

THEORY & OBJECTIVE

THERMODYNAMICS

*By
Team of
Engineers Academy*

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CORPORATE OFFICE

100-102, Ram Nagar, Bambala Puliya, Tonk Road, Pratap Nagar, Jaipur-302033

Ph.: + 91-8094441777

Website : www.engineersacademy.org | **Email:** info@engineersacademy.org

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CONTENTS

S.No.	Topic	Page No.
1.	Basic Concepts	1 – 14
	Practice Sheet.....	15 – 21
2.	Energy Interaction	22 – 40
	Practice Sheet.....	41 – 43
3.	First Law of Thermodynamics	44 – 67
	Practice Sheet.....	68 – 75
4.	Second Law of Thermodynamics	76 – 100
	Practice Sheet.....	101 – 110
5.	Availability and Irreversibility	111 – 120
	Practice Sheet.....	121 – 122
6.	Thermodynamics Relations	123 – 136
	Practice Sheet.....	137 – 141
7.	Ideal Gases and Processes	142 – 155
	Practice Sheet.....	156 – 160
8.	Real Gases	161 – 167
	Practice Sheet.....	168 – 170
9.	Properties of Pure Substances	171 – 180
	Practice Sheet.....	181 – 183
10.	Practice Sheet.....	184 – 213



BASIC CONCEPTS

THEORY

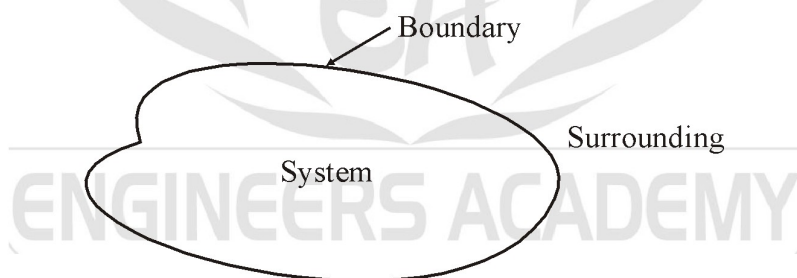
1.1 WHAT IS THERMODYNAMICS

Thermodynamics is the science of energy transfer and its effect on the physical properties of substances. It is based upon observation of common experience which have been formulated into thermodynamics laws. These law govern the principle found in all fields of energy technology, notable in steam and nuclear power plants, Internal combustion engine, gas turbines, air conditioning, refrigeration, gas dynamics, jet propulsion, compressor, chemical process plants and direct energy conversion devices.

1.2 THERMODYNAMIC SYSTEM AND SURROUNDINGS

An important concept in thermodynamics is the thermodynamic system, a precisely defined region of the universe under study. Everything in the universe, except the system is known as the surrounding.

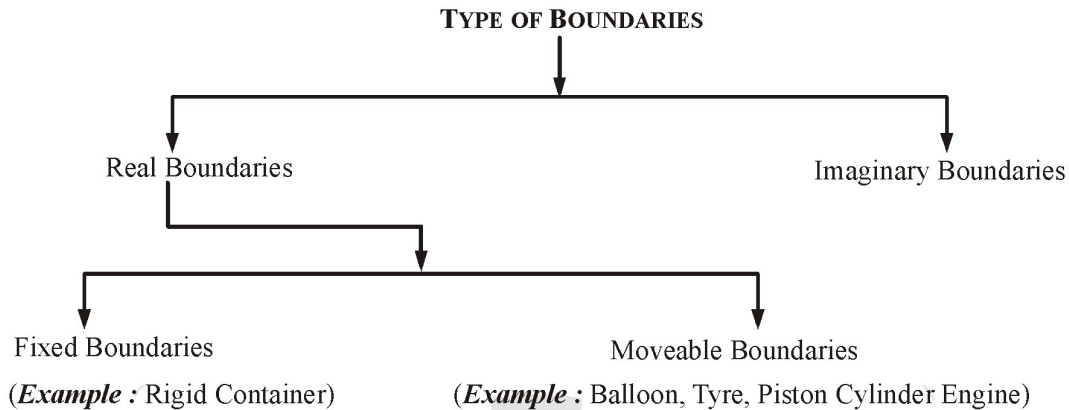
A system is separated from the remainder of the universe by a boundary which may be notional or not but which by convention delimits a finite volume. Exchanges of work, heat or matter between the system and the surrounding take place across this boundary.



System + Surrounding combined called universe

The boundary is simply a surface around the volume of interest. Any thing that passes across the boundary that effects a change in the internal energy need to be accounted for in the energy balance equation.

The volume can be the region surrounding a single atoms resonating energy. It can be the body of tropical cyclone. It could also be just one nuclide (i.e., system of quarks) as hypothesized in quantum thermodynamics.



Note: Adiabatic wall : It is a kind of wall made of insulator which will not allow heat transfer between system and surrounding.

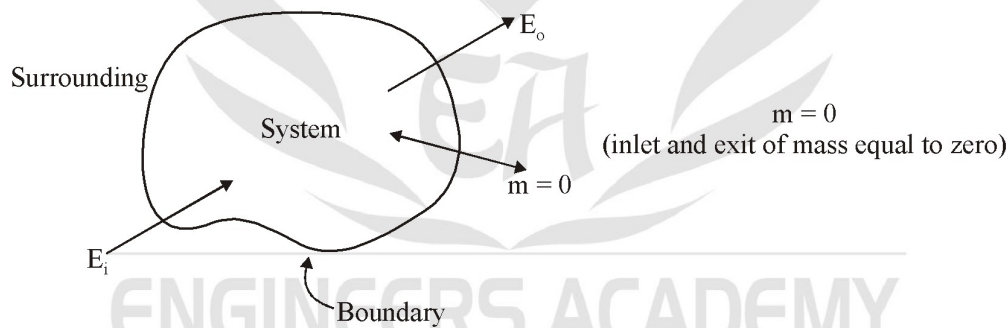
Metalic Wall or Diathermic Wall : It is a kind of wall made of conductor which will allow heat transfer between system and surrounding.

1.3 TYPES OF THERMODYNAMIC SYSTEM

There are three types of Thermodynamic system

1.3.1 CLOSED SYSTEM

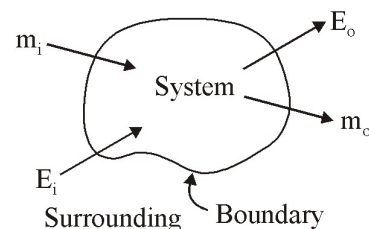
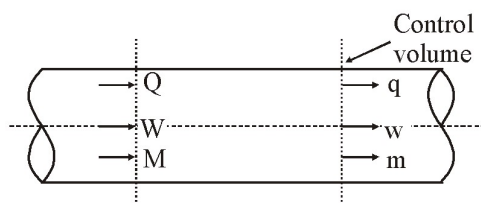
Energy in the form of heat and work can cross the boundary of the system, but there is no mass flow across the boundary. Boundary in closed system is control mass boundary.



Example: Piston cylinder arrangement without valve (heat and work cross the boundary but not mass)

1.3.2 OPEN SYSTEM

Both matter and energy can cross the boundary. Boundary use in these type of system is control volume boundary example flow of fluid in pipe



Heat, flow work and mass all can enter and leave the control volume

Example: Turbine, Pump, compressor, earth and it's atmosphere etc.

Piston cylinder arrangement without valve.

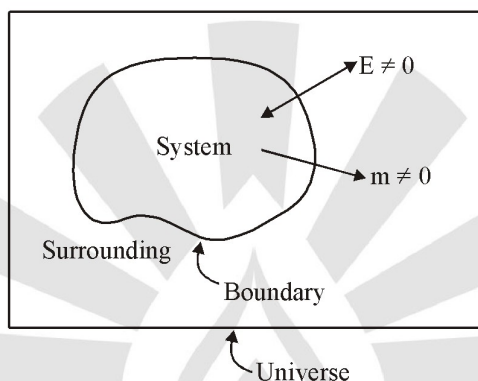
1.3.3 ISOLATED SYSTEM

A system that exchanges neither energy nor matter with its surrounding. In isolated system boundary of the system is adiabatic and control mass boundary

Example: Thermoflask, Universe

Note: Most of the thermodynamic system is taken as control volume or open system.

$$\text{Universe} = \text{System} + \text{Surrounding}$$



Hence universe is an e.g. of isolated system because no transfer of energy and matter takes place

1.4 THERMODYNAMICS PROPERTIES

Any measurable characteristics of the system is called the system Properties, properties of system define the position of system in space.

- All properties are point function
- Any variable whose change is fixed by the end states is a property (or we can say it an exact differential depends on limit only)

1.4.1 INTENSIVE PROPERTIES

It is the properties of the system which is independent of the mass or size of the system; pressure, temperature, specific enthalpy, specific entropy, density and velocity are examples since they are the same for the entire system or for parts of the system. If we bring two system together, intensive properties are not summed.

1.4.2 EXTENSIVE PROPERTIES

It is the properties of the system which depends on the mass of the system; volume, momentum and kinetic energy are example, if two system are brought together the extensive property of the new system is the sum of the extensive properties of the two system.

Note: If we divide an extensive property by the mass a specific property results. The specific volume thus defined to be

$$v = \frac{V}{m}$$

We will generally use on uppercase letter to represent an extensive property (Exception 'm' for mass) and a lowercase letter to denote the associated intensive property.

1.5 THERMODYNAMIC EQUILIBRIUM

A system is said to exist in a state of thermodynamic equilibrium when no change in any property is registered, if the system is isolated from its surroundings.

An isolated system always reaches in course of time a state of thermodynamic equilibrium and can never depart from it spontaneously.

Therefore, there can be no spontaneous change in any property if the system exist in an equilibrium state. Thermodynamics studies mainly the properties of physical system that are found in equilibrium states. A system will be in a state of thermodynamic equilibrium. If the conditions for the following three type of equilibrium are satisfied.

1.5.1 MECHANICAL EQUILIBRIUM

In the absence of any unbalanced force within system itself and also between the system and surrounding. The system is said to be in a state of mechanical equilibrium.

1.5.2 THERMAL EQUILIBRIUMS

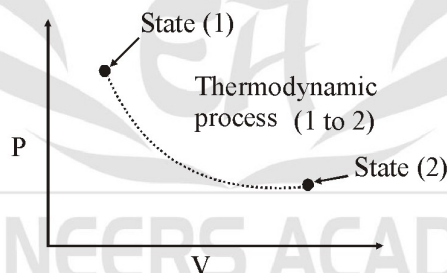
When a system existing in mechanical and chemical equilibrium is separated from its surroundings by a diathermic wall and if there is no spontaneous change in any property of the system. The system is said to exist in a state of thermal equilibrium.

1.5.3 CHEMICAL EQUILIBRIUM

If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to be exist in a state of chemical equilibrium.

1.6 THERMODYNAMIC PROCESS

When a system change its state from one equilibrium position to another equilibrium position it goes through a process, but these change is very fast and we cannot measure intermediate properties of the system. To measure intermediate properties thus we can assume quasi-static process.



Quasi-Static process

Quasi means 'Almost'

Static means 'Rest'

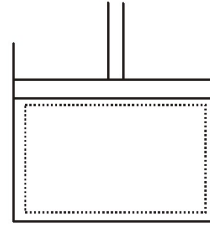
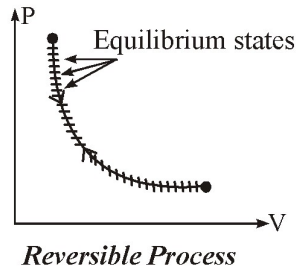
A process which carried out in a very slow manner with small difference in pressure is known as a quasi static process. To study the property change in between two state of the system we assume all thermodynamic process as quasi-static process

Note: To represent the process on 2-D curve we take all properties as intensive properties to make process independent of the size of system.

1.7 TYPE OF PROCESS

1.7.1 REVERSIBLE PROCESS

A reversible process (also sometimes known as quasi-static process) is one which can be stopped at any stage and reversed so that the system and surroundings are exactly restored to their initial states.



Friction less adiabatic piston cylinder engine is a follows reversible process

This process has the following characteristics

- (i) It must pass through the same states on the reversed path as were initially visited in the forward path.
- (ii) This process when undone will leave no history of events in the surroundings.
- (iii) It must pass through continuous series of equilibrium states.

No real process is truly reversible but some processes may approach reversibility, to close approximation.

Examples: Some examples of nearly reversible processes are :

- (1) Frictionless relative motion.
- (2) Expansion and compression of spring.
- (3) Frictionless adiabatic expansion or compression of fluid.
- (4) Polytropic expansion or compression of fluid.
- (5) Isothermal expansion or compression.
- (6) Electrolysis.

1.7.2 IRREVERSIBLE PROCESS

An irreversible process is one in which heat is transferred through a finite temperature.

Irreversibility are of two types

(i) External Irreversibilities

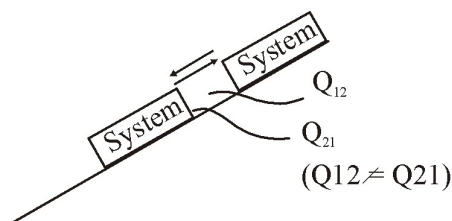
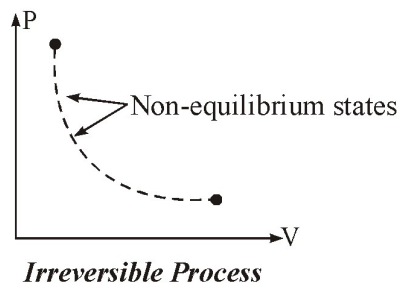
These are associated with dissipating effects outside the working fluid.

Example: Mechanical friction occurring during a process due to some external source.

(ii) Internal Irreversibilities

These are associated with dissipating effects within the working fluid.

Example: Unrestricted expansion of gas, viscosity and inertia of the gas.



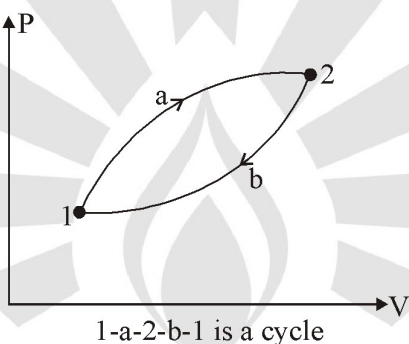
It is irreversible process

An irreversible process is usually represented by a dotted (or discontinuous) line joining the end states to indicate that the intermediate states are undetermined.

- Example:** (i) Relative motion with friction.
(2) Electricity flow through a resistance
(3) Plastic deformation
(4) Diffusion
(5) Throttling
(6) Heat transfer
(7) Combustion
(8) Free expansion

1.8 THERMODYNAMIC CYCLE

A system is said to have under goes a cycle if the initial and final point are same, Minimum number of process required for a cycle are two.



Note: The change in property in any cycle is equal to zero.

1.9 PURE SUBSTANCE

A pure substance is a system which is

1.9.1 HOMOGENEOUS IN COMPOSITION

The composition of each part of the system is the same as the composition of every other part. Composition means the relative proportions of the chemical elements into which the sample can be analysed. It does not matter how these elements are combined.

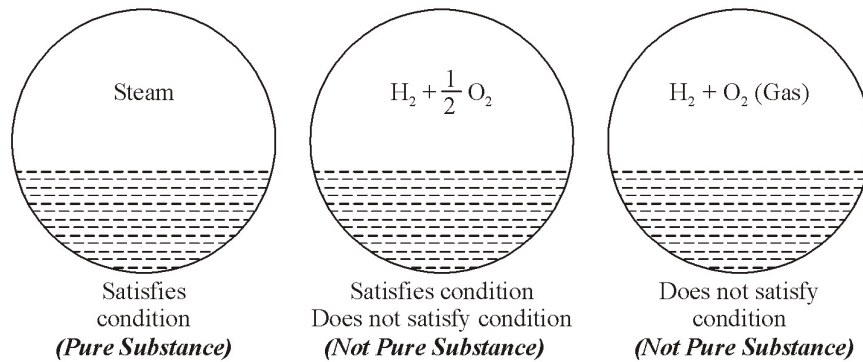
1.9.2 HOMOGENOUS IN CHEMICAL AGGREGATION

The chemical elements must be combined chemically in the same way in all parts of the system. Consideration of shown in figure that the system on the other hand is not homogeneous in chemical aggregation since in the upper part of the system the hydrogen and oxygen are not combined chemical (individual atoms of H and O are not uniquely associated), where as in the lower part of the system the hydrogen and oxygen are combined to form water.

1.9.3 INVARIABLE IN CHEMICAL AGGREGATION

The state of chemical combination of the system does not change with time (condition referred to variation with position).

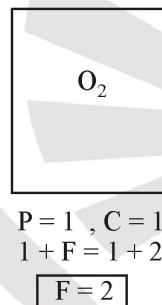
Thus a mixture of hydrogen and oxygen, which changed into steam during the time that the system was under consideration, would not be a pure substance.



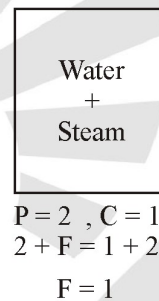
Note: However that a uniform mixture of steam, hydrogen gas, and oxygen gas would be regarded as homogeneous in both composition and chemical aggregation whatever the relative proportions of the components.

1.10 GIBBS PHASE RULE

These use to measure degree of freedom of the system. That means how many independent properties required to fix the state of the system.



It is pure substance also



It is pure substance also

Gibbs Phase Rule Formula :

$$P + F = C + 2$$

Where,

P = Number of phase in the system

F = Degree of freedom of the system (minimum number of independent intensive properties required to fix the state of the system)

C = Number of components in the system

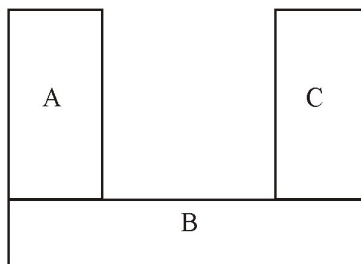
Note: Generally pure substance has two degree of freedom so we can represent them in two dimension curve.

1.11 THERMODYNAMICS RULES

1.11.1 ZEROth's LAW OF THERMODYNAMICS

The property which distinguishes thermodynamics from other science is temperature. One might say that temperature bears an important relation to thermodynamics as force does to static or velocity does to dynamics. Temperature is associated with the ability to distinguish hot from cold. When two bodies at different temperature are brought into contact, after some time they attain a common temperature and are then said to exist in thermal equilibrium.

Statement : When a body A is in thermal equilibrium with body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.



Note: When bodies A, B & C chemically react then zeroth law of thermodynamic will not apply.

Zeroth law of thermodynamic help to find out temperature of the body.

1.11.2 THERMOMETRIC PRINCIPAL

In order to obtain a quantitative measure of temperature, a reference body is used and a certain physical characteristic of this body which changes with temperature is selected. The change in the selected characteristic may be taken as an indication of change in temperature. The selected characteristic is called the thermometric property and the reference body which is used in the determination of temperature is called the thermometer.

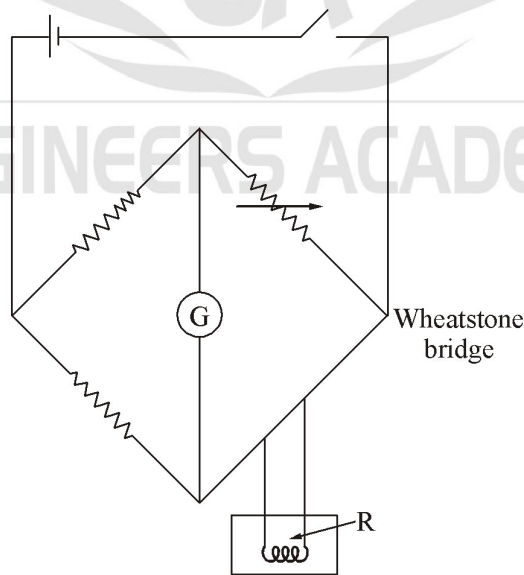
$$T = \phi(p)$$

P = It is the property of the system

1.12 TYPE OF THERMOMETERS

1.12.1 ELECTRICAL RESISTANCE THERMOMETER

In resistance thermometer shown in figure the change in resistance of metal wire due to its change in temperature is the thermometric property. The wire, frequently platinum, may be incorporated in a wheat stone bridge circuit. The platinum resistance thermometer measure temperature to a high degree of accuracy and sensitivity, which make it suitable as a standard for the calibration of other thermometers. In a restricted rang. The following quadratic equation is often used



Resistance Thermometer

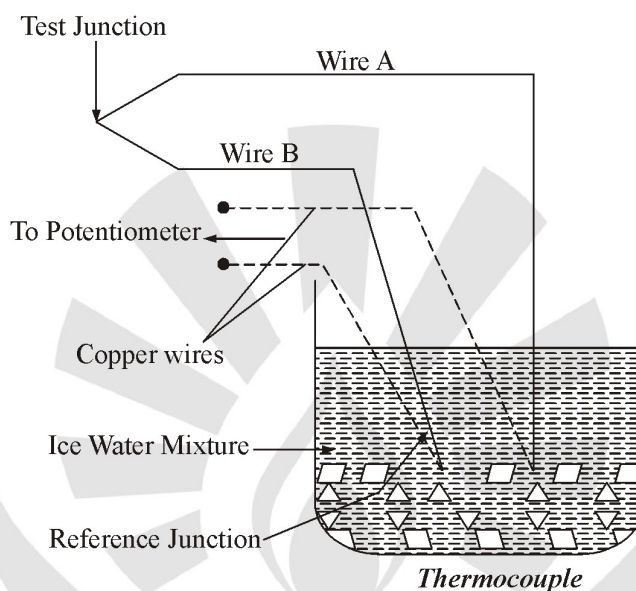
$$\frac{P}{Q} = \frac{R}{S}$$

$$R = R_0(1 + \alpha t + Bt^2)$$

Where, R_0 is the resistance of the platinum wire. When it is surrounded by melting ice and A and B are constant.

1.12.2 THERMOCOUPLE

A thermocouple circuit made up from joining two wire A and B made of dissimilar metals is shown in figure.



Due to seeback effect, a net e.m.f. is generated in circuit which depends on the difference in temperature between the hot and cold junction and is, therefore a thermometric property of the circuit the e.m.f. can be measured by a microvoltmeter to a high degree of accuracy.

The choice of metals depends largely on the temperature range to be investigated and copper-constantan, chromel-alumel and platinum-platinum-rhodium are typical combinations in used.

A thermocouple is calibrated by measuring the thermal e.m.f. at various known temperature, the reference junction being kept at 0°C . The results of such measurement on most thermocouple can usually be represented by a cubic equation of the form

$$\epsilon = a + bt + ct^2 + dt^3$$

Where, ϵ is the thermal e.m.f. and the constants a , b , c , and d are different from each thermocouple.

The advantage of the thermocouple is that of it comes to thermal equilibriums with the system. Whose temperature is to be measure, quite rapidly, because its mass is small.

1.12.3 CONSTANT VOLUME GAS THERMOMETER

In constant volume gas thermometer pressure is thermometric property

1.12.4 CONSTANT PRESSURE GAS THERMOMETER

In these volume plays the role of thermometric property.

1.12.5 INTERNATIONAL PRACTICAL TEMPERATURE SCALE

An international temperature scale was adopted at the Seventh General conference on weight and measures held in 1927.

TEMPERATURE OF FIXED POINT		
Fixed Point		Temperature °C
(i)	Normal boiling point of Oxygen	-182.97
(ii)	Triple point of water (Standard)	+0.01
(iii)	Normal boiling point of Water	100.00
(iv)	Normal boiling point of Sulphur	444.60
(v)	Normal melting point of zinc-suggested as an alternative to the sulphur point	419.50
(vi)	Normal melting point of Antimony	630.50
(vii)	Normal melting point of Silver	960.80
(viii)	Normal melting point of Gold	1063.00

(1) From 0 to 660°C

A platinum resistance thermometer with platinum wire whose diameter must lie between 0.05 to 0.20 mm is used and the temperature is given by the equation

$$R = R_0(1 + At + Bt^2)$$

Where, R_0 , A and B are computed by measurement at ice point, steam point and sulphur point.

(2) From -190 to 0°C

The same platinum resistance thermometer is used and the temperature is given by

$$R = R_0(1 + At + Bt^2 + C(t - 100)t^3)$$

Where, R_0 , A and B are the same before, and C is determined from a measurement of the oxygen point.

(3) From 660 to 1063°C

A thermocouple, one wire of which is made of platinum and the other of an alloy of 90% platinum and 10% rhodium is used with one junction at 0°C. The temperature is given by the formula

Where, a, b, and c are computed from measurement at the antimony point, Silver point and gold point. The diameter of each wire of the thermocouple must lie between 0.35 to 0.65 mm.

1.13 METHOD USED BEFORE 1954 FOR FINDING TEMPERATURE

The thermometer is first placed in contact with the system whose temperature $T(x)$ is to be measured and then in contact with an arbitrarily chosen standard system in an easily reproducible state where the temperature is T_1 thus assume linear relation between temperature and thermometric property.

$$t = ap + b$$

Where,

p = Thermometric property

At first reference point

$$t = t_1$$

$$P = P_1$$

$$t_1 = aP_1 + b \quad \dots(1)$$

Then the thermometer at the $T(x)$ is placed in contact with another arbitrarily chosen standard system in another easily reproducible state where the temperature is T_2 is given at second reference point

$$t = t_2$$

$$P = P_2$$

$$t_2 = aP_2 + b \quad \dots(2)$$

Solving equation (1) and (2)

$$t_1 = aP_1 + b$$

$$t_2 = aP_2 + b$$

$$t_1 - t_2 = a(P_1 - P_2)$$

$$a = \frac{t_1 - t_2}{P_1 - P_2}$$

Put value in equation (1)

$$t_1 = \left(\frac{t_1 - t_2}{P_1 - P_2} \right) P_1 + b$$

Then

$$b = t_1 - \left(\frac{t_1 - t_2}{P_1 - P_2} \right) P_1$$

Put value of a and b in equation

$$t = aP + b$$

$$t = \left(\frac{t_1 - t_2}{P_1 - P_2} \right) P + t_1 - \left(\frac{t_1 - t_2}{P_1 - P_2} \right) P_1$$

$$t - t_1 = \left(\frac{t_1 - t_2}{P_1 - P_2} \right) (P - P_1)$$

$$\frac{t - t_1}{t_1 - t_2} = \frac{P - P_1}{P_1 - P_2}$$

From these relation we can find temperature at any given value of 'P'.

Before 1954, there were two fixed points

- (i) The ice point, the temperature at which pure ice coexisted in equilibrium with air saturated water at one atmospheric pressure
- (ii) The steam point, the temperature of equilibrium between pure water and pure steam at one atmospheric pressure temperature interval, between these two fixed points was chosen to be 100 degree.

The use of two fixed points was found unsatisfactory and later abandoned because of (a) The difficulty of achieving equilibrium between pure ice and air saturated water (Since when ice melts, it surrounds itself only with pure water and prevent intimate contact with air saturated water) and (b) extreme sensitiveness of the steam point to change in pressure.

1.14 METHOD USED AFTER 1954 FOR FINDING TEMPERATURE

Since 1954 only one fixed point has been in use. The triple point of water. The state at which ice, liquid water and water vapour coexist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value 273.16 degree Kelvin, or 273.16 K. Designating the triple point of water by T_{tp} and with P_{tp} being the value of the thermometric property when the body whose temperature t is to be measured is placed in contact with water at triple point, it follows that

$$t = a P \quad \dots(1)$$