#### ISOCHORIC PROCESS

# Revision of First law of Thermodynamics

The first law of thermodynamics, or the law of conservation of energy, asserts that energy cannot be created nor destroyed; however, it can be converted from one form to another. Throughout any process, the sum of the change in the system's internal energy and the work executed by the system equals the total heat imparted to the system.

$$0 = W + \Delta U$$

This can also be written in terms of  $\Delta U$ , which is a state function.

$$\Delta U = Q - W$$

 $\Delta U$  = Change in the internal energy of a closed system

Q = Quantity of the energy supplied to the system as heat

W = Amount of thermodynamic work done by the system on its surroundings

The first law of thermodynamics can be written in the differential form as:

$$\delta Q = \delta W - dU$$

As heat and work done are path functions, they exhibit partial differentiability. In contrast, internal energy, being a state function, is fully differentiable.

Note: The internal energy (U) of a thermodynamic system represents the energy encompassed or stored within the system. It accounts for the aggregate energy possessed by individual molecules within the system.

Internal energy is a state function, and for an ideal gas, it is denoted as U = f(T). With an increase in temperature, the internal energy of the system also rises. Conversely, if the gas is cooling (experiencing a decrease in temperature), its internal energy decreases as well.

Ex. A thermodynamic process is shown in the figure. The pressures and volumes corresponding to some points in the figure are:  $P_A = 3 \times 10^4 Pa$ ,  $P_B = 8 \times 10^4 Pa$  and  $V_A = 2 \times 10^4 Pa$  $10^{-3}$  m<sup>3</sup>,  $V_D = 5 \times 10^{-3}$  m<sup>3</sup>.. In process AB, 600 J of heat is added to the system and in process BC, 200 J of heat is added to the system. What would be the change in internal energy of the system in process AC?



Sol. Heat added to the system in process AB,  $Q_{AB} = 600 \text{ J}$ Heat added to the system in process BC,  $Q_{BC} = 200 \text{ J}$ From the first law of thermodynamics, we get,

$$\Delta U_{AC} = \Delta Q_{AC} - \Delta W_{AC}$$
$$\Delta Q_{AC} = \Delta U_{AC} + \Delta W_{AC}$$

The heat exchange in process A to C is given as follows:

$$\begin{split} \Delta Q_{AC} &= \Delta Q_{AB} + \Delta Q_{BC} \\ \Delta Q_{AC} &= 600 J + 200 J \\ \Delta Q_{AC} &= 800 J \end{split}$$

The work done during process A to C is given as follows:

$$\Delta W_{AC} = \Delta W_{AB} + \Delta W_{BC}$$

The work done during process A to B is zero since the change in volume ( $\Delta V$ ) is zero.

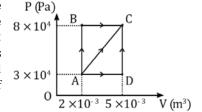
$$\Delta W_{AB} = 0$$

The work done during process B to C is given as follows:

$$\Delta W_{BC} = P\Delta V$$
 
$$\Delta W_{BC} = (8\times10^4)(3\times10^{-3})$$
 
$$\Delta W_{BC} = 240J$$
 The net work done is, 
$$\Delta W_{AC} = \Delta W_{BC} = 240J$$
 The change in internal energy is, 
$$\Delta U_{AC} = \Delta Q_{AC} - \Delta W_{AC}$$
 
$$\Delta U_{AC} = 800\ J - 240\ J$$
 
$$\Delta U_{AC} = 560\ J$$

Thus, option (A) is the correct answer.

The net work done is,



ΔU

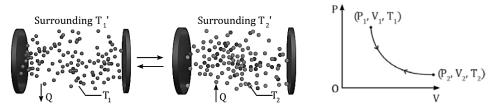
# Sign Convention - Internal Energy Change, Heat absorbed, Work done Sign Convention

| Process                     | Sign convention | Diagram                      |
|-----------------------------|-----------------|------------------------------|
| Heat drawn from the system  | Q is negative.  |                              |
| Heat supplied to the system | Q is positive.  |                              |
| Work done on the system     | W is negative.  | $W \rightarrow \blacksquare$ |
| Work done by the system     | W is positive.  | W                            |

# **Reversible and Quasic Static Process**

# **Reversible Process**

A reversible process is characterized by its ability to be reversed by infinitesimally adjusting the external conditions in the opposite direction.



With the indicator diagram, we can illustrate the reversible process as depicted in the graph.

#### **Quasi-Static Process**

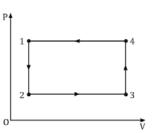
- It's a thermodynamic process that transpires at an infinitesimally gradual rate.
- Each state traversed during the quasi-static process gravitates toward equilibrium.
- "Quasi" denotes almost, and "static" refers to thermodynamic properties that remain unaltered with time.
- > Typically, a quasi-static process is also reversible.

# Cyclic and Non-cyclic Process Cyclic Process

A cyclic process is one in which a system returns to its initial state after undergoing any number of processes, while a non-cyclic process is characterized by having different initial and final states. For a cyclic process,

- 
$$U_i = U_f$$
 or  $\Delta U = 0$  or  $\Delta T = 0$   
-  $\Delta U = 0$  or  $W = \Delta Q$ 

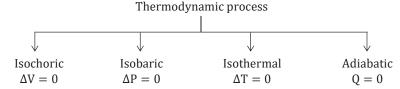
 $W = \Delta Q \Rightarrow It$  is the first law of thermodynamics for a cyclic process.



#### Thermodynamic Process - Isochoric, Isobaric, Isothermal and Adiabatic

A transition between two equilibrium states is referred to as a thermodynamic process.

The conventional thermodynamic processes comprise the following:



# Isochoric process

In an isochoric process, the volume remains constant.

$$V_i = V_f \text{ or } \Delta V = 0$$

From the first law of thermodynamics, we get,

$$\begin{aligned} \mathbf{Q} &= \mathbf{W} + \Delta \mathbf{U} & \dots \mathbf{(1)} \\ \mathbf{W} &= \mathbf{Q} - \Delta \mathbf{U} \end{aligned}$$

The work done in an isochoric process is,

$$W = \int_{V}^{V_f} P dV$$

 $W = P\Delta V = 0$  (Since the change in volume is zero)

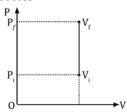
On substituting it in equation (i), we get the following:

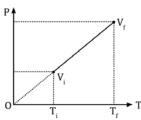
$$Q = W + \Delta U$$
$$Q = \Delta U$$

From this equation, we can observe that the heat supplied to the system is utilized in increasing the internal energy of the system.

$$Q = nC_V \Delta T$$
$$\Delta U = nC_V \Delta T$$

# Graphs of an isochoric process





**Note:** In the case of an ideal gas, internal energy solely relies on temperature. Hence, the alteration in internal energy is  $\Delta U = nC_v\Delta T$  for all thermodynamic processes. Given that temperature is a state function, internal energy likewise functions as a state function.

Ex. At a constant volume, 6000 J of heat is required to raise the temperature of two moles of a gas by 150 K. What is the specific heat capacity (Cv) of the gas?

(a) 
$$20 \text{Jmol}^{-1} \text{K}^{-1}$$

(b) 
$$20JK^{-1}$$

(d) 
$$900 \times 10^{3}$$
 J

Sol.

$$\begin{aligned} &Q = nC_{V}\Delta T \\ &C_{V} = \frac{Q}{n\Delta T} = \frac{6000J}{2mol \times 150 \text{ K}} \\ &C_{V} = 20J \text{mol}^{-1} \text{K}^{-1} \end{aligned}$$

Thus, option (a) is the correct answer.

**Ex.** At a constant volume, the temperature of a gas is increased from 200 K to 400 K. If the gas initially exerts a pressure of 3 kPa on the walls of the container, what is the final pressure of the gas?

(d) 
$$\sqrt{3}$$
kPa

Sol.

Initial temperature of the gas,  $T_1 = 200 \text{ K}$ 

Final temperature of the gas,  $T_2 = 400 \text{ K}$ 

Initial pressure on the walls of the container,  $P_1 = 3kPa$ 

$$\frac{\frac{P_1}{T_1} = \frac{P_2}{T_2}}{\frac{3}{200} = \frac{P_2}{400}}$$

$$P_2 = 6kPa$$

Thus, option (a) is the correct answer.

# **Isobaric Process**

In an isobaric process, the pressure remains constant.

$$P_i = P_f \text{ or, } \Delta P = 0$$

From the first law of thermodynamics,

$$Q = W + \Delta U \dots (i)$$

Work done in an isobaric process,

$$W = \int_{V_1}^{V_2} P dV$$

Since is constant,

$$W = P \int_{V_1}^{V_2} dV$$

$$W = P(V_2 - V_1)$$

$$W = P\Delta V$$

We know from ideal gas equation,

$$P\Delta V = nR\Delta T$$

The change in internal energy is given as follows:

$$\Delta U = nC_V \Delta T$$
  
$$\Delta U = nC_V (T_2 - T_1)$$

By substituting the values in equation (i), we get the following:

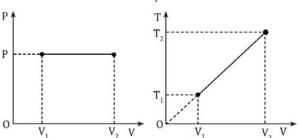
$$Q = W + \Delta U$$

$$Q = nR(T_2 - T_1) + nC_V(T_2 - T_1)$$

$$Q = n(T_2 - T_1)(R + C_V)(\because C_P - C_V = R)$$

$$Q = n(T_2 - T_1)(C_P)$$

$$Q = nC_p\Delta T$$



Heat transferred in an isobaric process,

$$Q = nC_p\Delta T$$

Change in internal energy,

$$\Delta U = nC_V \Delta T$$

# **Isothermal Process**

In an isothermal process, the temperature remains constant

$$T_i = T_f \text{ or } \Delta T = 0$$

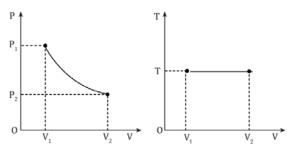
From the first law of thermodynamics,

$$Q = W + \Delta U$$

For an ideal gas, if  $\Delta T$  , then the change in internal energy is 0.

$$Q = W ....(i)$$

Every bit of warmth given to the system transforms into the tasks accomplished.



The tasks accomplished during an isothermal process are described as follows:

$$W = \int_{V_1}^{V_2} P dV$$
Also, PV = nRT
$$P = \frac{nRT}{V}$$
Therefore,
$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W = nRT \ln \frac{V_2}{V_1}$$

We can rewrite the work done as follows:

$$W = nRT \ln \frac{P_1}{P_2}$$

$$W = P_1 V_1 \ln \frac{V_2}{V_1} \text{ or, } W = P_2 V_2 \ln \frac{V_2}{V_1}$$

Or,

#### **Adiabatic Process**

In an adiabatic process, the heat exchange between the system and the surroundings is zero

$$(Q = 0)$$
.  
∴  $W = -\Delta U$ 

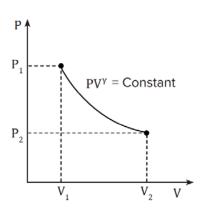
The work done by the system is at the expense of the internal energy.

The mathematical equation for an ideal gas undergoing a reversible adiabatic process is as follows:

$$PV^{\gamma} = Constant$$
 Where, 
$$\gamma = A diabatic index$$
 For a monoatomic ideal gas, 
$$\gamma = \frac{5}{3}$$
 For a diatomic ideal gas, 
$$\gamma = \frac{7}{5}$$

The work done in an adiabatic process is given as follows:

$$\begin{split} W &= \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{C}{V^{\gamma}} dV \text{ (Since PV}^{\gamma} = C) \\ W &= C \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} \\ W &= C [\frac{V^{-\gamma+1}}{1-\gamma}]_{V_1}^{V_2} = C \frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{1-\gamma} \\ \text{Also, } P_1 V_1^{\gamma} &= P_2 V_2^{\gamma} = C \\ W &= \frac{(P_2 V_2^{\gamma} \times V_2^{-\gamma+1}) - (P_1 V_1^{\gamma} \times V_1^{-\gamma+1})}{1-\gamma} \\ W &= \frac{P_2 V_2 - P_1 V_1}{1-\gamma} \end{split}$$



**Ex.** Which of the following holds true for an ideal gas that is undergoing an adiabatic change?

**Sol.** From the ideal gas equation, we get,

$$V = \frac{nRT}{P}$$

For an adiabatic change,

$$PV^{\gamma} = C$$

$$P\left(\frac{nRT}{P}\right)^{\gamma} = C$$

$$P(nRT)^{\gamma}P^{-\gamma} = C$$

$$P^{1-\gamma}T^{\gamma}=C$$

**Ex.** A diatomic gas that is initially at 18 °C is compressed adiabatically to  $\left(\frac{1}{8}\right)^{th}$  of its original volume.

What will be the temperature after compression?

Sol. Initial temperature of the gas,  $T_1 = 18 \,^{\circ}\text{C} = 18 + 273 \,^{\circ}\text{K} = 291 \,^{\circ}\text{K}$  From the ideal gas equation, we get,

$$PV = nRT$$
$$P = \frac{nRT}{V}$$

For an adiabatic change,

$$\begin{split} &PV^{\gamma} = C \\ &\left(\frac{nRT}{V}\right)V^{\gamma} = C \\ &TV^{\gamma-1} = C \end{split}$$

Therefore,

$$\begin{split} T_1 V_1^{\gamma-1} &= T_2 V_2^{\gamma-1} = C \\ T_2 &= T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} \\ T_2 &= 291 \times \left(\frac{V_1}{\frac{1}{8}V_1}\right)^{\gamma-1} = 291 \times 8^{0.4} \text{(Since } \gamma_{\text{diatomic gas}} = 1.4\text{)} \\ T_2 &= 291 \times 2.3 = 669.3 \text{ K} = 396.1^{\circ}\text{C} \end{split}$$