

Thermodynamics System

Definite quantity of matter bounded by some closed surface. There are 3 types of system.

a. Open System

It is a system where there is an exchange of both heat and molecules between system and surroundings.

b. Closed System

It is a system where there is an exchange of heat only.

c. Isolated System

It is a system where there is no any exchange of heat and molecules with its surroundings.

First Law of Thermodynamics

According to it, the total supplied heat to the system is used to increase the internal energy of the system and to do some work.

$$\text{i.e. } dQ = \cancel{dH} + \cancel{dU} + dU + dw$$

Since, $dw = Pdv$ then

$$dQ = dU + Pdv$$

Specific Heat Capacity of Gas

It is the amount of heat required to change the temperature of unit mass or unit mole of gas through unit temperature change.

i. Principal Specific heat Capacity at constant Volume

It is the amount of heat required to change the temperature of unit mass of gas through unit temperature at constant Volume. i.e. $C_V = \frac{dQ}{dT}$

ii. Principal Specific Heat at Constant Pressure

It is the amount of heat req. to change the temperature of unit mass of gas by unit temperature at constant pressure. i.e. $C_p = \frac{dq}{dT}$

iii. Molar Specific heat capacity of gas at constant pressure.

It is the amount of heat required to raise the temperature of unit mole of gas by unit temperature at constant volume pressure. i.e. $C_p = \frac{dq}{nDT}$

iv. Molar Specific heat capacity at constant volume.

It is the amount of heat required to change the unit temperature of a unit mole of gas ~~as~~ at constant volume.

$$\text{i.e. } C_v = \frac{dq}{nDT}$$

Why $C_p > C_v$?

We know,

$$dq = dU + PdV$$

$$\text{or, } dq = dU + PdV$$

$$\text{or, } dq = nC_vdT + PdV$$

When 'V' is constant

$$dq = nC_vdT \quad \dots \textcircled{1}$$

When 'P' is constant

$$dq = nC_vdT + PdV$$

$$\text{or, } dq' = (dq)_{P\text{constant}} + PdV$$

$$\text{or, } nC_pdT = nC_vdT + PdV$$

$$\therefore C_p > C_v$$

Here,

At constant pressure, there is work done along with the change in internal energy. Where at constant volume, only

internal energy change is there. That's why more heat is needed at constant pressure. So, C_p is always greater than C_v .

Derive $C_p - C_v = R$

By 1st Law of Thermodynamics,

$$d\varphi = dU + dW$$

$$\therefore d\varphi = nC_vdT + Pdv \quad \text{--- (i)}$$

At constant pressure

$$d\varphi = nC_pdT$$

$$\therefore nC_pdT = nC_vdT + Pdv \quad \text{--- (ii)}$$

From ideal gas equation for 'n' mole

$$PV = nRT$$

Differentiating both sides w.r.t. temperature at constant 'P'.

$$\therefore \frac{d(PV)}{dT} = \frac{d(nRT)}{dT}$$

$$\text{or, } P \frac{dv}{dT} = nR \cdot \frac{dT}{dT}$$

$$\text{or, } Pdv = nRdT \quad \text{--- (iii)}$$

from equation (i) and (ii), we get;

$$\therefore C_pdT = nC_vdT + nRdT$$

$$\text{or } C_pdT = C_vdT + RdT$$

$$\text{or, } C_p = C_v + R$$

Note: $\frac{C_p}{C_v} = \gamma$ 'gamma'

Also, $\gamma = 1 + \frac{2}{f}$, f = degree of freedom

Degree of freedom

For diatomic, f = 3 + 2 = 5

For triatomic, f = 3 + 3 = 6

For Monoatomic, $f = 3$

Thermodynamic Process

A thermodynamic process is said to take place when some changes occur in the state of a thermodynamic system i.e. the thermodynamic parameters of the system changes with time.

a. Isothermal Process (Slow Process)

The process in which pressure and volume of a system change without any change in its temperature is called an isothermal process.

b. Adiabatic Process (Rapid Process)

A process in which pressure, volume and temperature of the system change but there is no exchange of heat between the system and its surrounding is called adiabatic process.

c. Isochoric Process

If a substance undergoes a process in which the volume remains constant, the process is called an isochoric process.

d. Isobaric Process

If the working substance is taken in an expanding chamber in which the pressure is kept constant, the process is called isobaric process.

A. # Application of 1st Law in isothermal Process

From 1st Law of Thermodynamics, $d\varphi = dU + dW$

For isothermal process, $T = \text{constant}$

Since, internal energy of an ideal gas is only the function of temperature. Then, $dU = 0$

$$\therefore d\varphi = dW = PdV$$

Hence, for isothermal process, heat added / supplied to the system is used to do external work only.

Equation of an isothermal Process

From ideal gas equation;

$$PV = nRT$$

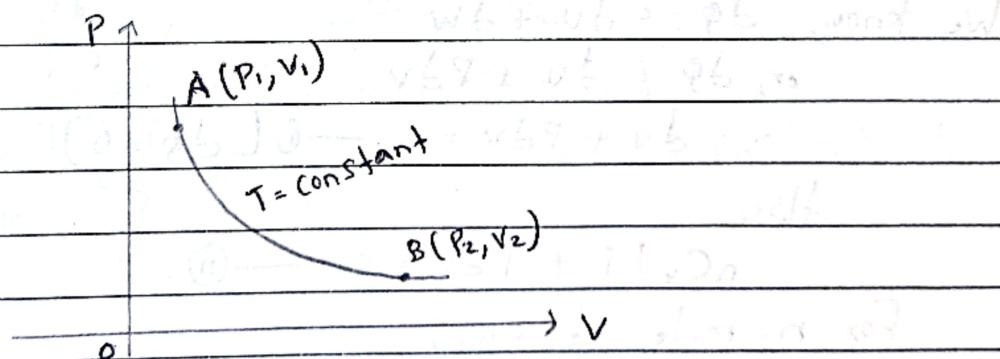
Since, (T) is constant for isothermal process

$$PV = \text{constant}$$

or, $V \propto \frac{1}{P}$, Thus equation of isothermal process is equivalent to Boyle's Law.

In general:

$$P_1 V_1 = P_2 V_2$$



Work done during Isothermal process

When small amount of work is done for small change in volume of a gas in a cylinder at constant pressure is

$$dW = PdV$$

Work done to change the volume V_1 to V_2 then,

$$W = \int_{V_1}^{V_2} PdV \quad \text{--- (1)}$$

For n mole of an ideal gas

$$PV = nRT$$

$$\text{or } P = \frac{nRT}{V} \quad \text{--- (II)}$$

from (I) and (II)

$$W = \int_{V_1}^{V_2} nRT \cdot dV$$

$$= nRT \left[\log_e V \right]_{V_1}^{V_2}$$

$$\therefore W = nRT \cdot \log_e \left(\frac{V_2}{V_1} \right)$$

B. # Application of 1st Law in Adiabatic Process

from 1st Law of thermodynamics

$$d\varphi = dU + PdV - dW$$

For adiabatic process, $d\varphi = 0$

$$\therefore dW = -dU$$

Equation of Adiabatic process

$$\text{We know, } d\varphi = dU + dW$$

$$\text{or, } d\varphi = dU + PdV$$

$$\text{or, } dU + PdV = 0 \quad \text{--- (I)} [d\varphi = 0]$$

Also,

$$nC_V dT + PdV = 0 \quad \text{--- (II)}$$

For n -mole of gas;

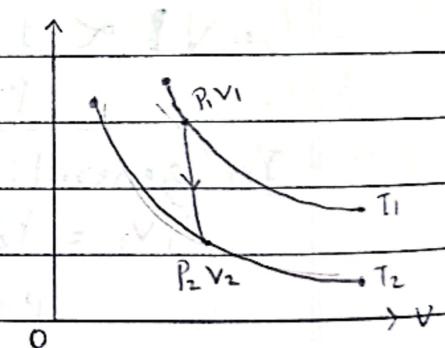
$$PV = nRT \quad \text{--- (III)}$$

Differentiating both sides w.r.t (T)

$$\frac{P \cdot \cancel{dV}}{\cancel{dT}} + V \cdot \frac{dP}{dT} = nR \cdot \frac{dT}{dT}$$

$$\text{or, } P \cdot \cancel{dV} + V \cdot \cancel{dP} = nR \cdot \cancel{dT}$$

$$\text{or, } \frac{dT}{nR} = \frac{P \cdot \cancel{dV} + V \cdot \cancel{dP}}{\cancel{nR}} \quad \text{--- (IV)}$$



From equation (ii) and (iv)

$$n C_V \left(\frac{P \cdot dV}{nR} + V \cdot dP \right) + P \cdot dV = 0$$

$$\text{or, } C_V \cdot P \cdot dV + C_V \cdot V \cdot dP + R P \cdot dV = 0$$

$$\text{or, } (C_V + R) P \cdot dV + C_V \cdot V \cdot dP = 0$$

$$\text{or, } C_p \cdot P \cdot dV + C_V \cdot V \cdot dP = 0 \quad [C_p - C_V = R]$$

Now,

Dividing both sides by $C_V \cdot P \cdot V$, we get

$$\frac{C_p \cdot dV}{C_V \cdot V} + \frac{dP}{P} = 0$$

$$\text{or, } \left(\frac{C_p}{C_V} \right) \frac{dV}{V} + \frac{dP}{P} = 0$$

$$\text{or, } \gamma \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

Integrating both sides

$$\text{or, } \int \frac{dV}{V} + \int \frac{dP}{P} = \int 0$$

$$\text{or, } \gamma \log V + \log P = \text{constant}$$

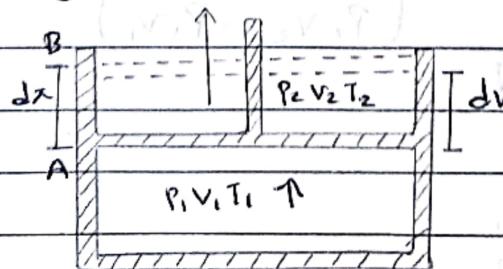
$$\text{or, } \log V^\gamma + \log P = \text{constant}$$

$$\text{or, } \log (P \cdot V^\gamma) = \log K \quad [\text{constant} = \log K]$$

$$\text{or, } P \cdot V^\gamma = K$$

$$\therefore P \cdot V^\gamma = \text{constant}$$

Work done during an adiabatic Process



P_1, V_1, T_1 = Initial state

P_2, V_2, T_2 = Final state

We know, $dW = PdV$

$$\text{or, } \int dW = \int_{V_1}^{V_2} P \cdot dV$$

$$\text{or, } W = \int_{V_1}^{V_2} P \cdot dV$$

$$\text{we have, } P \cdot V^\gamma = k$$

$$\text{or, } P = \frac{k}{V^\gamma}$$

$$\therefore P = kV^{-\gamma}$$

Therefore,

$$W = \int_{V_1}^{V_2} kV^{-\gamma} \cdot dV$$

$$\text{or, } W = k \int_{V_1}^{V_2} V^{-\gamma} \cdot dV$$

$$= k \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$= \frac{k}{1-\gamma} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

$$= \frac{k}{1-\gamma}$$

$$\text{Now, } P_1 V_1^\gamma = P_2 V_2^\gamma = k$$

$$\therefore W = \frac{1}{1-\gamma} (k \cdot V_2^{1-\gamma} - k \cdot V_1^{1-\gamma})$$

$$= \frac{1}{1-\gamma} (P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma})$$

$$= \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1)$$

Also,

$$P_1 V_1 = nRT_1$$

$$P_2 V_2 = nRT_2$$

$$\therefore W = \frac{1}{1-\gamma} [nRT_2 - nRT_1]$$

C.# Application of first law Isobaric Process

We know,

$$d\varphi = dU + dW$$

$$\text{or, } d\varphi = nC_v dT + Pdv$$

As the pressure is constant and the gas expand from V_1 to V_2 . Then total work done is given by:

$$W = \int_{V_1}^{V_2} Pdv$$

$$\text{or, } W = P \int_{V_1}^{V_2} dv$$

$$= P(V_2 - V_1)$$

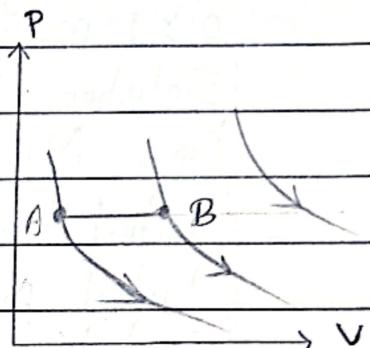


Fig: P-V diagram

D.# Application of first law in isochoric process

We know,

$$d\varphi = dU + dW$$

$$\text{or, } d\varphi = dU + Pdv$$

At isochoric process, $dv = 0$

$$d\varphi = dU$$

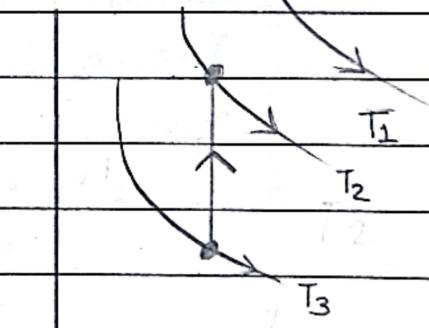


Fig: Isochoric Process