Thermochemistry

Major Concepts

Learning Outcomes

The students will be able to:

- Define thermodynamics. (Remembering)
- Classify reactions as exothermic or endothermic. (Understanding)
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance. (Remembering)
- Name and define the units of thermal energy. (Remembering)
- Relate a change in enthalpy to the heat of reaction or heat of combustion of a reaction. (Applying)
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure. (Applying)
- Define bond dissociation energy. (Remembering)
- Use the experimental data to calculate the heat of reaction using a calorimeter. (Applying)
- Specify conditions for the standard heat of reaction. (Applying)
- Apply Hess's Law to construct simple energy cycles. (Understanding)
- Describe how heat of combustion can be used to estimate the energy available from foods. (Analyzing)
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle) (Applying)

Introduction

The branch of chemistry which deals with heat changes during a chemical reaction is called thermochemistry.

The ability or capacity of a body to do work is called energy. There are two main types of energy; that is potential energy, and the kinetic energy.

The energy of an object due to its position relative to other objects or stored in a molecule due to its chemical bonds is called potential energy. The water held behind a dam has potential energy because of its height. The potential energy of water increases when the level (position) of water in the dam increases and the potential energy of water decreases when the level (position) of water decreases. This water has no kinetic energy because it is not moving.

The energy of a system due to its motion is called kinetic energy. All the moving objects have kinetic energy. The magnitude of the kinetic energy of a body depends on its mass and velocity. The greater the velocity of objects, the higher the kinetic energy or/and the heavier the objects, the higher the kinetic energy. When water is allowed to fall over the dam, its potential energy is converted into kinetic energy. The kinetic energy of falling water increases when the speed of flow of water increases. Kinetic energy of the given mass of water is directly proportional to the square of its speed.

The SI unit of energy and heat is joule which is defined as: the amount of energy expended when a force of one Newton moves an object (body) of 1kg through one meter in the direction of force. Joule (1818-1889) was a British scientist who probed work and heat. Joule is a small unit of energy; we therefore, use the unit kilojoule for energy (1kJ = 1000J). The non-SI unit of energy and heat which is used in large scale is calorie. It is denoted by cal and is defined as the amount of energy required to raise the temperature of one gram of water from 14.5°C to 15.5°C (1kcal = 1000cal).
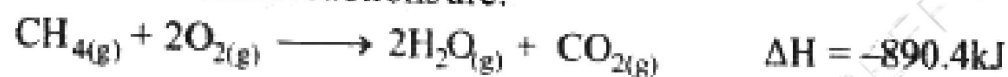
Energy is very important for us on the earth. For example, the food we eat provides the energy in the form of heat to regulate our body temperature and carry out all other bodily functions. The burning of logs, coal and natural gas provides energy in the form of heat to warm our homes. The burning of gasoline and diesel in the engine of automobiles provide energy to run engines. The energy released by the burning of fuel is used to generate electricity which in turn is used to light bulbs, run computers, refrigerators and other appliances. The main source of energy is sun and after that a large amount of energy comes from chemical reactions.

The transfer of energy between two objects due to difference in temperature is called heat. Heat flows from a hot body to cold body until both are at the same

temperature. Let us understand how energy is transferred from one piece of matter to another. When a red hot iron bar is placed in cold water, the temperature of the water increases, because the energy in the form of heat flows from iron bar (hot body) to water. On the other hand, the temperature of hot iron bar decreases, because the energy in the form of heat flows away from it to surrounding (water). This process of transferring of heat is continued till the temperature of the iron bar becomes equal to water.

11.1 Energy in Chemical Reaction

Chemical reactions may either be exothermic or endothermic. Those reactions or processes in which heat is evolved (from system to surrounding) are called exothermic reactions or processes (Greek: $ex\bar{o}$ = outside; hence heat flows out). The burning of gasoline, coal, and wood are the examples of exothermic reactions. The other examples of exothermic processes are freezing, condensation, and deposition. Some of the exothermic reactions are:
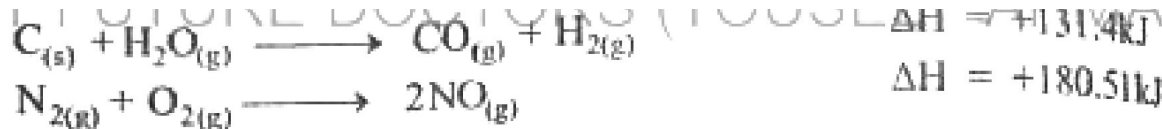
$$CH_{4(g)} + 2O_{2(g)} \longrightarrow 2H_2O_{(g)} + CO_{2(g)} \qquad \Delta H = -890.4 kJ$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.51 kJ$$

Amount of heat released is indicated by ΔH with negative sign because heat flows from system to surroundings. Majority of reactions which take place at ordinary temperature are exothermic.

During chemical reactions old bonds are broken and new bonds are formed. Bond breakage is an endothermic process while bond formation is an exothermic process. If the energy needed to break old bonds in the reactants is less than the energy evolved by new bond formation in the products, then the reaction is exothermic. In this case some of the potential energy is converted into thermal energy. The potential energy of the products is less than reactants, that is why, the products are more stable than reactants; that is, the bond in the products are more stronger than those of the reactants.

> **Keep in mind**
>
> A process that is endothermic in forward direction is exothermic in reverse direction, that is, evaporation is an endothermic process while condensation, the reverse of evaporation, is an exothermic process.

Those reactions or processes in which heat is absorbed (from surrounding to system) are called endothermic reactions or processes (Greek: **endon** = within; hence, heat flows in). The process of photosynthesis in plants is the example of endothermic reaction. The other examples of endothermic processes are melting, evaporation, and sublimation. Some of the endothermic reactions are:

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

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \qquad \Delta H = +180.51kJ$$

Amount of heat absorbed is indicated by ΔH with positive sign, because heat flows from surrounding to system.

If the energy needed to break old bonds in the reactants is greater than the energy evolved by new bond formation in the products, then the reaction is endothermic. In this case some of the thermal energy is converted into potential energy. The potential energy of the products is greater than reactants, that are why, the products are less stable than reactants; that is, the bond in the products are weaker than those of the reactants.

The amount of heat evolved or absorbed when reactants are converted into products during a chemical reaction is called heat of reaction. It may also called chemical energetic. The equation which shows the amount of heat evolved or absorbed during a chemical reaction is called thermochemical equation or reaction.

11.2 Thermodynamics

The study of energy, work, heat, temperature and their relationship is known as thermodynamics (Greek: **therme** = heat; **dunamis** = power). It may also concerned with energy transformation; that is, the transfer of energy from one object (or substance) to another. Chemists give preference to the branch of thermodynamics that is, thermochemistry.

There are four laws of thermodynamics, but only the first law of thermodynamics will be discussed in this chapter.

Some Thermodynamic Terms

System

Anything (substance or mixture) which is under observation or experiment (in the laboratory) is called system.

Types of System

i) Open system: It can exchange both energy and matter (mass) with its surroundings. Examples are open reaction flask, rocket, and an uncovered cup of tea. The energy and matter do not remain same in an open system.

ii) Closed system: It can exchange only energy but not the matter (mass) with surroundings. For example, a sealed reaction flask, a gas in a closed container. The system is most readily study in thermochemistry.

iii) Isolated system: It can exchange neither energy nor matter with surroundings. A thermos flask containing hot green tea approximates an isolated system.

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Surrounding

Everything in the universe which is not part of the system is called surrounding.

Universe

The system plus its surrounding is called universe. It is different from the astronomical universe.

Universe = System + Surrounding

Boundary

The real or imaginary surface which separates the system from surroundings is called boundary.

i) Suppose we have a cup full of tea, the tea is system, the cup and other things are surroundings. The tea plus cup and all other things is universe.

ii) Suppose we are studying the thermal decomposition of $Pb(NO_3)_2$ in a beaker.

System : $Pb(NO_3)_2$

Surrounding : Beaker + Source of heat + every thing else.

Universe : $Pb(NO_3)_2$ + Beaker + Source of heat + Everything else.

States of System

The condition of the system is called state of system. The variables such as temperature, pressure, volume, enthalpy etc. describe the state of system. State is of two types:

i) **Initial State of System:** The state of system before it undergoes a change is called initial state of system. Suppose we have a beaker of water. It has some temperature and volume, which is its initial state.

ii) **Final State of System:** The state of system after it undergoes a change is called final state of system. Suppose we heat the water, as a result of this temperature changes. It is its final state.

Change in State

The difference between two states (initial and final states) is called change in state. For example:

Change in temperature (ΔT) = $T_2 - T_2$

Change in pressure (ΔP) = $P_2 - P_1$

Change in volume (ΔV) = $V_2 - V_1$

Change in enthalpy (ΔH) = $H_2 - H_1$

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State Functions (State Variables)

A property which depends upon initial and final states of system and is independent of the path followed by the system is called state function.

For example, temperature, pressure, volume, enthalpy, internal energy are all state functions. The properties such as heat and work are path dependent and are not state functions.

11.3 Internal Energy

The sum of all kinds of energies (kinetic and potential energies) of the components of the system (particles) is called internal energy $(E = P.E + K.E)$. It is represented by symbol E. The SI unit of internal energy is joule and non-SI unit is calorie. The internal energy depends upon motion of particles, their arrangement, intermolecular and intra molecular forces. Internal energy is the sum of kinetic and potential energies as we know. Now we should know that, potential energy is due to intermolecular and intra molecular forces whereas the kinetic energy is due to translational, vibrational and rotational motions.

$$K.E = E_{Vibrational} + E_{Translational} + E_{Rotational}$$

Vibrational energy is due to vibrational motion, translational energy is due to translational motion and rotational energy is due to rotational motion.

The internal energy of a system cannot be measured. However change in internal energy (ΔE) can be calculated.

$$\Delta E = E_2 - E_1$$

Internal energy change (ΔE) of a system is the amount of energy evolved or absorbed by the system at constant volume. The change in internal energy has three portions:

i)   A number which shows the magnitude of the change.
ii) A unit which also shows the magnitude of the change.
iii) A sign that is used to give the direction.

If E is positive, then E_2 is greater than E_1 $(E_2 > E_1)$ and if E is negative, then E_2 is less than E_1 $(E_2 > E_1)$.

(Keep in mind that the increase in the energy of the system occurs with the decrease in the energy of the surrounding and vice versa.)

An increase in internal energy:

i)   Can cause a chemical reaction when it is enough to break the bonds.
ii) Can change the phase of the system; that is, fusion or evaporation may occur.
iii) Can increase the temperature of the system which in turn increases the kinetic energy of the system.

11.4 First Law of Thermodynamics

First law of thermodynamics is the law of conservation of energy and is stated as: energy can neither be created nor destroyed but can be changed from one form to another form. It may also be defined as: the energy lost by the system is equal to the energy gained by the surrounding but the total energy of the universe is always constant.

$$\Delta E_{Universe} = \Delta E_{System} + \Delta E_{Surrounding} = Zero$$

The internal energy changes when a system either gives off or gains energy (heat). Similarly, the internal energy changes when a work is either done by the system on the surrounding or done by the surrounding on the system. The total change in the internal energy is the sum of work (w) and energy (q).

$$\Delta E = q + w$$

This is the mathematical form of first law of thermodynamics. The internal energy of the system increases when work is done by the system on its surrounding and vice versa.

Work has to be done when:

i)   We increase the speed of car from 0 to 80 km/hour.
ii) We walk upstairs.
iii) We lift a hammer.
iv) An electron in an atom is forced to go away from the nucleus.
v)   A cation is isolated from anion in an ionic compound.
vi) A fixed amount of gas is compressed in to a smaller volume under the influence of an external pressure; that is, the pumping of air in the tyre.

In all of the above cases, the work has been done on the objects (system), hence the energy (P.E.) of the objects increase.

The work has to be done when:

i)   The stone throws down the mountain.
ii) Tears stream down the face.
iii) Water flows down the hill.
iv) Petrol burns inside the engine. *
v)   The wood and coal burns inside the stove.
vi) The tyre of the car bursts.

In these cases, the work has been done by the system on the surrounding, hence, the energy of the system decreases.

The sign conventions for heat (q) and work (w) are as under:

The q is positive when system absorbs energy; that is, for an endothermic

process and **q** is negative when system releases energy, that is, for an exothermic process.

The w is positive when the work is done on the system by the surroundings and w is negative when the work is done by the system on the surroundings.

The ΔE is positive when the system absorbs energy (heat) and ΔE is negative when the system loses energy.

Pressure-Volume Work

The product of force and distance is called work.

Work (w) = Force (F) × distance (S) .... (i)

SI unit of work is joule.

There are various kinds of work but in chemistry we most commonly deal with Pressure-Volume Work. Let us consider a gas confined in a cylinder with movable piston as shown in the figure. The internal energy of the system is E_1 at initial state. A quantity of heat (q) is given to the system. The internal energy of the system changes from E_1 to E_2 and the piston moves upward.
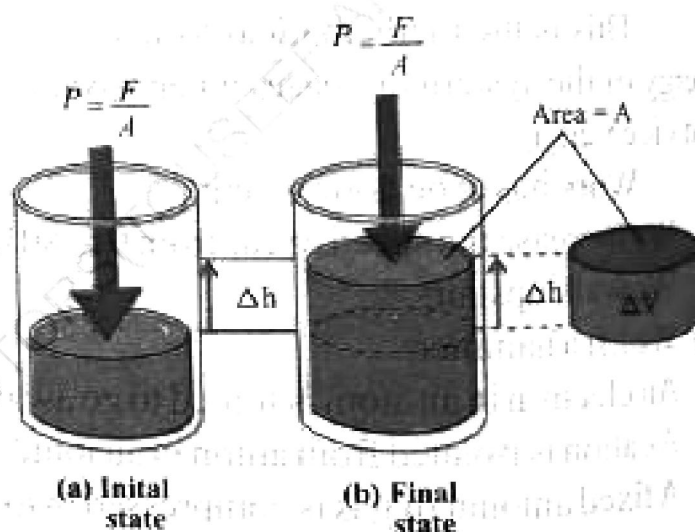

(a) Inital state (b) Final state

Figure 11.1: Pressure-volume Work

In the figure, A is the area of the piston, P is the external pressure on the piston, F is force exerted by the gas on piston and q is the heat absorbed by the gas.

As pressure is force per unit area, hence:

$$P = \frac{F}{A}$$

Therefore,

$$F = P \times A \qquad .... \text{(ii)}$$

Let us assume that, the gas expands. As a result of this, the piston moves from h_i (initial height) to h_f (final height). The difference of these heights is equal to Δh.

$$\Delta h = h_f - h_i \qquad .... \text{(iii)}$$

We know that, the volume of the gas in the cylinder is equal to cross section area (A) multiplied by the height of the column of the gas(h).

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Hence,

$$\Delta V = A \times h \qquad (Area = length \times width)$$

By applying the initial and final states of system, we get

$$V_i = A \times h_i \qquad \dots\dots\dots\dots \quad (iv)$$

$$V_f = A \times h_f \qquad \dots\dots\dots\dots \quad (v)$$

Change in volume (V) is

$$\Delta V = V_f - V_i \qquad \dots\dots\dots\dots \quad (vi)$$

By putting the values of equation (iv) and (v) in equation (vi), we get

$$\Delta V = Ah_f - Ah_i$$

$$\Delta V = A(h_f - h_i)$$

$$\Delta V = A\Delta h \qquad \dots\dots\dots\dots \quad (vii)$$

By rearranging the equation (vii), we get

$$\Delta h = \Delta V / A \qquad \dots\dots\dots\dots \quad (viii)$$

Where, h is change in height or the distance traveled by gas due to force.

By putting the values of equation (ii) and (viii) in equation (i), we get:

$$w = PA \times \Delta V / A$$

$$w = +P\Delta V$$

(Positive sign shows that work has been done on the system (gas) by the surrounding).

As, $w = P\Delta V$

Therefore,

$$\Delta E = q + P\Delta V$$

If the work is done by the system, then

$$\Delta E = q - P\Delta V \qquad (OR) \qquad \Delta E = q - w$$

1.4.1 Heat Changes at Constant Pressure

The heat content of a system is called enthalpy. It may also be defined as: the internal energy E plus product of pressure (P) and volume (V) is called enthalpy. It is represented by H. Mathematically,

$$H = E + PV$$

It is impossible to measure enthalpy of a system. However change in enthalpy (ΔH) can easily be measured.

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$$\Delta H = H_2 - H_1 \qquad \dots\dots\dots\dots \quad (vi)$$

$$H_2 = E_2 + P_2 V_2$$

$$H_1 = E_1 + P_1 V_1$$

By putting the values of H_2 and H_1 in eq. (i)

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1) \qquad \dots\dots\dots\dots \quad (ii)$$

or $\qquad \Delta H = (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$

or $\qquad \Delta H = \Delta E + \Delta PV$

When P is constant whereas the gas is expanding, then we can write,

$$\Delta H = \Delta E + P\Delta V$$

or $\qquad \Delta H = \Delta E + w \qquad \dots\dots\dots\dots \quad (iii) \qquad$ (Where $P\Delta V = w$)

According to the first law of thermodynamics,

$$\Delta E = q - w$$

By putting the value of ΔE in equation (iii), we get

$$\Delta H = q - w + w$$

or $\qquad \Delta H = q \qquad\qquad$ (q = Amount of heat supplied)

This relationship is usually written as,

$$\Delta H = q_P$$

Where, subscript p means constant pressure.

11.4.2 Heat Changes at Constant Volume

Consider a gas in a closed container, the volume of the gas is not changed. Therefo

$$\Delta V = O$$

According to first law of thermodynamics:

$$\Delta E = q - w$$

or $\qquad \Delta E = q - P\Delta V$

As volume is constant i.e. $\Delta V = O$, therefore,

$$\Delta E = q - P \times O$$

or $\qquad \Delta E = q - O \qquad$ or $\qquad\qquad \Delta E = q$

This relationship is usually written as:

$$\Delta E = q_v$$

Where, subscript v means constant volume. All the heat given to the sys

(gas) is used to increase internal energy of the system.

11.5 Standard State and Standard Enthalpy Changes

The physical state of substance at 25°C and at one atmosphere which is the most stable state is called standard state. It is denoted by $\Delta H°$. Where, Δ (delta) stands for change, the symbol H for enthalpy, and the superscript degree sign (°) for standard states. Hence, the $\Delta H°$ means standard enthalpy change.

The amount of heat released or absorbed (enthalpy change) during a chemical reaction when all the reactants and products are in their standard states is called standard enthalpy of reaction. It may also called heat of reaction. It is denoted by $\Delta H°_{rxn}$. Substances are said to be in the standard state at 1 atm; hence we use the term "standard enthalpy." Here the subscript "rxn" stands for reaction. Hence, is read as the standard enthalpy change of reaction. Its unit is $kJmol^{-1}$.

For exothermic reactions $\Delta H°_{rxn}$ values are shown by negative signs and for endothermic reactions the $\Delta H°_{rxn}$ values are shown with positive signs.

For example:

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad \Delta H°_{rxn} = -285.8 \text{ kJmol}^{-1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H°_{rxn} = -393.51 \text{ kJmol}^{-1}$$

The magnitude of ΔH is directly proportional to the quantity of reactant consumed in the process (or to the quantity of product formed in the process). For example, 393.51kJ of heat is produced when 1 mol of carbon is burnt at standard states. Because the combustion of 1 mol of carbon with 1 mol of O_2 releases 393.51kJ of heat, the combustion of 2 mol of carbon with 2 mol of O_2 releases twice as much heat, 787.02kJ.

$$2C + 2O_2 \longrightarrow 2CO_2 \qquad \Delta H°_{rxn} = -787.02 \text{ kJ}$$

11.5.1 Standard Enthalpy of Atomization ($\Delta H°_{at}$)

The enthalpy change when one mole of gaseous atoms is formed from the element at standard states is called standard Enthalpy of atomization. It is denoted by $\Delta H°_{at}$. Its unit is $kJ\,mol^{-1}$. For example, the standard enthalpy of atomization of hydrogen is:

$$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H°_{at} = 218\text{kJmol}^{-1}$$

The standard enthalpy of atomization of sodium is:

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H°_{at} = 107\text{kJmol}^{-1}$$

11.5.2 Standard Enthalpy of Formation (ΔH_f°)

The enthalpy change when one mole of a compound is formed from its elements in their standard states is called standard enthalpy of formation. It is denoted by ΔH_f° and its unit is $kJmol^{-1}$.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_f^\circ = -393.51 \ kJmol^{-1}$$

$$Mg_{(s)} + 1/2O_{2(g)} \longrightarrow MgO_{(s)} \qquad \Delta H_f^\circ = -692 \ kJmol^{-1}$$

A negative ΔH_f° means that the compound is more stable than reactants. For example, CO_2 and MgO are more stable than their reactants. On the other hand, the positive ΔH_f° means that the compound is less stable than their reactants. For example, NO is less stable than their reactants. Consider the reaction.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \qquad \Delta H_f^\circ = +90.37 \ kJmol^{-1}$$
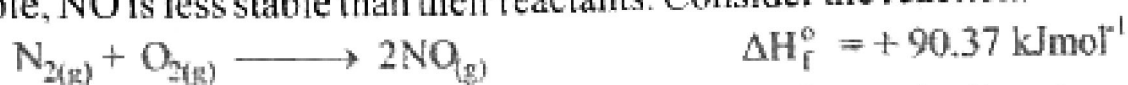
The reactions which are exothermic in forward direction will be endothermic in reverse direction. The enthalpy change for a reverse reaction is equal in magnitude to that for the corresponding forward reaction but opposite in sign; that is, heat of decomposition of a compound is equal and opposite to heat of formation of that compound. For example, the amount of heat released is 46.11kJ for the formation of one mole of ammonia. The amount of heat required to decompose one mole of ammonia is 46.11kJ which is equal to heat of formation of ammonia but apposite in sign because the reaction in reverse direction is endothermic.

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H^\circ = -46.11 \ kJmol^{-1}$$

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad \Delta H^\circ = +46.11 \ kJmol^{-1}$$

Table 11.1: Standard Enthalpies of Formation of Some Common Substance at 25°C

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_{2(g)}$	226.7	Glucose	$C_6H_{12}O_{6(s)}$	-1273
Ammonia	$NH_{3(g)}$	-46.19	Hydrogen chloride	$HCl_{(g)}$	-92.30
Benzene	$C_6H_{6(l)}$	49.00	Methane	$CH_{4(g)}$	-74.80
Carbon dioxide	$CO_{2(g)}$	-393.51	Sodium chloride	$NaCl_{(s)}$	-410.9
Ethyl alcohol	$C_2H_5OH_{(l)}$	-277.7	Sucrose	$C_{12}H_{22}O_{11(s)}$	-2221
Ethylene	$C_2H_{4(g)}$	52.26	Water	$H_2O_{(l)}$	-285.8

The stability of a compound has close relation with enthalpy of formation. The enthalpy of formation of a compound will enable you to identify a stable compound. A compound is said to be unstable which has positive or low negative values of enthalpy of formation and a compound is said to be very unstable which has high positive values of enthalpy of formation. On the other hand, the compound with high negative values of enthalpy of formation is said to be very stable.

11.5.3 Standard Enthalpy of Combustion (ΔH_c^0)

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen at standard states is called standard enthalpy of combustion. It is denoted by ΔH_c^0. Its unit is $kJmol^{-1}$. For example, heat of combustion of CH_4, CO_2 and CO is shown by the reactions:
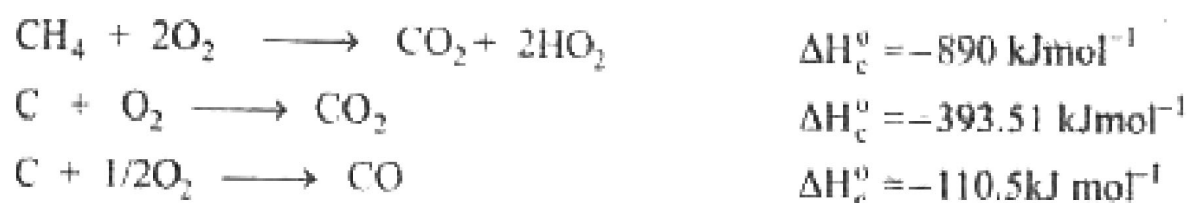
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2HO_2 \qquad \Delta H_c^0 = -890 \ kJmol^{-1}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H_c^0 = -393.51 \ kJmol^{-1}$$

$$C + 1/2O_2 \longrightarrow CO \qquad \Delta H_c^0 = -110.5 kJ \ mol^{-1}$$

Table 11.2: Standard Enthalpies of Combustion of Some Common Substance at 25°C

Substance	Formula	ΔH_c^0 (kJ/mol)	Substance	Formula	ΔH_c^0 (kJ/mol)
Hydrogen	$H_{2(g)}$	−286	Ethylene	$C_2H_{4(g)}$	−1412
Methane	$CH_{4(g)}$	−891	Acetylene	$C_2H_{2(g)}$	−1300
Butane	$C_6H_{6(l)}$	−2880	Benzene	$C_6H_{6(l)}$	−3270
Octane	$C_8H_{18(l)}$	−5474	Carbon monoxide	$CO_{(g)}$	−283

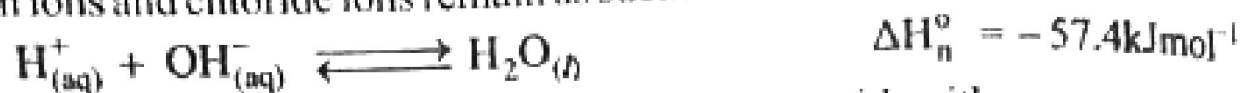### 11.5.4 Standard Enthalpy of Neutralization (ΔH_n^0)

The enthalpy change when one mole of hydrogen ions (H^+) from an acid react with one mole of hydroxide ions (OH^-) from a base to form one mole of water at standard states is called standard enthalpy of neutralization. It is denoted by ΔH_n^0. Its unit is $kJmol^{-1}$. The strong acids and bases are ionized completely when dissolved in water as:

$$HCl_{(g)} \xrightleftharpoons{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(s)} \xrightleftharpoons{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$
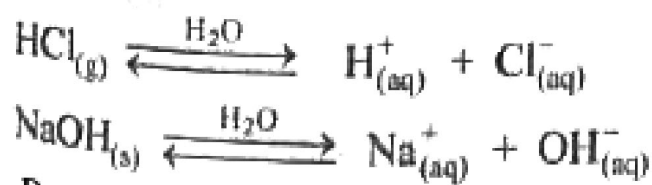
By mixing the hydrochloric acid and sodium hydroxide solutions, the following situation occurs:

$$\left(H^+_{(aq)} + Cl^-_{(aq)}\right) + \left(Na^+_{(aq)} + OH^-_{(aq)}\right) \rightleftharpoons H_2O_{(l)} + Na^+_{(aq)} + Cl^-_{(aq)}$$
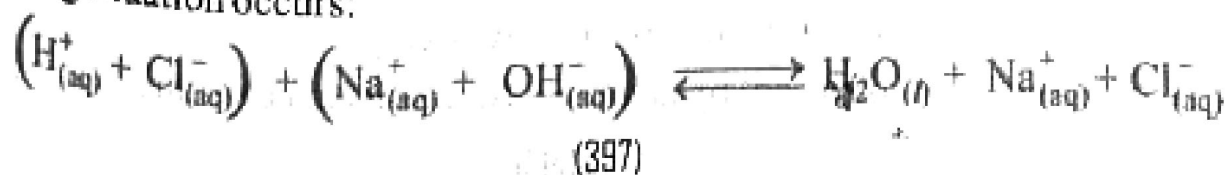
In the above reaction, the H⁺ ions .... The sodium ions and chloride ions remain as such. Hence, the actual reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \qquad \Delta H^o_n = -57.4 \text{kJmol}^{-1}$$

The heat of neutralization of any strong acid with any strong base is approximately equal to –57.4kJ/mol, because the reaction involves only the combination of hydrogen and hydroxide ions.

11.6 Heat Capacity

The amount of energy required to raise the temperature of an object or a substance by one degree Celsius (or one Kelvin) is called heat capacity. It is denoted by C. Its unit is joules per gram per degree Celsius ($J/g\,^\circ C$) or joules per mole per degree Celsius ($J/mol\,^\circ C$). It is measured at constant pressure or constant volume.

Heat capacity may further be classified into specific heat capacity and molar heat capacity.

The amount of energy required to raise the temperature of one gram of a substance (element or compound) by one degree Celsius ($1^\circ C$) or one Kelvin (1K) at constant pressure is called specific heat capacity or just specific heat. It is denoted by C_s. Its unit is $J/g\,^\circ C$. The specific heat for water at 15°C is 4.184J/g°C and that of iron is 0.45J/g °C. It means 4.184 Joules energy is required to raise the temperature of one gram of water by one degree Celsius and 0.45 Joules energy is required to raise the temperature of one gram of iron by one degree Celsius; that is, water needs about nine times more heat to raise the temperature of one gram of water by one degree Celsius as compared to iron metal. It can be determined experimentally by measuring the temperature change (ΔT), the mass of substance and quantity of heat released or absorbed. The following equation is used to calculate the specific heat.

$$C_s = \frac{q}{m \times \Delta T}$$

Where, C_s is the specific heat capacity, m is the mass of a substance, ΔT is the change in temperature, and q is the amount of heat released or absorbed. The q is positive for an endothermic process and negative for an exothermic process.

The amount of energy required to raise the temperature of a substance is equal to the product of specific heat, mass of a substance and rise in temperature.

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

As C_s is the specific heat capacity, by taking mass constant, the amount of heat (q) released (or absorbed) by an object (or a substance) is directly proportional

to its temperature change. The increase in temperature increases the quantity of heat of an object.

The amount of energy required to raise the temperature of one mole of a substance by one degree Celsius (1°C) or one Kelvin ($1K$) is called molar heat capacity. It is denoted by C_m. its unit is J/mol $^\circ$C.

The specific heat capacity of a substance can easily be converted into molar heat capacity by multiplying specific heat capacity of a substance with its molar mass.

<u>**Molar heat capacity = Specific heat capacity × molar mass of a substance**</u>

Every object or substance has its own heat capacity.

Table 11.3: The heat capacities of some common substances and objects at room temperature (25°C)

Element	Heat Capacity (J/g $^\circ$C)	Compound	Heat Capacity (J/g $^\circ$C)	Object	Heat Capacity (J/g $^\circ$C)
Aluminum (s)	0.900	Ammonia (g)	2.09	Cement	0.88
Copper (s)	0.385	Benzene (l)	1.74	Glass	0.84
Gold (s)	0.129	Carbon tetrachloride(l)	0.862	Granite	0.79
Graphite (s)	0.711	Ethanol (l)	2.44	Steel	0.45
Iron (s)	0.450	Ethylene glycol (l)	2.42	Wood	1.76
Mercury (l)	0.140	Water (l)	4.184		

The water has high value of specific heat capacity, hence

i) It plays an important role in regulating the temperature of the earth.

ii) It is also used in the radiators of automobiles as a coolant.

iii) It keeps our body temperature constant to a certain degree. Hence, our body needs much energy transfer to increase or decrease the temperature of our body.

11.7 Calorimetry

The measurement of heat of reaction is called calorimetry. The amount of heat released or absorbed (ΔH) during a physical and chemical process can be measured with a device, known as calorimeter. For example, a calorimeter is used to measure the heat of neutralization of a strong acid with a strong base and heat of combustion of an organic compound burnt in oxygen. There are two types of calorimeters.

i) Simple calorimeter

ii) Bomb calorimeter

i) Simple Calorimeter

It consists of an insulated container with a thermometer and stirrer. It can be used to measure heat of neutralization of a strong acid with a strong base and heat of solution. The known quantities of reactants are placed in the calorimeter. The amount of heat released or absorbed during a chemical reaction is calculated from the temperature change. Knowing the mass of reactants in the calorimeter, the specific heat of the reaction mixture and the temperature change, we can calculate the heat of reaction using the equation:

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

Because the pressure inside the calorimeter is constant (1 atm), hence, heat change (q) for the process is equal to enthalpy change.

$$q = \Delta H_p = C_s \times m \times \Delta T$$

The heat of neutralization of a strong acid with a strong base is calculated by simple calorimeter.

Figure 11.2: Simple Calorimeter

ii) Bomb Calorimeter

It consists of an insulated steel vessel called a bomb. It has an ignition coil and a platinum cup inside the bomb. The bomb has an inlet valve for adding oxygen and electrical leads for the ignition of mixture. It is generally used to measure the enthalpy of combustion of food, fuel and other compounds.

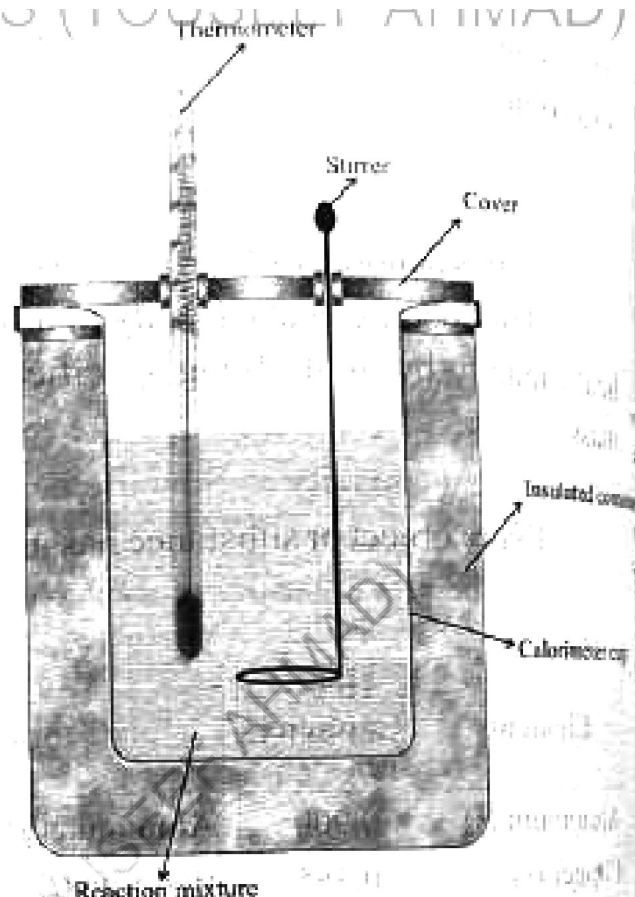The known quantity of a sample is placed in a small platinum

Figure 11.3: Bomb Calorimeter

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cup inside the bomb. The bomb is sealed and oxygen is added in through an inlet valve until the pressure inside the bomb is about 20atm. The bomb is then placed in an insulated steel vessel containing known mass of water. The initial temperature of water is noted by thermometer. The sample is ignited by passing an electric current through the ignition coil. The heat evolved during the combustion of sample raises the temperature of bomb, water and other parts of the calorimeter. The rise in temperature of water is noted after every 30 seconds. Knowing the mass of sample in the calorimeter, the heat capacity of the calorimeter and the temperature change, we can calculate the heat of combustion by the following equation:

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

Example 11.1

Calculate the heat of neutralization when 50mL of 0.5M HCl is mixed with 50mL of 0.5M NaOH in a calorimeter at 25°C. The final temperature after stirring the reaction mixture is 27.25°C. The specific heat of water is 4.184 J/g°C and the density of solution is 1g/mL.

Solution:

Change in temperature (ΔT) $= T_2 - T_1 = 27.25°C - 25.00°C = 2.25°C$

Total volume of solution $= 50mL + 50mL = 100mL$

Total mass of solution $=$ Density $\times$ Total volume $= 1g/mL^{-1} \times 100mL = 100g$

Number of moles of HCl or NaOH $= \dfrac{50mL}{1000mL\ L^{-1}} \times 0.5mol\ L^{-1} = 0.025mol$

Heat of a neutralization of solution $= \Delta H_n = ?$

The equation used to calculate heat of neutralization is:

$$\Delta H_n = q_p = C_s \times m \times \Delta T$$

By putting the values we get,

$$\Delta H_n = -(4.184Jg^{-1}°C^{-1} \times 100g \times 2.25°C)$$
$$= -941.4J$$

The value of ΔH_n in kilo joule $= \dfrac{-941.45J}{1000J/kJ} = -0.9414kJ$

ΔH_n for one mole of HCl and NaOH $= \dfrac{-0.9414kJ}{0.025mol} = -37.656kJ/mol$

The value of ΔH_n is negative because the heat is released.

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11.8 Hess's Law of Constant Heat Summation

Consider the formation of two moles of carbon monoxide from two moles of carbon and one mole of oxygen.

$$2C_{(Graphite)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$
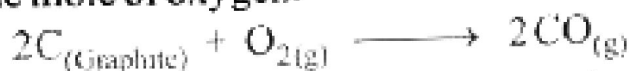
The enthalpy change for this reaction cannot be measured directly although the CO gas is the major product, because the CO gas formed during the reaction further reacts with oxygen and forms some CO_2 gas. The enthalpy change for the above reaction can be measured indirectly using Hess's law.

In 1840, the Swiss chemist German Henri Hess (1802-1850), a professor of St. Petersburg university, Russia formulated this law. He is known as the father of thermochemistry. Hess's law states that the enthalpy change during chemical reaction is same whether reaction takes place in one step or in a series of steps. Enthalpy is a state function; hence, its change is independent of the path between initial and final states.

Consider a general reaction in which A is reactant and D is product. In this reaction A is converted into D by direct and indirect methods. In a multi-step reaction B and C are intermediate states.
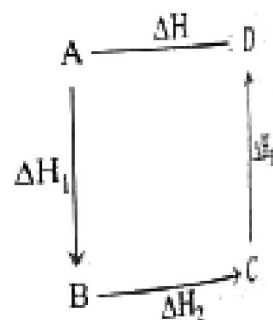
According to Hess's Law, the enthalpy change for the overall reaction is equal to the sum of the enthalpy changes of the individual steps in a multistep reaction.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Applications of Hess's Law

The enthalpy change (heat of formation) of methane, ethyne, CO, benzene, alcohol etc. cannot be calculated directly. They can be determined indirectly using Hess's law. Some examples of Hess's law are:
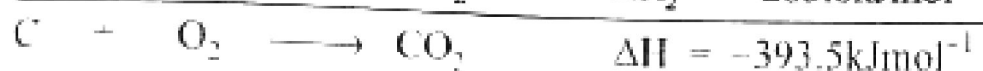
Formation of CO_2

The formation of CO_2 takes place by two methods:

Direct method:

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.51 kJmol^{-1}$$

Indirect method:

$$C + 1/2O_2 \longrightarrow CO \qquad \Delta H_1 = -110.5 kJmol^{-1}$$

$$\underline{CO + 1/2O_2 \longrightarrow CO_2 \qquad \Delta H_2 = -283.0 kJmol^{-1}}$$

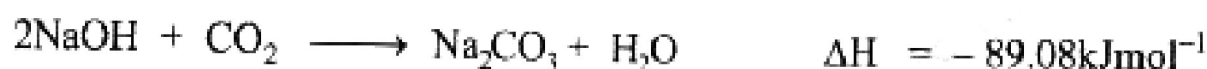$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.5 kJmol^{-1}$$

The enthalpy change remains same whether reaction takes place in one step or in several (many) steps.

Formation of Sodium Carbonate

It takes place by two methods:

Direct Method:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H = -89.08 kJmol^{-1}$$

Indirect Method:

$$NaOH + CO_2 \longrightarrow NaHCO_3 \qquad \Delta H_1 = -48.06 kJmol^{-1}$$

$$\underline{NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H_2 = -41.02 kJmol^{-1}}$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad \Delta H = -89.08 kJmol^{-1}$$
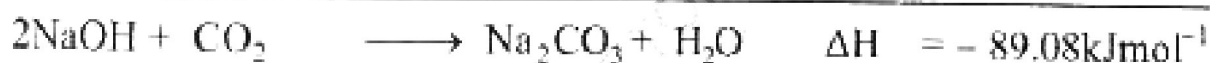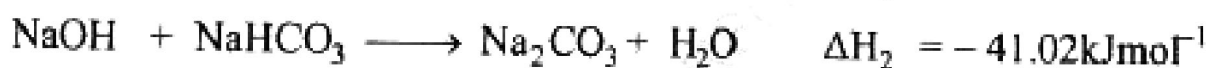
The enthalpy change remains same whether reaction takes place in one step or in several steps.

11.9 Born-Haber Cycle

The Born-Haber cycle was developed by the German physicist Max Born and the German chemist Fritz Haber to calculate the lattice energies of binary ionic compounds such as MX. The Born-Haber cycle states that the sum of all the enthalpy changes is always equal to zero. It is a special application of Hess's law.

Calculation of Lattice Energy of NaCl

The formation of NaCl occurs by two methods:

Direct method:

One mole of sodium combines with half mole of chorine to produce one mole of NaCl. The amount of energy released when one mole of NaCl is produced from its elements is called heat of formation of NaCl. The heat of formation of sodium chloride is -411kJ/mol.

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_f = -411 kJmol^{-1}$$
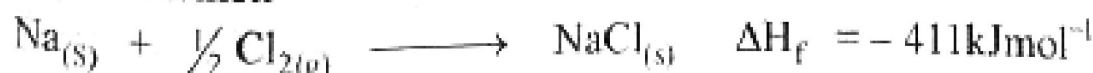
Indirect method:

Lattice energy of compounds cannot be determined directly by experiments. It can be determined indirectly by means of an energy cycle because an ionic compound is thought to be formed in a series of steps.

The energy triangle diagram for NaCl is:

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \xrightarrow{\Delta H^o} Na^+_{(g)} + Cl^-_{(g)}$$
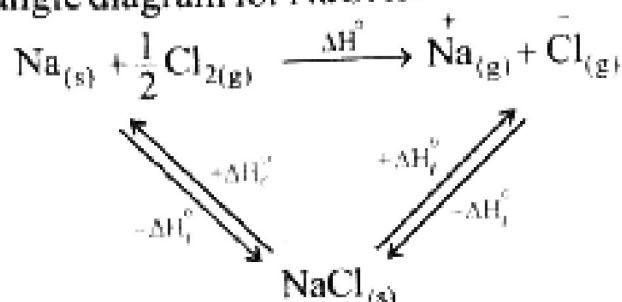
The complete energy cycle called Born-Haber cycle for the formation of NaCl is:
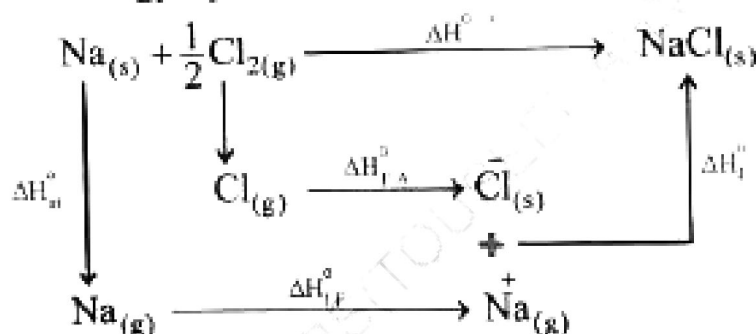
We can calculate the lattice energy of NaCl with help of five steps that are given below:

i) One mole of solid sodium is directly converted into sodium vapours. This process is called sublimation. It is an endothermic process. The enthalpy of sublimation for sodium is 107.7 kJ/mol.

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad\qquad \Delta H^o_1 = +107.7 \text{kJ/mol}$$

ii) One mole of sodium ions are obtained by the ionization of one mole of gaseous sodium atoms. It is an endothermic process. The enthalpy of ionization for sodium is 496 kJ/mol. This is the first ionization energy of sodium.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1\bar{e} \qquad\qquad \Delta H^o_2 = +496.0 \text{kJ/mol}$$

iii) One mole of chlorine atoms are obtained by the dissociation of half mole of Cl_2 gas. It is also an endothermic process. The enthalpy of atomization for Cl_2 gas is 121.7 kJ/mol.

$$\frac{1}{2}Cl_2 \longrightarrow Cl_{(g)} \qquad\qquad \Delta H^o_3 = +121.7 \text{kJ/mol}$$

iv) One mole of chloride ions are formed from chlorine atoms by the addition of electrons. It is an exothermic process. The enthalpy of ionization for chlorine is –349 kJ/mol. This is the electron affinity of chlorine.

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$Cl_{(g)} + 1e^- \longrightarrow Cl^-_{(g)}$ $\Delta H^\circ_4 = -349.0 kJ/mol$

v) One mole of solid sodium chloride is formed by the combination of one mole of sodium ions and one mole of chloride ions. This is the process of lattice formation. It is an exothermic process. The amount of energy released during the formation of NaCl is called lattice energy.

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$ $\Delta H^\circ_5 = ?$
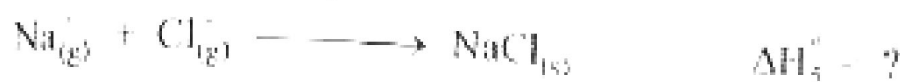
We cannot determine lattice energy directly. It can be determined by using Hess's law as:

$$\Delta H_f = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 + \Delta H^\circ_5$$
$$-411 = 107.7 + 496.0 + 121.7 + (-349.0) + \Delta H^\circ_5$$
$$-411 = 725.4 - 349.0 + \Delta H^\circ_5$$
$$-411 = 376.4 + \Delta H^\circ_5$$
$$\Delta H^\circ_5 = -411 - 376.4 = -787.4 kJ/mol$$

The lattice energies of other compounds can be calculated in the same way.

Practice Exercise 2:
Calculate the lattice energy of KBr with the help of the following information:
i) The enthalpy of formation for KBr is –392.2kJ/mol
ii) Heat of sublimation for potassium is 89kJ/mol
iii) The ionization energy for potassium is 419kJ/mol
iv) The enthalpy of atomization for bromine is 112kJ/mol
v) The electron affinity of bromine is –324kJ/mol

Summary of Facts and Concepts

➤ Thermochemistry is the study of heat changes associate with chemical reactions and physical changes.
➤ Energy is the capacity of a body to do work or heat transfer. It includes kinetic energy and potential energy. The SI unit of energy is joule.
➤ Kinetic energy is due to motion of the object or particles of substance. It depends on mass and velocity of an object or particle of substance. $(K.E = 1/2mv^2)$. Potential energy is due to the position of an object or stored in a molecule because of its composition.
➤ Internal energy is the sum of the kinetic energies and potential energies of the particles of the substance.

> According to first law of thermodynamics, the energy of the universe is constant and the internal energy change (ΔE) is the sum of heat (q) and work (w): $\Delta E = q + w$

> The change in internal energy (ΔE) is the amount of energy (heat) evolved or absorbed by the system at constant volume: $\Delta E = q_v$

> In an exothermic process, the heat flows out of the system while in an endothermic process, the heat flows into a system.

> Enthalpy is a state function. It is the heat content of a system. It is equal to the sum of internal energy (E) and product of pressure (P) and volume (V).

> Enthalpy change (ΔH) is the amount of heat evolved or absorbed by the system at constant pressure: $\Delta H = q_p$

> Thermochemical equation is the equation that shows the amount of heat change during a chemical reaction.

> The enthalpy change for exothermic reaction is negative and for endothermic reaction it is positive.

> The amount of heat evolved or absorbed during a chemical reaction or physical process is measured experimentally by using calorimeter.

> According to Hess's law of constant heat summation, the enthalpy change during chemical reaction is same whether reaction occurs in a single step or in a series of steps.

> The standard enthalpy of formation is the enthalpy change when one mole of a compound is formed from its elements in their standard states; that is, at 25 °C and 1 atm.

> The amount of energy required to break all bonds in mole of substance is called bond dissociation energy.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

(i) The study of heat changes that accompany a chemical reaction is called:
(a) Thermochemistry   (b) electrochemistry
(c) nuclear chemistry   (d) chemical kinetics

(ii) Which one of the following is NOT the unit of heat:
(a) Joule   (b) Kelvin   (c) calorie   (c) kilojoule

(iii) Anything which is under observation or experiment is called:
(a) Universe   (b) boundary   (c) system   (d) surrounding

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(iv) The energy of the system during endothermic reactions is:
- (a) Increased
- (b) decreased
- (c) neither increased nor decreased
- (d) first increased and then decreased

(v) The sum of kinetic energy and potential energy of the particles of substance is called:
- (a) Heat capacity
- (b) specific heat
- (d) enthalpy of the system
- (d) internal energy

(vi) Internal energy depends upon:
- (a) Intermolecular forces
- (b) intramolecular forces
- (c) motion of particles
- (d) all of them

(vii) The enthalpy change is positive for:
- (a) Combustion
- (b) exothermic process
- (c) ionization energy
- (d) electron affinity

(viii) One calorie is equal to:
- (a) 4.184 J (b) 41.84 J (c) 418.4 J (d) 4184.0 J

(ix) The heat of formation of carbon dioxide is:
- (a) 3.9351 kJ/mol
- (b) 39.351 kJ/mol
- (c) 393.51 kJ/mol
- (d) 3935.1 kJ/mol

(x) Which one of the following is **NOT** a state function:
- (a) Temperature
- (b) work
- (c) pressure
- (d) internal energy

Q.2. Fill in the blanks with suitable words given in the brackets:

(i) The majority of reactions which give stable products are _____ . (Endothermic/exothermic)

(ii) The w is _____ when the work is done on the system by the surroundings. (positive/negative)

(iii) The energy of the system is _____ during an endothermic process. (decreased/increased)

(iv) Melting of ice is an _____ process. (exothermic / endothermic)

(v) The amount of energy required to raise the temperature of one gram of a substance one Kelvin at constant pressure is called _____. (specific heat capacity/molar heat capacity)

(vi) The energy is provided to the ~~~~ ~~~~ ~~~~ ~~~~ to change the enthalpy of the system. (pressure/volume)

(vii) The energy is provided to the system at constant _____ to change the internal energy of the system. (pressure/volume)

(viii) The heat of formation of a compound is _____ . to heat of decomposition of a compound. (equal/not equal)

(ix) The equation for first law of thermodynamics is _____ . ($E = q + w/\Delta E = q + w$)

(x) The enthalpy change when one mole of a _____ is formed from its elements is called standard enthalpy of formation. (Substance / compound)

Q.3. Label the following statements as True or False:

(i) Thermochemistry is the study of heat, energy and work.

(ii) Enthalpy is not a state function.

(iii) A balanced chemical equation which shows the enthalpy change of a reaction is called thermochemical equation.

(iv) According to Hess's law, the enthalpy change is equal to the sum of the enthalpy changes of the individual steps in a multi-step reaction.

(v) The energy can be created or destroyed during a physical change or chemical change.

(vi) In chemistry, we most commonly deal with pressure-volume work.

(vii) The Born-Haber cycle is different from Hess's law.

(viii) The heat of neutralization for a strong acid and a strong base is equal to -57.4kJ/mol.

(ix) The unit of specific heat capacity is $J/mol°C$.

(x) Bomb calorimeter is used to determine the heat transfer at constant volume.

Q.4: Define the following terms: thermochemistry, joule, and calorie.

Q.5: Define heat. Explain with example, how energy is transferred from one piece of matter to another?

Q.6: Define energy. What is the difference between kinetic energy and potential energy? Give the importance of energy.

Q.5: What is the difference between temperature and heat?

Q.6: What is thermochemical equation? What are exothermic and endothermic reactions? Give an example of each.

Q.7: What is system? What do you know about types of system?

Q.8: Give definitions for the following terms:

   (a) Thermodynamics
   (b) Surrounding
   (c) Boundary
   (d) Universe
   (e) State of system

Q.9: What is meant by state function? Explain enthalpy is a state function but heat is not a state function.

Q.10: Define and explain internal energy of the system.

Q.11: What is first law of thermodynamics? Prove that:

   (a) $\Delta H = q_p$
   (b) $\Delta E = q_v$

Q.12: What is meant by enthalpy? What is the difference between ΔH and ΔE? The value of $\Delta H \approx \Delta E$ in case of solids and liquids, why?

Q.13: Give the sign of ΔH for exothermic and endothermic reactions.

Q.14: Give precise definitions for the terms given below:

   (a) Standard enthalpy change
   (b) Standard enthalpy of atomization
   (c) Standard enthalpy of combustion
   (d) Standard enthalpy of formation
   (e) Standard enthalpy of neutralization

Q.15: What is meant by the term heat capacity of a substance? Define and explain specific heat capacity and molar heat capacity. Give units of each.

Q.16: Why we prefer to sit on a bench made of wood rather than a bench made of iron in a hot summer day?

Q.17: Define calorimetry.

   (a) How do you measure the enthalpy of neutralization by simple calorimeter?

   (b) How do you measure the enthalpy of combustion by bomb calorimeter?

Q.18: What is Hess's law of constant heat summation? Give its applications.

Q.19: What is lattice energy? How does the Born-Haber cycle helps to calculate the lattice energy of NaCl?

in a thermochemical equation?

Q.21: Why the heat of neutralization of any strong acid with any strong base is approximately equal to -57.4kJ mol^{-1}?

Q.22: The white precipitate of AgCl is formed when 20mL of 0.50mol/dm^3 solution of $AgNO_3$ is added to 20mL of 0.50mol/dm^3 solution of NaCl. The rise in temperature is $8.0\,°C$. Calculate the heat of solution in kilojoules per mole. The specific heat of the solution is assumed to be $4.184 \text{J/g.}°C$ and density is 1.00g/mL.

Q.23: Calculate the lattice energy of lithium fluoride (LiF) with the help of the following information:

a)   The enthalpy of formation for LiF is -594kJ mol^{-1}.
b)   Heat of sublimation for lithium is 155kJ mol^{-1}.
c)   The ionization energy for lithium is 520kJ mol^{-1}.
d)   The enthalpy of atomization for F_2 is 75kJ mol^{-1}.
e)   The electron affinity of fluorine is -328kJ mol^{-1}.