CHEMICAL ENGINEERING

Thermodynamics

Comprehensive Theory
with Solved Examples *and* Practice Questions

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Thermodynamics

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Thermodynamics

Basic Concepts and Zeroth Law of Thermodynamics

CHAPTER

1

1.1 Introduction

Thermodynamics is the branch of science which deals with the energy and energy interactions. More specifically it deals with energy conversions, energy exchange and the direction of exchange.

1.1.1 Macroscopic and Microscopic Approach

- Macroscopic Approach: In this approach individual molecular behaviour of a gas is not taken into consideration and the average behaviour of all the molecules is studied. This approach is applied when the continuum concept is valid.

Do You Know ?

- Continuum hypothesis suggests that the matter is continuously distributed with no voids being present.
- In case of gases it is valid when mean free path (average distance travelled by a molecule between two successive collisions) is much smaller than the system dimensions.

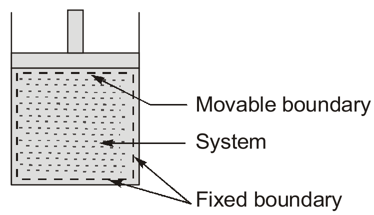
- Microscopic Approach: In this the individual molecular behaviour is taken into consideration. For example: It is used in space exploration.

Remember : For our use, in classical thermodynamics, we often use macroscopic approach.

1.2 System, Surroundings and Properties

1.2.1 System, Surroundings and Properties

- System: A thermodynamics system is defined as the fixed mass or fixed region in space (also called control volume) upon which our study is focused.
- Surroundings: Everything external to the system is called surroundings.
- Boundary: It is a real or imaginary surface which separates system from the surroundings. A boundary can be fixed or movable. A boundary has zero thickness, no mass and no volume.



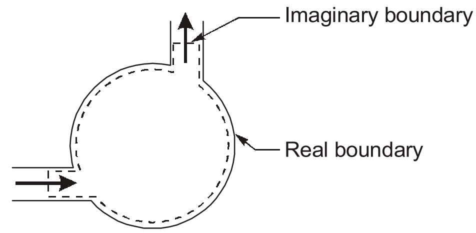


Figure 1.1 Fixed Mass System

Figure 1.2 Fixed Region in Space (Control Volume)

1.2.2 Types of System

Based on energy-mass interaction with the surroundings the system has been categorized as given below.

Type of system	Energy transfer	Mass transfer	Example
Open	Yes	Yes	Piston cylinder arrangement with valves
Closed	Yes	No	Piston cylinder arrangement without valves
Isolated	No	No	Universe

Remember : Control volume is a volume surrounding an open system on which study is focused. The boundaries of a control volume is called control surface.

1.2.3 Properties of a System

- Properties are macroscopic characteristics of a system such as mass, volume, energy, pressure and temperature to which numerical values can be assigned at a given time without knowledge of the past history of the system. They have been classified as follows:

  1. **Intensive (Intrinsic) Properties:** The properties which are independent of the mass of system under consideration.

     For examples: Pressure, temperature, density, viscosity etc.

Remember

- All specific properties are intensive properties, eg. specific volume, specific heat, specific internal energy etc.
- Density is an intensive property.

  2. **Extensive (Extrinsic) Properties:** The properties which are dependent on the mass of system under consideration.

     For examples: Mass, energy, volume etc.

NOTE : While deciding the type of property we should not change the system under consideration.

- An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition as shown in figure 1.3. Each part will have same value of the property in case it is intensive but half the value in case it is extensive.

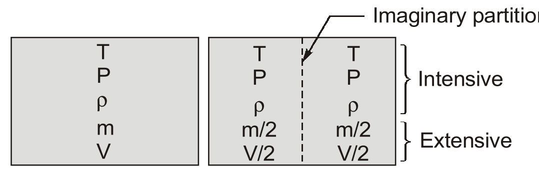


Figure 1.3

- Important points with respect to properties:
  1. They are point or state functions.
  2. They are independent of past history.
  3. They are exact differentials.

1.3 State of The System and Process

- Any equilibrium condition of the system is called state of the system. At a given state all the properties of a system have fixed values throughout the entire system [may/may not be uniform]
- A change in state is called a process.
- The infinite number of states through which the system passes while going from an initial to a final state is called the path of the process. A process can be classified as:

1. **Quasistatic and Non-Quasistatic Process:** If a process takes place infinitely slowly it is called a quasistatic process, otherwise a non-quasistatic process.
   - A quasistatic process is generally represented by a joined line on property diagrams. Whereas a non-quasistatic process is represented by dotted lines. (Fig. 1.4) [i.e. every point on the path represents an equilibrium state and hence can be represented on the curve.]

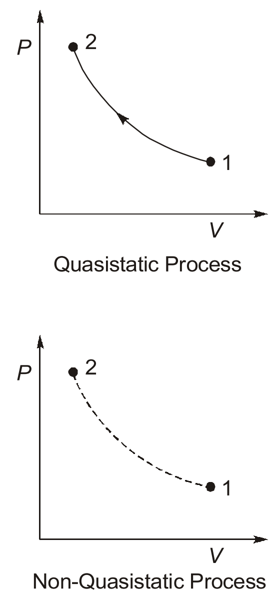


Figure 1.4

2. **Reversible and Irreversible Process:** A process is said to be reversible if it can be reversed in direction following the same path as that of the forward process without leaving any change in the system as well as the surroundings. The process is said to be irreversible otherwise.

NOTE

- Quasistatic and reversible processes are not always same but for our study we take them as same.
- All reversible processes are quasistatic but all quasistatic processes might not be reversible.
- Frictionless quasistatic process is reversible.

Remember

- The reversibility of a process in problems can be conveyed in following ways:
  (a) Quasistatic compression/expansion
  (b) Ideal flow (open system)

1.4 Pure Substances

- A substance is said to be a pure substance if it is of homogeneous chemical composition throughout.
- It does not have to be a single chemical element or compound. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as mixture is homogeneous. For example: air.
- Some more examples are shown in figure 1.5.

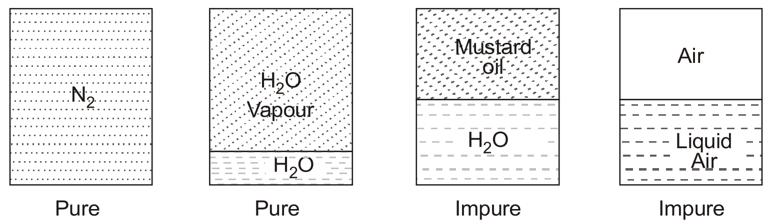


Figure 1.5

Remember

- The mixture of refrigerants which behaves as a pure substance is called Azeotrope.
- Mixture of ethyl alcohol and water is also a pure substance due to molecular level hydroxyl bond formation.

1.4.1 Gibbs Phase Rule

- Phase is defined as a quantity of mass that is homogeneous throughout in chemical composition and physical structure. Eg. solid, liquid, vapour, gas.
- In general the minimum number of independent intensive variables required to fix the state of the system for multiphase, multi-component system is given by the Gibbs phase rule, expressed as:

$$F = C - P + 2$$

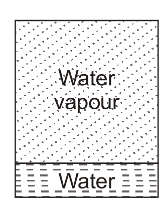
where,
F = Degree of freedom or minimum number of independent intensive variables required
C = Number of chemical components
P = Number of phases present in equilibrium

Example 1.1 Determine the degree of freedom of the following systems and comment on the result:

(1) Water and water vapour system
(2) A mixture of oxygen and nitrogen gas as system
(3) Water at its triple point

Solution **:**

(1)



In the given system it can be asserted that:

Number of phases, $P = 2$ (liquid + vapour)
Number of components, $C = 1$ (only water)

$\therefore$ From Gibbs phase rule, we know

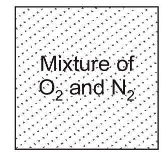
$$F = C - P + 2$$

Substituting the values in above equation

$$F = 1 - 2 + 2 = 1$$

Comment : Only one variable is enough to fix the state of the system eg: two phase systems in evaporators of a RAC system.

(2) It can be asserted that in the given system



$$P = 1 \quad \text{(only gas)}$$

$$C = 2 \quad (O_2 + N_2)$$

From the Gibbs phase rule, we know $F = C - P + 2$

Substituting the values in above equation

$$F = 2 - 1 + 2 = \mathbf{3}$$

Comment : We will require three independent intensive variables to fix the state of the system.

Remember : Triple point of any substance is a state at which it can exist in equilibrium in solid, liquid and gaseous phase i.e. all 3 phases can co-exist.

(3) $\therefore$ It can be asserted from above definition that at triple point of water

$$P = 3 \quad \text{(solid, liquid and gas)}$$

$$C = 1 \quad \text{(only water)}$$

From the Gibbs phase rule, we know $F = C - P + 2$

Substituting the values in above equation

$$F = 1 - 3 + 2 = 0$$

Comment : The degree of freedom comes out to be zero which suggests that the triple point of water is a very specific condition and occurs at a particular value of temperature and pressure.

Remember : At triple point of water

$T = 0.01°C = 273.16$ K, $P = 0.6112$ kPa

NOTE : Even through air is mixture of several gases but it is considered as one component (in gaseous phase).

1.5 Zeroth Law of Thermodynamics

- It states that if two bodies (A and B) are in thermal equilibrium with a third body C then A and B are also in thermal equilibrium with each other.

  Explanation :
  Let us say T_A, T_B and T_C are the temperatures of 3 bodies A, B, and C respectively.
  Given: A and C are in thermal equilibrium *i.e.*, $T_A = T_C$ and B and C are in thermal equilibrium *i.e.*, $T_B = T_C$ then as a consequence of zeroth law: A and B will also be in thermal equilibrium *i.e.*, $T_A = T_B$

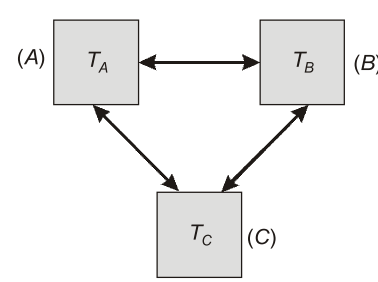


Figure 1.6

Do You Know?

- Zeroth law was first formulated by R. H. Fowler in 1931.
- Its fundamental value was recognized more than half a century after the formulation of the first and second laws and hence it was named zeroth law as it should have preceded the first and second laws.

1.5.1 Thermometry

- It is based on finding the thermometric property.
- The temperature cannot be quantified on the basis of feeling and hence we need a property which is easily measurable and then that property is used to find the temperature of the body.

1. Thermistor or Resistance Thermometer

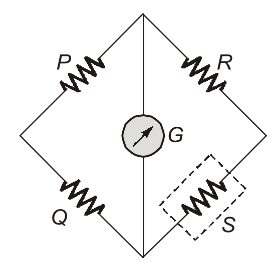


Figure 1.7

- It is based on working of a balanced Wheatstone bridge circuit.

here: P and Q = Resistance with fixed known values
G = Galvanometer
R = Variable resistance (helps in balancing of Wheatstone bridge)
S = Resistance very sensitive to temperature change

- Initially let us assume that the circuit is balanced, hence there will be no deflection in the Galvanometer G.
- By balanced Wheatstone bridge equation we can write

$$\frac{P}{Q} = \frac{R}{S} \quad \text{...(i)}$$

- Now if we change the temperature of S, its resistance will change to S' (unknown value) and the bridge will become unbalanced.
- Thus we will change value of R (variable resistance) to R', to again balance the bridge.

Now $$\frac{P}{Q} = \frac{R'}{S'} \quad \text{...(ii)}$$

- From equation (ii) we get the value of unknown S' at the new temperature.
- The resistance as a function of temperature for resistor S will be known to us and from that we can calculate the temperature.

Remember : In thermistor, resistance is the thermometric property used to calculate temperature.

2. Thermocouple

- It's working is based on principle of Seebeck effect.
- Seebeck effect: If two different metals are joined at two different junctions which are kept at different temperatures then an EMF is generated between the two junctions which is directly proportional to the temperature difference between them.

According to seebeck effect:

$$\text{EMF} \propto T_2 - T_1$$

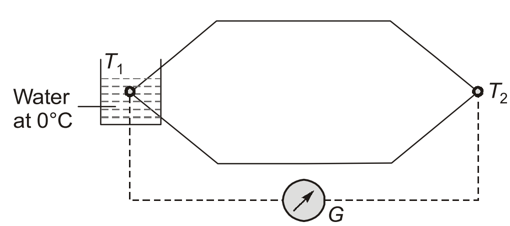


Figure 1.8

- Hence, if one of the temperatures is known, the other can be found easily using the above relation.

Remember : In thermocouple, EMF is the thermometric property.

Do you know? The opposite of Seebeck effect is called Peltier effect and it is used in thermoelectric refrigeration.

3. Constant Volume Gas Thermometer

- It is based on Gay-Lussac's law which states that for a given mass and constant volume of an ideal gas, the pressure is directly proportional to the absolute temperature, assuming closed system.

$$P \propto T$$

or
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

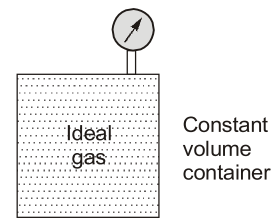


Figure 1.9

- Hence here temperature is measured by pressure change.

Remember : Pressure is the thermometric property in this case.

4. Constant Pressure Gas Thermometer

- It is based on Charle's law which states that, for a given mass of an ideal gas at constant pressure, the volume is directly proportional to the absolute temperature, assuming closed system.

$$V \propto T$$

or
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

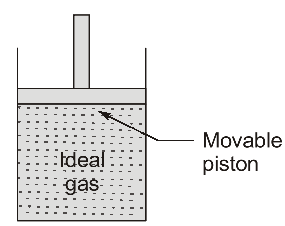


Figure 1.10 Piston Cylinder Arrangement

- Here temperature is measured by volume change.

Remember : Volume is the thermometric property in this case.

NOTE : Both constant volume and constant pressure gas thermometers are independent of the material of construction (which is ideal gas) i.e. any type of ideal gas can be used whether it is Oxygen, Nitrogen, Air etc.

1.5.2 Temperature Scales

- Temperature is the measure of random energy of molecules. Temperature scales enable us to use a common basis for temperature measurements and several have been used till date.
- All scales are based on some easily reproducible states such as the freezing and boiling points of water also called ice point and steam point respectively.
- The Celsius scale and Fahrenheit scale are two most widely used scales.

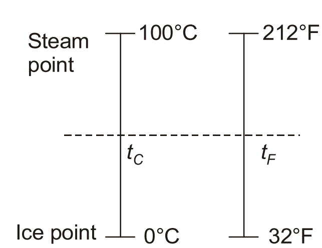


Figure 1.11

Let t_c be a temperature on Celsius scale and t_F, the corresponding value on Fahrenheit scale.
We assume that the scale are linear

$$\therefore \quad \frac{t - t_i}{t_s - t_i} = \text{Constant \{for any scale\}} \quad \ldots(i)$$

t_i = Temperature at ice point
t_s = Temperature at steam point
t = Temperature to be found

Applying equation (i) to Celsius and Fahrenheit scale

$$\frac{t_C - 0}{100 - 0} = \frac{t_F - 32}{212 - 32} \quad \ldots(ii)$$

Solving equation (ii), we get

$$t_F = \frac{9}{5}t_C + 32$$

or

$$t_C = \frac{5}{9}(t_F - 32)$$

- The above scales of °C and F are called relative temperature scales.
- Later the second law of thermodynamics will help us define an absolute temperature scale. Kelvin, which is the absolute temperature scale defined on Celsius scale.

$$T_k = t_c + 273.15$$

Remember : Kelvin is also called the thermodynamic temperature scale.

- Before 1954, temperature measurement was based on two reference points, namely ice point and stream point. After 1954, the temperature measurement has been based upon single reference point i.e. triple point of water.
- According to internationally accepted convention

$$1\text{K} = \left(\frac{1}{273.16}\right)^{\text{th}} \text{ of triple point of water}$$

Example 1.2 What does a temperature difference of 10 on °C scale correspond to on a Fahrenheit scale?

Solution :

Given: $\Delta t_c = 10$

We know $t_F = \frac{9}{5}t_c + 32$ ...(i)

Applying Δ on both sides of equation (i), we get

$$\Delta t_F = \frac{9}{5}\Delta t_c$$

Putting the value of Δt_c, we get $\Delta t_F = \frac{9}{5} \times 10 = 18$

NOTE : $\Delta t_F = 1.8\,(\Delta t_c)$

1.5.3 Calibration of Thermometers

- If two different thermometers using alcohol and mercury respectively, are calibrated at ice point and steam point and the distance between ice point and steam point is divided into 100 equal parts then they are not guaranteed to give the same reading anywhere between the calibration points, but they will always give the same readings at the calibration points itself.

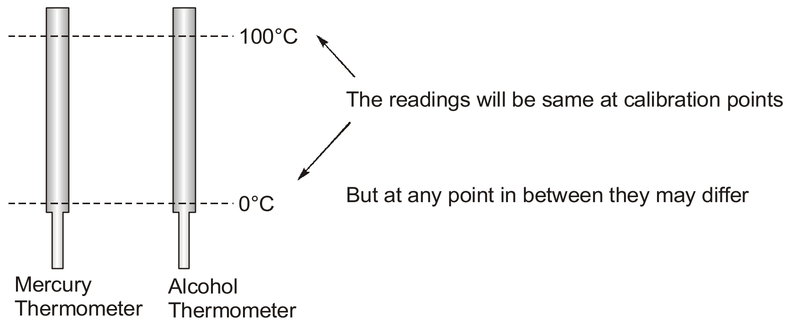


Figure: 1.12

Summary

- Thermodynamics is the science that primarily deals with energy.
- A system with fixed mass is called a closed system and a system that involves mass transfer across it boundary is called an open system.
- Mass dependent properties are called extensive properties and mass independent properties are called intensive properties.
- All temperature measurements are based on Zeroth law.
- Temperature scales are arbitrary/random in nature.

Objective Brain Teasers

Q.1 An open system is one in which
(a) Heat and work cross the boundary, but the mass does not
(b) Mass crosses the boundary, but the heat and work do not
(c) Heat, work and mass cross the boundary
(d) None of heat, work and mass cross the boundary

Q.2 Which of the following is not a point function?
(a) Temperature (b) Pressure
(c) Energy (d) Power

Q.3 Which of the following is an intensive property of a thermodynamics system?
(a) Volume (b) Temperature
(c) Mass (d) Energy

Q.4 Which of the following is the basis of temperature measurement?
(a) Zeroth law of thermodynamics
(b) First law of thermodynamics
(c) Second law of thermodynamics
(d) Third law of thermodynamics

Q.5 The absolute zero pressure will be
(a) When molecular momentum of the system becomes zero
(b) at sea level
(c) at a temperature of –273.15 K
(d) under vacuum conditions

Q.6 The standard fixed point of thermometry is the
(a) ice point
(b) triple point of water

(c) boiling point of water
(d) sulphur point

Q.7 A system comprising of a single phase is called
(a) Closed system
(b) Open system
(c) Heterogeneous system
(d) Homogeneous system

Q.8 A mixture of air and liquid air is
(a) a pure substance
(b) not a pure substance
(c) homogeneous and invariable in chemical composition throughout its mass
(d) one having relative proportions of oxygen and nitrogen constant in gas and liquid phases

Q.9 When mean free path of the molecules of a gas approaches the order of magnitude of the dimensions of the vessel, which concept of the following loses its validity?
(a) Continuum (b) Stability
(c) Equilibrium (d) Entropy

Q.10 Most of the real processes are
(a) quasi-static (b) non-quasi-static
(c) adiabatic (d) isothermal

■ ANSWERS

1. (c)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (a)
6. (b)	**7.** (d)	**8.** (b)	**9.** (a)	**10.** (b)

STUDENT'S ASSIGNMENTS

1. A new temperature scale *N* is to be defined. The boiling and freezing points of water on this scale are 100°N and 400°N respectively. Then (a) What will be the reading on the new scale corresponding to 60°C? (b) At what temperature both the Celsius and the new temperature scale reading would be same?

[**Ans.** (a) 220°N, (b) 100°]

2. The reading t_A and t_B for centigrade thermometer *A* and *B* graded at ice point 0°C and steam point 100°C are related by the equation $t_A = l + mt_B + nt_B^2$ where l, m, n are constants. When both are immersed in a liquid, *A* reads 51°C and *B* reads 50°C. Determine the reading of *A* when *B* reads 25°C? Comment on which thermometer is correct.

[**Ans.** (a) 25.75°C; (b) not possible to say]

■■■■