b) Internal energy

(c) Heat (d) State function

(v) Heat of ________ of a substance is always negative.

(a) Formation (b) Combustion

(c) Decomposition (d) Solution

(vi) A balloon filled with oxygen is placed in a freezer. Identify system;

(a) Balloon (b) Oxygen

(c) Freezer (d) All of these

(vii) A bomb calorimeter is used in ________ calorimetry.

(a) Constant volume (b) Constant pressure

(c) Both a and b (d) Constant temperature

(viii) Born Haber cycle is used to determine lattice energies of;

(a) Molecular solids (b) Ionic solids

(c) Covalent solids (d) Metallic solids

(ix) Enthalpy of combustion for C is -393.5 kJmole^{-1}

$C_{(s)} + O_2(g) \rightarrow CO_{2(g)}$ $\Delta H^{\circ}_{Combustion}$ = -393.5 kJmole^{-1}

Enthalpy of formation of CO_2 would be;

(a) +393.5 kJ (b) -393.5 kJ

(c) Zero (d) Cannot be predicted form the given equation.

(x) Which of the following is not a state function of a system?

(a) Thermal energy at constant pressure

(b) Enthalpy (c) Internal energy

(d) Work done

(xi) For writing a thermochemical equation for enthalpy of combustion of an element requires;

(a) 1 mole of element as reactant

(b) 1 mole of oxide of element as product

(c) Standard states of all the substances

(d) Balanced equation of 1 mole of element

1. a 2. a, b 3. a, c, d 4. a, b, c, d

2. Name and define units of thermal energy

3. Define the terms system, surrounding, boundary, state function, heat capacity, internal energy, enthalpy of a substance.

4. Classify reactions as exothermic or endothermic.

5. Define bond dissociation energy.

6. When ethanol burns in oxygen, carbon dioxide and water are formed.

(a) Write the equation which describes this reaction.

(b) Using the following data, calculate the enthalpy of combustion for ethanol C_2H_5OH.

ΔH°_f for ethanol(l) = -277.0 kJmole^{-1}

ΔH°_f $CO_{2(g)}$ = -393.5 kJ mole^{-1}, ΔH°_f water$_{(l)}$ = -285.8kJmole^{-1}

7. Calculate from the data in table 11.1 and 11.2, the enthalpy changes of the following reaction at standard conditions.

$C_6H_{6(l)} \longrightarrow 6C_{(s)} + 3H_{2(g)}$ (Ans: -49.6 kJ/mole)

8. The heat of combustion of liquid benzene, C_6H_6 to form H_2O and CO_2 at 1 atm and 25°C is -3268 kJmole^{-1} of benzene. What is the heat of formation of liquid benzene under these conditions? (Ans: +49.6 kJ/mole).

10. Camphor ($C_{10}H_{16}O$) has a heat of combustion of 5903.6 kJ/mole. A sample of camphor having mass of 0.1204g is burned in a bomb calorimeter. The temperature increases by 2.28°C. Calculate heat capacity of the calorimeter. (Ans: 2.04531kJK^{-1})

11. In a coffee-cup calorimeter 100cm^3 of 1.0M HCl and 100 cm^3 of 1.0M NaOH are mixed at 24.6°C raised temperature by 6.9°C. Calculate the enthalpy of neutralization of HCl by NaOH from the given data. Heat capacity of water is 4.18 J/gK. (Ans: -57.684 kJ/mole).

12. Calculate ΔH° for the reaction

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

from the following data

$$S_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)} \qquad \Delta H^\circ = -395.2\,kJ$$

$$2SO_{2(g)}O_{2(g)} \longrightarrow 2SO_{3(g)} \qquad \Delta H^\circ = -198.2\,kJ$$

13. An aluminium frying pan weighs 745g is heated on a stove from 25°C to 205°C. What is q for the frying pan? C_P for Al is 24.35 Jmole^{-1}K^{-1} (Ans: 120938.3 J)

14. Write the balanced equation for the formation reaction of each of the following substances

(a) C_4H_9OH (Butanol) (b) Rust, Fe_3O_4 (c) Acetic acid CH_3CO_2H (d) Urea $(NH_2)_2$ CO

15. The human body burns glucose for energy. Burning 1.0g of glucose produces 15.65 kJ of heat.

(a) Write the balanced equation for the combustion of glucose.

(b) Determine the molar heat of combustion of glucose. (Ans: -2817kJ mole^{-1})

(c) Heats of combustions of C and H_2 are -393.5kJmole^{-1}and -285.8kJmolre^{-1} respectively. Determine the heat of formation of glucose. (Ans: -1258.8 kJ/mole)

16. The standard combustion enthalpies of carbon, hydrogen and acetic acid are -393.5 kJ mole$^{'}$, -285.8kJmole^{-1} and -875 kJmole^{-1} respectively. Deduce the value of standard enthalpy of formation of acetic acid, CH_3COOH. (Ans: -483.6 kJ/mole)

17. Is the conversion of magnetite, Fe_3O_4 to hematite, Fe_2O_3 by oxygen is endothermic or exothermic? Justify your answer.

$$3Fe(s) + 2O_{2(g)} \longrightarrow Fe_3O_{4(s)} \quad \Delta H^\circ = -1118\,kJ$$

$$2Fe_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow Fe_2O_{3(s)} \quad \Delta H^\circ = -824.2\,kJ$$

18. Calculate ΔH for the conversion of graphite to diamond. Heats of combustions of graphite and diamond measured at 25°C and 1 atm pressure are -393.5 kJ and -395.4 kJ respectively.

(Ans: +1.9 kJ/mole)

19. Develop a hypothetical reaction and calculate the Gibbs free energy. Discuss conditions under which reaction wood be spontaneous or non-spontaneous.

20. Arrange the following compounds in order of increasing entropy. Justify your order.

CH_3OH (s), CH_3OH (g), CH_3OH (l)

21. Strontium fluoride is an ionic solid. It dissolves in water and can be used as an optical coating for lenses.

a. Draw Born-Haber cycle for the enthalpy change of solution of SrF_2(s).

b. Label each enthalpy change.

c. Calculate the enthalpy change of solution of SrF_2, using the following data.

Enthalpy Change	ΔH°, kJ mol^{-1}
Lattice energy of SrF_2	-2492
Enthalpy of hydration for Sr^{2+} ion	-1480
Enthalpy of hydration for F^{-1} ion	-506

d. Write the names of factors the affect enthalpy of hydration.

e. Differentiate enthalpy of hydration from lattice energy.

Project:

Research and review the fundamental concepts of enthalpy, entropy, and Gibbs free energy.