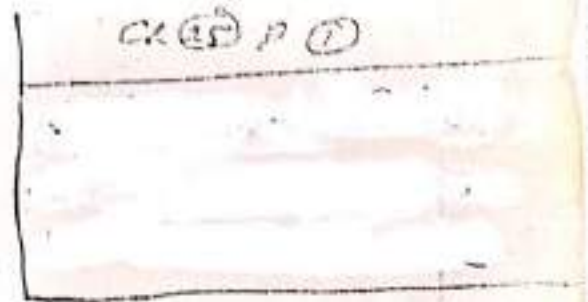


Heat And The First Law Of Thermodynamics

Heat

Let a hot object
(cup of coffee) and a
cold object (a glass of ice
water)



are placed in a room. Then, after some
time both of them are at the same
temperature (room temperature). It means that
the hot object has lost the heat and
the cold object has gained the heat.

Therefore heat is that energy which flows
from a body at higher temperature to a
body at lower temperature.

Therefore heat is a form of energy,
which may be defined as.

"Heat is energy that flows between a
system and its environment by virtue
of a temperature difference between them."

Units of Heat. The unit of heat is Calorie,
which may be defined as

It is the amount of heat energy required
to raise the temperature of 1 gm of ice
water from 14.5 °C to 15.5 °C.

The unit of energy is Joule in SI system.

Therefore

$$1 \text{ Cal} = 4.186 \text{ J}$$

British Thermal Unit
(Btu),

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$$1 \text{ Btu} = 1055 \text{ J}$$

Also $1 \text{ cal} = 4.186 \text{ J}$

$$1 \text{ Kilo cal} = 1 \text{ Cal} = 4186 \text{ J.}$$

Misconceptions About Heat . Heat is similar to work because both of them represent energy. When heat is given to a substance or positive work is done on the system, in both of those cases, the temperature of the system increase hence internal energy increases. Therefore heat can be converted into work and work into heat through the change in the internal energy of the system.

The Mechanical Equivalent of Heat

In 1850, James Joule performed an experiment to determine the value of mechanical equivalent of heat.

The apparatus shown in the fig. The falling weights turn paddles that stir the water in the container, thus raising its temperature.

In this experiment
the work W done
on the water

(mechanical energy)
is converted into heat Q , due to which
the temperature of the water increases.

Therefore the unit of energy or work, Joule,
can be related with the unit of heat,

Calorie, as a result of Joules' experiment.

$$1 \text{ cal} = 4.186 \text{ J}$$

Hence 4.186 J/cal is known as
mechanical equivalent of heat.

Q. Define and explain heat capacity and specific heat.

HEAT CAPACITY The heat capacity of a
substance may be defined as, "It is the
amount of heat energy required to raise the
temperature of a substance through one degree."

Let Q heat is given to a substance
so that its temperature increases by ΔT , then

$$Q = C \Delta T \quad \text{or} \quad C = \frac{Q}{\Delta T}$$

Hence C is the heat capacity of the substance,
which may also be defined as, "The ratio of
the amount of heat Q supplied to a body in
any process to its corresponding temperature change
 ΔT ."

SPECIFIC HEAT

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The specific heat of a substance may be defined as,

"It is the amount of heat energy required to raise the temperature of unit mass of the substance through one degree."

Let 'Q' heat is given to a substance of mass 'm', so that its temperature is increased by ΔT . Then we have

$$Q = mc \Delta T$$

$$c = \frac{Q}{m \Delta T}$$

As heat capacity is given by $C = \frac{Q}{\Delta T}$

Therefore

$$c = \frac{C}{m}$$

This is the relation between specific heat and heat capacity. These are the average values. Heat capacity and specific heat both change slightly with respect to temperature.

Let a substance of mass 'm' is heated so that its temperature increases from initial temperature T_i to final temperature T_f . As the specific heat change with respect to temperature, therefore the temperature range is divided into N small intervals, each of ΔT_n assuming that c_n is constant in each small interval. Then the total heat given to the substance for all intervals of temperature is

$$Q = \sum_{n=1}^N m c_n \Delta T_n$$

where $n=1, 2, 3, \dots, N$

In the differential limit, this becomes

$$Q = m \int_{T_i}^{T_f} c \, dT$$

Here 'm' is constant and 'c' depends on temperature.

If the temperature interval ($T_f - T_i$) is not too large, then the specific heat varies less than 1%, therefore it may be taken as constant.

Hence above equation may be written as

$$Q = mc(T_f - T_i) \text{ end}$$

HEAT OF TRANSFORMATION

It is defined as

The amount of heat required to change the phase or state (from solid to liquid or gas) of unit mass of the substance is called heat of transformation or latent heat 'L'.

The total heat required to change the state of the substance of mass 'm' at constant temperature is

$$Q = mL$$

Heat of Fusion. The amount of heat energy transferred required to change the state from solid to liquid or liquid to solid at freezing or melting point of unit mass of the substance is called heat of fusion.

Heat of vaporization

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For unit mass of the substance, the amount of heat transferred to change the state from liquid to gas or from gas to liquid at boiling point is called heat of vaporization.

Q. Discuss molar specific heats or molar heat capacities of solids, also explain Dulong-Petit law.

MOLAR HEAT CAPACITY. The amount of heat energy required to raise the temperature of one mole of the solid substance through one degree is known as molar heat capacity.

Let 'Q' heat is given to 'n' moles of the substance (solid) so that its temperature is increased by ΔT , then we have

$$Q = n C \Delta T$$

or

$$C = \frac{Q}{n \Delta T}$$

Here 'C' is the molar heat capacity of the solid. Heat capacity is given by

$$C' = \frac{Q}{\Delta T}$$

Therefore the relation between molar heat capacity and heat capacity is

$$C = \frac{C'}{n}$$

DULONG-PETIT LAW

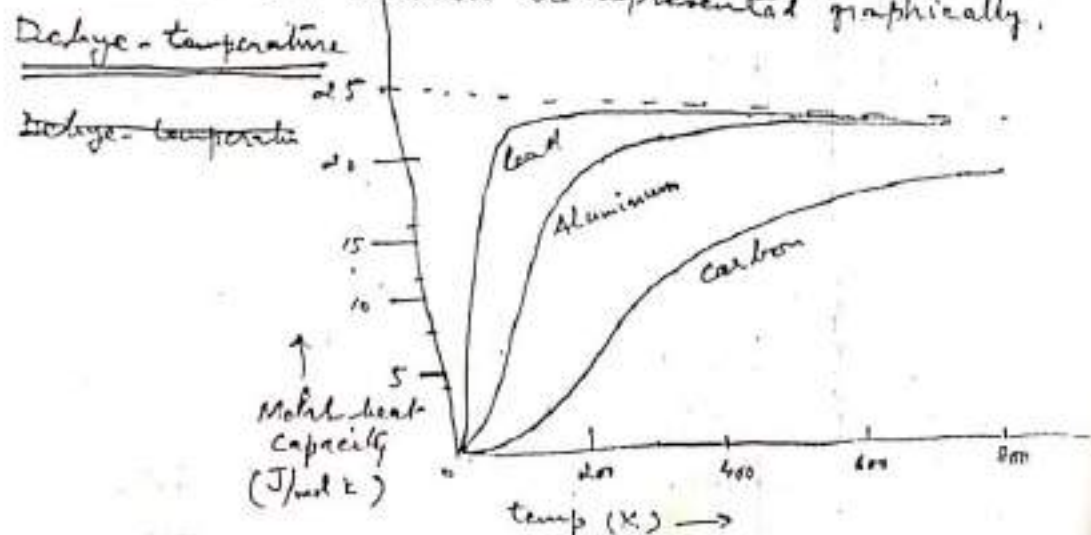
This law may be stated as:-

"The molar heat capacities of elemental solids, with few exceptions, have values close to $25 \text{ J/mol}\cdot\text{K}$ "

In solid the atoms have vibrational motion only, also one mole of any solid element contains the same number of atoms (Analogous Avogadro's number 6.02×10^{23})

Therefore the same amount of heat energy must be required to raise the temperature of one mole of the solid element through one degree.

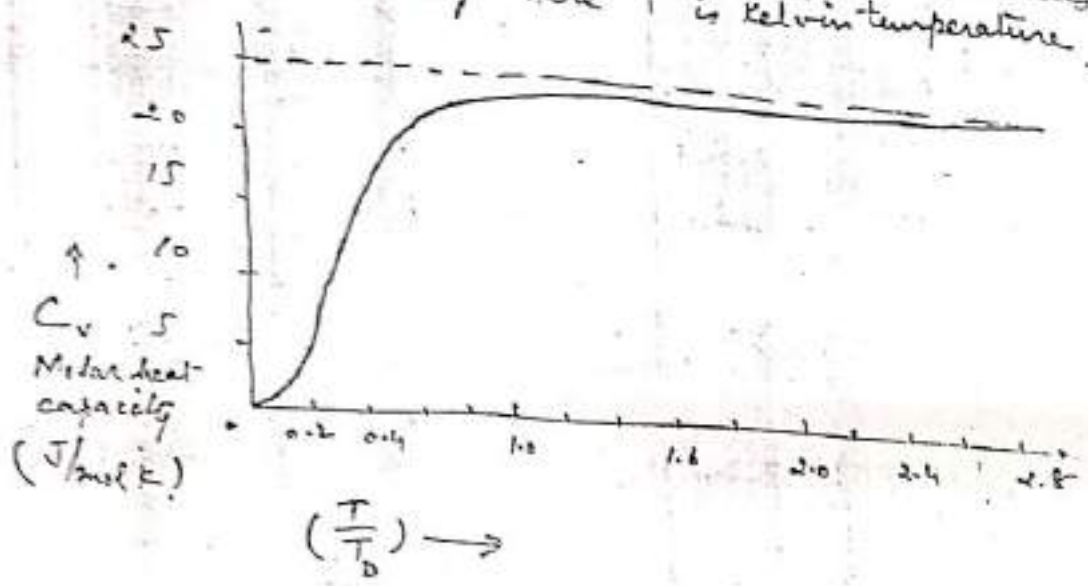
But the molar heat capacity of a solid element is also the function of temperature, its value increases with the increase in temperature, but the limiting value of molar heat capacity at high temperature is almost $25 \text{ J/mol}\cdot\text{K}$ for most of the solid elements, as shown by the graphs. The molar heat capacities of lead, aluminium and carbon are represented graphically.



Debye-Temperature

The Debye-temperature ' T_D ' is that at which the molar heat capacity of solid element approaches to 90% of its limiting value. (25 J/mol.K)

A graph is also drawn between $\frac{T}{T_D}$ and C_v , molar heat capacity of solid elements as shown in the fig. Here T is Kelvin temperature.



INTERNAL ENERGY AND MOLAR HEAT CAPACITY

The atoms of solid vibrate in three directions; also each direction has two degrees of freedom, one for potential energy and one for kinetic energy. Any value of potential energy and kinetic energy can be given to an oscillator. Therefore there are $(3 \times 2 = 6)$, six degrees of freedom. According to law of equipartition of energy, each atom has an average energy of $\frac{1}{2} kT$ per degree of freedom.

Therefore the internal energy per mole of the solid element is

$$E_{int} = 6 N_A (\frac{1}{2} kT) = 3RT \quad \because R = \frac{N_A k}{A}$$

Here 'k' is Boltzmann constant and 'R' is molar gas constant. When the temperature of the solid element increases from T_i to T_f then the increase in its internal energy is

$$\Delta E_{int} = 3R (T_f - T_i) = 3R \Delta T \quad \because \Delta T = T_f - T_i$$

~~So, $\Delta T = T_f - T_i$, then~~

the increase in the internal energy of one mole of solid element for one degree rise in temperature is

$$C_v = \frac{\Delta E_{int}}{\Delta T} = 3R = 3 \times 8.3145 = 24.9 \text{ J/mol K}$$

Here C_v is the molar heat capacity of the solid element, which is just equal to 25 J/mol K. This is the 'classical'

Dulong and Petit value of the molar heat capacity of the solid elements. For $T < T_D$ (Debye-temperature), however, the classical theory fails. In this region, the effects of quantum theory become important which was first developed and Einstein and later by Debye.

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Q. ^{Stat} Define molar heat

capacities of a gas and also derive a relation between them.

MOLAR HEAT CAPACITY AT CONSTANT VOLUME 'C_v'

The molar heat capacity at constant volume of a gas may be defined as, an

'C_v' It is the amount of heat energy required to raise the temperature of ^{one mole of} the gas through one degree at constant volume.

Consider ^{n moles of} a gas enclosed in a cylinder fitted with a piston. When the piston is fixed then the volume of the system remains constant, therefore the heat energy given to the system, (Q)_v, causes ~~a change~~ an increase in its internal energy only, or

$$(Q)_v = \Delta E_{int} \dots \text{I}$$

If 'ΔT' is the increase in the temperature of the system, then

$$(Q)_v = n C_v \Delta T \dots \text{II}$$

Comparing Eq I and Eq II we get:

$$\Delta E_{int} = n C_v \Delta T \dots \text{III}$$

MOLAR HEAT CAPACITY AT CONSTANT PRESSURE 'C_p'

The molar heat capacity at constant pressure of a gas may be defined as

'C_p'. It is the amount of heat energy

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Ch. E. C. U. U. U.

required to raise the temperature of one mole of the gas through one degree at constant pressure."

Let C_p is the molar heat capacity of the gas at constant pressure, if Q heat is given to the n moles of the gas then its temperature increases by ΔT at constant pressure, therefore

$$Q = n C_p \Delta T \quad \text{--- IV}$$

During the expansion of the gas at constant pressure, negative work is done on the system, therefore

$$W = - (P \Delta V) \checkmark$$

As

$$PV = nRT$$

n

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

Therefore

$$W = - P \Delta V = - nR \Delta T \quad \text{--- V}$$

The net change in the internal energy of the gas is equal to the heat energy given to the system plus the work done on the system, therefore we have

$$\Delta E_{int} = Q + W \quad \text{--- VI}$$

Putting the values from Eq III, Eq IV and Eq V we get,

$$nC_v \Delta T = nC_p \Delta T - nR \Delta T$$

$$C_v = C_p - R$$

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

This is the relation between molar heat capacities of a gas; here R is molar gas constant.

Monatomic Gas. In case of monatomic gas, the atom has translational motion only, which further has three degrees of freedom, therefore.

$$C_v = \frac{3}{2} R = 12.47 \text{ J/mol K}$$

$$\text{and } C_p = C_v + R = \frac{3}{2} R + R = \frac{5}{2} R = 20.8 \text{ J/mol K}$$

Diatomic Gas. In case of diatomic gas, a molecule has three degrees of freedom due to translational motion and two degrees of freedom due to rotational motion, therefore

$$C_v = \frac{5}{2} R = 20.8 \text{ J/mol K}$$

$$C_p = C_v + R = \frac{5}{2} R + R = \frac{7}{2} R = 29.1 \text{ J/mol K}$$

Polyatomic Gas. A molecule of polyatomic gas has eight degrees of freedom due to translational, rotational and vibrational motions, therefore

$$C_v = \frac{8}{2} R = 4R = 33.3 \text{ J/mol K}$$

$$C_p = C_v + R = 4R + R = 5R = 41.5 \text{ J/mol K}$$

Ratio between C_p and C_v

The ratio between C_p and C_v is a constant, which is given by

$$\gamma = \frac{C_p}{C_v}$$

$$\gamma = \frac{5}{3} = 1.67 \quad (\text{for monatomic gas})$$

$$\gamma = \frac{7}{5} = 1.4 \quad (\text{for diatomic gas})$$

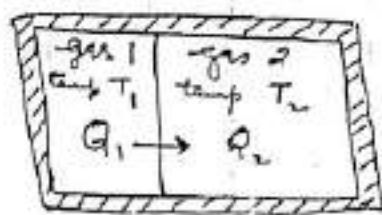
$$\gamma = \frac{4}{3} = 1.33 \quad (\text{for polyatomic gas})$$

Here ' γ ' is known as ratio of specific heats or specific heat ratio.

Q. State and explain first law of thermodynamics.

THE FIRST LAW OF THERMODYNAMICS

Consider two different gases enclosed in a container separated by a wall, the volumes of the gases are constant, while the container is isolated from the environment. The first gas is at higher temperature T_1 and the second gas is at lower temperature T_2 .



Here $T_1 > T_2$

After a sufficient time in thermal contact, the two gases attain the same intermediate temperature T .

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During the thermal contact,
Let Q_1 heat is transferred
lost by hotter gas (gas 1), therefore Q_1 is
negative for gas 1, while the heat gained
by cooler gas 2 is Q_2 , therefore Q_2 is
positive for gas 2.

But the heat lost is equal to the heat
gained in magnitude, hence

$$|Q_1| = |Q_2|$$

As gas 1, loses Q_1 heat therefore its internal
energy decreases, or the change in internal
energy is negative.

$$\begin{aligned} \text{or } -\Delta E_{\text{int.1}} &= -Q_1 \\ \text{or } \Delta E_{\text{int.1}} &= Q_1 \quad (\text{mathematically}) \end{aligned}$$

Similarly the gas 2, gains Q_2 heat, therefore
its internal energy increases, or the change in the
internal energy of is positive.

$$\Delta E_{\text{int.2}} = Q_2$$

It means that the signs of ΔE_{int} and Q are
always the same. In general, the above
equation may be applied to either gas, in the
absence of external work.

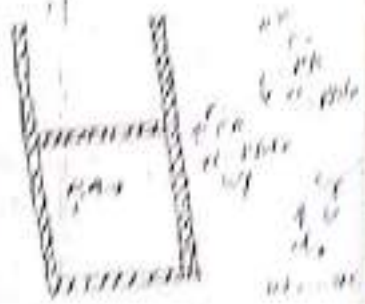
$$\Delta E_{\text{int}} = Q \quad \text{--- I}$$

Now consider a gas enclosed in a
cylinder fitted with a piston, the whole
system is isolated from the environment
(surroundings).

If the system is isolated, therefore no heat can enter or leave the system.

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If the pressure on the piston is decreased, then the gas will expand; also during this process negative work is done



on the system, due to which the internal energy of the gas increases, or the change in the internal energy is negative, or

$$\Delta E_{int} = -W \quad \checkmark \quad \text{B.U. 19/10}$$

$$\text{or } \Delta E_{int} = W \quad (\text{mathematically})$$

when the pressure on the piston is increased, then the gas will be compressed, during this process a positive work is done on the system due to which the internal energy of the system increases, or the change in the internal energy is positive, therefore:

$$\Delta E_{int} = W \quad \text{--- (i)}$$

Here the signs of ΔE_{int} and W are also the same.

It means that the change in the internal energy ΔE_{int} of a system depends on the exchange of heat energy Q , and the external work done W .

Let the system is taken from its initial

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state i to a final state f , along a variety of different paths. We know that the external work done ' W ' and the heat-energy ' Q ' depend on the path followed, but here we find that the term $(Q+W)$ has the same value, and it is independent of the path followed, depending only on the initial and final equilibrium states i and f of the gas. This quantity $(Q+W)$ must be equal to a function of thermodynamic coordinates, which is the change in internal energy of the gas ΔE_{int} .

ΔF is not const then W & Q does not depend on path

ΔF is const.

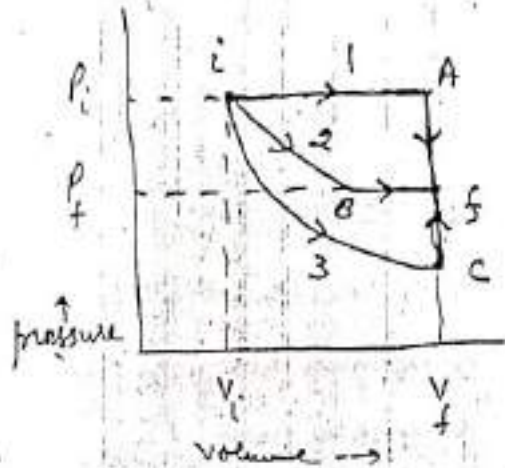
$$\Delta E_{int} = Q + W.$$

Therefore ' ΔE_{int} ', the change in the internal energy of the system does not depend on the path followed, but it depends only on the initial and final conditions of the state of the gas.

The internal energy of the system (gas) E_{int} is equal to the sum of translational, rotational and vibrational kinetic energies of its molecules. In the case of real gas it might ^{also} include the potential energies between the atoms in a molecule as well as the potential energies between different molecules.

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The internal energy of a system may also include the excitations of the electrons in the atoms, and also the binding energy of the atoms in the lattice. (in case of solid system).



Let a system is taken from its initial state i to final state f , along three different paths, as shown in the fig; but the change in the internal energy of the remains the same along three different paths, therefore which is equal to the difference

Therefore
$$\Delta E_{int} = E_{int,f} - E_{int,i}$$
 between the final and initial internal energies.

Here $E_{int,i}$ depends on the coordinates of state i and $E_{int,f}$ depends on the coordinates of state f only.

Therefore the first law of thermodynamics may be stated as, "In any thermodynamic process between equilibrium states i and f , the quantity $(Q+W)$ has the same value for any path between i and f . This quantity is equal to the change in the value of a state function called 'the internal energy'."

The mathematical form of first law of thermodynamics is

$$\Delta E_{int} = Q + W \quad \dots \text{I}$$

Here,

i, Q is positive when heat enters the system which causes an increase in the internal energy.

ii, Q is negative when heat leaves the system due to which the internal energy decreases.

iii, W (work done on the system) is negative during the expansion of the system (when volume increases) which causes a decrease in the internal energy.

iv, W (work done on the system) is positive during the compression of the system (when volume decreases due to increase in pressure) which causes an increase in the internal energy.

If the system undergoes only an infinitesimal change in state (very small), then the differential form of first law of thermodynamics is

$$dE_{int} = dQ + dW \quad \dots \text{II}$$

Applications of the first law of thermodynamics

Q. Define and explain adiabatic process. Also derive a relation for it.

ADIABATIC PROCESS. The process during which no heat enters or leaves the system, is called adiabatic process.

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In adiabatic process, the system must be well insulated so that no heat can enter or leave the system, therefore $Q = 0$

Hence the first law of thermodynamics for adiabatic process is

$$\Delta E_{int} = W$$

Adiabatic Expansion. If the pressure is decreased and the gas is allowed to expand adiabatically, then negative work is done on the system due to which its internal energy decreases, and temperature decreases. Hence adiabatic expansion causes cooling effect, for which we have

$$-\Delta E_{int} = -W$$

Adiabatic Compression. If the pressure is increased and the gas is compressed adiabatically, then positive work is done on the system, which causes an increase in the internal energy and also an increase in its temperature. Therefore adiabatic compression causes heating effect, for which we have

$$\Delta E_{int} = W$$

RELATION FOR ADIABATIC PROCESS

Let C_v and C_p are the molar heat capacity at constant volume and constant pressure, respectively, of a gas. If n moles of the gas is heated at constant volume so that its temperature is increased by dT .

then the change in internal energy is

$$dE_{int} = n C_v dT \quad \dots \text{I}$$

During a very small expansion at constant pressure P , the work done on the system is,

$$PdV = -dW \quad \dots \text{II}$$

But $dW = dE_{int} = n C_v dT$ by first law at dT, dW = 0

Putting the value of dW in Eq II, we get.

$$PdV = -n C_v dT \quad \dots \text{III}$$

The equation of state of an ideal gas is

$$PV = nRT$$

Differentiating, we get.

$$d(PV) = d(nRT)$$

$$\text{or } PdV + VdP = nRdT$$

$$\text{or } VdP = nRdT - PdV$$

Putting the value of PdV from Eq III, we get.

$$VdP = nRdT - (-n C_v dT)$$

$$= nRdT + n C_v dT$$

$$= n dT (R + C_v)$$

$$= n C_p dT \quad \dots \text{IV}$$

$$\left[\begin{array}{l} \therefore \\ C_p = C_v + R \end{array} \right]$$

Dividing Eq IV by Eq III, we get.

$$\frac{VdP}{PdV} = \frac{n C_p dT}{-n C_v dT}$$

$$\text{or } \frac{VdP}{PdV} = - \frac{C_p}{C_v} = -\gamma$$

$$\text{or } \int \frac{dP}{P} = -\gamma \int \frac{dV}{V}$$

$$\ln P = -\gamma \ln V + \ln A$$

$$\ln P + \gamma \ln V = \ln A$$

$$\ln PV^\gamma = \ln A$$

$$PV^\gamma = A = \text{const}$$

$$PV^\gamma = \text{const.}$$

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

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

81

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Ch. 2, C.C. L. L.H.R.

As $nR = \text{constant}$.

Therefore $TV^{\gamma-1} = \text{constant}$. or $\left[\frac{T}{T_i} \left(\frac{V}{V_i}\right)^{\gamma-1} = \frac{T_i}{T_i} \left(\frac{V_i}{V_i}\right)^{\gamma-1} \right]$

This is also the equation for adiabatic process in terms of temperature and volume.

Again we have

$$PV^\gamma = \text{constant}$$

or $(P)^{\frac{1}{\gamma}} V = (\text{constant})^{\frac{1}{\gamma}} = \text{constant}$.

From equation of state, we have

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

Therefore

$$(P)^{\frac{1}{\gamma}} \frac{nRT}{P} = \text{constant}$$

or $(P)^{\frac{1}{\gamma}-1} T = \frac{\text{constant}}{nR}$

As nR is also constant, therefore.

$$(P)^{\frac{1-\gamma}{\gamma}} T = \text{constant} \quad \text{or} \quad \left[\left(\frac{P}{P_i}\right)^{\frac{1-\gamma}{\gamma}} \frac{T}{T_i} = \left(\frac{P_i}{P_i}\right)^{\frac{1-\gamma}{\gamma}} \frac{T_i}{T_i} \right]$$

This is also the equation for adiabatic process in terms of pressure and temperature.

The work done during adiabatic process is

$$W = \frac{1}{\gamma-1} (P_f V_f - P_i V_i) \quad \text{End.}$$

Q. Define and explain isothermal process.

ISOTHERMAL PROCESS. It is the process during which the temperature of the system remains constant.

If the temperature of the system is kept constant, then its internal energy also remains constant; therefore the change in internal energy must be equal to zero. or

$$\Delta E_{int} = 0$$

In isothermal process the first law of thermodynamics may be written as

$$Q + W = 0 \quad \text{--- I}$$

As the temperature remains constant, therefore Boyle's law is applied to this process.

$$P_f V_f = P_i V_i \quad \text{or} \quad PV = \text{constant}$$

Isothermal Expansion. Eq I may be written as

$Q = -W$ It means during isothermal expansion (when pressure is decreased slowly), negative work is done on the system and to keep the temperature constant, 'Q' heat must be given to the system. This is a slow process.

Isothermal Compression. Eq I may also be written as $-Q = W$

It means that during isothermal compression when the pressure is increased slowly, positive work is done on the system. To keep the temperature constant, 'Q' heat must be rejected by the system slowly.

Q. Define and discuss constant-volume process.