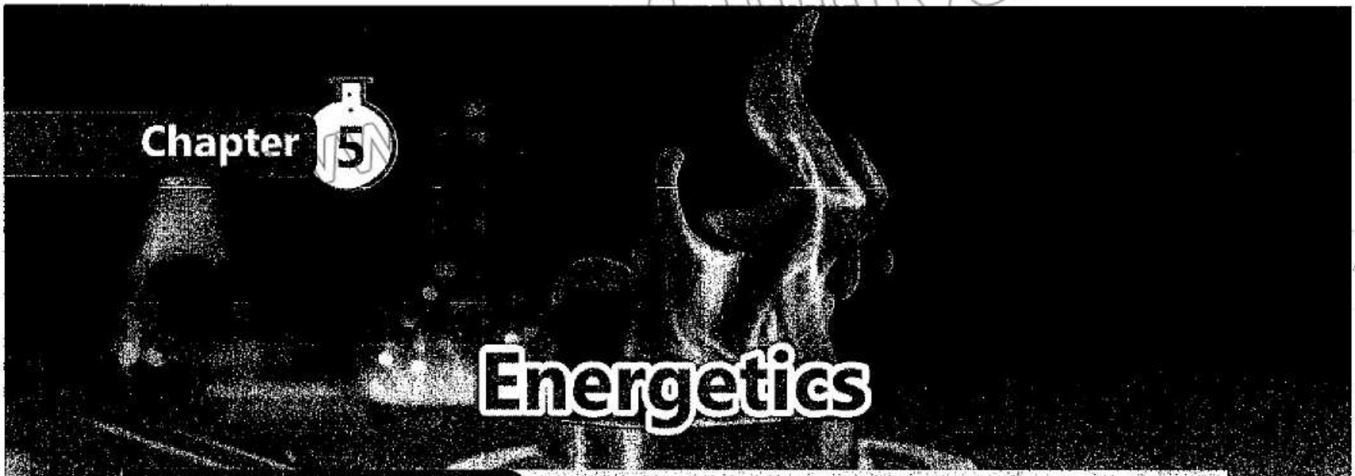


Chapter 5

Energetics

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the idea of a chemical system and its connection with its surroundings influences energy transfer during a chemical reaction.
- Differentiate between exothermic and endothermic reactions by giving examples.
- State that thermal energy is called enthalpy change and recognize its sign as negative for exothermic and positive for endothermic reactions
- Define activation energy as the minimum energy that colliding particles must have for a successful collision.
- Explain that activation energy depends on reaction pathway which can be changed using catalysts or enzyme (detailed pathways not required)
- Draw, label and interpret reaction pathway diagram for exothermic and endothermic reaction which includes enthalpy change, activation energy (uncatalyzed and catalyzed), reactants and products
- Recognize that bond breaking is endothermic and bond making is exothermic processes.
- Explain that enthalpy change is sum of energies absorbed and released in bond breaking and bond forming
- Calculate enthalpy change of a reaction given bond energy values
- Explain how respiration (aerobic and anaerobic), an exothermic process, provides energy for biological systems and lipids as reserve stores of energy.

Introduction

Energy exists in different forms which are often interconvertable. In chemical energetics we are mainly concerned with two forms of energy.

1. Chemical Energy: This energy is stored in a molecule in which atoms are bonded to each other.
2. Heat Energy: This form of energy is released when a bond is formed and absorbed when it is broken.

In energetics we study the energy changes that take place during a chemical reaction. These changes are caused by the making and breaking of bonds during a reaction. In most of the reactions the weak bonds of reactants break while in products new strong bonds are formed. Since energy is needed to break a bond while energy is evolved when a bond is formed, such reactions take place always with the evolution of heat. If a reaction is accompanied with the evolution of heat it is called an exothermic reaction and if heat is absorbed during a reaction it is called an endothermic reaction.

In energetics we not only encounter heat which comes out of a chemical reaction but also another quantity which is called enthalpy.

Enthalpy (H) or heat content, is defined as the total amount of thermal energy stored in a compound. The unit of its measurement is $kJ\ mol^{-1}$.

When the energy is absorbed during a reaction, the total enthalpy of the system increases. When energy is evolved during a reaction, the total enthalpy of the system decreases.

Chemical energetics is part of a broader field of chemistry called Thermodynamics. In energetics we study the flow of energy in a chemical reaction. Thermodynamics deals with how the energy changes during chemical reaction affect the properties of a chemical system.

Thomas Young was the first to use the word 'energy' to the field of physics in 1802.

5.1 System and Surounding

In Chemistry, any physical or chemical change under study may also be called a system. The chemical reaction includes reactants, products, catalyst, solvent and anything else which is important to study this reaction. Everything else which does not fall in this system is called the surrounding. For example, if you are boiling water in the beaker, the water molecules will be called a system while everything surrounding this like beaker, burner, etc. will be called the surrounding. When energy is transferred from surrounding to the system, the change is called endothermic and it has a positive sign. When energy is transferred from system to surrounding, the change is called exothermic and it carries negative sign.

Interesting Information!

Energy evolved during a chemical reaction is used in everyday life for cooking, heating, lighting, transportation, communication, entertainment and much more.

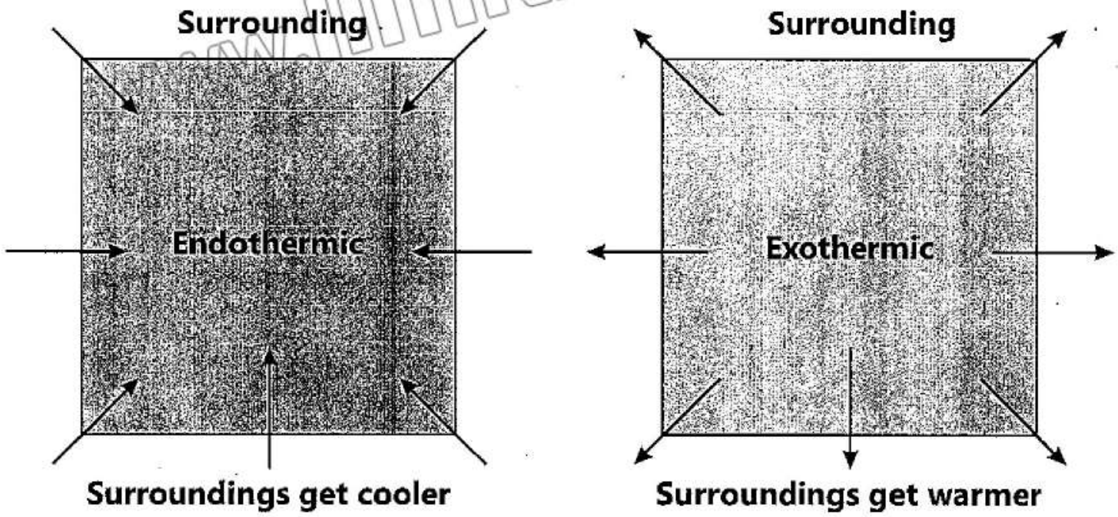


Fig (5.1) System and surrounding exchanging energy

Exercise

Does boiling water in a beaker endothermic or exothermic change? Which form of energy is being transferred in this system.

Interesting Information!

Enthalpy is important because it tells us how much heat is present in a system. Heat is important because we can extract useful work from it.

5.2 Enthalpy

The total amount of heat energy present in a molecule under standard conditions (0°C temperature and 760 mm pressure) is also called its heat content. Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy is equal to the total heat content of a system. Enthalpy of a system is represented by (H) while the change in enthalpy which a system undergoes is represented by ΔH. The total enthalpy (H) of a system cannot be measured directly. However, the change in enthalpy ΔH brought about in a system can be measured comparatively easily.

In Chemistry, the standard enthalpy of reaction (ΔH°) is the enthalpy change when reactants in their standard states undergo reaction to produce products in their standard states. This quantity is called the standard enthalpy change or heat of reaction at constant pressure.

$$2\,CO_{(g)} + O_{2(g)} \longrightarrow 2\,CO_{2(g)} \quad \Delta H^\circ = -566.0\ kJ$$

The reaction in this system is thus exothermic evolving 566 kJ of heat energy which is given to the surrounding.

How is enthalpy different from heat?

Heat is a form of energy that flows from hot body to a cold body because of a difference in temperature. We measure heat in joules. Heat is what we call the transfer of thermal energy. Contrary to this, enthalpy is an essential part of a system since it depends on the number of molecules present in that system, its chemical composition and its structure. Heat is not essential part of a system, it just comes and goes. When heat leaves or enters a system, it results in a change of enthalpy. At a constant pressure the enthalpy change is equal to heat evolved or absorbed.

Exercise

Can energy be transferred in a form other than heat during a chemical reaction?

Exercise

Why it is not possible to calculate the enthalpy of a system?

5.3 Exothermic and Endothermic Reactions

A physical or a chemical change is almost always accompanied with either absorption or evolution of heat. Heat, which is evolved or absorbed during a chemical reaction, is called the heat of that reaction.

Chemical reactions in which heat energy is evolved are called exothermic reactions while those in which heat energy is absorbed are called endothermic reactions. Heat, which is evolved during an exothermic reaction, goes to the surrounding and the container in which such a reaction is being carried out, gets hot. Conversely, in an endothermic reaction, the absorption of heat from the surrounding will decrease the temperature of the container.

Example: Hydrogen gas and oxygen gas react to give liquid water in an exothermic reaction.

$$\underset{\text{Hydrogen}}{2H_2(g)} + \underset{\text{Oxygen}}{O_2(g)} \longrightarrow \underset{\text{Water}}{2H_2O(l)} + 571.6\ kJ$$

571.6 kJ heat energy is evolved during this reaction. If the energy evolved is shown separately it is expressed as $\Delta H = -571.6\ kJ$. The same amount of energy will be absorbed when the reaction will move in the backward direction i.e. water will decompose to give hydrogen and oxygen back.

Example: Carbon dioxide gas is produced when solid carbon burns in oxygen gas.

$$\underset{\text{Carbon}}{C(s)} + \underset{\text{Oxygen}}{O_2(g)} \longrightarrow \underset{\text{Carbon dioxide}}{CO_2(g)} + 393.5 \text{ kJ}$$

It is also an exothermic reaction and 393.5 kJ heat energy is evolved during this reaction. When this reaction moves in the backward direction, the same amount of energy i.e. 393.5 kJ will be absorbed. This reaction has ΔH - 571.6 kJ mol^{-1} of CO_2.

Both the reactions mentioned above are the examples of exothermic changes.

The following reactions represent endothermic changes.

$$\underset{\text{Hydrogen}}{H_2(g)} + \underset{\text{Iodine}}{I_2(s)} \longrightarrow \underset{\text{Hydrogen Iodide}}{2HI(g)} - 53.08 \text{ kJ}$$

The enthalpy change for the reaction is ΔH = 53.08 kJ

Hydrogen gas reacts with solid iodine only at high temperature and 53.08 kJ of heat energy is absorbed.

Formation of NO in air due to lightening in the clouds.

$$\underset{\text{Nitrogen}}{N_2(g)} + \underset{\text{oxygen}}{O_2(g)} \longrightarrow \underset{\text{Nitric Oxide}}{2NO(g)} - 180.6 \text{ kJ}$$

The enthalpy change for the reaction is ΔH = 180.6 kJ.

Interesting Information!

Heat evolved or absorbed during a reaction is used in self-heating or self-cooling packs. These packs contain reactants that undergo an exothermic or an endothermic reaction providing high or low temperature.

Our present-day living conditions depend heavily on the availability of energy in its various forms. Exothermic chemical reactions are extensively used to fulfill this requirement. In such reactions, chemical energy is converted into heat energy. We burn fuels like gas, oil and coal to cook food and for other heating purposes in our homes and industry. During this burning process called combustion, compounds present in fuels react with oxygen of the air to produce a large amount of heat.

Foods such as fats and carbohydrates are important biological fuels. During metabolism, the chemical energy present in this food is converted to heat to keep us warm.

A large portion of electricity is produced at power stations by burning fuels such as natural gas and coal. The heat which comes out from their combustion is used to produce steam at high pressure. This high pressure steam is then used to rotate turbines, which in turn generate electricity.

While driving a vehicle, it is the combustion of petrol or diesel that gives off energy and drives it forward. The one example of exothermic reactions people seem to enjoy the most is that of fireworks. Fireworks are the result of combustion reactions that yield heat, light and sound. Different metal powders alongwith oxidising agents produce a variety of colours when burut.

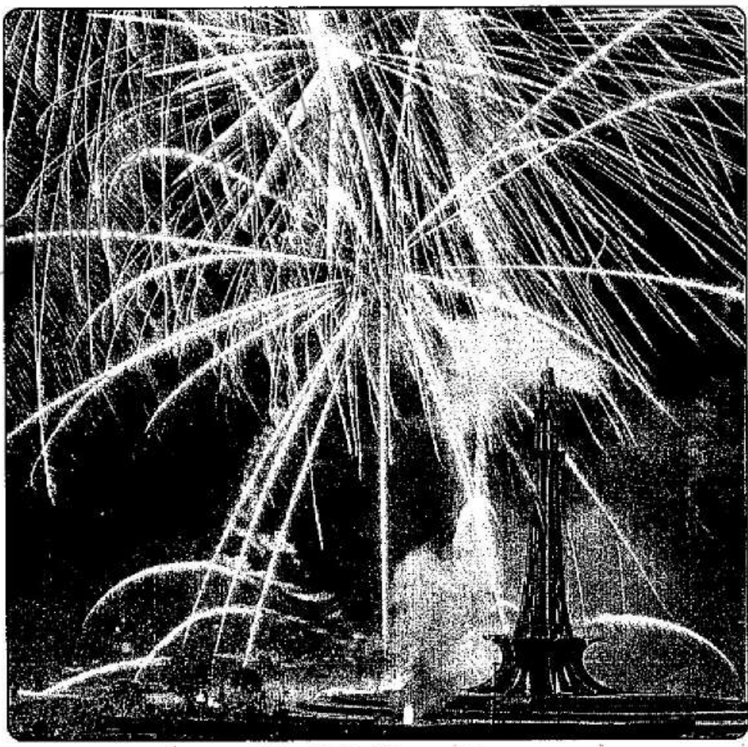


Fig (5.2) Fireworks

Exercise

Why the chemical reaction between sodium metal and water proceeds violently?

Exercise

Is melting of ice an exothermic or endothermic change?

Exercise

Can exothermic reaction be reversed?

Let us now examine the reason why the chemical reactions are either exothermic or endothermic.

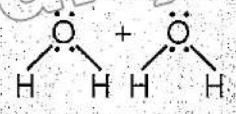
A chemical reaction mainly involves the processes which involve bond breaking and bond formation. In the following reaction, the chemical bonds between the atoms present in the molecules of H_2 and O_2 first break to give their atoms.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

$$\underset{\text{Molecule}}{2H_2(g)} \longrightarrow \underset{\text{Atoms}}{4H(g)} \qquad \underset{\text{Molecule}}{O_2(g)} \longrightarrow \underset{\text{Atoms}}{2O(g)}$$

These atoms of hydrogen then form bonds with oxygen atoms to form two molecules of gaseous H_2O.

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



Breaking of bonds of H_2 and O_2 absorb energy (endothermic process) while making of bonds between H and O evolve energy (exothermic process). In this reaction, weaker bonds are broken i.e of H_2. Hence less energy is absorbed in the system. While the bonds which are formed in water molecule are stronger and thus greater energy is evolved. Hence, the energy which is evolved is more than the energy which is absorbed. The overall reaction is thus exothermic.

$2H_2(g) \longrightarrow 4H(g) + 435\ kJ/mol$		(Endothermic)
$O_2 \longrightarrow 2O + 498\ kJ/mol$		(Endothermic)
$O + H \longrightarrow O-H - 484\ kJ/mol$		(Exothermic)

Since two moles of H_2 take part in the reaction so total energy absorbed in the reaction

$$2H_{2(g)} \longrightarrow 4H + 870\ kJ/mol$$

$$O_{2(g)} \longrightarrow 2O_{(g)} + 498\ kJ/mol$$

$$2H_{2(g)} + O_{2(g)} \longrightarrow 4H_{(g)} + 2O_{(g)} + 1368\ kJ/mol$$

It means 1368 kJ energy is absorbed when 2 moles of H_2 and one mole of O_2 break their bonds to convert themselves into atoms.

Bond dissociation energy of H_2 is 435 kJ/mol while that of O_2 is 498kJ/mol. Bond formation energy of one O – H bond is 484 kJ/mol.

Interesting Information!

Nitrogen of the atmosphere reacts with oxygen to produce not only in the presence of lightening. This is because reaction is highly endothermic, so only lightening can provide enough energy for this reaction to take place.

Total energy evolved in the formation of 4 O—H bonds.

$$2\,O_{(g)} + 4H_{(g)} \longrightarrow 2\,H_2O_{(g)} - 1936\text{ kJ/mol}$$

This is the energy evolved when two moles of water are formed from 4 moles of hydrogen atoms and 2 moles of oxygen atoms. Thus for the formation of one mole of water, the energy evolved will be 968 kJ mol^{-1}.

Hence the overall energy evolved in this reaction is = –1936 + 1368 = –568kJ for two moles of water.

$$2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(g)} + 568\text{ kJ/mol} \text{ or } \Delta H = -568\text{ kJ}$$

The enthalpy change for the formation of two moles of gaseous water is thus –568kJ. So the enthalpy change for the formation of one mole of gaseous water will be

$$= -\frac{568\text{ kj}}{2\text{ mol}} = -284\text{ kJ mol}^{-1}$$

The experimental value of formation of gaseous water is -284.3 kJ which is quite close to this calculated value.

Sample Problem:

Calculate the enthalpy of the following chemical reaction.

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

Bond energies of H_2, I_2 and HI are 436, 151, and -299 kJ mol^{-1} respectively.

Exercise

Calculate the enthalpy change for the formation of one mole of liquid water.

5.4 How does a Reaction take place?

A reaction takes place when the reactant molecules collide with each other to give a transition state. Let us study the following hypothetical reaction.

$$A_2 + B_2 \longrightarrow 2AB$$

Before mixing, the molecules of reactants A and B are in a state of random motion separately colliding with each other and with the walls of container. Kinetic energies possessed by these molecules are not the same. Majority of these molecules possess average kinetic energy but a few possess more than average energy while yet others possess less than average kinetic energy. The molecules which possess more than average kinetic energy may also be called excited molecules.

When the two reactant molecules are mixed together, all these molecules start colliding with each other. The collisions which result by colliding molecules having average or less than average kinetic energies may not be able to produce any result. But when the two excited molecules from both the reactants collide with each other they may be able to produce the transition state as shown in the following Fig (5.3).

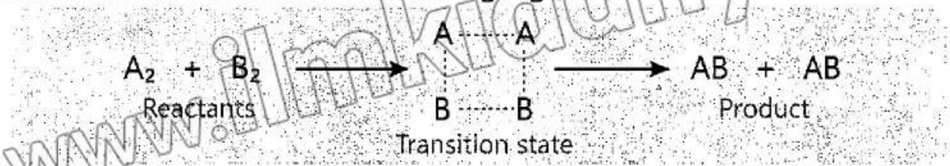


Fig (5.3) Formation of Transition state

The transitation state is shown at the peak of curve. After a very short period of time the transition state either returns to the reactants or to the products. The progress of the reaction can be shown in the form of the following energy profile diagram drawn between path of the reaction and the energy of the reactants and products.

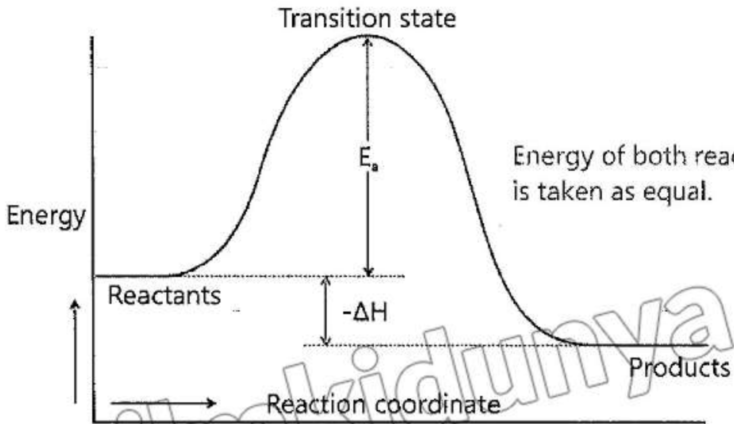


Fig (5.4) Path of Exothermic Reaction

Interesting Information!

Washing clothes at 140°F uses almost twice the energy as at 140°F wash. 90% of the energy used by the traditional electric bulb is wasted in producing heat.

The energy of the transition state is higher than that of reactants or products because the bonds between the reactant or product molecules are being cleaved progressively. The energy absorbed by the reactant or product molecules in order to be converted into the transition state is called the activation energy (E_a) of the reaction. The difference between the energy of reactant and that of the product comes out in the form of heat representing enthalpy (ΔH) of the reaction. This graph represents the path of an exothermic reaction Fig (5.4). A similar graph can be drawn for an endothermic reaction Fig (5.5).

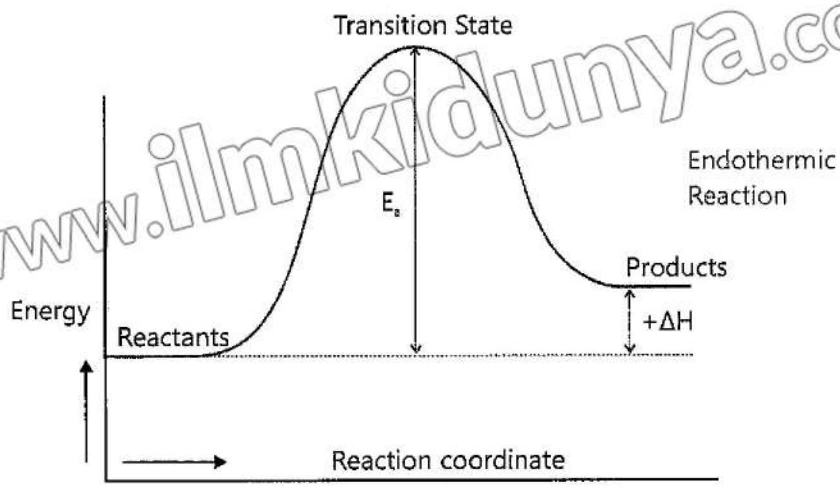


Fig (5.5) Path of Endothermic Reaction

Exercise

Are energy diagrams useful?

Exercise

Draw an energy profile diagram for a hypothecal reaction which does not evolve or absorb heat.

An addition of the catalyst in a reaction increases the rate of reaction because it changes the path adopted by the reactants whereby the activation energy value of the reaction is substantially decreased. As a result, more reactants are now able to be converted into product molecules and hence the rate of reaction will increase Fig (5.6).

A catalyst is thus, defined as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. **For example,** Ni acts as a catalyst in the hydrogenation of oil to give banaspati ghee. Platinum acts as a catalyst in the production of H_2SO_4. Chlorine acts as a catalyst promoting the breakdown of ozone.

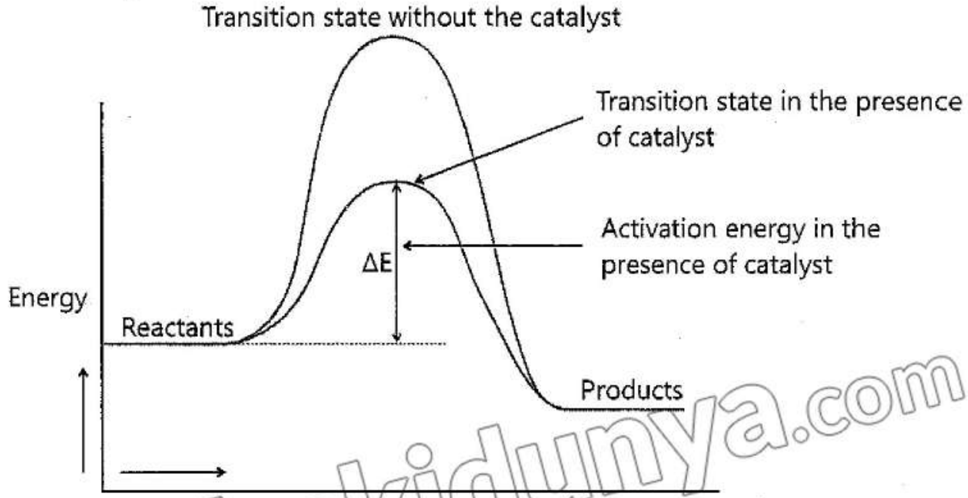


Fig (5.6) Path of Reaction in the absence and presence of a catalysist

5.5 Aerobic and Anaerobic Respiration

The process of respiration in human beings is a continuous process. During this process, we breathe in oxygen and breathe out carbon dioxide. Respiration also carries complex chemical reactions inside the human body. This process that occurs in the presence of oxygen is called aerobic respiration. Aerobic respiration is an exothermic process and involves the following reactions.

$$\underset{(C_6H_{12}O_6)}{\text{Glucose}} \xrightarrow{\text{in cytoplasm}} \underset{\text{Energy}}{\overset{(C_3H_4O_3)}{\text{Pyruvate}} \atop +} \xrightarrow{O_2} 6CO_2 + 6H_2O + \text{Energy}$$

Glycolysis

During glycolysis one molecule of glucose is split into two molecules of pyruvate. This process involves a series of reactions catalysed by enzymes, with a net production of 2 ATP (Adenosine Triphosphate). When cells of our body require energy for performing the metabolic activities, they use this ATP and break it down to get the required energy. The food we eat undergoes digestion in our body and the digested food molecules that are absorbed by the cells undergo oxidation to produce energy.

In certain organisms like bacteria and algae respiration occurs in the absence of oxygen and it is called anaerobic respiration. This is also an exothermic process and during this process glucose is converted into carbon dioxide and ethanol with the evolution of energy.

$$\text{Glucose} \xrightarrow{\text{in cytoplasm}} \underset{\text{Energy}}{\underset{+}{\text{Pyruvate}}} \xrightarrow[\text{Yeast}]{\text{Absence of oxygen}} \underset{\text{Energy}}{\underset{+}{C_2H_5OH}} + CO_2$$

Lipids are a group of organic compounds which include fats, waxes, sterols, etc. Lipids serve as an energy reserve within our body. About half of the fuel our body needs comes from lipids. If you eat more food than you need in a day, the excess food is stored as lipids in adipose cells. In between meals and during exercise our body relies on this resource to provide energy. Glycogen is the primary storage form of glucose. It is stored in the liver and muscles.

Key Points

1. Any physical or chemical change under study is called a system. Everything else which does not fall in this system is called surrounding.
2. The total amount of heat energy present in a system at standard conditions is called its heat content. The quantity of enthalpy of a system is also called its total heat content.
3. The standard enthalpy of a reaction is the enthalpy change that occurs when reactants in their standard states undergo reaction to produce products in their standard states.
4. Chemical reactions which take place with the evolution of heat are called exothermic reactions while those which proceed with the absorption of heat are called endothermic reactions.
5. A chemical reaction always involves breaking and formation of chemical bonds.
6. When weaker bonds are broken while stronger bonds are formed, the reaction is overall exothermic and vice versa.
7. A reaction takes place when the reactant particles collide to give a transition state which then change into the products.
8. The energy needed by the reactant particles to change into transition state is called activation energy.
9. The difference between the energy of reactants and that of products is called enthalpy change of the reaction.
10. The reaction is exothermic if the energy of the products is less than that of reactants and endothermic if the energy of the products is more them that of reactants.
11. A catalyst increases the rate of reaction by decreasing its activation energy.
12. The process of respiration in human beings takes place in the presence of oxygen and it is called an aerobic respiration. In some organisms, the respiration occurs in the absence of oxygen which is called anaerobic respiration.

Exercise

1. Tick (✓) the correct answer.

(i) The following reaction is an exothermic reaction.

$$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$$

From where does the energy come to break the bond of H_2 and Cl_2?

(a) By collisions between the molecules

(b) From sunlight

(c) From the surrounding

(d) By collisions of the molecules with the walls of the container

(ii) Which of the following reactions has the least value of activation energy?

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

(b) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

(c) $NaCl_{(ac)} + AgNO_3 (aq) \longrightarrow AgCl_{(s)} + NaNO_3$

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

(iii) Formation of which hydrogen halide from the elements is an endothermic reaction?

(a) HCl (b) HF

(c) HBr (d) HI

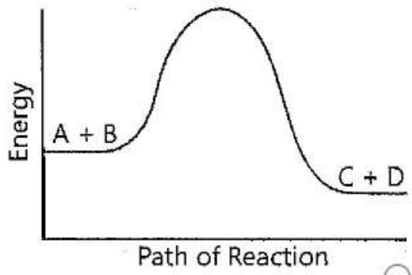
(iv) What are the products of anaerobic respiration?

(a) ATP + CO_2 + H_2O (b) CO_2 + H_2O

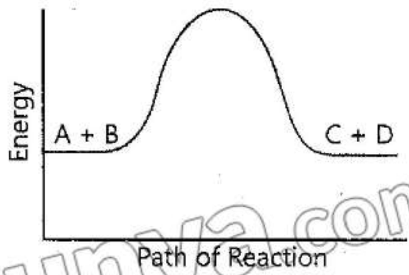
(c) ATP + Ethanol + H_2O (d) Ethanol + H_2O

(v) Which reaction do you expect to be a reversible reaction?

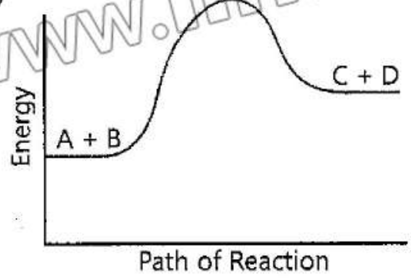
(a)



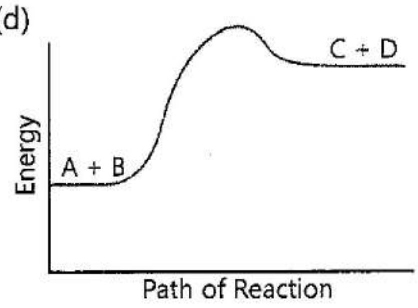
(b)



(c)



(d)



(vi) What does it show when a chemical reaction is exothermic?

(a) It shows the bonds which break are weaker than those are formed.

(b) It shows the bond which break are stronger than those are formed.

(c) Exothermic nature of the reaction is not concerned with bond formation or bond breakage.

(d) It shows that the reactants are more stable than the products.

(vii) When NaOH and HCl are mixed the temperature increases. The reaction is:

(a) endothermic with a positive enthalpy change.

(b) endothermic with a negative enthalpy change.

(c) exothermic with a positive enthalpy change.

(d) exothermic with a negative enthalpy change.

(viii) The average bond dissociation energy for the C-H bond is 412 kJ mol^{-1}. Which of the following process will have enthalpy change close to 412 kJ mol^{-1}?

(a) $CH_{4(g)} \longrightarrow C_{(g)} + 2H_{2(g)}$

(b) $CH_{4(g)} \longrightarrow C_{(g)} + 2H_{2(g)}$

(c) $CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)}$

(d) $CH_{4(g)} \longrightarrow CH_{3(g)} + H_{(g)}$

(ix) The average bond energies for 0 - 0 and 0 = 0 are 146 and 496 kJ mol^{-1} respectively. Find the enthalpy in kJ for the following reaction?

$$H—O—O—H_{(g)} \longrightarrow H—O—H_{(g)} + \frac{1}{2} O = O_{(g)}$$

(a) -102kJ

(b) +102kJ

(c) +350kJ

(d) +394kJ

(x) Why does the following exothermic reaction not occur?

$$C\,(Diamond) \longrightarrow C\,(Graphite) \qquad \Delta H = -3 kJ\,mol^{-1}$$

(a) Structure of diamond is more stable than that of graphite.

(b) Diamond has strong covalent bonds than does the graphite.

(c) The change from diamond to graphite has high activation energy.

(d) Density of graphite is less then that of diamond.

2. Questions for Short Answers

i. What is the difference between enthalpy and enthalpy change?

ii. Why is breaking of a bond an endothermic process?

iii. Depict the transition state for the following reaction.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

iv. Draw the reaction profiles for two exothermic reactions one of which moves faster than the other.

v. What is the role of glycogen in our body?

3. Constructed Response Questions

i. Physical changes which usually occur around us are given in the table. Write down whether they are exothermic or endothermic.

Physical change	Exothermic or Endothermic	Physical change	Exothermic or Endothermic
Conversion of hydrated salt into anhydrous salt		Conduction of electricity by metals	
Burning paper		Dissolving ammonium chloride in water	
Vapourizing liquid nitrogen		Formation of rain from clouds	
Evaporation of dry ice		Dissolving sodium carbonate in water	

ii. Explain why the reaction between atmospheric gases oxygen and nitrogen does not take place under normal conditions? But in the presence of lightening these gases react to give NO. The reaction stops as soon as the lightening stops.

iii. A reaction between natural gas (CH_4) and atmospheric oxygen does not take place when you mix them. As soon as you show a burning match stick, the reaction starts immediately and then it continues until one or both of the reactants is/are used up. Explain.

4. Descriptive Questions

i. Find out the enthalphy change of the following reaction using the given data.

$$N_2 + O_2 \longrightarrow 2NO$$

Bond dissociation energy of N_2 = 958.38 kJ/mol

Bond dissociation energy of O_2 = 498 kJ/mol

Bond formation energy of NO = -626 kJ/mol

ii. Explain the difference between the terms heat and enthalpy.

iii. Explain why formation of a bond is always an exothermic process.

iv. Explain the role of lipids in our body.

v. Explain the following terms.
Activation energy, Transition state, Aerobic respiration

5. Investigative Questions

i. Why is it essential to cook some of the food items while others we can eat without cooking?

ii. Why does fireworks look spectacular. What type of chemical compounds undergo chemical reactions during this activity.