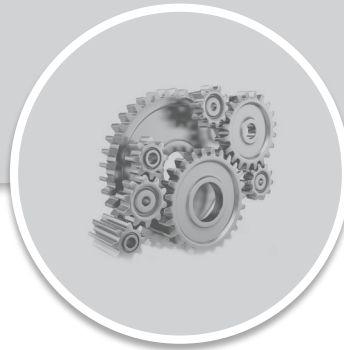


# MECHANICAL ENGINEERING

## Thermodynamics



Comprehensive Theory  
*with Solved Examples and Practice Questions*





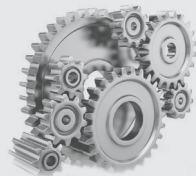
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## **Thermodynamics**

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# Energy and its Interactions

## 2.1 INTRODUCTION

- Energy can exist in numerous forms such as thermal, mechanical, kinetic, potential, electrical, magnetic, chemical and nuclear, and their sum constitutes **total energy**  $E$  of the system. The absolute value of energy is not that important in any thermodynamic analysis. All the analysis can easily and accurately be done by considering the **change** in total energy only. Since we deal with the changes only, the total energy of a system can be assigned a value of zero ( $E = 0$ ) at some convenient reference point. The change in total energy of a system is **independent** of the reference point selected.
- In thermodynamics, the various forms of energy that constitute the total energy are considered in two groups: **macroscopic** and **microscopic** forms of energy.
- The energy possessed by the **system as a whole** with respect to an external reference frame constitute macroscopic forms of energy, such as kinetic and potential energies.
- The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity and surface tension.

The energy that a system possesses as a result of its **motion** relative to some reference frame is called kinetic energy (K.E.) when all parts of a system move with the same velocity, the kinetic energy is given by,

$$\text{K.E.} = \frac{mv^2}{2}$$

- The energy that a system possesses as a result of its **elevation in a gravitational field** is called potential energy (P.E.) and is given by,

$$\text{P.E.} = mgz$$

- The energy possessed by the system with respect to the molecular structure and **molecular level interactions** constitute microscopic forms of energy. The sum of all microscopic forms of energy of a system is called its **internal energy** and is denoted by  $U$ . The microscopic forms of energy are independent of outside reference frames.



Fig : The macroscopic energy of an object changes with velocity and elevation

- The magnetic, electric and surface tension effects are significant in some specialized cases only and are usually ignored. In the absence of such effects, the total energy of a system consists of the kinetic, potential and internal energies and is expressed as,

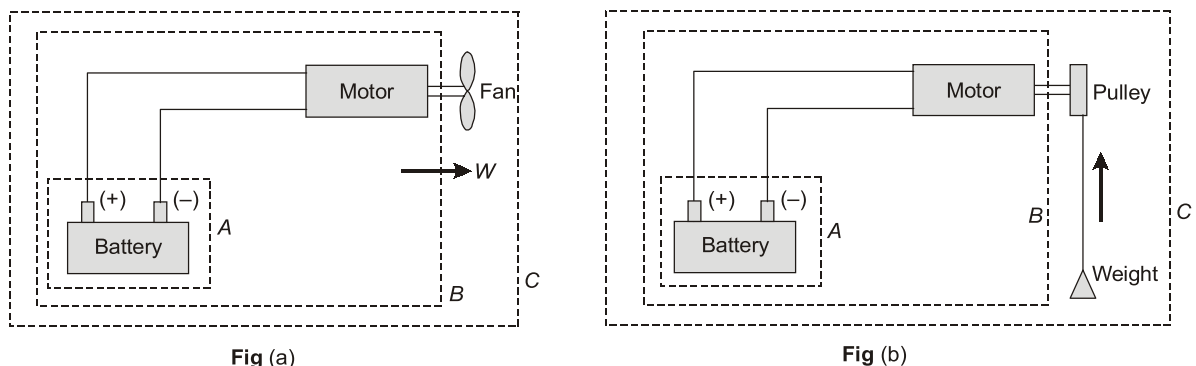
$$E = U + \text{K.E.} + \text{P.E.}$$

The following types of energy form a part of microscopic energy:

- Sensible energy:** This is the form of internal energy of a system which is associated with the kinetic energies of molecules. This form of energy varies directly with temperature as molecular motions are higher at higher temperature.
  - Latent energy:** This is the form of internal energy which is associated with its phase. To convert a solid or liquid into gas, some energy is to be supplied to overcome the higher molecular forces present in solid or liquid. This energy is nothing but latent energy which is associated with phase change.
  - Chemical energy:** This is the form of internal energy which is associated with the atomic bonds in a molecule.
  - Nuclear energy:** This is the form of internal energy which is associated with the strong bonds between protons and electrons within the nucleus of the atom itself.
- Energy interaction for a closed system with its surroundings can take place by:
    - work transfer
    - heat transfer
  - Work and heat are modes of energy transfer and these bring about changes in the properties of the system. The discussion related to their quality will be done later in chapter 5.

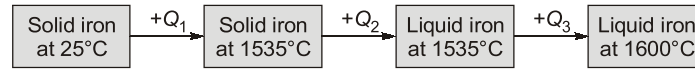
## 2.2 WORK TRANSFER

- Work transfer is one of the basic modes of energy transfer.
- The work is said to be done by a force when it acts on a body which moves in the direction of force. This definition of work is more suitable from mechanics point of view.
- In thermodynamics, work transfer is considered as a boundary phenomenon i.e. when work crosses the boundary of the system. Work is said to be done by the system if the sole effect on the things external to the system can be converted into raising of weights, though the weight may not be actually raised.
- In Fig. (a), a battery is connected to a motor which is, in turn, driving a fan. The system is doing work on the surroundings. When the fan is replaced by a pulley and a weight as shown in Fig. (b), the sole effect on things external to the system is then the raising of the weight.



**Solution: (d)**

The figure below shows the phase transformation of iron.



Heat required to melt iron from 25°C to 1600°C per kg is given by,

$$Q = Q_1 + Q_2 + Q_3 = c_s(\Delta T_1) + L_f + c_l(\Delta T_2)$$

where,  $c_s$  is specific heat in solid state

$L_f$  is latent heat of fusion

$c_l$  is specific heat in liquid state

Given,

$$c_s = 0.5 \text{ kJ/kgK}, L_f = 280 \text{ kJ/kg}$$

$$c_l = 0.535 \text{ kJ/kgK}$$

∴

$$Q = 0.5 \times (1535 - 25) + 280 + 0.535 (1600 - 1535) \\ = 1069.78 \text{ kJ/kg}$$

Given,

$$\text{Melting rate} = 5 \times 10^3 \text{ kg/hour}$$

$$\text{So, Rate of heat supply} = Q_{\text{per kg}} \times \text{Melting rate} = \frac{1069.78 \times 5 \times 10^3}{3600} = 1485.8 \text{ kW}$$

$$\text{Electric furnace is 65\% efficient, therefore rating of the furnace} = \frac{1485.8}{0.65} = 2285.85 \text{ kW}$$

■■■■

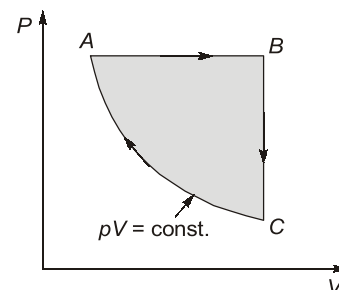


### OBJECTIVE BRAIN TEASERS

- Q.1** On a hot summer day, the air in a well sealed room is circulated by a 0.60 HP fan driven by a 70% efficient motor. The rate of energy supply from the fan motor assembly to the room is \_\_\_\_\_ kJ/s [Correct upto 3 decimal places]
- Q.2** Thermodynamic work is the product of
- two intensive properties
  - two extensive properties
  - an intensive property and change in an extensive property
  - an extensive property and change in an intensive property
- Q.3** Which of the following is/are correctly matched?
- Volume - Extensive property
  - Density - Intensive property
  - Work - Point function
  - Heat - Imperfect differential

[MSQ]

- Q.4** A man is pulling a bucket of water up to the roof of a building of 6 m height. The total weight of the rope is 20 N and the weight of the bucket with water is 100 N. The work done by the man is \_ Nm.
- Q.5** One kg of a perfect gas is compressed from pressure  $P_1$  to pressure  $P_2$  by
- Isothermal process
  - Adiabatic process
  - The law  $PV^{1.1} = \text{constant}$
- The correct sequence of these processes in increasing order of their slope on P-V diagram is
- 1, 2, 3
  - 1, 3, 2
  - 2, 3, 1
  - 3, 1, 2
- Q.6** A cyclic process ABC is shown on a P-V diagram in figure below





## CONVENTIONAL BRAIN TEASERS

**Q.1** A gas is expanded from an initial volume of  $0.1 \text{ m}^3$  at 3 bar to a final volume of  $0.3 \text{ m}^3$  at 1 bar. The pressure and volume are related linearly during the process. Determine the work done.

**1. Solution :**

Given data:  $V_1 = 0.1 \text{ m}^3$ ;  $p_1 = 3 \text{ bar} = 300 \text{ kPa}$ ;  $V_2 = 0.3 \text{ m}^3$ ;  $p_2 = 1 \text{ bar} = 100 \text{ kPa}$

Let  $A$  is any point on process 1–2.  $p$  and  $V$  are the pressure and volume at point  $A$ . Based on the given data, the  $p$ - $V$  relation can be expressed by the linear equation

$$\frac{p_2 - p_1}{V_2 - V_1} = \frac{p - p_1}{V - V_1}$$

$$\frac{100 - 300}{0.3 - 0.1} = \frac{p - 300}{V - 0.1}$$

$$\frac{-200}{0.2} = \frac{p - 300}{V - 0.1}$$

$$-1000 = \frac{p - 300}{V - 0.1}$$

or-  $1000V + 100 = p - 300$

or  $p = 400 - 1000V$

where  $p$  is in kPa and  $V$  is in  $\text{m}^3$ .

The work done is calculated by

$$W_{1-2} = \int_{V_1}^{V_2} p dV = \int_{0.1}^{0.3} (400 - 1000V) dV = \left[ 400V - \frac{1000V^2}{2} \right]_{0.1}^{0.3}$$

$$= 400 \times 0.3 - 500 \times (0.3)^2 - 400 \times 0.1 + 500 \times (0.1)^2$$

$$= 120 - 45 - 40 + 5 = 40 \text{ kJ}$$

**Q.2** One mole of an ideal gas at 0.5 MPa and 300 K is heated at constant pressure till the volume is doubled and then allowed to expand at constant temperature till the volume is doubled again. Sketch the processes on  $P$ - $V$  diagram. Also determine the net work done.

**2. Solution :**

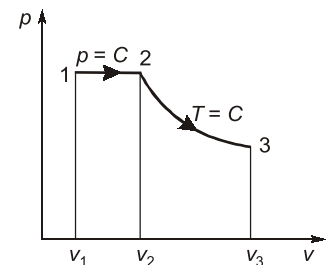
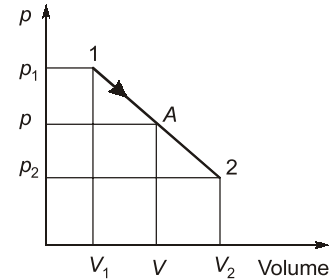
Given data: Number of mole:  $n = 1$ ;  $p_1 = 0.5 \text{ MPa} = 500 \text{ kPa} = p_2$ ;  $T_1 = 300\text{K}$ ;

Let  $V_1 = V$ ; and  $V_2 = 2V_1 = 2V$ ;

$V_3 = 2V_2 = 4V$ ;  $T_2 = T_3$

Work done during process 1–2:

$$W_{1-2} = \int_1^2 p dV = p \int_1^2 dV = p[V]_1^2 = p(V_2 - V_1)$$





# First Law of Thermodynamics

## 3.1 INTRODUCTION

In the early part of nineteenth century the scientists developed the concept of energy and the hypothesis that it can neither be created nor be destroyed; this came to be known as the **law of conservation of energy**. The first law of thermodynamics is merely one statement of this general law with particular reference to heat and work.

So, far, we have considered various forms of energy such as heat  $Q$ , work  $W$ , and total energy  $E$  individually, and no attempt is made to relate them to each other during a process. The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and its interactions. Based on experimental observations, the first law of thermodynamics states that energy can be neither created nor destroyed during a process, it can only change forms.

## 3.2 The First Law of Thermodynamics (Joule's Law or Law of Conservation of Energy)

- When a closed system undergoes a complete cycle, net work is done on or by the system. The only other energy involved in the cycle is heat which is supplied or rejected during various processes.
- The first law relates these two forms of energy in the following statement:

“For a closed system undergoing a cycle the net energy interaction in the form of heat is equal to the net energy interaction in the form of work”

Let us consider a closed system which consists of a known mass of water,  $m$ , contained in an adiabatic vessel having a thermometer and a paddle wheel, as shown in figure (a). Let a certain amount of work  $W_{1-2}$  be done upon the system by the paddle wheel.

The quantity of work can be measured by the fall of weight which drives the paddle wheel through a pulley. The system was initially at temperature  $t_1$ , the same as that of atmosphere, and after work transfer let the temperature rises to  $t_2$ .

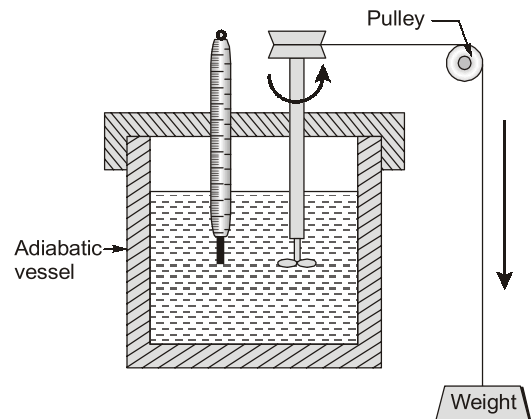


Fig. (a) Adiabatic work

Given: Initial pressure,  $P_1 = 200$  kPa; Mass of air,  $m = 3$  kg; Initial temperature,  $T_1 = 27^\circ\text{C} = 300$  K;  
 $P_2 = 400$  kPa =  $P_3$ ,  $V_1 = V_2$  and  $V_3 = 2V_2 = 2V_1$

Assumptions:

- (i) Closed system
- (ii) Quasi-static process
- (iii)  $\Delta KE = \Delta PE = 0$
- (iv) Air is an ideal gas

Applying first law between states 1 and 3

$$Q_{1-3} = \Delta U_{1-3} + W_{1-3}$$

Work done,  
for  $V_1$ ,

$$W_{1-3} = W_{1-2} + W_{2-3}$$

$$P_1 V_1 = mRT_1$$

$$200 \times V_1 = 3 \times 0.287 \times 300$$

$$V_1 = 1.292 \text{ m}^3$$

$\therefore$   
now

$$V_2 = 2V_1 = 2.584 \text{ m}^3$$

$$W_{1-2} = 0 \quad \text{(as constant volume)}$$

$$W_{2-3} = P_2(V_3 - V_2) \quad \text{(as isobaric process)}$$

$$= 400(2.584 - 1.292) = 516.6 \text{ kJ}$$

$\therefore$   
Change in internal energy,  
assuming

$$W_{1-3} = 0 + 516.6 = \mathbf{516.6 \text{ kJ}}$$

$$\Delta U_{1-3} = mc_v(T_3 - T_1) \quad \text{(as ideal gas)}$$

$$c_v = 0.718 \text{ kJ/kgK}$$

and for  $T_3$ , using equation

$$\frac{P_1 V_1}{T_1} = \frac{P_3 V_3}{T_3}$$

$$T_3 = \left(\frac{P_3}{P_1}\right)\left(\frac{V_3}{V_1}\right) \times T_1 = \frac{400}{200} \times 2 \times 300 = 1200 \text{ K}$$

$\therefore$   
now,

$$\Delta U_{1-3} = 3 \times 0.718 (1200 - 300) = 1938.6 \text{ kJ}$$

$$Q_{1-3} = \Delta U_{1-3} + W_{1-3} = 1938.6 + 516.6$$

$$= \mathbf{2455.2 \text{ kJ}}$$

Hence, options (a), (b) and (d) are correct.

■■■■



**OBJECTIVE  
BRAIN TEASERS**

- Q.1** The specific heat of a material is given in a strange unit to be  $c = 2.8$  kJ/kg $^\circ\text{F}$ . The specific heat of this material in the SI units of kJ/kg $^\circ\text{C}$  is \_\_\_\_\_. [Correct upto 2 decimal places]
- Q.2** Which one of the following phenomenon occurs when gas in a piston cylinder assembly expands reversibly at constant pressure?
- (a) Heat is added to the gas
  - (b) Heat is removed from the gas

- (c) Gas does work from its own stored energy
- (d) Gas undergoes adiabatic expansion

- Q.3** A piston cylinder arrangement contains 2 kg of air at 300 kPa and  $27^\circ\text{C}$ . During a reversible isothermal expansion process 20 kJ of displacement work is done by air and 5 kJ work is done on the system through a heating coil. The heat transfer during the process is \_\_\_\_ kJ.
- Q.4** A frictionless piston-cylinder device and a rigid tank each contain 2 kmol of an ideal gas at the same temperature, pressure and volume. The temperature of both the systems is raised by

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{L_2}{L_1}\right)^{\gamma-1}$$

$$= \left(\frac{L_2}{L_1}\right)^{\frac{4}{3}-1} = \left(\frac{L_2}{L_1}\right)^{\frac{1}{3}}$$

$$\Rightarrow \frac{L_2}{L_1} = \left(\frac{T_1}{T_2}\right)^3$$

$$\Rightarrow L_1 T_1^3 = L_2 T_2^3$$

21. (c)

If a compression or expansion of a gas takes place in a short time, it would be nearly adiabatic, such as compression stroke of a gasoline or a diesel engine.

22. (b)

$$F = 200 \text{ N}; \quad d = 80 \text{ mm}$$

$$t = 10 \text{ min} = 10 \times 60 = 600 \text{ sec}$$

Initially rod was the system but finally machined rod and chips become the system.

$$\Delta U = 100 \text{ kJ},$$

$$N = 250 \text{ rpm} = \frac{250}{60} \text{ rps}$$

$$\therefore W = -T \times \theta = -(F \times r) \times (\omega t)$$

$$= -(F \times r) \times (2\pi N \times t)$$

$$\Rightarrow W = -200 \times 0.04 \times 2\pi \times \frac{250}{60} \times 600$$

$$\Rightarrow W = -125663.7 \text{ J} = -125.6 \text{ kJ}$$

[Work done on system]

$$\therefore \Delta U = Q - W$$

$$\Rightarrow 100 = Q - (-125.6)$$

$$\Rightarrow Q = -25.6 \text{ kJ}$$



## CONVENTIONAL BRAIN TEASERS

**Q.1** Air is contained in a vertical piston cylinder assembly fitted with an electrical resistor. The atmosphere exerts a pressure of 1 bar on the top of the piston, which has a mass of 45 kg and a face area of 0.09 m<sup>2</sup>. Electric current is passed through the resistor and the volume of the air slowly increases by 0.045 m<sup>3</sup> while its pressure remains constant. The mass of the air is 0.27 kg and its specific internal energy increases by 42 kJ. The air and piston are at rest initially and finally. The piston cylinder material is a ceramic composite and is thus a good insulator. Friction between the piston and cylinder wall can be ignored, and the local acceleration of gravity  $g = 9.81 \text{ m}^2/\text{s}$ . Determine the heat transfer from the resistor to the air, in kJ, for a system consisting of (a) the air alone (b) the air and the piston.

1. **Solution**

(a) Refer figure (a),

Given:  $P_{\text{atm}} = 1 \text{ bar}$ ,  $m_{\text{piston}} = 45 \text{ kg}$ ,  $A_{\text{piston}} = 0.09 \text{ m}^2$ ,  $m_{\text{air}} = 0.27 \text{ kg}$

$\Delta V = 0.045 \text{ m}^3$ ,  $\Delta u_{\text{air}} = 42 \text{ kJ/kg}$

**Assumptions:**

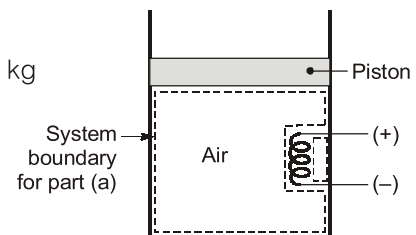
1. The system is only air (i.e. excluding heating element).
2. Changes in kinetic and potential energy is zero.
3. Only heat transfer is through resistor.

$$\text{as } \Delta KE = \Delta PE = 0$$

$$\therefore \text{For the system } Q = \Delta U + W \quad \dots(i)$$

as air undergoes constant pressure process

$$\therefore W = \int_1^2 P dV = P \Delta V$$



**Fig. (a)**

# Thermodynamic Relations

## 8.1 INTRODUCTION

In the preceding chapters we made extensive use of the property tables. We tend to take the property tables for granted, but thermodynamic laws and principles are of little use to engineers without them. In this chapter, we focus our attention on how the property tables are prepared and how some unknown properties can be determined from limited available data.

It will come as no surprise that some properties such as temperature, pressure, volume and mass can be measured directly, other properties such as density and specific volume can be measured directly. Other properties such as density and specific volume can be determined from these using some simple relations. However, properties such as internal energy, enthalpy and entropy are not so easy to determine because they cannot be measured directly or related to easily measurable properties through some simple relations. Therefore, it is essential that we develop some fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties.

## 8.2 MATHEMATICAL THEOREMS

### Theorem 1

If a relation exists among the variables  $x$ ,  $y$  and  $z$ , then  $z$  may be expressed as a function of  $x$  and  $y$  or

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

If 
$$\left( \frac{\partial z}{\partial x} \right)_y = M \text{ and } \left( \frac{\partial z}{\partial y} \right)_x = N$$

then, 
$$dz = Mdx + Ndy$$

where  $z$ ,  $M$  and  $N$  are functions of  $x$  and  $y$ .

Differentiating  $M$  partially with respect to  $y$ , and  $N$  with respect to  $x$ .

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \cdot \partial y}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \cdot \partial x}$$

$$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This is the condition of exact (or perfect) differential.

### Theorem 2

If a quantity  $f$  is a function of  $x$ ,  $y$  and  $z$ , and a relation exists among  $x$ ,  $y$  and  $z$ , then  $f$  is a function of any two of  $x$ ,  $y$ , and  $z$ . Similarly, any one of  $x$ ,  $y$  and  $z$  may be regarded to be a function of  $f$  and any one of  $x$ ,  $y$  and  $z$ . Thus if

$$x = x(f, y)$$

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy$$

Similarly, if

$$y = y(f, z)$$

$$dy = \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz$$

Substituting the expression of  $dy$  in the preceding equation,

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f \left[ \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz \right] \\ &= \left[ \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z \right] df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f dz \end{aligned}$$

Again,

$$dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)_f dz$$

$$\therefore \left(\frac{\partial x}{\partial z}\right)_f = \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

### Theorem 3

Among the variables  $x$ ,  $y$  and  $z$ , any one variable may be considered as a function of the other two. Thus

$$x = x(y, z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Similarly,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

**Example 8.12**

A 3.27 m<sup>3</sup> tank contains 100 kg of nitrogen at 175 K. The pressure in the tank is calculated as  $P_1$  with the help of ideal gas equation and as  $P_2$  with the help of van der Waal's equation. If  $R_{N_2} = 0.297$  kJ/kgK,  $T_C = 126.2$  K and  $P_C = 3.39$  MPa, the value of  $P_1 - P_2$  is

- (a) 93.52 Pa                      (b) 93.52 MPa  
(c) 93.52 kPa                    (d) 93.52 bar

**Solution : (c)**

Given,                      Volume of tank,  $V = 3.27$  m<sup>3</sup>  
                                  Mass of nitrogen,  $m = 100$  kg  
                                  Temperature,  $T = 175$  K

Thus the specific volume,             $v = \frac{V}{m} = \frac{3.27}{100} = 0.0327$  m<sup>3</sup>/kg

From the ideal gas equation of state

$$P_1 = \frac{RT}{v} = \frac{0.297 \times 175}{0.0327} = 1589.45 \text{ kPa}$$

The van der Waal's constant for nitrogen are determined as

$$a = \frac{27R^2T_C^2}{64P_C} = \frac{27 \times (0.297)^2 (126.2)^2}{64 \times 3.39 \times 10^3} = 0.175 \text{ m}^6 \text{ kPa/kg}^2$$

$$b = \frac{RT_C}{8P_C} = \frac{0.297 \times 126.2}{8 \times 3.39 \times 10^3} = 0.00138 \text{ m}^3/\text{kg}$$

Then from van der Waal's equation

$$P_2 = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{0.297 \times 175}{0.0327 - 0.00138} - \frac{0.175}{(0.0327)^2} = 1495.93 \text{ kPa}$$

$$\therefore P_1 - P_2 = 1589.45 - 1495.93 = 93.52 \text{ kPa}$$



**OBJECTIVE BRAIN TEASERS**

**Q.1** For a given volume of dry saturated steam, Clapeyron's equation is given by

(a)  $v_g - v_f = \frac{dT_s}{dP} \times \frac{T_s}{h_g - h_f}$

(b)  $v_g - v_f = \frac{dT_s}{dP} \times \frac{h_g - h_f}{T_s}$

(c)  $v_g - v_f = \frac{dP}{dT_s} \times \frac{h_g - h_f}{T_s}$

(d)  $v_g - v_f = \frac{dP}{dT_s} \times \frac{T_s}{h_g - h_f}$

**Q.2** To get the cooling effect for a refrigerant, it has to be precooled at least below the

- (a) critical temperature  
(b) triple point temperature  
(c) maximum inversion temperature  
(d) minimum inversion temperature

**Q.3**  $Tds$  equation can be expressed as

(a)  $Tds = c_v dT + \frac{T\beta}{K_T} dv$

(b)  $Tds = c_v dT + \frac{T}{K_T} dv$

(c)  $Tds = c_v dT + \frac{TK_T}{\beta} dv$

(d)  $Tds = c_v dT + \frac{T\beta}{K_T} dP$



**CONVENTIONAL BRAIN TEASERS**

**Q.1** For a perfect gas, shown that

$$c_p - c_v = \left[ P + \left( \frac{\partial u}{\partial v} \right)_T \right] \left( \frac{\partial v}{\partial T} \right)_P = Pv\beta + v\beta \left( \frac{\partial u}{\partial v} \right)_T$$

where  $\beta$  is the coefficient of cubical/volume expansion.

**1. Solution :**

The first law of thermodynamics applied to a closed system undergoing a reversible process states as follows:

$$\delta Q = du + Pdv$$

and as per second law

$$ds = \left( \frac{\delta Q}{T} \right)_{\text{rev}}$$

Combining above two equation we have

$$Tds = du + Pdv$$

also we know,

$$h = u + Pv$$

$\therefore$

$$\begin{aligned} dh &= du + Pdv + vdP \\ &= Tds + vdP \end{aligned}$$

Thus,

$$Tds = du + Pdv = dh - vdP$$

Now, if  $u$  is assumed to be a function of  $T$  and  $v$  then

$$du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv = c_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv$$

Also if  $h$  is assumed to be a function of  $T$  and  $P$  then

$$dh = \left( \frac{\partial h}{\partial T} \right)_P dT + \left( \frac{\partial h}{\partial P} \right)_T dP = c_p dT + \left( \frac{\partial h}{\partial P} \right)_T dP$$

In the equation of  $Tds$ , substituting  $du$  and  $dh$  values

$$c_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv + Pdv = c_p dT + \left( \frac{\partial h}{\partial P} \right)_T dP - vdP$$

or

$$c_v dT + \left[ P + \left( \frac{\partial u}{\partial v} \right)_T \right] dv = c_p dT + \left[ \left( \frac{\partial h}{\partial P} \right)_T - v \right] dP$$

Since above equation is true for any process, it will also be true for constant pressure process i.e.  $dP = 0$

$$\therefore (c_p - c_v)(dT)_P = \left[ P + \left( \frac{\partial u}{\partial v} \right)_T \right] (dv)_P$$

$$(c_p - c_v) = \left[ P + \left( \frac{\partial u}{\partial v} \right)_T \right] \left( \frac{\partial v}{\partial T} \right)_P$$

By definition,

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P$$