

APPENDIX (IX)
CONTENT OF ENERGY

LEARNING OBJECTIVES

I. SOURCES OF ENERGY

- (a) Sun as primary source of energy.
- (b) Consumption of fuels
- (c) And Pollution

II. ENERGY TERMS ASSOCIATED WITH MATTER

- (a) Internal energy
- (b) Enthalpy
- (c) Hess's law of heat summations
- (d) Entropy
- (e) Free energy
- (f) Predicting the directions of a reaction using the entropy and free energy concepts.

III. NATURE OF ENERGY CHANGES DURING CHEMICAL REACTION

- (i)
 - (a) Distinction between exothermic and endothermic reaction
 - (b) Heat of reaction
 - (c) Heat of Neutralization
 - (d) Heat of combustion
 - (e) Heat of Fusion
 - (f) Heat of vaporization.

(ii) EXAMPLES RELATED TO ENERGY CHANGES DURING CHEMICAL REACTION

Enthalpy and bond energy changes in gaseous state.
Calculation of bond energy with the help of enthalpy changes

UNIT - I

SOURCES OF ENERGY

- (i) Coal
- (ii) Petroleum
- (iii) Natural Gas

Are presently our major sources of energy. These are known as fossil fuels. These carbon containing substances that were formed from the remains of the organisms that lived millions of years ago, under the influence of high temperature and pressure in the interior of earth.

Some other unconventional energy sources which have not been exploited significantly are

Wind Energy
Tidal Energy
Geothermal Energy

Most of these energy sources have not so far been exploited significantly.

Much research is presently focused on nuclear and solar energy.

Solar energy is the world's largest source of energy.

1. Plants absorb energy from the sun through the processes of photosynthesis.
- * Plants serve as food for animals.
 - * Plants and animals are fossilized to coal, petroleum and natural gas.
 - * Plants also supply wood which acts as fuel.
 - * Solar energy causes evaporation of sea water which on subsequent condensation on mountains and other places returns to the sea in the form of rivers. As water flows from higher level to lower level, it can be made to generate electricity.
 - * Other alternative sources of energy.

Source	Renewable or Nonrenewable
1) Biomass	Renewable
2) Wind	Renewable
3) Ocean waves	Renewable
4) Tidal waves	Renewable
5) Solar energy	Renewable
6) Nuclear Fusion (This is to create energy the way stars Produce energy)	Renewable since hydrogen would be the prime source & is available in plenty.
7) Nuclear Fission.	Non - renewable.

CONSUMPTION OF FUELS AND POLLUTION

To meet daily requirements of energy such as

- * Transportation
- * Cooking

Fossil fuels (Coal, Petrol, Diesel etc.) are burnt which causes pollution of atmosphere, in many ways.

1. Combustion of fossil fuel results in the formation of carbon dioxide i.e. CO_2

Fossil fuel + O_2 Combustion \rightarrow CO_2 + H_2O + other
gases + heat.

Carbon dioxide has ability to absorb infrared rays and re-radiate it back. This effect is known as "Greenhouse effect". This would lead to increasing of average temperature of earth.

2. Combustion of fuel in insufficient supply of oxygen produces carbon monoxide (CO), CO combines with Hemoglobin in the blood and forms carboxy - hemoglobin and makes it incapable of transporting oxygen. Many hydrocarbons are carcinogenic and hence, causes serious health hazards.
3. Fossil fuel contains compounds of Sulfur and Nitrogen. During combustion these compounds are oxidised to form oxides of sulfur and nitrogen. Which are corrosive and poisonous. During rains these oxides dissolve in rain water to cause "acid rain".

Part I Questions :-

Note : * Indicates correct answer

Q.1 Following pairs of fuel is non renewable source of fuel.

- (a) Water and noble gas
- * (b) Petroleum and coal
- (c) Sun and wind
- (d) Petroleum and tidal energy

Q.2 Green house effect is caused due

- (a) increase in proportion of noble gas
- (b) increase in the pollution of air
- (c) increase in proportion of nitrogen in air.
- * (d) increase in amount of carbon dioxide in air.

Q.3 Following is known as Green-house effect

- (a) increase in lead content of atmosphere
- * (b) carbon dioxide having ability to absorb IR radiations and radiating them back.
- (c) Formation of carbon monoxide due to incomplete combustion of fuel.
- (d) increase of polluting agents in the atmosphere.

Q.4 Following is the pollution caused by burning fuel.

- * (a) causes acid rain due to the presence of oxide of sulfur and nitrogen in the atmosphere.
- (b) causes soil pollution
- (c) increases chlorine content of water
- (d) increases oxygen content of the atmosphere

UNIT -II

ENERGY TERMS ASSOCIATED WITH MATTER

INTERNAL ENERGY : 'E' Energy possessed by the substance. The various energies which contribute towards internal energy are.

- a) Translational energy of the molecules (E_t)
- b) Rotational Energy of the molecules (E_r)
- c) Vibrational energy of the molecules (E_v)
- d) Electronic energy. (E_e)
- e) Nuclear energy (E_n)
- f) Interaction energy of molecules (E_i)

Therefore, absolute value of internal energy cannot be determined as it is not possible to determine the exact values for the constituent energy.

But, we can determine the change in internal energy which occur during chemical reaction.

Change in internal energy "E" of a reaction is the difference between the internal energy of the product and the reactant.

$$\begin{aligned}\Delta E &= E_{(\text{product})} - E_{(\text{reactant})} \\ &= E_p - E_R.\end{aligned}$$

Internal energy (E) is a state function i.e. it's value depends upon the state of the substance but does not depend upon how that state is achieved.

e.g. CO_2 can be obtained by various methods.

- 1) by heating calcium carbonate.
- 2) by burning coal.

However, one mole of CO_2 at N.T.P. is associated with a definite amount of internal energy which does not depend upon the source from which it is obtained.

FIRST LAW OF THERMODYNAMICS OR LAW OF CONSERVATION OF ENERGY

"Energy can neither be created nor be destroyed, although it may be changed from one form to another".

Total energy of the universe i.e. system + surrounding is always constant during any physical or chemical process.

If a system has internal energy E_1 absorbs certain amount of energy (q)

It's internal energy = $q + E_1$

Let a 'W' amount of work be done on it, so it's internal energy changes to E_2

$$E_2 = E_1 + q + W$$

$$E_2 - E_1 = q + W$$

$$\Delta E = q + W$$

i.e.

Change in internal energy = heat absorbed + work done on the system.

If the volume during the process is V at constant pressure, then work is referred to as pressure-volume work given as

$$W = -P \Delta V.$$

equation 1 can be written as

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

According to internal energy conventions :

q is +ve, if heat is absorbed by the system.
 q is -ve, if heat is given out by the system.
 W is +ve' if work is done on the system.
 W is -ve' if work is done by the system.

If during the change, the volume remains constant, then no work is done i.e. $P \Delta V = 0$ Hence,

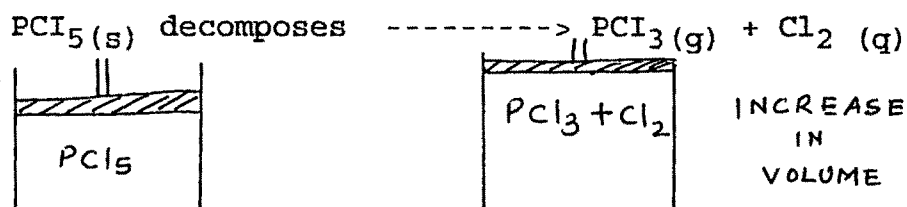
$$q.v = \Delta E$$

ENTHALPY 'H' :

Energy change occurring during the reaction at constant 'T' (temperature) and 'V' (volume) is given by internal energy change.

But when a reaction is carried out at constant pressure two possibilities arises :

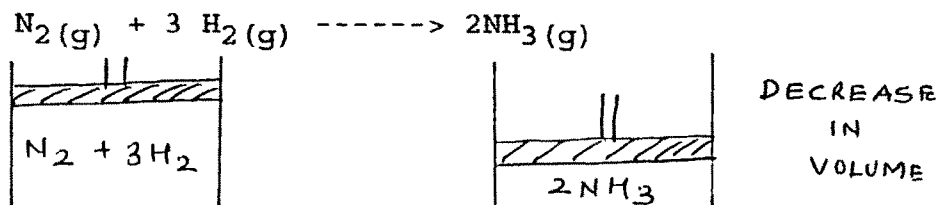
- (i) If reaction proceeds with increase in volume.



reaction system has to expand against the atmospheric pressure and energy is required for this purpose.

that is heat evolved would be little less than the heat evolved at constant volume.

- (ii) if reaction proceeds with decrease in volume at constant pressure



Work is done on the system and heat evolved will be little greater than the heat evolved at constant volume.

Hence, to study the heat changes at constant 'T' and 'P' A new function, enthalpy is introduced.

Enthalpy is total energy associated with any system which includes it's internal energy and also energy due to environmental factors such as pressure-volume conditions.

Mathematically, it may be put as

$$H = E + PV$$

It is not possible to determine the absolute value of enthalpy because 'E' is not known. ΔH , change in enthalpy during chemical process can be determined.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$
$$\Delta H = H_p - H_R$$

'ENTROPY' 'S' :

"The randomness or disorder in system is expressed in terms of function called entropy" Represented by 'S' It is a state function measured in joules per degree kelvin (Jk)

$$\Delta S = S_{\text{(final stage)}} - S_{\text{(initial stage)}}$$

Change in Entropy

To understand the term randomness

Let us consider the Criterion of spontaneity : "It is known that spontaneous process have a natural urge to occur under a particular set of conditions.

This indicates that there is some driving force that makes a process to take place by itself after proper initiation.

"Now, let us find out criterion for spontaneity of a process"

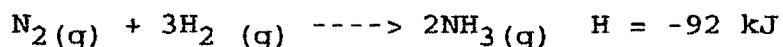
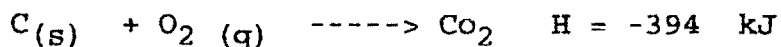
IS ΔH THE CRITERION ?
(ENTHALPY CHANGE)

It is known that all the system in this universe tend to acquire a state of minimum energy.

That is the processes which are accompanied by evolution of heat are called exothermic reaction. That is exothermic reactions should be spontaneous.

For exothermic reactions ΔH is negative.

e.g.

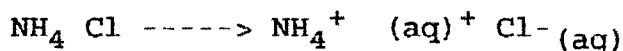


But negative value of ΔH can not be taken as only criterion of spontaneity of a reaction.

e.g.

(i) Endothermic reactions.

Dissolution of ammonium chloride $\text{NH}_4\text{Cl(s)}$ in water.



$$\Delta H = +15 \text{ kJ.}$$

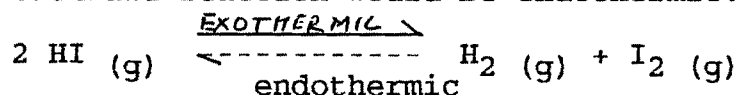
b) Reactions do not go to completion

Most of spontaneous exothermic reactions when carried out in a closed vessel do not go to completion and proceed only upto a state of equilibrium.

c) Reversible nature of the reaction

There are many reaction in which forward and backward reactions take place simultaneously.

In such cases if forward reaction is exothermic then backward reaction would be endothermic.



The above facts indicate that ΔH is not the only criterion of spontaneity.

ANOTHER CRITERION OF SPONTANEITY IS THE TENDENCY TO HAVE MAXIMUM RANDOMNESS

Let us consider a process in which H is almost equal to zero and hence is not favouring the feasibility of the process.

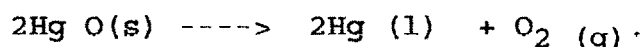
The diffusion of two gases which do not react chemically is one such process.

Here, air and Bromine Vapours are taken in two vessels which are separated by a movable partition when the partition is removed. The two gases get uniformly distributed.

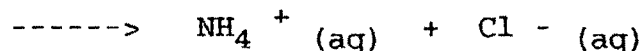
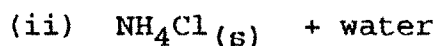
Intermixing of gases results in increase in randomness or disorder of the system.

That is increase in randomness is the other criterion for spontaneity.

In endothermic reactions where ΔH is +ve There is increase in randomness.



Here, randomness increases because products are in liquid or in gaseous state whereas reactant is in solid state. Randomness of gaseous state is greater than that of liquid state, which is in turn greater than that of solid state.



ions which were previously held together in the crystal lattice in solid state are now free and moving about in all direction, It means disorder has increased.

Thus, factor that determine spontaneity is the tendency of the system to attain the state of maximum randomness.

Randomness is expressed in terms of a function called entropy. Represented by 'S'

- * It is a state function.
- * It is measured in Joules per degree kelvin (JK^{-1})
- * A system having greater disorder has greater entropy.
- * Entropy change ΔS in any process is given as

$$\Delta S = S(\text{final stage}) - S(\text{initial stage})$$

Thus, spontaneity of a process is determined in terms of two tendencies.

- (i) Tendency to have minimum energy
- (ii) Tendency to have maximum randomness

FREE ENERGY 'G'

The two tendencies which determine the spontaneity of a process act independent of each other and may work in the same or opposite directions.

If these two tendencies work in opposite directions then the direction of spontaneous change is determined by the tendency having greater magnitude.

Gibbs free energy is related to enthalpy (H) and entropy (S) and temperature (T) as

$$G = H - TS$$

Change in free energy is given as

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

This equation is known as Gibbs - Helmholtz equation.

One can predict from these equations whether a particular process is spontaneous or not at a particular temperature and pressure.

For a spontaneous process ΔG should be negative.

(i) $\Delta G = -ve$ (negative)

reaction is spontaneous

(ii) $\Delta G = 0$

the reaction is in equilibrium,

(iii) $\Delta G = \text{positive (+ve)}$

The reaction is non - spontaneous

CONDITIONS FOR SPONTANEOUS PROCESSES :

(i) Both energy as well as entropy factor are favourable i.e. ΔH is negative and ΔS is positive. Under these conditions ΔG would certainly be negative and the process would occur spontaneously

(ii) Energy factor favours but entropy factor opposes i.e. ΔH is negative, under these conditions ΔG would be negative.

(iii) Energy factor opposes but entropy factor favours i.e. ΔH is positive
 ΔS is positive

Under these conditions ΔG would be negative.
Signs of ΔH , ΔS , ΔG to predict spontaneity

ΔH	ΔS	ΔG	Remarks	Example
-	+	-	Spontaneous at all temperature	$2O_3 \rightarrow 3O_2$
-	-	-		
-	-	-	at low temp spontaneous	
		+	at high temp non-spontaneous at high temp.	$H_2O(g) \rightarrow H_2O(l)$
+	+	+	at low temp Non-spontaneous	
		-	at high temp spontaneous	$H_2O(s) \rightarrow H_2O(l)$
+	-	+	Non spontaneous at all temp.	$3O_2(g) \rightarrow 2O_3(g)$

Part II Questions

Note : * Indicates correct answer

Q.1 Internal Energy 'E' is

- *(a) specific for a particular substance.
- (b) Which depends upon the path followed to obtain the substance.
- (c) absolute value of energy
- (d) None of the above.

Q.2 The relationship between E (internal energy); work done (w) and heat absorbed (q) is best represented by;

- (a) $E = q - P \Delta V$
- (b) $P \Delta V = E + q$
- *(c) $E = q - P \Delta V$
- (d) $P \Delta V = q + E$

Q.3 What is the mode of transfer of energy when petrol is subjected to combustion in engine of a scooter ?

- (a) as heat only.
- (b) partly as work and partly as light
- *(c) partly as heat and partly as work
- (d) as work only.

- Q.4 Internal energy of a molecule is....
- (a) Kinetic energy only
 - * (b) Kinetic as well as potential
 - (c) Potential energy only
 - (d) None of these
- Q.5 A system gives out 20 joule of heat and 40 joules of work. What is the internal energy change ?
- (a) + 80 joule
 - (b) - 102 joule
 - (c) + 20 joule
 - * (d) - 60 joule
- Q.6 200 joule of work is done on the system and 140 joule of heat is given out. What is the change in internal energy ?
- * (a) + 60 joule
 - (b) - 40 joule
 - (c) 60 joule
 - (d) + 340 joule
- Q.7 Enthalpy of a system is
- * (a) Total energy of a system including, internal energy and energy due to environmental factors
 - (b) It is the energy of product
 - (c) It is the difference in energy of product and reactant
 - (d) It is the energy associated with change in environmental factors like T,P.
- Q.8 IF the enthalpy change of the reaction
- $$\text{CH}_4 (\text{g}) + \text{C}_2\text{H}_4 (\text{g}) \longrightarrow \text{C}_3\text{H}_8 (\text{g}) \text{ is } - 19.4 \text{ kcal}$$
- What will be the enthalpy change of the reaction.
- $$\text{CH}_3\text{H}_8 (\text{g}) \longrightarrow \text{CH}_4 (\text{g}) + \text{C}_3\text{H}_4 (\text{g})$$
- (a) -38.8 kcal
 - (b) -20.0 kcal
 - (c) -19.4 kcal
 - (d) +19.4 kcal
- Q.9 Predict which of the following processes proceed with increase in randomness ?
- a) Liquification of a gas
 - b) Crystallization of sugar
 - c) Combination of atoms to form bond
 - * d) Melting of ice

- Q.10 Which of the following are spontaneous processes ?
- a) Raising of water level with pump
 - b) Electrolysis of NaCl solution
 - *c) burning of wood
 - d) solidification of water.
- Q.11 The heat change taking place during the reaction at a particular temperature, which does not involve any change of volume is represented by
- a) G
 - b) H
 - c) N
 - *d) E
- Q.12 Which of the following processes proceeds with the positive value of ΔS ?
- *a) $\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$
 - b) $\text{SO}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{SO}_3\text{(g)}$
 - c) Freezing of icecream
 - d) $\text{H}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$
- Q.13 Entropy denoted by ' S ' measures
- a) heat of a reaction
 - *b) disorder of a system
 - c) rate of a reaction
 - d) reversibility of a reaction
- Q.14 Spontaneity of a process is determined in terms of two tendencies.
- a) Tendency to have maximum energy and maximum randomness.
 - b) Tendency to have minimum energy and minimum randomness.
 - c) Tendency to have average energy and randomness
 - *d) Tendency to have maximum randomness and minimum energy.
- Q.15 For a spontaneous process the value of ΔG should be ..
- a) positive
 - b) Zero
 - *c) negative
 - d) fractional

UNIT III

ENDOTHERMIC AND EXOTHERMIC REACTIONS :

Depending upon the evolution or absorption of energy the chemical reactions can be classified into two types; exothermic and endothermic

Exothermic reactions :

The chemical reaction's which proceed with the evolution of heat energy are called exothermic reactions.

Enthalpy change ΔH can be written as

$$\Delta H = H_p - H_r$$

$$\text{if } H_p < H_r.$$

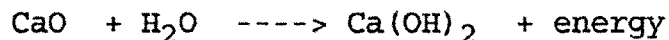
That is $H = -ve.$

H_p - enthalpy of products

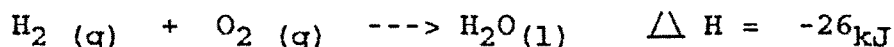
H_r - enthalpy of reactants.

Examples :

(i) when CaO lime is added to water which is used for white washing purpose large amount of heat is produced.



$$\Delta H = -ve.$$



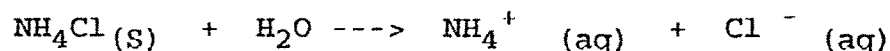
Heat evolved is expressed in the unit joules (J) or kilojoules (kJ).

ENDOTHERMIC REACTIONS : Chemical reactions which proceed with the absorption of heat energy are called endothermic reactions.

When, endothermic reaction is carried out at constant temperature and pressure. Due to absorption of heat the enthalpy of products (H_p) increases.

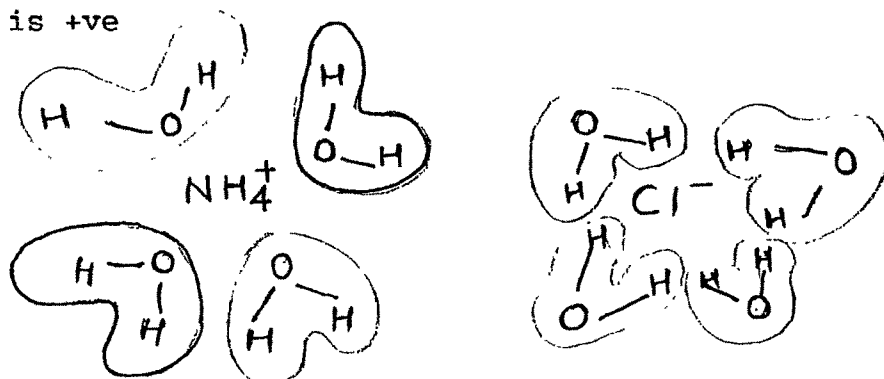
$$\begin{aligned} \Delta H &= H_p - H_r. \\ \text{As } \Delta H_p &> \Delta H_r. \\ \Delta H &= +ve \end{aligned}$$

When ammonium chloride NH_4Cl is added to water, cooling effect is observed due to following reaction.



Here energy is required to break bond the between NH_4^+ and $\text{Cl}^- (\text{aq})$

ΔH is +ve



Energy changes during chemical reaction depends upon the nature of bonds, that are to be broken up.

Energy can also be liberated in the form of

- 1) radiation,
- 2) electrical energy
- 3) Mechanical energy.

Due to chemical reaction occurring in a battery. Chemical energy is converted into electrical energy.

By using battery of high efficiency cars, buses etc. can operate which is an example of conversion of electrical energy into mechanical energy.

HEAT OF A REACTION :

It is the amount of heat absorbed or evolved during a chemical reaction is called the enthalpy change of the reaction, it is represented by H . A standard state of a substance is it's most stable state under one atmospheric pressure and 298°K .

The enthalpy change at the standard state conditions is called standard enthalpy of the reaction denoted by H° . Superscript (o) indicates standard state.

Na, Ag, Cu etc. are solid in their standard state. Represented as $\text{Na}(\text{s})$, $\text{Ag}(\text{s})$ $\text{Cu}(\text{s})$ respectively. Similarly $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ are gaseous under standard conditions

The enthalpy of each element in a standard state is regarded as zero.

ΔH is expressed in either in kcal or kilojoules.

HESS'S LAW OF CONSTANT HEAT SUMMATION :

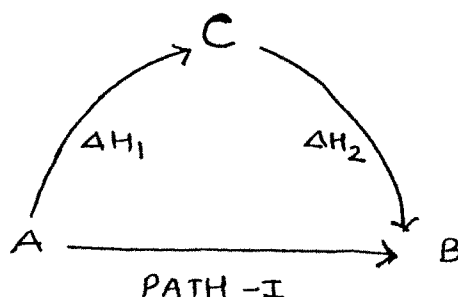
Law states that " The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps

ΔH by path II -

(i) $\Delta H = H_1 + H_2$

ΔH by Path I is

(ii) ΔH PATH-II

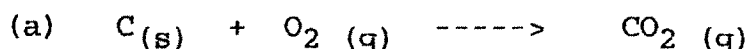


It implies that the enthalpy change of reaction depends only on the state of reactants and products and not on the way by which the change is brought about.

Let us consider the formation of carbon dioxide from carbon and oxygen.

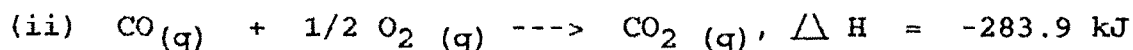
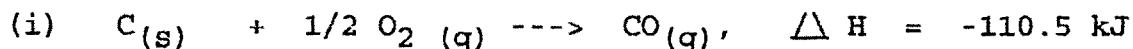
There are two ways by which the change can be brought about :

Conversion of carbon to carbon dioxide



$\Delta H = -393.5 \text{ kJ}$

(b) Conversion of carbon to carbon monoxide then conversion into carbon dioxide.



$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 \\ -393.5 \text{ kJ} &= -116.5 + (-283.9) \text{ kJ} \\ &= -393.5 \text{ kJ}\end{aligned}$$

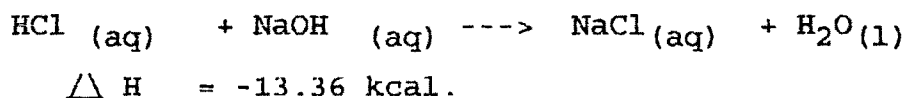
The important result of the Hess's law is that thermochemical equations can be added or subtracted.

Therefore, it is possible to calculate the heat changes which cannot be measured experimentally e.g.

- * heat of reaction
- * heat of combustion
- * heat of neutralization so on...

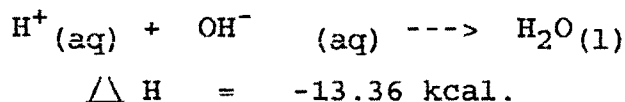
HEAT OF NEUTRALIZATION

It is the enthalpy change accompanying the complete neutralization of one gram equivalent of an acid by a base in dilute aqueous solutions.



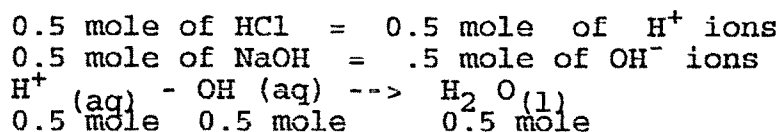
Acid + base Neutralization process \longrightarrow Salt + water

Heat of neutralization of strong acid with strong base is always 13.3 kcal. As strong acids and strong bases are completely ionized in dilute aqueous solutions Neutralization simply involves the combination of H^+ ion (from acid) and OH^- ion (from base) to form water molecule.



Examples :

- (1) What would be heat released when
 - i) 0.5 mole of HCl is neutralized by 0.5 mole of NaOH in aqueous solution.

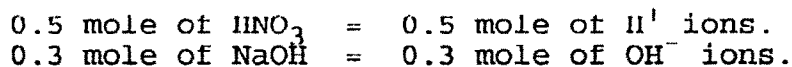


When 1 mole of water is formed by combination of H^+ and OH^- ion 13.36 kcal of heat is produced.

Heat produced during formation of 0.5 mole of water formation of 0.5 mole of water would be

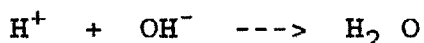
$$\begin{aligned}&= 13.36 \times 0.5 \\ &= 6.68 \text{ kcal.}\end{aligned}$$

- (2) 0.5 mole of HNO_3 is mixed with an aqueous solution containing 0.3 mole of NaOH



Now

0.3 mole OH^- ions would react with 0.3 mole of H^+ to give 0.3 mole of H_2O



$$\begin{aligned} 0.3 \text{ mole } & 0.3 \text{ mole } & 0.3 \text{ mole} \\ \text{Energy liberated} &= 0.3 \times 13.36 \\ &= 4.008 \end{aligned}$$

- (3) 100 cm^3 of 0.2 M HCl solution is mixed with 200 cm^3 of 0.3 M KOH .

100 cm^3 of 0.2 M HCl contain

$$\frac{0.2 \times 100}{1000} = 0.02 \text{ mole HCl}$$

200 cm^3 of 0.3M KOH contain

$$\frac{0.3 \times 200}{1000} = 0.06 \text{ mole KOH}$$

0.02 mole H^+ ions would react with 0.02 mole of OH^- ions to form 0.02 mole of H_2O .

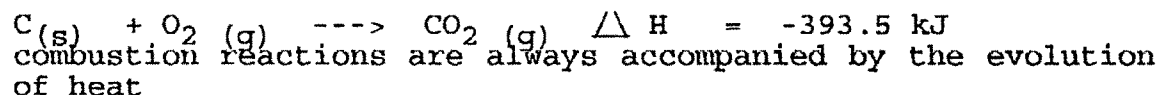
$$\begin{aligned} \text{The heat liberated} &= 13.36 \times 0.02 \\ &= 0.2672 \text{ kcal.} \end{aligned}$$

HEAT OF COMBUSTION

It is the heat change accompanying the complete combustion of one mole of a substance in excess of oxygen or air.

Examples :

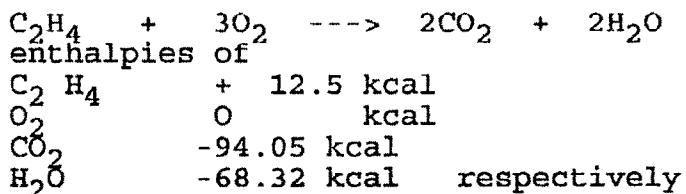
- (1) Combustion of carbon.



for such reaction ΔH is always negative.

$$\begin{aligned} \Delta H &= H_p - H_r \\ \Delta H &= (\text{enthalpy of product}) - (\text{enthalpy of reactants}) \end{aligned}$$

For a given reaction

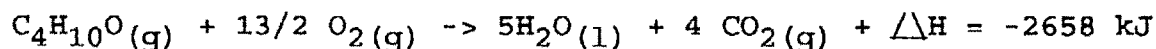


Using this data calculate heat of combustion of ethylene (C_2H_4) $\Delta H = H_p - H_r$

$$\begin{aligned}\Delta H &= (2 \times \text{enthalpy of } \text{CO}_2 + 2 \times \text{enthalpy of } \text{H}_2\text{O}) - \\ &\quad (\text{Enthalpy of } \text{C}_2\text{H}_4 + 3 \times \text{enthalpy of } \text{O}_2) \\ &= [2(-94.05) + 2 \times (-68.32)] - [12.5 + 3 \times (0)] \\ \Delta H &= -337.24 \text{ kcal is the heat of combustion of ethylene.}\end{aligned}$$

Example

- (1) A cylinder of cooking gas is assumed to contain 11.2 kg of butane the thermochemical equation, for the combustion of butane is



If a family needs 1500 kJ of energy per day for cooking, how long would the cylinder last.

Solution :

Molecular mass of butane (C_4H_{10})

$$= 58 \text{ g / mole}$$

58g of butane gives 2658 kJ of heat

11.2 kg of butane would yield

$$= \frac{2658 \times 11.2 \times 1000}{58} \text{ kJ}$$

daily requirement of energy is = 15000 kJ
The cylinder would last for.....days

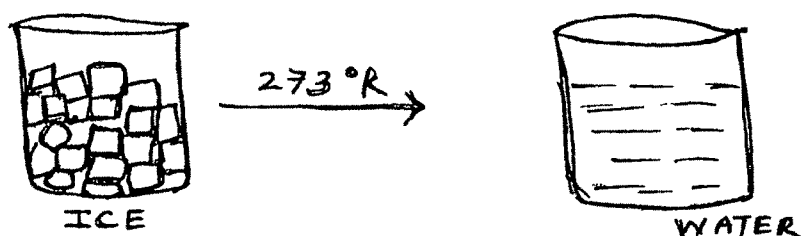
$$= \frac{2658 \times 11.2 \times 1000}{58 \times 15000} \text{ days.....}$$

$$= 34 \text{ days.}$$

HEAT OF FUSION :

It is the enthalpy change (ΔH) accompanying the conversion of mole of a solid substance into the liquid state at its melting point.

When 1 mole of ice changes into water at it's melting point (273°K) 6.0 kJ of heat is absorbed.



The value of ΔH fusion gives idea about magnitude of force of attraction between the molecules of solid.

Example : Ionic solid like NaCl have strong force of attraction between the ions therefore ΔH fusion is also very high.

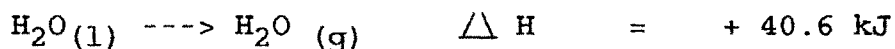
Enthalpies of fusion of substances

substance	M.P $^{\circ}\text{K}$	ΔH fus. kJ/mole
Oxygen	55	+ 0.45
CC 14	250	+ 2.5
NaCl	1074	29.0
MgCl ₂	1260	+ 43.0

ENTHALPY OF VAPORIZATION

It is the enthalpy change ΔH accompanying the conversion of one mole of a liquid into it's vapours at the boiling point.

When one mole of water is converted into steam at 100°C . the enthalpy change accompanying the process is 40.6 kJ.



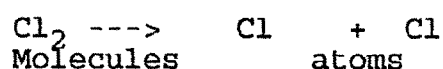
The values of ΔH vap. gives an idea about interparticle forces among the molecules. Stronger the interparticle force higher is the value of ΔH of vaporization.

Substance	B.P. °K	Hvap. kJ/mole
Oxygen	90	+ 0.67
Ethyl alcohol	351	+ 34.7
Sodium chloride	1738	+ 170.0
Magnesium chloride	1691	+ 137.0

(ii) **ENTHALPY AND BOND ENERGY CHANGES IN GASEOUS STATE :**

Theoretical values of heat of reaction can be calculated by the use of bond energy values

Bond energy is the amount of energy required to break bond and form respective atoms, ions or radicals.



Bond energy of different bonds.

Bond	Bond Energy kcal/mole	Bond	Bond energy kcal/mole
H - H	103	Br-Br	46
C - H	98	N - H	92
Cl - Cl	57	C = C	145

Examples :

- (1) Calculate ΔH for the following reaction using bond energy values $2\text{C}_{(s)} + 3\text{H}_{2(g)} \text{ ----> } \text{C}_2\text{H}_6$

Bond energies of reactants

$$\begin{aligned}
 &= 2 \text{ atom (Cs --> Cg)} + 3 (\text{H} - \text{H}) \\
 &= 2 (170) + 3 (103) \\
 &= 649 \text{ kcal}
 \end{aligned}$$

Bond energies of products -

$$\begin{aligned}
 &= 1 \times (\text{C-C bond}) + 6 (\text{C} - \text{H}) \\
 &= 1 (80) + 6 (98) \\
 &= 80 + 588 \\
 &= 668 \text{ kcal}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H &= \text{bond energies of reactants} - \text{bond energies of products} \\
 &= 649 - 668 \\
 &= -19 \text{ kcal}
 \end{aligned}$$

Part III Questions

Note : * indicates correct answer

Q.1 Which of the following reactions are exothermic

- *a) $4\text{C (s)} + 5\text{H}_2\text{(g)} \rightarrow \text{C}_4\text{H}_{10}\text{(g)}; \quad \text{H} = -123 \text{ kJ}$
- b) $\text{Hgo(s)} + 180.04 \text{ kJ} \rightarrow \text{Hg(l)} + \text{O}_2\text{(g)}$
- *c) $.5 \text{ N}_2\text{(g)} + 1.5 \text{ H}_2\text{(g)} \rightarrow \text{NH}_3\text{(g)} + 45 \text{ kJ}$
- d) $\text{SnO}_2\text{(s)} + 2\text{CO (g)} \rightarrow \text{Sn (s)} + 2\text{CO}_2 - 360 \text{ kJ}$

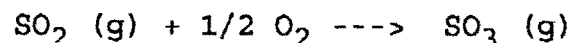
Q.2 Will the process
 $\text{Mg(g)} \rightarrow \text{Mg}^{+2}\text{(g)} + 2\text{e}^-$ be

- a) exothermic
- *b) endothermic
- c) evolving no heat change
- d) exothermic as well as endothermic

ANS KEY $\text{Mg (g)} \rightarrow \text{Mg}^{+2} + 2\text{e}^-$

This reaction involves removal of two electrons from magnesium atom forming magnesium ion. Therefore, energy is required to remove electron to form ion. Hence the above reaction would be endothermic.

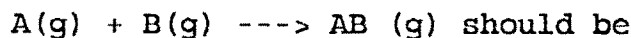
Q.3 Should the following spontaneous reaction be



- *a) exothermic
- b) endothermic
- c) endothermic as well as exothermic

ANS KEY Exothermic, Because randomness decreases energy factor must favour

Q.4 The chemical reaction



- *a) exothermic
- b) endothermic
- c) neither exothermic nor endothermic
- d) unpredictable

Q.5 IF $H^\circ \text{CO}_2 = -111.3 \text{ kJ/mole}$
 $H^\circ \text{O}_2 = 0$ "
 $H^\circ \text{CO} = -110.5 \text{ kJ/mole}$ "

predict about following reaction
 $2\text{CO(g)} + \text{O}_2 \text{(g)} \rightarrow 2\text{CO}_2 \text{(g)}$

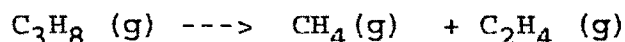
- a) exothermic $H = -293.4 \text{ kJ}$
- b) endothermic $H = +463.5 \text{ kJ}$
- *c) exothermic, $H = -564.4 \text{ kJ}$
- d) exothermic, $H = -393.5 \text{ kJ}$

ANS KEY

$$\begin{aligned} H &= H_p - H_r \\ &= 2 \cdot \text{CO}_2 - (2 \cdot \text{CO} + \text{O}_2) \\ &= 2 \times -393.5 - (2 \times -111.3 + 0) \\ &= -787.0 - (-222.6) \\ &= -787.0 + 222.6 \\ H &= -564.4 \text{ kJ Exothermic} \end{aligned}$$

Q.6 If enthalpy change of the reaction,

$\text{CH}_4 \text{(g)} + \text{C}_2\text{H}_4 \text{(g)} \rightarrow \text{C}_3\text{H}_8 \text{(g)}$ is -19.4 kcal .
 What will be the enthalpy change of the reaction.



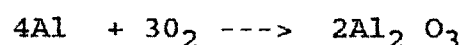
- a) -19.4 kcal
- b) $+38.8 \text{ kcal}$
- c) -38.8 kcal
- *d) $+19.4 \text{ kcal}$

ANS KEY As the given reaction $\text{CH}_4 \text{(g)} + \text{C}_2\text{H}_4 \text{(g)} \rightarrow \text{C}_3\text{H}_8 \text{(g)}$ $H = -19.4 \text{ kcal}$

is exothermic. The reverse of above reaction, i.e.
 $\text{C}_3\text{H}_8 \text{(g)} \rightarrow \text{CH}_4 \text{(g)} + \text{C}_2\text{H}_4 \text{(g)}$
 would be endothermic with

$$H = +19.4 \text{ kcal}.$$

Q.7 H for Al_2O_3 is -1670 kJ what is the enthalpy change of the reaction.



- a) $+1670 \text{ kJ}$
- b) $+3340 \text{ kJ}$
- *c) -3340 kJ
- d) -1670 kJ

ANS KEY

$$\begin{aligned} H &= H_p - H_r \\ H &= 2HAl_2O_3 - (4 HAl + 3 HO_2) \\ &= 2 \times -1670 - (4 \times 0 + 3 \times 0) \\ H &= -3340 - (0 + 0) \\ H &= -3340 \text{ kJ} \end{aligned}$$

Q.8 Consider the following reactions, both of which produce C,D, from A and B.

- 1) $A + B \rightarrow Q ; Q \rightarrow C + D$
- 2) $A + B \rightarrow AB ; AB \rightarrow C + D.$

will the enthalpy change for net process in two cases be same or different ?

- a) different
- b) Zero
- c) negative
- *d) same

Q.9 The enthalpy of neutralization of HCl and NaOH is

- a) Zero
- *b) - 13.36 kcal
- c) +57.3 kJ
- d) can not be predicted.

Q.10 In which of the following reactions, heat of neutralization has highest numerical value.

- a) NH_4OH and HCl
- b) CH_3COOH and NaOH
- *c) NaOH and HCl
- d) NH_4OH and CH_3COOH

Q.11 From the following equation which will give heat of combustion.

- a) $N_2 + 3H_2 \rightarrow 2NH_3$
- *b) $C + O_2 \rightarrow CO_2$
- c) $NH_4OH + HCl \rightarrow NH_4Cl + H_2O$
- d) $H_2C = CH_2 + H_2 \rightarrow CH_3 - CH_3$

Q.12 From the following equation which equation represents fusion and which equation represents vaporization.

- a) $H_2(g) \rightarrow H_2(l)$
- b) $C_2H_4(g) \rightarrow C_2H_4(l)$
- c) $C_2H_6(l) \rightarrow C_2H_6(g)$
- d) $S(s) \rightarrow S(l)$
- e) $H_2O(l) \rightarrow H_2O(g)$
- f) $H_2O(s) \rightarrow H_2O(l)$