KINETIC THEORY & FIRST LAW OF THERMODYNAMICS

GAS LAWS AND KINETIC THEORY OF GASES :

Concept of ideal gas :

An ideal gas should

i) All molecules are identical and spherical.
Therefore perfect ideal gas is essentially monatomic and pure. Mixture of gases will have different molecules.
ii) Have exactly equal coefficients of pressure and volume.
iii) Have the molecules of infinitesimally small size.
iv) Have no force of interaction between molecules.
Therefore there exist no potential energy due interaction between molecules.
v) All collisions between the gas molecules are perfectly elastic.
vi) There is no effect of gravity.
Therefore density of gas can be assumed constant with height.
vii) Strictly obey the Boyle's law, the Charle's law and the law of pressure in all conditions of pressure and temperature.
Therefore the perfect ideal can never be liquefied.

Gas Laws :

Boyle's law (Isothermal law) :
Volume of a given mass of an ideal gas is inversely proportional to its pressure at constant absolute temperature.

$$V \propto 1/P$$

$\Rightarrow$ PV = constant

$\Rightarrow$ $P_1V_1 = P_2V_2$

Charle's Law (Isobaric law) :
Volume of a given mass of an ideal gas is directly proportional to its absolute temperature at constant pressure.

$$V \propto T$$

$\Rightarrow$ V/T = constant

$\Rightarrow$ $V_1/T_1 = V_2/T_2$

$$V_t = V_0\left(1+\frac{t}{273}\right)$$

Pressure Law (Isochoric law) :
Pressure of a given mass of an ideal gas is directly proportional to its absolute temperature at constant volume.

$$P \propto T$$

$\Rightarrow$ P/T = constant

$\Rightarrow$ $P_1/T_1 = P_2/T_2$

$$P_t = P_0\left(1+\frac{t}{273}\right)$$

Ideal Gas Equation :

From the gas law it is clear that pressure, volume and temperature of a given mass of an ideal gas are interrelated. This relation is called Ideal gas equation.

$$PV = nRT$$

$$\Rightarrow \quad \frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \text{ and}$$

$$\frac{PV}{T} = \frac{m}{M}R$$

$$\Rightarrow \quad \frac{m}{V}=\frac{PM}{RT}$$

$$\Rightarrow \quad \rho=\frac{PM}{RT}$$

n is number of moles of the gas, m total mass of gas molecules and R is universal gas constant. The ideal gas equation is always true, what ever may be the process.

Number of molecules per unit volume (the number density)

$$\frac{nN}{V}=\frac{PN}{RT}=\frac{P}{kT}$$

Avogadro's hypothesis :

One mole of each substance contains same number of particles. It is

$N = 6.02 \times 10^{23}$ particles per gram-mole

Dalton's law of partial pressure :

The pressure exerted by a mixture of mutually inert gases is the sum of the pressures exerted by the individual gases (their partial pressures) occupying the same volume alone.

The pressure that a gas would exert if it occupied the container alone and if it behaved perfectly is called the partial pressure of the gas.

$$P = \sum p_i \text{ where}$$

$$p_i = \frac{n_iRT}{V}$$

Grahm's law of diffusion :

Rate of diffusion of a gas is inversely proportional to square root of the density of the gas

$$r \propto 1/\sqrt{\rho}$$

$$\Rightarrow \quad \frac{r_1}{r_2}=\sqrt{\frac{\rho_2}{\rho_1}}=\sqrt{\frac{M_2}{M_1}}$$

Degree of freedom of gas molecules :

The number of velocity components needed to describe the motion of a molecule completely in three dimensional space is called the number of degree of freedom. In other words it is the total no of coordinates required to fix the position and orientation of a molecule in three dimensional space.

To understand it easily we may define the degree of freedom as the number of possible kinetic energies associated with the molecule due its translation along three axes, due to its rotation about three axes and due to its vibration in various modes.

In perfect ideal gas and gases behaving like ideal gas, there exists no force of interaction between the molecules. Therefore intermolecular vibration is not possible for these gases. At normal temperatures inter-atomic vibrations in polyatomic gases do not associate sufficient kinetic energy with the gas molecules. Therefore no degree of freedom is attributed to vibration of atoms in a polyatomic gas molecule at normal temperatures.

In all molecules, translation along three axes is always possible hence three kinetic energies due to the translation of molecule along three axes exist, but for a monatomic gas molecule (or molecules of perfect ideal gas) the moment of inertia about all the three axes is almost zero as they are point masses. Hence even if they rotate the kinetic energy associated with the molecule due to its rotation about any axis remains practically zero. Therefore monatomic gas molecules have only three degrees of freedom, all attributed to its translation along three axes.

In diatomic molecule of gases like ideal gas there exist a line passing through two atoms of the molecule about which the moment of inertia of the molecule remain zero as both the atoms lie on the axis of rotation. About rest of the two axes the moment of inertia of the gas molecule is finite. Hence the degree of freedom of the diatomic gas molecule is five. Three attributed to translation of the molecule along three axes and two for the rotation of molecule about the two axes perpendicular to line joining the atoms. From the same logic the linear polyatomic gas molecules have five degrees of freedom.

Degree of freedom of a nonlinear polyatomic gas molecule is six. Three for translation along three axes and rest of the three for rotation about three axes as its moment of inertia remains nonzero about all the three axes.

The number of degree of freedom is related with adiabatic constant γ as

$$\gamma = 1 + {}^{2}\!/_{f}$$

$\Rightarrow \quad f = \dfrac{2}{(\gamma - 1)}$ (This relation is established with definition of adiabatic process later in this chapter)

Law of equipartition of energy :

The law of equipartition of energy states that the average kinetic energy per degree of freedom for a gas molecule is ${}^{1}\!/_{2}kT$, where k is Boltzmann's constant. Thus for a gas with f degrees of freedom, on an average the total kinetic energy associated with the gas molecules is

$$U_k = \left({}^{f}\!/_{2}\right) kT \times nN \text{ or}$$

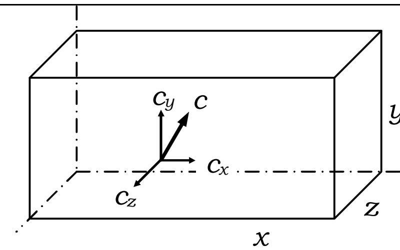
$$U = {}^{f}\!/_{2}\, nRT = \frac{nRT}{(\gamma - 1)}$$

Pressure formula for Ideal Gas :

From law of equipartition of energy

$${}^{1}\!/_{2}\, m\overline{c_x^{\,2}} = {}^{1}\!/_{2}\, m\overline{c_y^{\,2}} = {}^{1}\!/_{2}\, m\overline{c_z^{\,2}}$$

$$\Rightarrow \quad \overline{c_x^{\,2}} = \overline{c_y^{\,2}} = \overline{c_z^{\,2}}$$



but

$$c^2 = c_x^2 + c_y^2 + c_z^2 \text{, therefore}$$

$$\overline{c^2} = \overline{c_x^2} + \overline{c_y^2} + \overline{c_z^2}$$

$$\Rightarrow \quad \frac{\overline{c^2}}{3} = \overline{c_x^2}$$

Let us consider a molecule colliding with wall *bc*,
Change of momentum of molecule is

$$(-mc_x) - (mc_x) = -2mc_x$$

therefore change of momentum of wall due to collision of one molecule

$$+2mc_x$$

this molecule will collide with the wall after traveling a distance $2a$ with velocity v_x, again in a time interval

$$\frac{2a}{c_x}$$

hence the molecule will collide with the same wall with a frequency

$$\frac{c_x}{2a}$$

therefore change of momentum of wall due to one molecule in one second is

$$(2mc_x)\frac{c_x}{2a} = \frac{mc_x^2}{a}$$

If the total number of molecules inside the container is η then the total change in momentum of wall *bc* due to collision with all molecules in one second, i.e. force experienced by wall is

$$F = \frac{m}{a}\sum c_x^2$$

$$\Rightarrow \quad F = \frac{\eta m}{a}\frac{\sum c_x^2}{\eta}$$

$$\Rightarrow \quad F = \frac{\eta m}{a}\overline{c_x^2}$$

Therefore pressure applied by gas on the wall *bc* is

$$P = \frac{F}{bc} = \frac{\eta m}{abc}\overline{c_x^2} = \tfrac{1}{3}\rho\,\overline{c^2}$$

where ρ is density of gas and $\overline{c^2}$ is mean square velocity of gas molecules.
From this we can get

$$c_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{as} \quad \rho = \frac{PM}{RT}$$

Here

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} \text{, and}$$

$$c_{mp} = \sqrt{\frac{2RT}{M}}$$

Barometric Formula :
Let there be a tall vertical cylinder (free fall acceleration g and temperature T of gas remains constant) of gas with are of cross section S. Now consider a disk of thickness dh at a height h, thus

$S\,dP = -S\rho g\,dh$ (–ve sign is because as h increases P decreases.)

$\Rightarrow \quad dP = \frac{PM}{RT} g dh$ as $\rho = \frac{PM}{RT}$,

$$\Rightarrow \quad \int_{P_0}^{P} \frac{dP}{P} = \frac{Mg}{RT}\int_0^h dh$$

$$\Rightarrow \quad P = P_0\, e^{-\frac{Mgh}{RT}}$$

Kinetic interpretation of Temperature :
The mean kinetic energy of n mole of ideal gas

$$\langle E_k \rangle = \frac{1}{2}(m)\bar{c}^2$$

$$\Rightarrow \quad \langle E_k \rangle = \frac{1}{2} nM \times \frac{3RT}{M} = \frac{3}{2} nRT.$$

Thus the average kinetic energy of gas molecules is directly proportional to its absolute temperature.

Internal Energy of the Ideal Gas :
Internal energy of the gas is the sum of kinetic and potential energy of all its molecules. As ideal gas molecules have no interaction force amongst them, the potential energy of molecules is zero. Then

$$U = E_k = \tfrac{3}{2} nRT.$$

For any other gas behaving ideally

$$U = \tfrac{f}{2} nRT$$

where f is degree of freedom of gas molecules.
It shows that the Internal energy of ideal gas is a pure function of its absolute temperature and does not depend on pressure or volume of gas.

Vapour and gas :
A gaseous state at a temperature above its critical temperature is called a gas where it can not be liquefied by the application of pressure only, until it is cooled down below its critical temperature.

THERMODYNAMICS :

Thermodynamic variables :
The pressure (P), volume (V) and the absolute temperature (T) of the given mass of gas are called its thermodynamic variables.

Thermodynamic system :
A system in which the thermodynamic variables of a given mass of the gas can be easily changed is called a thermodynamic system. Since all the three thermodynamic variables of a given mass of gas are always related by the relation

$PV = nRT$ (The ideal gas equation)

therefore it is not possible to change only one variable keeping rest of the two constant for a given mass of gas.

A thermally conducting cylinder fitted with an easily movable piston is a simple thermodynamic system. By heating it temperature of the gas can be changed, by moving the piston the gas volume can be changed and by applying force on the piston pressure of the gas inside the cylinder can be changed.

Thermodynamic state of the gas :

A set of all the three thermodynamic variables for a given mass of gas defines its particular thermodynamic state. If one or more than one variables change the thermodynamic state of the gas has changed.

State diagram :

When thermodynamic state of the gas is presented in plane consisting of any two thermodynamic variables (popularly P-V) of the gas, the representation is called state diagram. A point in the state diagram, which tells the value of two state variables, represents a particular thermodynamic state of the gas and the third variable can be calculated using ideal gas equation.

Thermodynamic process :

When thermodynamic state of the gas is changed from one particular state to another, the path followed by gas on state diagram from initial state to final state is called thermodynamic process. The mathematical relation between state variables (popularly between P and V) representing this curve on the state diagram is called process equation. Infinite number of curves can join the initial thermodynamic state and final thermodynamic state therefore between two states infinite processes are possible.

Energies involved in the thermodynamic system :

Change in internal energy (ΔU) :

Internal energy of the thermodynamic system defined earlier is

$$U = \left(f/2\right)nRT$$

therefore change in internal energy is always

$$\Delta U = \left(f/2\right)nR\left(\Delta T\right)$$

$$\Rightarrow \qquad \Delta U = \frac{f}{2}\left(P_2V_2 - P_1V_1\right)$$

It is a pure function of temperature therefore it is independent of thermodynamic process. It only depends on the initial and final thermodynamic state of the gas. ΔU is considered positive when there is increment in the internal energy (hence increment in absolute temperature of the gas) otherwise negative.

Work done by thermodynamic system :

When gas expands it does work against external pressure which is considered positive. For ideal gas we assume that the pressure of gas at any instant is same throughout inside the gas and the piston is in equilibrium with the external pressure therefore if gas pressure is P then work done by gas for small increment in the volume of thermodynamic system is

$$dw = PdV$$

$$w = \int_{V_1}^{V_2} PdV$$

In P-V diagram, area under the curve gives the work done by gas against external pressure. Therefore work done by a gas in a thermodynamic system is path dependent. Depending on the process P will be a different function of V thus the value of the above integral will be different in the deferent process.

Heat exchange with the thermodynamic system :
Heat received by a thermodynamic system is considered is positive where as heat rejected by it is considered negative.

First law of thermodynamics:
The heat energy given to a thermodynamic system is partly consumed by the system in doing work against external pressure and rest increases the internal energy of the system.

$dQ = dU + dw$* or

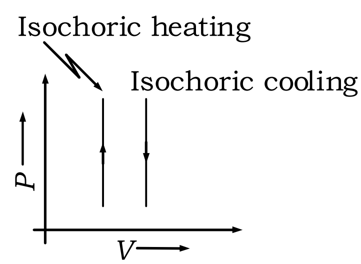
$Q = \Delta U + W$

$$\Rightarrow \quad Q = \frac{f}{2} nR(\Delta T) + \int_{V_1}^{V_2} PdV$$

Thermodynamic Processes :

a) Isochoric Process :
Rule : volume of the gas remains constant
Process equation :

V = Constant



$$\Delta U = \frac{f}{2}(P_2V - P_1V) = \frac{f}{2}V(\Delta P)$$

$w = \int PdV = 0$ as $dV = 0$, since V is constant

Thus $Q = \Delta U$

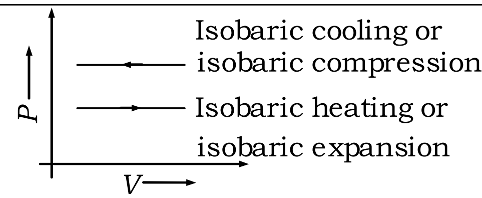
$$\Rightarrow \quad Q = \frac{f}{2}V(\Delta P) = \frac{f}{2}nR(\Delta T)$$

Two isochoric lines never intersect each other, as they are parallel straight lines perpendicular to volume axis.

b) Isobaric Process :
Rule : pressure of the gas remains constant
Process equation :

P = Constant

*w and Q are not actual functions of the state of a system, that is, they do not depend on the values of the system's coordinates. Hence, dw and dQ are not exact differentials as the term is used in mathematics. All they mean here is a very small quantity. More advanced books write them as δQ and δw to indicate their inexact nature. However, dU is an exact differential, for U is an exact function of the system's coordinates.



$$\Delta U = \frac{f}{2}(PV_2 - PV_1) = \frac{f}{2}P(\Delta V)$$

$$w = \int_{V_1}^{V_2} PdV$$

$\Rightarrow$ $$w = P\int_{V_1}^{V_2} dV$$

$\Rightarrow$ $$w = P(\Delta V)$$

Thus $Q = \Delta U + w$

$\Rightarrow$ $$Q = \frac{f}{2}P(\Delta V) + P(\Delta V)$$

$\Rightarrow$ $$Q = \left(\frac{f}{2}+1\right)P(\Delta V) = \left(\frac{f}{2}+1\right)nR(\Delta T)$$

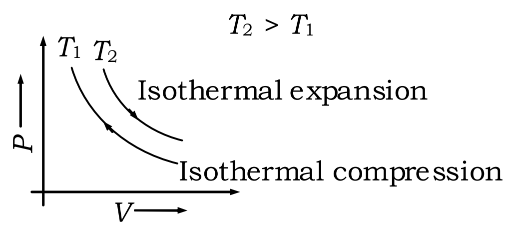
Two isobaric lines never intersect each other, as they are parallel straight lines perpendicular to presser axis.

c) <u>Isothermal Process</u> :
Rule : temperature of the gas remains constant
Process equation :

T = Constant

$\Rightarrow$ PV = Constant

$\Rightarrow$ $P_1V_1 = P_2V_2$



$$\Delta U = 0$$

$$w = \int_{V_1}^{V_2} PdV$$

$\Rightarrow$ $$w = \int_{V_1}^{V_2} \frac{nRT}{V}dV = nRT\int_{V_1}^{V_2}\frac{dV}{V}$$

$\Rightarrow$ $$w = nRT\ln\left(V_2/V_1\right) = nRT\ln\left(P_1/P_2\right)$$

Thus $Q = w$

$\Rightarrow$ $$Q = nRT\ln\left(V_2/V_1\right) = nRT\ln\left(P_1/P_2\right)$$

Two isothermal curves never intersect each other. Larger the distance of the curve from origin greater will be the temperature on it.

d) Adiabatic Process :
Rule : heat exchange with the thermodynamic system is restricted
Process equation :

$dQ = 0$ Therefore

$dU = -\,dw$

$\Rightarrow \quad \frac{f}{2} nRdT = -P\,dV$

$\Rightarrow \quad P\,dV + V\,dP = -\frac{2}{f} P\,dV$

$\Rightarrow \quad V\,dP + \left(1 + \frac{2}{f}\right) P\,dV = 0$

$\Rightarrow \quad \left(1 + \frac{2}{f}\right) \frac{dV}{V} + \frac{dP}{P} = 0$

$\Rightarrow \quad \left(1 + \frac{2}{f}\right) \ln V + \ln P = \text{constant}$

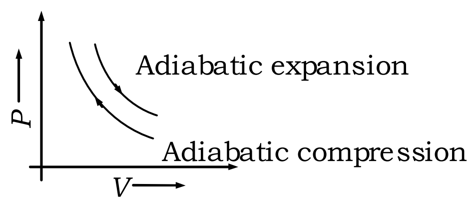
$\Rightarrow \quad P V^{\left(1+\frac{2}{f}\right)} = \text{constant}$

Since f is a constant thus $\left(1 + \frac{2}{f}\right)$ is also a constant known as adiabatic exponent γ.

Therefore process equation is

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

$\Rightarrow \quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$



Volume temperature relationship in adiabatic process :

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

$\Rightarrow \quad (PV)V^{(\gamma-1)} = \text{constant}$

$\Rightarrow \quad (nRT)V^{(\gamma-1)} = \text{constant}$

$\Rightarrow \quad TV^{(\gamma-1)} = \text{constant}$

Pressure temperature relationship in adiabatic process :

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

$\Rightarrow \quad \frac{P^{\gamma} V^{\gamma}}{P^{(\gamma-1)}} = \text{constant}$

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

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

$\Delta U = \frac{f}{2}\left(P_2 V_2 - P_1 V_1\right) = \frac{f}{2} nR(\Delta T)$

$$\Rightarrow \quad \Delta U = \frac{(P_2V_2 - P_1V_1)}{\gamma - 1} = \frac{nR(\Delta T)}{\gamma - 1}$$

$$w = \int_{V_1}^{V_2} PdV$$

Now from process equation

$$PV^{\gamma} = k = P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$\Rightarrow \quad w = \int_{V_1}^{V_2} \frac{k}{V^{\gamma}} dV = k\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$\Rightarrow \quad w = k\left(\frac{V^{1-\gamma}}{1-\gamma}\right)_{V_1}^{V_2}$$

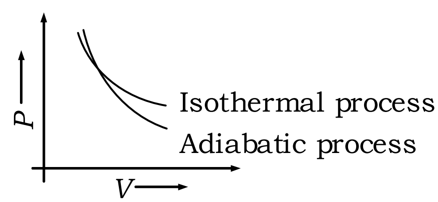
$$\Rightarrow \quad w = \frac{1}{1-\gamma}\left(\frac{kV_2}{V_2^{\gamma}} - \frac{kV_1}{V_1^{\gamma}}\right)$$

$$\Rightarrow \quad w = \left(\frac{P_2V_2 - P_1V_1}{1-\gamma}\right)$$

Thus $Q = \Delta U + w = 0$

Two adiabatic curves also never intersect each other.

For isothermal process.



$$PV = \text{constant}$$

$$\Rightarrow \quad \left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{P}{V} \qquad \text{... (1)}$$

For adiabatic process

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

$$\Rightarrow \quad \left(\frac{dP}{dV}\right)_{\text{adia}} = -\gamma\frac{P}{V}\text{, therefore} \qquad \text{... (2)}$$

$$\left(\frac{dP}{dV}\right)_{\text{adia}} = \gamma\left(\frac{dP}{dV}\right)_{\text{iso}}$$

Thus at same point in the P-V diagram the adiabatic curve has slope γ times greater then the slope of the isotherm.

e) Polytropic process :

Think of a process PV^{η} = constant. As η increases the slope of the curve on P-V diagram increases. When we consider the expansion of gas in a processes of the form PV^{η} = constant. For η = 1 the process is isothermal and the temperature remains constant. For $\eta < 1$, gas heats up ($P_2V_2 > P_1V_1$) during expansion and for $\eta > 1$ gas cools down ($P_2V_2 < P_1V_1$) during expansion.

For $\eta = 0$ the process is isobaric

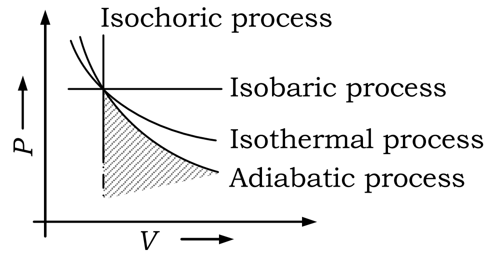
For $\eta = 1$ the process is isothermal

For $\eta = \gamma$ the process is adiabatic

For $\eta \to \infty$ the process is isochoric

When $\eta > \gamma$ and finite the process is said to be polytropic.
Process equation :

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



$$\Delta U = \frac{f}{2}\left(P_2V_2 - P_1V_1\right) = \frac{f}{2}nR\left(\Delta T\right)$$

$$\Rightarrow \quad \Delta U = \frac{\left(P_2V_2 - P_1V_1\right)}{\gamma - 1} = \frac{nR\left(\Delta T\right)}{\gamma - 1}$$

$$w = \int_{V_1}^{V_2} PdV$$

Similar to adiabatic process we can calculate

$$\Rightarrow \quad w = \frac{P_2V_2 - P_1V_1}{1-\eta}$$

$$Q = \left(P_2V_2 - P_1V_1\right)\left(\frac{1}{\gamma-1} - \frac{1}{\eta-1}\right)$$

$$\Rightarrow \quad Q = nR\left(\Delta T\right)\left(\frac{1}{\gamma-1} - \frac{1}{\eta-1}\right)$$

As $\eta > \gamma$ and $\Delta T < 0$, Q is negative for polytropic expansion.

<u>Specific Heat Of An Ideal Gas</u> :

<u>Mass specific heat</u> :
Amount of heat absorbed by unit mass of gas to increase its temperature through 1 K is defined as its mass specific heat.

$$c = \frac{dQ}{mdT}$$

<u>Molar heat capacity</u> :
When the amount of gas is taken in gm. moles the specific heat calculated is called molar heat capacity or molar specific heat. It is the amount of heat absorbed by 1 mole of gas to increase its temperature through 1 K.

$$C = \frac{dQ}{n\,dT}$$

$$\Rightarrow \quad C = \frac{dQ}{\left(m/M\right)dT} = M\frac{dQ}{mdT}$$

$$\Rightarrow \quad C = mc$$

Since for gas the amount of heat absorbed to increase its temperature of unit amount of gas by 1 K is different for different processes thus its specific heat is also different for different processes.

$$C\Big|_{\text{process}} = \frac{dQ}{ndT}\Big|_{\text{process}}$$

Since internal energy of the gas is independent of the process, where as work done by gas is process dependent therefore

$$\Rightarrow \quad C\Big|_{\text{process}} = \frac{dU}{ndT} + \frac{dw}{ndT}\Big|_{\text{process}}$$

here $U = \frac{f}{2}nRT = \frac{nRT}{\gamma - 1}$

$$\Rightarrow \quad dU = \frac{nRdT}{\gamma - 1}$$

$$\Rightarrow \quad \frac{dU}{ndT} = \frac{R}{\gamma - 1}, \text{ hence}$$

$$C\Big|_{\text{process}} = \frac{R}{\gamma - 1} + \frac{PdV}{ndT}\Big|_{\text{process}}$$

If it is isochoric process then

$$dw = PdV = 0$$

$$\Rightarrow \quad C_V = \frac{dQ}{n\,dT}\Big|_V = \frac{dU}{n\,dT} = \frac{R}{\gamma - 1}, \text{ thus}$$

$dU = nC_V dT$ (Which is always true)

From this we can also write

$$C\Big|_{\text{process}} = C_V + \frac{PdV}{ndT}\Big|_{\text{process}}$$

If it is isobaric process then form ideal gas equation

$$PV = nRT$$

$$\Rightarrow \quad PdV = nRdT$$

$$\Rightarrow \quad \frac{dw}{ndT}\Big|_P = \frac{PdV}{ndT}\Big|_P = R$$

$$\Rightarrow \quad C_P = \frac{dQ}{n\,dT}\Big|_P = \frac{dU}{n\,dT} + \frac{PdV}{ndT}\Big|_P$$

$$\Rightarrow \quad C_P = \frac{R}{\gamma - 1} + R, \text{ hence}$$

$$C_P = C_V + R = \frac{\gamma R}{\gamma - 1}$$

$\Rightarrow \quad C_P - C_V = R$ called Mayor's result, and

$C_P / C_V = \gamma$ called poisson's ratio.

To find out specific heat in any process, try calculating $\frac{PdV}{ndT}\Big|_{\text{process}}$, for this differentiate ideal gas equation getting

$$PdV + VdP = nRdT$$

and differentiate the process equation to eliminate the term VdP.

Mixture of gases :

Average molecular weight :
Is defined as the total mass of gas divided by the number of moles of the gas.

$$\langle M \rangle = \frac{\sum n_i M_i}{\sum n_i}$$

Molar specific heat :
Is defined as the total heat energy delivered to the gas (at constant pressure for C_P and at constant volume for C_V) divided by the number of moles of the gas.

$$C_P = \frac{\sum n_i (C_P)_i}{\sum n_i} \text{ and } C_V = \frac{\sum n_i (C_V)_i}{\sum n_i}$$

Adiabatic constant :
Total internal energy of mixture of gases is the sum of individual internal energies of the components. As all the components are at the same temperature

$$\sum \frac{n_i RT}{(\gamma_i - 1)} = \frac{\left(\sum n_i\right) RT}{(\gamma_{eq} - 1)}$$

$$\Rightarrow \quad \gamma_{eq} = 1 + \frac{\sum n_i}{\sum \frac{n_i}{(\gamma_i - 1)}}$$

Adiabatic constant of the mixture of gases can also be defined as

$$\gamma_{eq} = \frac{\sum n_i C_P}{\sum n_i C_V}$$

$$\Rightarrow \quad \gamma_{eq} = \frac{\sum n_i \frac{\gamma_i R}{(\gamma_i - 1)}}{\sum n_i \frac{R}{(\gamma_i - 1)}} = \frac{\sum n_i \left\{\frac{1}{(\gamma_i - 1)} + 1\right\}}{\sum n_i \frac{1}{(\gamma_i - 1)}}$$

$$\Rightarrow \quad \gamma_{eq} = 1 + \frac{\sum n_i}{\sum \frac{n_i}{(\gamma_i - 1)}}$$

Volume elasticity of gases :
Suppose a given mass of an ideal gas has a pressure P and volume V. When the pressure is increased to $(P + \Delta P)$, the volume decreases to $(V - \Delta V)$. Thus a pressure increase ΔP results in a volume change ΔV. Then normal stress = ΔP and volume strain = $\Delta V / V$, therefore modulus of elasticity is

$$E = \left(\frac{\Delta P}{\Delta V / V}\right) = \frac{V \Delta P}{\Delta V}$$

Isothermal elasticity :

$$P V = \text{constant}$$

$$\Rightarrow \quad P V = (P + \Delta P)(V - \Delta V)$$

$$\Rightarrow \quad \Delta P\, V - P_f \Delta V = 0$$

$\Rightarrow \quad \dfrac{\Delta P}{\left(\Delta V/V\right)} = P_f = E_{\text{isothermal}}$

Adiabatic elasticity :

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

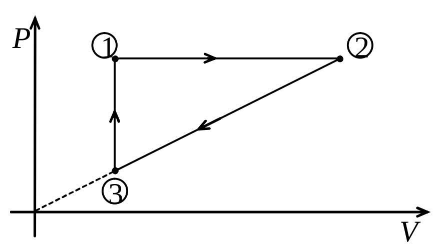
$\Rightarrow \quad PV^{\gamma} = (P + \Delta P)\,(V - \Delta V)^{\gamma} = (P + \Delta P)\; V^{\gamma}\,(1 - \gamma\, \Delta V/V\,)$

$\Rightarrow \quad P_f \Delta P - \gamma P_f\, \Delta V/V\, = 0$

$\Rightarrow \quad \dfrac{\Delta P}{\left(\Delta V/V\right)} = \gamma P_f = E_{\text{adiabatic}}$

Conversion of P-V diagram in to P-T and T-V diagrams :
To convert one diagram in to the other for every process the process equation in the one set of variables should be converted in to the other set of variables with help of ideal gas equation. Plotting these new process equations in the new diagram and carefully choosing the states of the gas in the new diagram using the fact that when one variable increases in the first diagram how the other variable in the new diagram changes for the same process, will complete the job.

Representative example 3 :
Convert the adjacent P-V diagram in to P – T diagram.



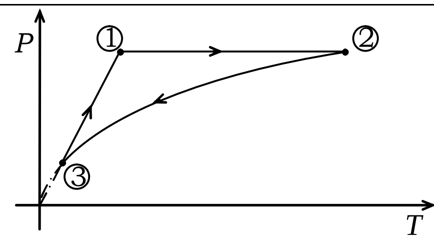
Solution :
From the P-V diagram it is clear that,

⇨ The process 1→2 is isobaric thus the same process will also remain isobaric in P-T diagram. In isobaric process $V \propto T$ thus between states 1 and 2,

⇨ $V_1 < V_2 \Rightarrow T_1 < T_2$
The process 3→1 is isochoric. In isochoric process

⇨ $P \propto T \Rightarrow P = kT$,
The process equation for isochoric process in P-T diagram. Between states 3 and 1, $P_3 < P_1$.
The process 2→3 is obviously $P = kV$, in P-V diagram. The corresponding process equation in the P-T diagram is

⇨ $P = kV$ and $PV = nRT$ thus $P^2 = k'T$
Is a parabola whose axis is temperature axis.

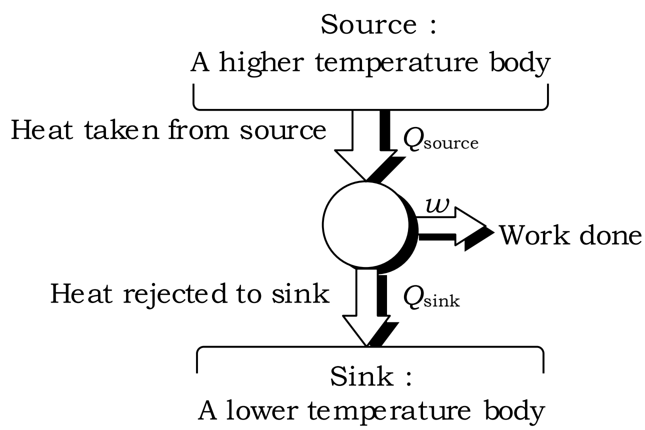


Cyclic process :
When a thermodynamic system attains the initial thermodynamic state following certain thermodynamic process then the set of theses processes is called a cyclic process. A clockwise cycle in P-V diagram represents the heat engine while the anti clockwise cycle represents the heat pump or refrigerator.

Efficiency of a heat engine operating in a cyclic process :
Suppose an engine takes an amount Q_{source} of heat from a high-temperature body and converts a part w of it into work then it has to reject Q_{sink} (= $Q_{source} - w$) amount of heat to low temperature body. If the working substance inside the engine attains the same final state as initial state then, by first law of thermodynamics

$$w = Q_{source} - Q_{sink}.$$

Thus the efficiency of the engine is defined as



$$\eta = \frac{\text{work done by the engine}}{\text{heat supplied to it}}$$

$$= \frac{w}{Q_{source}} = \frac{Q_{source} - Q_{sink}}{Q_{source}}$$

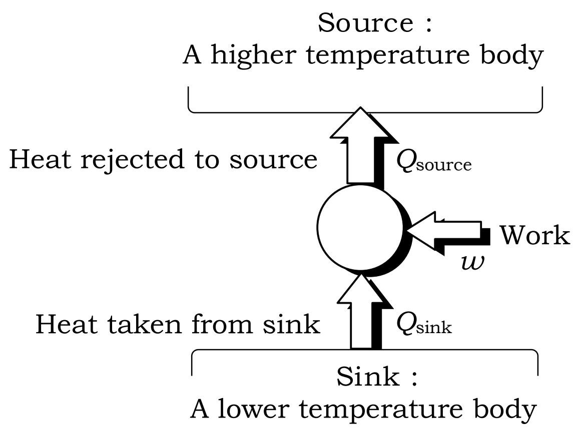
$$= 1 - \frac{Q_{sink}}{Q_{source}}$$

In a cycle calculate the Q_{source} or Q_{sink} for each process, then apply above relation to calculate the efficiency of the cycle.

Efficiency of a heat pump (Refrigerator) operating in a cyclic process :
Suppose it takes an amount Q_{sink} of heat from a low-temperature body and an amount of work w is done on the system to reject Q_{source} (= $Q_{sink} + w$) amount of heat to high-temperature body. If the working substance inside the engine attains the same final state as initial state then, by first law of thermodynamics

$w = Q_{source} - Q_{sink}$.

Thus the efficiency of the refrigerator is defined as

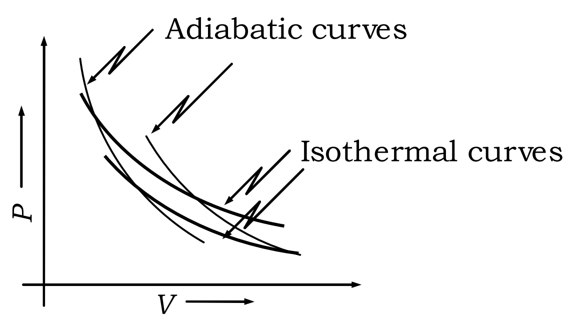


$$\varepsilon = \frac{\text{Heat drawn from the sink}}{\text{work done on the refrigerator}}$$

$$\Rightarrow \quad \varepsilon = \frac{Q_{sink}}{w} = \frac{Q_{sink}}{Q_{sink} - Q_{source}}$$

$$\Rightarrow \quad \varepsilon = \frac{1}{1 - \frac{Q_{source}}{Q_{sink}}}$$

<u>Carnot cycle</u> :
A cyclic process consisting of two adiabatic and two isothermal processes is called Carnot cycle.

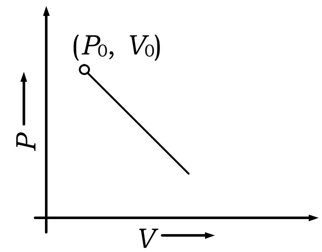


<u>Carnot's theorem</u> :
All reversible engines (operating in a cyclic process) operating between the same temperature limits have equal efficiency and no engine operating between the same temperature limits can have an efficiency greater than this. It is a consequence of the second law of thermodynamics and puts a theoretical limit to the efficiency of the heat engine

$$\eta = 1 - \frac{T_{sink}}{T_{source}}$$

Use this formula to calculate the efficiency of Carnot's cycle.

Equation of the process is



$$P + kV = C$$

$\Rightarrow$ $dP + kdV = 0$

From ideal gas equation

$$PV = nRT$$

$\Rightarrow$ $pdV + VdP = nRdT$

$\Rightarrow$ $pdV - kVdV = nRdT$

The point at which

$$dQ = 0 = dU + dw$$

$\Rightarrow$ $nRdT + PdV = 0$

$\Rightarrow$ $PdV - kVdV = -PdV$

$\Rightarrow$ $P = \dfrac{kV}{2}$

$\Rightarrow$ $P = \dfrac{C}{3}, V = \dfrac{2C}{3k}$