

## Thermodynamics

1. Thermodynamics means flow of heat. This deals with the quantitative relationship existing between heat and other forms of energy in physicochemical transformations.
2. The four laws are namely zero, first, second and third laws of thermo dynamics have been arrived on the basis of experimental facts and there is no theoretical proof for any of these laws.
3. A specified part of the universe under constant observation is called System.

**Ex:** i) A crystal (for a crystallographer)  
ii) Chemical reaction (for a chemist)

4. The part of the universe other than the system is called Surroundings.

Universe = system +surroundings.

5. Systems are classified on the basis of their interaction with the surroundings as follows

i. A system that can exchange both matter and energy with the surroundings is called open system.

**E g.** Boiling water in an open vessel.

ii. A system that can exchange only energy with the surroundings but not matter is called closed system.

**E.g.** Hot water in a closed steel vessel.

iii. A system that can exchange neither matter nor energy with the surrounding is called isolated system.

**E.g.** Hot water in an insulated (or) thermos flask.

6. On the basis of composition, there are two types of systems.

**i) Homogeneous System:** A system consisting of one phase only.

**Ex:** Pure solid, a liquid or a mixture of gases.

**ii) Heterogeneous System:** It may consist of two or more phases.

**Ex:** a solid in contact with liquid state.

7. Thermodynamics deals with macroscopic properties only Macroscopic Properties are those that arise due to collective behaviour of the individuals  
E.g. Pressure, Volume, Temperature, Surface Tension, Viscosity, Density etc.
8. Macroscopic properties whose value is independent of the total quantity of matter contained in the system is called Intensive property  
E.g. Temperature, Viscosity, Pressure, Surface Tension, Dielectric constant, Specific Heat, Refractive Index, Molarity, Normality,  $p^H$ , boiling point, freezing point, Vapour pressure and molar properties such as molar volume, molar entropy, molar heat capacity.
9. Macroscopic properties whose value depends on the total quantity of matter contained in the system is called Extensive Property.  
E.g. Mass, Volume, Internal Energy, Heat Capacity, Energy, Enthalpy, Entropy etc.,
10. The condition of existence of a system when the macroscopic properties have a definite value is called a State of System.  
Those macroscopic properties whose value decides the state of a system are called state variables.  
E.g. Pressure, Volume, Temperature and Number of Moles.
11. A thermodynamic parameter (or) quantity whose value depends only on the state of system and it is independent of path is called State Function  
E.g. Pressure, Volume, Temperature, E, H, S, G etc.,
12. A thermodynamic parameter whose value depends on the path of trans-formation is called Path Function.  
E.g. Heat, Work
13. The operation which brings about the changes in the state of the system is termed as Thermo dynamic process.
- 14: Types of Thermo dynamic process
- i)

**Isothermal Process:** ( $\Delta T=0$ ) A process in which temperature of system does not change throughout the studies.

For an isothermal process  $dT =0$  and  $dE=0$ .

An isothermal process is achieved by using thermostatic control.

ii) **Adiabatic Process** ( $\Delta q=0$ ): In this process heat is not exchanged between system and surroundings.

For an adiabatic process  $q = 0$ .

It can be achieved by insulating the system boundaries.

iii) **Isobaric Process**: In this process pressure of the system remains constant through out the studies.

For an isobaric process,  $\Delta P=0$

iv) **Isochoric Process**: In this process volume of the system remains constant through out the studies made in.

For an isochoric process,  $\Delta V=0$

v) **Cyclic Process**: In this process initial state of system is regained after a series of operation.

For a cyclic process  $\Delta U=0$  and  $\Delta H=0$

vi) **Reversible Process**: A reversible process is one in which all changes occurring at any part process are exactly reversed when change is carried out in opposite direction.

It gives rise to maximum work

vii) **Irreversible Process**: An irreversible process is one in which direction of the change cannot be reversed by small change in variables. An irreversible process is a real one and all process which naturally occur are irreversible.

It gives rise to network i.e. somewhat lesser work than the reversible work or

$$W_{\text{rev}} > W_{\text{irrv.}}$$

## 15. Work, Heat and Energy

These are important thermodynamically useful concepts. These are algebraic quantities hence these can be positive (or) negative.

**Mechanical Work (W)**: -The displacement of an object through a distance  $dx$  against a force ( $F$ ) is called work. Work is a path function.

$$W = F \times dx$$

$$W = \text{force} \times \text{distance} = P_{\text{ex}} \cdot A \cdot l$$

It is measured in Joules (J), Kilo Joules (KJ), erg. Cal., lit.atm etc.

It is calculated as the product of external pressure and change in Volume

$$W = - (P \Delta V); (\Delta V = V_{\text{final}} - V_{\text{initial}})$$

'W' is +ve when work is done on the system.

'W' is -ve when work is done by the system

- i) If the pressure is not constant at every stage of compression, but changes in number stage of finite steps, work done on the gas will be summed over all the steps and will be equal to  $-\sum p\Delta V$
- ii) If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount,  $dV$ . In such a case we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} p_{\text{ext}} dV$$

$$1 \text{ lit. atm} = 101.3\text{J} = 1.013 \times 10^9 \text{ erg} = 24.2 \text{ cal.}$$

### I) Work Done In Isothermal Reversible Expansion Of Ideal Gas

$$W_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$$

$$W_{\text{rev}} = -2.303nRT \log \frac{P_1}{P_2}$$

### II) Work Done In Isothermal Irreversible Expansion

$$W = -P_{\text{ext}}\Delta V$$

### III) Work Done In Isothermal Reversible Compression Of Ideal Gas :

$$W_{\text{compression}} = 2.303nRT \log \frac{V_1}{V_2}$$

$$W_{\text{compression}} = 2.303nRT \log \frac{P_2}{P_1}$$

**16. Free Expansion:** Expansion of a gas in vacuum [ $P_{\text{ext}}=0$ ] is called free expansion.

No work is done during free expansion of an ideal gas whether the process is reversible (or) Irreversible.

For isothermal ( $T=\text{constant}$ ) expansion of an ideal gas into vacuum  $W=0$  since  $P_{\text{ext}}=0$

### Solved Problem

Q. Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres.

i) How much heat is absorbed and how much work is done in the expansion?

**Solution:** We have

$$q = -w = p_{\text{ext}}(10 - 2) = 0(8) = 0$$

No work is done; no heat is absorbed.

ii) Consider the same expansion against a constant external pressure of 1 atm.

**Solution:** We have  $q = -w = P_{\text{ext}}(\Delta V) = 1 \times (10 - 2) = 8$  litre-atm.

iii) Consider the same expansion to a final volume of 10 litres conducted reversibly.

**Solution:** We have  $q = -w = 2.303 \times 10 \log \frac{10}{2}$   
= 16.1 litre - atm

17. **Heat (Q):**- It is the form of energy which flows between a system and surroundings by virtue of temperature difference.

**Calorie:** The heat required to raise the temperature of 1 gram of water by  $1^{\circ}\text{C}$  is known as calorie. SI unit is Joule.

18. **Energy**

It is defined as the capacity to do work. The property that is obtained through work or property that can be converted into work is known as **energy**.

The unit of measurement of energy is same as that of work (J or Cal or ergs)

Generally energy is two types.

i) **Potential Energy:** It is the energy associated with a body or a system by virtue of its position or state. Potential energy =  $mgx$

**Ex :** Water stored at an elevated place

(ii) **Kinetic Energy:** it is the energy associated with a body or a system of mass 'm', moving with a velocity 'v'.  $KE = \frac{1}{2} mv^2$

**Ex:** Electron moving in an atom.

### 19. Zeroth Law of Thermodynamics (Or) Law of Thermal Equilibrium

It states that "If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other."

It introduces the concept of temperature to measure hotness or coldness of a body.

### 20. First Law of Thermodynamics (OR) Law of conservation of energy.

It can be stated as "energy is neither created nor destroyed but it may be transformed from one form to another form".

(Or)

"It is impossible to construct a perpetual motion machine of 1st kind that can work without consuming any form of energy" (or) "The net energy change in a closed system is equal to heat absorbed plus the work done by the system"

It is mathematically expressed as  $\Delta E = \Delta Q + W$  (or) according to IUPAC  $q = \Delta E + w$

$\Delta E$  = Change in Internal energy;

$\Delta Q$  = heat gained or lost by the system;

$W$  = Work done by the system (or) on the system.

a) For absorption of heat 'Q' is +ve and for release 'Q' is -ve

b) When work is done on the system 'W' is +ve.

c) When work is done by the system 'W' is -ve.

**Case .i)** When  $W=0$ ,  $\Delta E=q_v$

i.e. internal energy increases If heat is absorbed by system, internal energy decreases If heat is lost by system.

**Case.ii)** When  $q = 0$ ,  $\Delta E=W$

i.e. internal energy increases If work is done on the system and internal energy decreases If work is done by the system,

In adiabatic process work is done by the system at the expense of internal energy.

**Case.iii)** When  $\Delta E=0$ ,  $q=-W$

i.e. Heat absorbed by the system is equal to work done by the system.

If  $W = -q$  Work is done on the system (when  $\Delta E = 0$ ) and heat flows from system to surroundings.

**Case.iv)** For a Cyclic process  $\Delta E = 0, q = -W$

Work done by the system is equal to heat absorbed.

## 21. Internal Energy (E (OR) U)

i) It is the sum of all types of potential and kinetic energies of constituent particles of a given substance at given temperature.

ii) It is an extensive property and a state function.

iii) Its absolute value can't be determined but the change of Internal energy ( $\Delta E$ ) can be determined.  $\Delta E$  of a chemical reaction is determined by Bomb calorimeter.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

iv. For any chemical reaction  $\Delta E = E_P - E_R$

$E_P$  = Total internal energy of the products,  $E_R$  = Total internal energy of the reactants.

a. For any exothermic reaction  $E_P < E_R$  and  $\Delta E$  is negative.

b. For any endothermic reaction  $E_P > E_R$  and  $\Delta E$  is positive.

v. For a given substance Internal energy in vapour phase > liquid state > solid state.

## 22. Enthalpy (H)

i. It is the total heat content of a system at constant pressure and temperature.

ii. It is a state function and an extensive property.

iii. Its absolute value can't be determined but the change in Enthalpy ( $\Delta H$ ) can be determined.  $\Delta H$  of a chemical reaction is determined by calorimeter.

iv. It is related to internal energy as  $H = E + PV$

v. For finite changes at constant pressure, we can write equation  $\Delta H = \Delta E + \Delta pV$

Since P is constant, we can write  $\Delta H = \Delta E + p\Delta V$

vi.  $\Delta H$  is negative for exothermic reactions,  $\Delta H$  is positive for endothermic reactions

vii. For a given substance Enthalpy in vapour phase > liquid state > solid state

**23. Relation Between  $\Delta H$  &  $\Delta E$**  for any chemical reaction, at any constant temperature is

$$\Delta H = \Delta E + \Delta n RT, \text{ where}$$

T = absolute temperature of the reaction, R = Universal gas constant

$$\Delta n = n_2 - n_1$$

$n_2$  = Total number of moles of gaseous products

$n_1$  = Total number of moles of gaseous reactants

For any process which does not involve gases  $\Delta H = \Delta E$

**Solved Problem:** If water vapour is assumed to be perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and  $100^\circ\text{C}$  is 41 kJ/mole. Calculate the internal energy change, when

i) 1 mol of water is vaporised at 1 bar pressure and  $100^\circ\text{C}$

ii) 1 mol of water is converted into ice.

**Solution**

i) The change,  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$   $\Delta H = \Delta U + \Delta n RT$

Substituting the values, we get  $\Delta U = \Delta H - \Delta n RT$

$$= 41 \text{Kj/mole}$$

$$- 1 \times 8.314 \times 10^{-3} \times 373 = 37.904 \text{kj/mole}$$

ii) The change  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$

There is negligible change in volume, so, we can put  $P\Delta V = \Delta n RT$  in this case,  $\Delta H = \Delta U$

So,  $\Delta U = 41 \text{Kj/mole}$ .

**24. Heat Capacity and Specific Heat**

i. Heat Capacity (C) of a substance is the amount of heat required to raise its temperature through one degree

ii. Heat capacity is the ratio of heat absorbed by a system to the resulting increase in temperature

$$C = \frac{q}{dT} \quad q = \text{Heat absorbed by the system}$$



$dT$  = rise in temperature

iii. For gases, heat capacity is of two types - Heat capacity at constant volume ( $C_V$ ) and heat capacity at constant pressure ( $C_P$ ).

a. Heat capacity at constant volume ( $C_V$ ) gives the measure of the change of internal energy ( $E$ ) of a system with temperature

$$C_V = \left[ \frac{\partial E}{\partial T} \right]_v = \frac{q_v}{dT}$$

b. Heat capacity at constant pressure ( $C_P$ ) gives the measure of the change of enthalpy ( $H$ ) of a system with temperature

$$C_P = \left[ \frac{\partial H}{\partial T} \right]_p = \frac{q_p}{dT}$$

**For An Ideal Gas I.  $C_P - C_V = R$**

**II.  $C_P/C_V = \gamma$**

**III.  $C_P - C_V = \frac{R}{M}$**

iv. Molar heat capacity or molar heat = Specific heat X molecular weight of the substance.

Molar heat capacity at constant pressure

$$C_P = \frac{q_P}{dT} = \frac{dH}{dT} = \left( \frac{\partial H}{\partial T} \right)_P$$

a. The molar heat capacity at constant volume  $C_V = \left( \frac{3}{2} \right) R$

b. Molar heat capacity at constant pressure  $C_P = \left( \frac{3}{2} \right) R + R = \left( \frac{5}{2} \right) R$

c.  $\gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.66$

$\gamma$  Values depend upon the atomicity of gaseous molecules due to degree of freedom for molecules to have vibrational and rotational energy in addition to translation energy in case of diatomic molecules and poly atomic molecules.

$\gamma = 1.66$  the gas is mono atomic **Ex:** He, Ne, Ar, Kr.

$\gamma = 1.40$  the gas is diatomic **Ex:** O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub> etc.

$\gamma = 1.33$  the gas is poly atomic **Ex:** CO<sub>2</sub>, SO<sub>2</sub>, K<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> etc.,

**25. Specific Heat Capacity (C):** It is the quantity of heat required to raise the temperature of 1 gram of substance through 1K (or 1°C)

$$\text{Specific heat capacity } (C) = \frac{\text{Heat capacity}}{\text{Mass}} = \frac{C}{M}$$

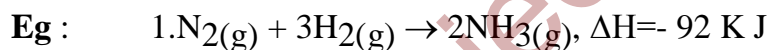
$$C = \frac{q}{m\Delta T} \quad (\text{or}) \quad q = C \times m \times \Delta T$$

Units of "C"  $Jg^{-1}K^{-1}$  (or)  $Jg^{-1}(^{\circ}C^{-1})$

The specific heat capacity (C) and molar heat capacity (C<sub>m</sub>) as of the substance are related as  $C_m = C \times \text{molar mass}$

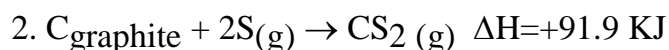
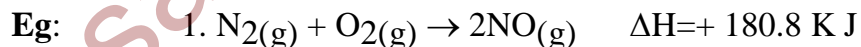
## 26. Exothermic Reactions

A chemical reaction, in which heat is liberated, is known as **exothermic reaction**.



## Endothermic Reactions

A chemical reaction, in which heat is absorbed, is known as **endothermic reaction**.



27. The physical state of a substance under standard conditions ( $t = 25^{\circ}C$ ,  $P = 1 \text{ atm}$ ) is known as standard physical state.

The enthalpies of all elements in their standard state are taken as zero.

32. Stable form of carbon, sulphur and phosphorous are graphite, rhombic sulphur and black phosphorous respectively.

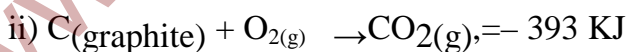
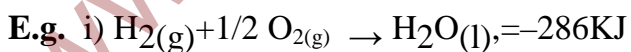
33. The amount of heat evolved or absorbed when the chemical reaction takes place between the reactants as indicated in the stoichiometric equation is called the heat of reaction.
34. The heat of a reaction  $\Delta H$  depends upon
- 1) The physical state of reactants and products
  - 2) Whether the reaction is conducted at constant pressure or constant volume.
  - 3) Temperature
  - 4) Stoichiometry of equation
35. Heat of a reaction at constant volume is equal to the change in intrinsic energy ( $\Delta E$ ).
36. Heat of a reaction at constant pressure ( $\Delta H$ ) is equal to sum of the change in internal energy and external work done
37.  $\Delta H = \Delta E + P\Delta V$ , Where  $P.\Delta V =$  work done
38.  $\Delta H = \Delta E + \Delta n RT$

Where  $\Delta n =$  total number of moles of the gaseous products - total number of moles of the gaseous reactants.

- i) If  $\Delta n$  is positive, then  $\Delta H > \Delta E$
- ii) If  $\Delta n$  is negative, then  $\Delta H < \Delta E$
- iii) If  $\Delta n$  is zero, then  $\Delta H = \Delta E$

**Types of heat of reactions:**

- 39 **Standard heat of Formation:** It is the change in heat content when one mole of a compound in the standard state is formed from its constituent elements in their standard state.



40. A compound formed with evolution of heat is called an exothermic compound.

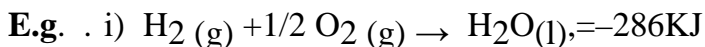
**E.g.** .  $CO_2, SO_2, H_2O, CH_4$  etc;

A compound formed with absorption of heat is called an endothermic compound.

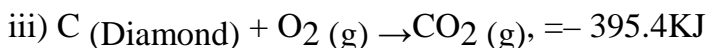
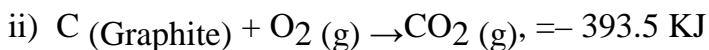
**E.g.**  $CS_2, NO, C_2H_4, C_6H_6,$  etc;

41. Exothermic compounds are more stable than endothermic compounds.

42. The enthalpy of a compound is equal to its standard heat of formation.
43. The change in enthalpy when one mole of the substance is completely burnt in oxygen is called the heat of combustion or the enthalpy of combustion.

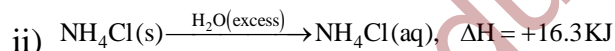
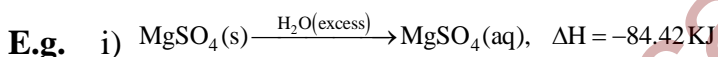


Here,  $\Delta H$  represents enthalpy of combustion of  $\text{H}_2$  or enthalpy of formation of  $\text{H}_2\text{O}$



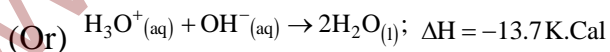
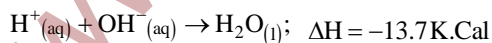
Here,  $\Delta H = -393.5 \text{KJ}$  represents enthalpy of combustion of graphite and also enthalpy of formation of  $\text{CO}_2$ . But  $\Delta H = -395.4 \text{KJ}$  represents heat of combustion of diamond only.

44. All combustion reactions are exothermic.
45. The change in enthalpy when 1 mole of the solute is dissolved in a large quantity (infinite quantity) of the solvent is known as heat of solution.



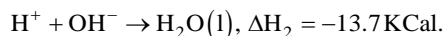
46. The change in enthalpy when one gram equivalent weight of an acid is completely neutralised by one gram-equivalent weight of a base in dilute solution is called the heat of neutralisation or enthalpy of neutralisation.
47. The heat of neutralisation of any strong acid by any strong base is equal to  $-13.7 \text{Kcal}$  Or  $-57.3 \text{KJ}$ .

This is because the strong acid and strong base are completely ionized in aqueous solution. Net reaction is given by



48. If the acid is weak or the base is weak the heat of neutralisation is less than  $13.7 \text{Kcal}$  because a part of it will be used up to dissociate the weak acid or base.
49. Heat of neutralisation is the algebraic sum of heat of neutralisation of  $\text{H}^+$  and  $\text{OH}^-$  and heat of ionisation of weak component.

**E.g.**  $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}, \Delta H = -13.3 \text{KCal}$  the reaction takes place in two steps



As per Hess law,  $\Delta H = \Delta H_1 + \Delta H_2$

50. Hess Law of constant heat summation states that “the enthalpy change in a reaction is always the same whether the reaction is conducted in one step or in several steps”.

51. The amount of energy required to break one mole of a particular bond in a given compound and to separate the resulting gaseous atoms or free radicals from one another is called bond dissociation energy.

For example, the bond dissociation energy of H – H bond in  $\text{H}_2$  molecule is  $435.9 \text{KJ.mol}^{-1}$ .

52. In case of molecules having more than one bonds of same type, bond dissociation energy of all bonds are not equal. Thus average of bond dissociation energies of all bonds to be taken as the bond energy.

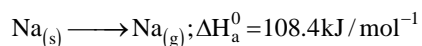
For example, in methane ( $\text{CH}_4$ ) bond energy of all C–H bonds are not equal. Average of four C–H bonds in  $\text{CH}_4$  is to be taken as C–H bond energy.

53. The heat required to dissociate one mole of a simple molecule in the gaseous state into its constituent atoms in the gas phase is called enthalpy of atomization.



54. In case of diatomic molecules, like dihydrogen, the enthalpy of atomization is the bond dissociation enthalpy.

55. In case of metals and monoatomic nonmetals, the enthalpy of atomisation is same as the enthalpy of sublimation.



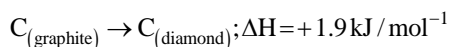
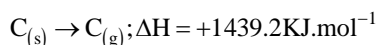
56. The amount of heat required to convert one mole of a simple substance in the solid state into the gaseous state without decomposition of the substance is called enthalpy of sublimation.

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{evap}}$$

57. The temperature and pressure at which the vapour, liquid and solid phases of a substance are in equilibrium is called triple point. For water triple point occurs at  $0.008^{\circ}\text{C}$  and  $4.6\text{ mm}$ .

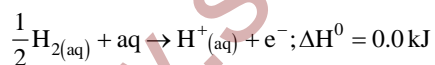
58. Sublimation of solids takes place when it is heated at the pressure less than the triple point pressure. For most of the solids triple point pressure is lesser than atmospheric pressure.

59. The enthalpy change involved in the change of phase or physical state of one mole of compound at atmospheric pressure is called enthalpy of phase transformation.



60. The change in enthalpy, when an ion of unit activity (or concentration) in aqueous solution is formed from its constituent elements in the standard state is called enthalpy of ionization in aqueous solution.

61. The absolute value is not possible. Therefore, the enthalpy of  $\text{H}^+_{\text{aq}}$  at  $298\text{ K}$  is taken as zero arbitrarily and the enthalpy of ionization of other ions calculated by using it.



62. The change in enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to another concentration is called enthalpy of dilution.

63. The technique of measuring heats of reaction is called calorimetry. The apparatus used is called calorimeter.

64. Bomb Calorimeter is commonly used to find the heat of combustion of organic compounds.

65. Since the bomb calorimeter is a closed vessel (constant volume), heat of reaction calculated in this experiment is  $\Delta E$ .

66. Heat of combustion  $\Delta E = Z \times \theta \times \frac{M}{m}$

Where  $Z$  – heat capacity of calorimeter + water

$\theta$  – rise in temperature

$m$  – weight of substance

$M$  – Molecular weight of substance

67. Heat of combustion at constant pressure ( $\Delta H$ ) is calculated by using the formula.

$$\Delta H = \Delta E + \Delta n RT$$

68. Water Calorimeter is a simple type of calorimeter used for calculation of heat of neutralisation, heat of solution.

69. Heat capacity of the calorimeter together with stirrer and the thermometer is called water equivalent of calorimeter.

70.  $m_1$ g of water at low temperature  $t_1$ <sup>0</sup>C is mixed with  $m_2$ g of water at high temperature  $t_2$ <sup>0</sup> C in calorimeter. The resultant temperature is  $t_3$ <sup>0</sup>C .

$$W = \left( \frac{m_2(t_2 - t_3)}{(t_3 - t_1)} - m_1 \right) \text{cal}$$

$$W = \left( \frac{m_2(t_2 - t_3)}{(t_3 - t_1)} - m_1 \right) \times 4.18 \text{J}$$

82. Now the reaction is conducted in the calorimeter and the rise in temperature  $\Delta T$  is measured. Heat liberated = (W + Volume of reaction mixture)  $\times \Delta T$  Cal.