Law of Thermodynamics (2nd sem & 4th sem)
Phys - H - G.E - T-02 (Thermal Physics)

Thermodynamic Description of system : Zeroth law of thermodynamics and temperature :∞

⊕ Thermodynamics is that branch of Physics which deals with the transformation of heat energy into other forms of energy and vice-versa.

Thermal equilibrium is the state reached by two (or more) systems placed in thermal contact through a conducting wall.

Zeroth law of thermodynamics :→

Let us consider two systems A and B. They are separated from each other by an insulating wall so that no heat exchange takes place between them. Each of these two systems are brought into thermal contact with a third system C through conducting walls.

Experimental facts are expressed in the form of a law known as Zeroth law of thermodynamics. The law states that " Two systems are in thermal equilibrium with a third are in thermal equilibrium with each other.

System C

System A   Sysk m B
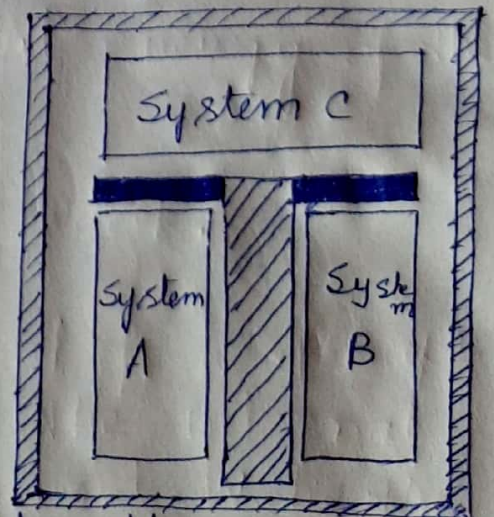
Concept of temperature :→

This law immediately leads us to the concept of temperature. A number of systems in thermal equilibrium with one another must possess a common value of some property. So if the property is the same for some systems, then they will be in thermal equilibrium and if not, then they there will be exchange of thermal energy among them till this property is the

same for all of them, when they reach thermal equilibrium with one another. This property is called temperature.

Definition of temperature :→

The temperature of a system is defined as that property which determines whether or not the system is in thermal equilibrium with other systems.
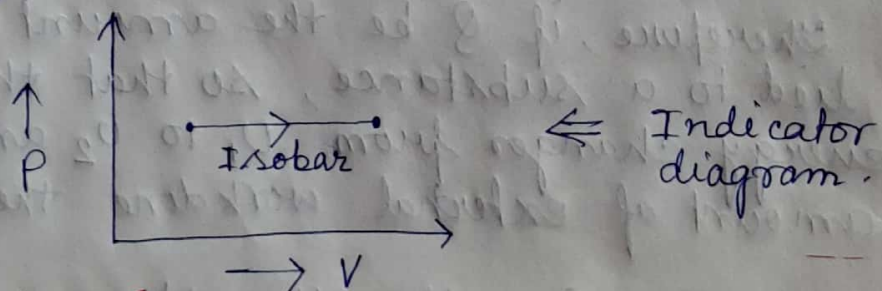
ɸ Thermodynamic Process :→

When the values of the thermodynamic variables of a system change from one equilibrium to another, the system is said to have undergone thermodynamic process.

There are different types of thermodynamic processes.

Thermodynamic Process

| Iso-baric process | Isochoric process | Cyclic process | Isothermal process | Adiabatic Process |
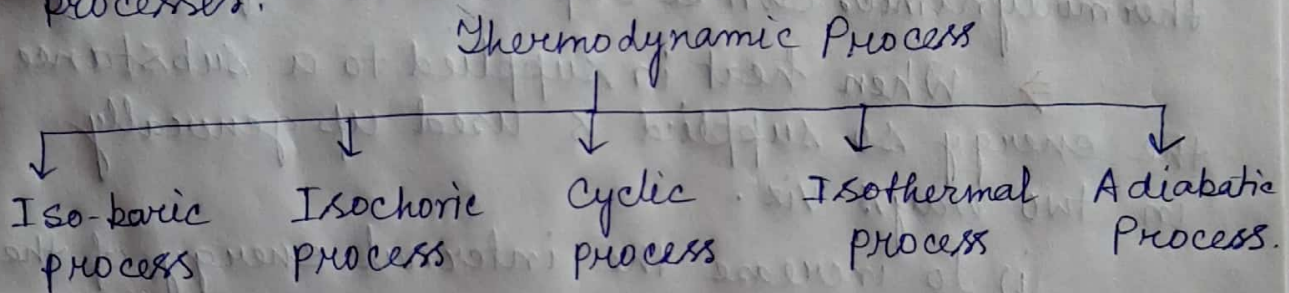
§ Isobaric Process :→
A thermodynamic process that takes place at constant pressure is called iso-baric process.
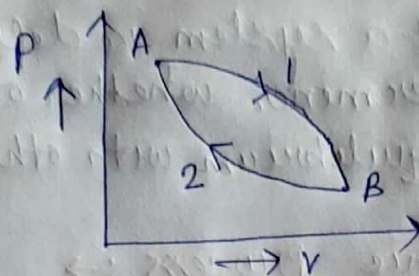
P ↑ — Isobar — ← Indicator diagram.

→ V

§ Isochoric process :→

A thermodynamic process in which the volume of the system remains constant is called the Isochoric process.

P ↑ ↑ ← Isocore ← Indicator diagram

→ V
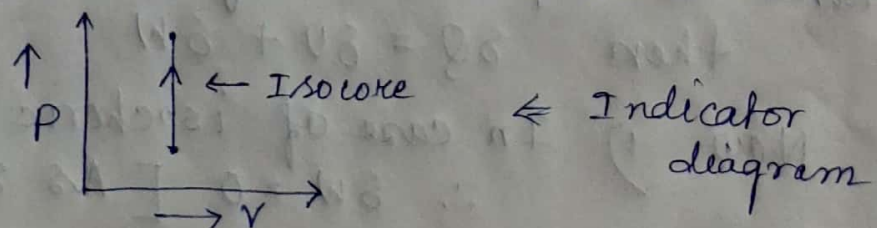
§ Cyclic Process :→

A thermodynamic process in which the system returns to its initial state after undergoing a series of processes is called cyclic.

← Indicator Diagram

Note :→
Isothermal and Adiabatic processes will be discussed in detail later on.

⊕ First law of thermodynamics :→

As suggested by Clausius, the first law of thermodynamics can be expressed in a general form.

⇒ When heat is supplied to a substance, the energy so supplied is used up generally in two ways viz.

i) to increase the internal energy of the substance

ii) to perform external work.

Therefore, if Q be the amount of heat supplied to a substance, so that the internal energy changes from U_1 to U_2 and W be the amount of external work done then

$$Q = U_2 - U_1 + W$$

If the amount of heat supplied to a substance is infinitesimally small viz. δQ.

then $\delta Q = \delta U + \delta W$

Now i) In case of isochoric process $\delta V = 0$

∴ $\delta W = 0$ $[AS\ \delta W = P\delta V]$

$$\therefore \quad \delta Q = \delta U.$$

ii) In cyclic process the change of Internal energy is nil. $\therefore \quad \delta U = 0.$

$$\therefore \quad \delta Q = \delta W.$$

❖ 22.9. Internal energy.

By the internal energy of a system, we mean the sum of the kinetic energy (translational, rotational and vibrational) of its molecules and the potential energy due to configuration (separation) of the molecules. Therefore if the total kinetic energy and potential energy of molecules of the system be E_k and E_p respectively, the internal energy of the system $U = E_k + E_p$. A part of the heat energy supplied, therefore, goes towards increasing the energy of the molecules. So a change in the internal energy can occur if a transfer of energy between the system and the surroundings takes place. The increase in internal energy is manifested by a rise in temperature or a change in state. The actual amount of internal energy possessed by a body can never be measured. But this possesses no problem, because in practice we are concerned only with the changes in internal energy; this can always be measured with certainty.

Sometimes a substance may acquire extra energy due to other causes. For example, a substance at the top of a high tower has more potential energy than that on the ground, or if it is carried in a fast moving car, its kinetic energy as a whole is greater than that when it is at rest. However, this extra energy is not considered as a part of internal energy; it is external energy.

❖ 22.10. Internal energy of a gas.

The thermal state of a gas is defined by its temperature T, pressure P or the volume V. Evidently, it may be argued that internal energy of a gas depends on all these factors. This matter was investigated experimentally by Joule and the result is known as **Joule's law** or **Mayer's hypothesis**. It states that—

The internal energy of a given amount of gas depends only upon its temperature and is independent of its pressure or volume.

The law implies that the change in internal energy of a given mass of a gas can be known provided its change in temperature is given, no matter what the pressure or volume may be. Evidently, if the temperature of a gas does not change, its internal energy remains the same, though the pressure and the volume of the gas might vary.

The hypothesis holds exactly only for an ideal gas. In practice, for real gases, the internal energy is found to depend on its volume. The effect is however, very small so that the hypothesis holds extremely closely for all real gases. For our work, we shall disregard this small departure in the behaviour of real gas from that of an ideal gas.

❖ 22.13. Specific heats of gases.

Two specific heats of a gas : The specific heat of a substance is defined as the amount of heat absorbed per unit mass per unit rise in temperature. There is no difficulty about this definition when applied to solids and liquids; but special considerations are necessary to apply this definition in the case of gases, becuase with change in temperature both the volume and the pressure of a gas vary considerably. The amount of heat absorbed by a gas depends upon the conditions of its volume and pressure; hence it is customary to define the specific heat of a gas by keeping either of the two factors, P and V, constant. Accordingly, two specific heats of a gas have come in vogue, viz., **specific heat or specific heat capacity at constant volume** (c_v) and the **specific heat or specific heat capacity** at constant **pressure** (c_p).

☛ **Definition :** *The specific heat of a gas at constant volume* (c_v) *is the amount of heat required to raise the temperature of unit mass of the gas through* $1°$, *when its volume is kept constant throughout.*

Thus, the heat required to raise the temperature of the mass m of a gas through $t°$ at constant volume is given by

$$Q = mc_v t \qquad \ldots \qquad \ldots \qquad (22.7)$$

So in **c.g.s. system**, the specific heat of a gas at constant volume is the amount of heat in calorie required to raise the temeprature of 1 g of the gas through 1°C without any change in volume. Its unit is calorie/gm °C.

In **S.I.**, the specific heat of a gas at constant volume is the amount of heat in Joule required to raise the temperature of 1 kg of the gas through 1 K when its volume is kept constant. Its unit is Joule/kg K.

In **F. P. S. system**, the corresponding unit is B. Th. U./lb°F

It is often convenient to deal with one mole of the gas, instead of one gram or one kilogram of the gas. The corresponding specific heat (C_v) is then called **molar specific heat or molar specific heat capacity of the gas at constant volume**. If M be the molar mass of the gas, then

$$C_v = Mc_v$$

☛ **Definition :** *The molar specific heat of a gas at constant volume is the amount of heat required to raise the temperature of 1 mole of the gas through* $1°$, *when its volume is kept constant throughout.*

So the heat required to raise the temperature of n mole of the gas through $t°$ at constant volume is given by

$$Q = nC_v t \qquad \ldots \qquad \ldots \qquad (22.8)$$

The unit of C_v in **C.G.S.** system is calorie/mol °C and in **S.I.** it is joule/mol K. The **F.P.S.** unit is B. Th. U./mol °F.

- **Definition :** *The specific heat of a gas at constant pressure (c_p) is the amount of heat required to raise the temperature of unit mass of the gas through 1°, when its pressure is kept constant throughout.*

So the heat required to raise the temperature of the mass m of a gas through $t°$ at constant pressure is given by

$$Q' = mc_p t \qquad \qquad (22.9)$$

The definition of c_p in different systems of units may be given in a similar way as c_v, the only change being that instead of constant volume we should substitute constant pressure. Also c_p is expressed in the same unit as c_v.

As before, **the molar specific heat or molar specific heat capacity of the gas at constant pressure** is given by

$$C_p = Mc_p$$

- **Definition :** *The molar specific heat of gas at constant pressure is the amount of heat required to raise the temperature of 1 mole of the gas through 1°, when its pressure is kept constant throughout.*

Thus the heat required to raise the temperature of n mole of a gas through $t°$ at constant pressure is given by

$$Q' = nC_p t \qquad \qquad (22.10)$$

The unit of C_p is the same as that of C_v.

- **An important discussion :** We have said earlier that the amount of heat absorbed by a gas depends upon the conditions of its volume and pressure. First law of thermodynamics gives $\delta Q = \delta U + \delta W$. For a given rise in temperature δT of the gas, δU remains the same. But $\delta W = P\delta V$ depends upon the manner of change in P and V as the gas absorbs the heat δQ. For example if the gas absorbs heat at constant volume, $\delta W = 0$ and at constant pressure, $\delta W = P \times$ change in volume. So δW actually depends on the process involved. Consequently the heat absorbed δQ also depends on the process even if the rise of temperature δT remains the same. Hence the specific heat of the gas is also dependent on the process and it is meaningless to define it unless the process is clearly specified. We shall see later that in isothermal processes, specific heat of a gas is infinity and in adiabatic processes it is zero. So the specific heat of a gas can have any value from zero to infinity depending upon the manner in which it is being heated. The absorption of heat at constant volume and at constant pressure were chosen because these two processes are most important. Correspondingly we defined two specific heats for a gas.

This discussion is also valid for solids and liquids. However, their expansion in volume due to heating is very small. Hence the external work done in a process is so small that it is neglected. So the heat energy supplied is utilised in producing only an increase of internal energy i.e., an increase of temperature.

● Relation between C_p and C_v :

To find the relation between the two specific heats, let us consider n moles of an ideal gas. If its temperature is raised at constant volume from T_1 to T_2, then the heat supplied is

$$Q = nC_v (T_2 - T_1)$$

where C_v is the molar specific heat at constant volume. Since there is no change in volume (i.e., $dV = 0$), no external work is done and the first law of thermodynamics gives

$$nC_v (T_2 - T_1) = U_2 - U_1 \qquad \qquad \ldots \qquad \ldots \qquad (22.11)$$

where U_1 and U_2 are the internal energies at the temperatures T_1 and T_2 respectively.

If, however, the same amount of the gas is heated at constant pressure P, so that the same rise in temperature takes place, the heat supplied is

$$Q' = nC_p(T_2 - T_1)$$

where C_p is the molar specific heat at constant pressure.

If the volume of the gas changes from V_1 to V_2, the external work done by the gas during expansion is $P(V_2 - V_1)$. Since the internal energy of the gas depends only on temperature, the changes in the internal energy must be the same as in the previous case, Hence,

$$nC_p(T_2 - T_1) = U_2 - U_1 + P(V_2 - V_1)$$

Substituting for $U_2 - U_1$ from equation (22.11), we get

$$nC_p(T_2 - T_1) = nC_v(T_2 - T_1) + P(V_2 - V_1)$$
$$\text{or,} \quad n(C_p - C_v) (T_2 - T_1) = P(V_2 - V_1) \qquad \ldots \qquad \qquad \ldots \qquad (22.12)$$

But we know that for n moles of an ideal gas, $PV = nRT$, where R is the gas constant for one mole of the gas. Hence, $PV_1 = nRT_1$ and $PV_2 = nRT_2$. Substituting these in equation (22.12), we get

$$C_p - C_v = R \qquad \qquad \ldots \qquad \qquad \ldots \qquad (22.13)$$

Thus, the difference in the molar specific heats of a gas at constant pressure and constant volume is equal to the universal gas constant.

❖ 22.15. Isothermal process.

☞ **Definition :** *When the change of pressure and volume of a gas takes place without any change in temperature, it is called an isothermal change or an isothermal process.*

In general, however, *any process that takes place without any change in temperature of the system $(\delta T = 0)$ is called an isothermal process.*

● **Explanation :** In order to explain how such a change can be brought about, let us consider a quantity of gas in a metal cylinder fitted with a frictionless movable metal piston. If the gas is now allowed to expand *very slowly,* some work is done by the gas, which will tend to produce a decrease in its internal energy. The temperature of the gas therefore, falls slightly. But the metal cylinder being a good conductor of heat, heat flows from the surroundings through the cylinder to the gas and exactly compensates the loss in internal energy. The temperature of the gas, therefore, remains constant and the gas is said to have undergone an isothermal expansion.

Similarly, let us suppose that the gas is compressed *very slowly.* This time, the work is done on the gas, and the internal energy and hence the temperature of the gas tends to increase. The heat, so produced, escapes through the cylinder to the surroundings and the temperature of the gas is thereby maintained constant. This reverse process is called the *isothermal compression* of the gas.

● **Conditions to be satisfied :** From the above discussions, it follows that to allow the exchange of heat between the gas and the surroundings, *isothermal changes must always be performed in a thin-walled, highly conducting vessel.* But, in practice, there is no such conductor known through which conduction of heat takes place as rapidly as required to maintain the temperature of the system constant. A fairly close approximation to isothermal change may be obtained by causing the movement of the piston at a very slow rate, thus allowing sufficient time for transfer of heat between the gas and the surrounding by conduction through the walls of the enclosure. Hence, *isothermal change is essentially a very slow process.*

Fig. 22.13 : Isothermals of a gas

● **Relation between P and V ; Isothermals :** It is obvious that *a gas undergoing isothermal change obeys Boyle's law,* PV = constant. A plot of P against V will be a rectangular hyperbola [Fig. 22·13]. Similar shaped curves will be obtained at different constant temperatures. These curves are called the isothermals of the gas, the lower ones corresponding to smaller values of temperature.

● **Application of the first law :** As the internal energy of a gas depends only upon its temperature,
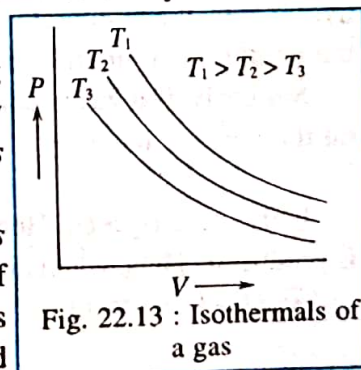
the internal energy of the gas remains unchanged during an isothermal process. From the first thermodynamics, since $U_2 = U_1$, $Q = W$. Hence *in an isothermal expansion, the heat supplied equ... external work done by the gas.*

As the change in temperature is zero, then from definition, the molar specific heat in an is... process is

$$C_{isothermal} = \frac{Q}{nt} = infinity$$

● **Work done :** The equation of state for n moles of an ideal gas is

$$PV = nRT$$

Here T is constant. If the initial and final volumes of the gas be V_1 and V_2 respectively, then th... done by the gas is

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

$$= nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$= 2 \cdot 303 \, nRT \log \left(\frac{V_2}{V_1} \right) \qquad \cdots$$

If the initial and final pressures of the gas be P_1 and P_2 respectively, then since $P_1V_1 = P_2$...

$$W = 2 \cdot 303 \, nRT \log \left(\frac{P_1}{P_2} \right) \qquad \cdots$$

Adiabatic process.

☞ **Definition** : *If the change of pressure and volume of a gas takes place under such a condition that no heat enters or leaves the gas, it is said to have undergone an adiabatic change or an adiabatic process.* The heat content of the gas therefore, remains constant during such a change.

In general, however, *any process that takes place under such a condition that no heat enters or leaves the system ($\delta Q = 0$) is called an adiabatic process.*

● **Application of the first law** : Now, if a gas in an enclosure is allowed to expand adiabatically then $Q = 0$. Evidently, the first law of thermodynamics gives,

$$U_2 - U_1 = -W \qquad \qquad \ldots \qquad \qquad \ldots \qquad (22.16)$$

∴ $U_2 < U_1$. Thus in doing external work, the internal energy content of the gas is lowered. From Mayer's hypotheses, the temperature of the gas also falls by a certain amount. It is a common experience that when the compressed air in a bicycle tire is released, the air on rushing out becomes colder.

Similarly, if a gas is compressed adiabatically, then $Q = 0$ and since W is negative when work is done on the gas, we have

$$U_2 - U_1 = W \qquad \qquad \ldots \qquad \qquad \ldots \qquad (22.17)$$

In this case $U_2 > U_1$. Hence the internal energy of the gas increases, and a consequent rise in temperature is produced. Thus, when air is pumped into a bycycle tire, the air becomes hotter which can be easily felt.

As $Q = 0$, so from definition, the molar specific heat in an adiabatic process is

$$C_{isothermal} = \frac{Q}{nt} = \text{zero}$$

● **Conditions to be satisfied** : A gas undergoing an adiabatic change must be kept in an enclosure surrounded by a thick layer of heat insulating material, so that no heat enters or leaves the enclosure.

The process should be performed quickly. The flow of heat is a slow process so that if the changes are brought about rapidly, no appreciable exchange of heat takes place. *Adiabatic change is, therefore, a quick one.*

● **Relation among P, V and T** : Unlike isothermal changes, Boyle's law does not hold for adiabatic changes. In this case, the pressure-volume changes of the gas obeys the law,

$$PV^{\gamma} = \text{constant} \qquad \ldots \qquad \ldots \qquad (22.18)$$

where, γ is the ratio of the specific heat of the gas at constant pressure to the specific heat at constant volume, i.e., $\gamma = \dfrac{C_p}{C_v}$. Since $C_p > C_v$, γ is always greater than unity. For monatomic gases like argon, helium etc., $\gamma = 5/3$; for diatomic gases and air, $\gamma = 7/5$.

The equation $PV = RT$, which is always true under all possible conditions, holds for adiabatic changes also. Eliminating either P or V from the equation (22.18) with the help of this expression, we get the following relations for an adiabatic change,

$$TV^{\gamma-1} = \text{constant} \qquad \ldots \qquad \ldots \qquad (22.19)$$

$$\dfrac{P^{\gamma-1}}{T^{\gamma}} = \text{constant} \qquad \ldots \qquad \ldots \qquad (22.20)$$

● **Adiabatics** : The plot of P vs V as shown in Fig. 22.14 is called an *adiabatic curve*. A complete family of adiabatics for a fixed mass of a gas is obtained for different initial values of the pressure and volume of the gas. The figure also illustrates the isothermals for the same mass of the gas. From the inspection of the curves, it follows that the adiabatics are steeper than the isothermals.

● **Slopes of isothermals and adiabatics** : The slope of the adiabatic through any point is γ times the slope of the isothermal through the same point. This can be proved simply by using calculus. The slope of the curve is given by $\dfrac{dP}{dV}$. For isothermals, $PV = \text{constant}$. Differentiation gives $PdV + VdP = 0$,
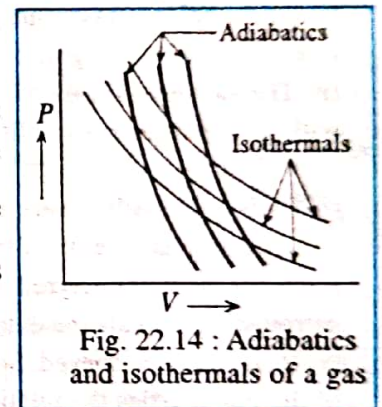

Fig. 22.14 : Adiabatics and isothermals of a gas

$$\dfrac{dP}{dV} = -\dfrac{P}{V}$$

For adiabatics, $PV^{\gamma} = \text{constant}$. Differentiating we get,

$$\gamma PV^{\gamma-1}dV + V^{\gamma}dP = 0, \qquad \text{or,} \quad \dfrac{dP}{dV} = -\gamma\dfrac{P}{V}$$

● **Work done** : Let us consider n moles of an ideal gas. If it undergoes an adiabatic expansion so that the initial and final values of its pressure, volume and temperature be P_1, V_1, T_1 and P_2, V_2, T_2 respectively, then

$$P_1V_1 = nRT_1 \text{ and } P_2V_2 = nRT_2$$

The change in its internal energy is

$$U_2 - U_1 = n\,C_v\,(T_2 - T_1)$$

So the work done by the gas is

$$W = -(U_2 - U_1) = n\,C_v\,(T_2 - T_1) \qquad \ldots \qquad \ldots \qquad (22.21)$$

$$= \dfrac{C_v}{R}(P_1V_1 - P_2V_2) = \dfrac{C_v}{C_p - C_v}(P_1V_1 - P_2V_2) = \dfrac{1}{\gamma-1}(P_1V_1 - P_2V_2) \qquad \ldots \qquad (22.22)$$

$$= \dfrac{nR}{\gamma-1}(T_1 - T_2) \qquad \ldots \qquad \ldots \qquad (22.23)$$

where $\gamma = C_p/C_v$

● Alternative deduction :

For an adiabatic change $PV^{\gamma} = $ constant $= K$ (say)

The work done by the gas is

$$W = \int_{V_1}^{V_2} P\,dV = K \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = \frac{K}{1-\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right)$$

But $K = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$. So

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

● Applications : The adiabatic expansion has many important applications, as cooling prod the sudden adiabatic expansion of compressed gases. An example for such cooling effe solidification of carbon dioxide gas, called dry ice. If a cylinder containing compressed carbo gas is suddenly opened and a piece of wet cloth is held before it, the issuing gas is deposited in of solid carbon dioxide. Oxygen was first liquefied by utilising this principle. In some refrigera required cooling is produced by the adiabatic expansion of compressed air.

Example 22.19 : *Find out the molar specific heats C_p and C_v for an ideal gas for which $\gamma = 1.67$.*

Solution : Since $\gamma = C_p/C_v = 1.67$, therefore, $C_p = 1.67\ C_v$. From equation (22.13)

$$C_p - C_v = 8.31; \quad \text{or, } (1.67 - 1)\ C_v = 8.31$$

$$\therefore\ C_v = 12.40 \text{ J/mol K} \quad \text{and } C_p = 20.71 \text{ J/mol K}$$

Example 22.20 : *The specific heat of oxygen at constant volume is 651 J/kg K. Find its specific heat at constant pressure. (Molar mass of O_2 = 32 kg/k mol. Universal gas constant = 8.4 J/mol K)*

Solution : Molar specific heat of oxygen at constant volume $C_v = 32 \times 10^{-3} \times 651$ J/mol K

From equation (22.13), $\quad C_p = C_v + R = (32 \times 10^{-3} \times 651 + 8.4)$ J/mol K

$$= 29.232 \text{ J/mol K}$$

Hence the specific heat at constant pressure,

$$c_p = C_p/M = 29.232/32 \times 10^{-3} \text{ J/kg K}$$

$$\equiv 913.5 \text{ J/kg K}$$

Example 22.21 : *At S.T.P. one litre of hydrogen weighs 8.96×10^{-5} kg and its specific heat at constant volume is 2.47×4200 J/kg K. Calculate its specific heat at constant pressure, Given, density of mercury at 0°C = 13.6×10^3 kg/m³.*

Solution : At S.T.P. 1 kg of hydrogen occupies the volume $V = \dfrac{1 \times 10^{-3}}{8.96 \times 10^{-5}} = 11.161$ m³. The pressure $P = 0.76 \times 9.8 \times 13.6 \times 10^3$ N/m² and temperature $T = 273$ K.

$$PV = rT \text{ for 1 kg mass}$$

$$\therefore\quad r = \frac{PV}{T} = \frac{(0.76 \times 9.8 \times 13.6 \times 10^3)(11.161)}{273} = 4141.13$$

$$c_p - c_v = r = 4141.13$$

$$\therefore\quad c_p = c_v + 4141.3 = 2.47 \times 4200 + 4141.13 = 14515.13 \text{ J/kg K}$$