

PHYSICS

JEE and NEET CRASH COURSE

Kinetic Theory of Gasses and Thermodynamics



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Kinetic Theory of Gases

To state the conditions of a gas, its volume, pressure and temperature must be specified.

	N.T.P.	S.T.P.
Temperature	0 C - 273.15 K	0.01 C - 273.16K
Pressure	1 atm - 1.01325×10^5 N/m ² - 1.01325×10^5 Pascal	1 atm
Volume	22.4 lit.	22.4 lit

Equation of State for Ideal Gas

$$PV = n RT \quad \text{where, } n = \frac{M}{M_0}$$

$$P = \frac{\rho RT}{M_0} \quad \text{where, } \rho = \frac{M}{V}$$

Properties/Assumptions of Ideal gas

- ⊙ All the molecules of a gas are identical as regards their shape and mass. The molecules of different gases are different.
- ⊙ The gas molecules behave as rigid, elastic and smooth spheres. The molecules collide with the walls of the container. These collisions are perfectly elastic i.e., there is no loss of kinetic energy in these collisions.
- ⊙ The molecules of a gas are in a state of continuous random motion. They move with all possible velocities in all possible directions. They obey Newton's law of motion.

Mean momentum = 0;

Mean velocity = 0.

$$\langle \vec{v} \rangle = 0 \quad ; \quad \langle v^2 \rangle \neq 0 \text{ (Non zero)} \quad ; \quad \langle v^3 \rangle = \langle v^5 \rangle = 0$$

- ⊙ The average distance travelled by a molecule between two successive collisions is called as **mean free path** (λ_m) of the molecule.
- ⊙ The time during which a collision takes place is negligible as compared to time taken by the molecule to cover the mean free path so NTP ratio of time of collision to free time of motion $10^{-8} : 1$.
- ⊙ When a gas taken into a vessel it is uniformly distributed in entire volume of vessel such that its density, molecular density, motion of molecules etc. all are identical for all direction, therefore

$$\text{root mean velocity } \bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 \quad \rightarrow \quad \text{equal}$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

Pressure exerted by the gas in all direction $P_x = P_y = P_z = P \quad \rightarrow \quad \text{equal}$

- ⊙ All those assumptions can be justified, if number of gas molecules are taken very large i.e., 10^{23} molecules/cm³.

Gas Law's

$$PV = nRT$$
$$R = 8.314 \text{ J/mol}\cdot\text{K}$$
$$= \frac{25}{3}$$

Boyle's Law

$$V \propto \frac{1}{P} \quad \text{If } M \text{ and } T \text{ are constant} \quad \text{or} \quad PV = \text{constant}$$

Charle's Law

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{constant}$$

Gay Lussac's Law

$$P \propto T \quad \text{or} \quad \frac{P}{T} = \text{constant} \quad (\text{Volume and Mass are kept constant})$$

Avogadro's Law

At same temperature and pressure equal volumes of all gases contains equal number of molecules.

If $P, V,$ and T are same then $N_1 = N_2$

Dalton's Law

The pressure exerted by a mixture of several gases equals the sum of the pressure exerted by each component gas present in the mixture.

$$P_{\text{mix.}} = P_1 + P_2 + P_3 \dots$$

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$$P = \frac{\rho R T}{M_0}$$

Expression for Pressure of an Ideal Gas

$$P = \frac{1}{3} \rho \langle v^2 \rangle$$

$\langle v^2 \rangle$ = mean square speed of molecules

$$\langle v^2 \rangle = \frac{3P}{\rho} = \frac{3RT}{M_0}$$

T. to. K.E. = $\frac{1}{2} m v_1^2 + \frac{1}{2} m v_2^2 + \dots$
 $= \frac{1}{2} m \frac{(v_1^2 + v_2^2 + \dots + v_n^2)}{N}$

As $PV = nRT$, then **Total translational K.E. of gas** = $\frac{1}{2} M \langle v^2 \rangle = \frac{3}{2} PV = \frac{3}{2} nRT$

Translational kinetic energy of 1 molecule = $\frac{3}{2} kT$ (it is independent of nature of gas)

$$\langle v^2 \rangle = \frac{3P}{\rho} \quad \text{or} \quad v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M_{mole}}} = \sqrt{\frac{3kT}{m}}$$

Where v_{rms} is root mean square speed of the gas.

\downarrow Molar Mass

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

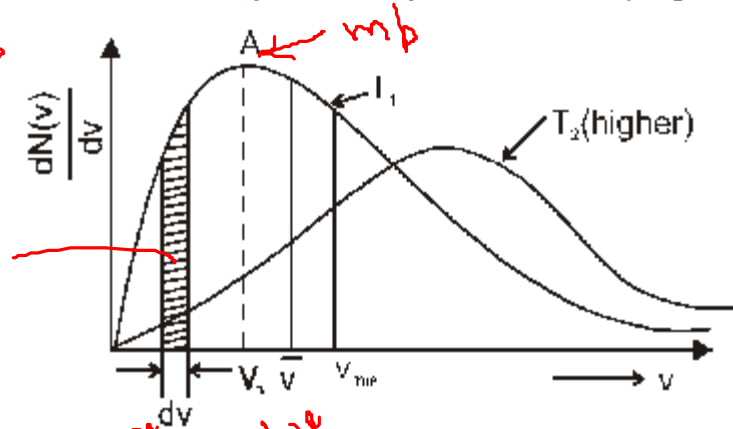
$$k = \frac{R}{N_A}$$

\uparrow Boltzmann's const.

Maxwell's Distribution Curve

A plot of $\frac{dN(v)}{dv}$ (number of molecules per unit speed interval) against v is known as Maxwell's distribution curve.

Area = no. of molecules having speed v



Total area = Total no. of molecules
 $V_{rms} > V_{avg} > V_{mp}$

Average (or Mean) Speed	RMS Speed	Most Probable Speed
$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = 1.59 \sqrt{kT/m}$	$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = 1.73 \sqrt{\frac{kT}{m}}$	$v_p = \sqrt{\frac{2kT}{m}} = 1.41 \sqrt{kT/m}$

From the above expression, we can see that

$\sqrt{\frac{3kT}{m}} > \sqrt{\frac{8kT}{\pi m}} > \sqrt{\frac{2kT}{m}}$

$\sqrt{\frac{3RT}{M_0}}$

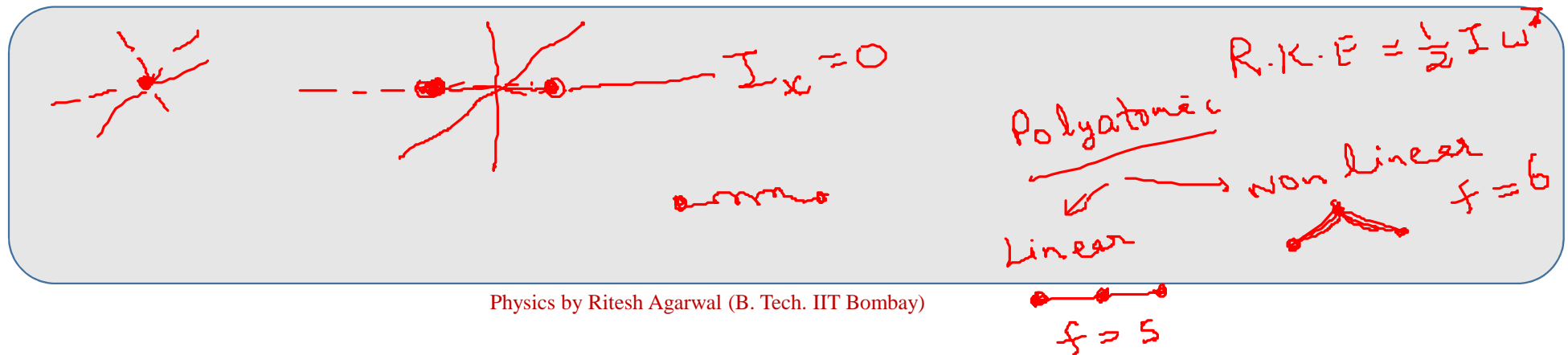
$\sqrt{\frac{2RT}{M_0}}$

Degree of Freedom

The number of independent ways in which a molecule or an atom can exhibit motion is called it's degrees of freedom.

The number of independent coordinates required to specify the dynamical state of a system is called it's degrees of freedom.

Mono atomic : (all inert gases Ex. He , Ar etc.)	$f = 3$	(translational)
Diatomic : (gases like H_2 , N_2 , O_2 etc.)	$f = 5$	(3 translational + 2 rotational)
If temp > 5000 K	$f = 7$	[3 translational.+ 2 rotational + 2 vibrational]



Maxwell's Law of Equipartition of Energy and Internal Energy

Maxwell's Law of Equipartition of Energy

Energy associated with each degree of freedom = $\frac{1}{2} kT$. If degree of freedom of a molecule is f , then

$$\text{total kinetic energy of that molecule} = \frac{1}{2} f k T$$

Internal Energy

The internal energy of a system is the sum of kinetic and potential energies of the molecules of the system. It is denoted by U . Internal energy (U) of the system is the function of its absolute temperature (T) and its volume (V). i.e. $U = f(T, V)$

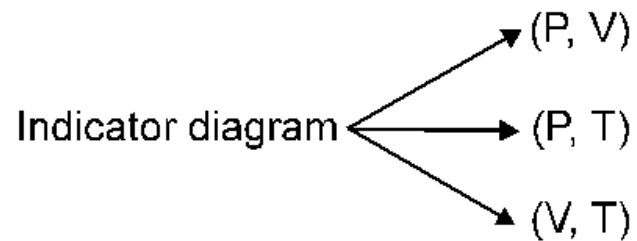
In case of an ideal gas, intermolecular force is zero. Hence its potential energy is also zero. In this case, the internal energy is only due to kinetic energy, which depends on the absolute temperature of the gas. i.e. $U = f(T)$.

For an ideal gas internal energy $U = \frac{f}{2} nRT$.

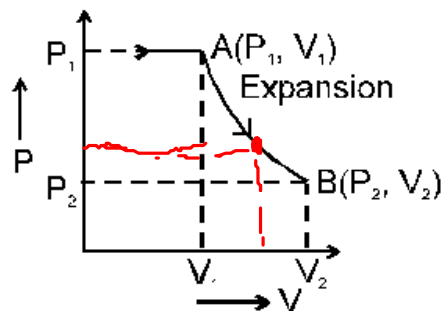
State function
 $\Delta U = \frac{f}{2} n R \Delta T$

Indicator Diagram

A graph representing the variation of pressure or variation of temperature or variation of volume with each other is called indicator diagram.



- (A) Every point of Indicator diagram represents a unique state (P, V, T) of gases.
- (B) Every curve on Indicator diagram represents a unique process.



$$PV = nRT$$

Thermodynamics and Thermodynamic System

Thermodynamics is mainly the study of exchange of heat energy between bodies and conversion of the same into mechanical energy and vice-versa.

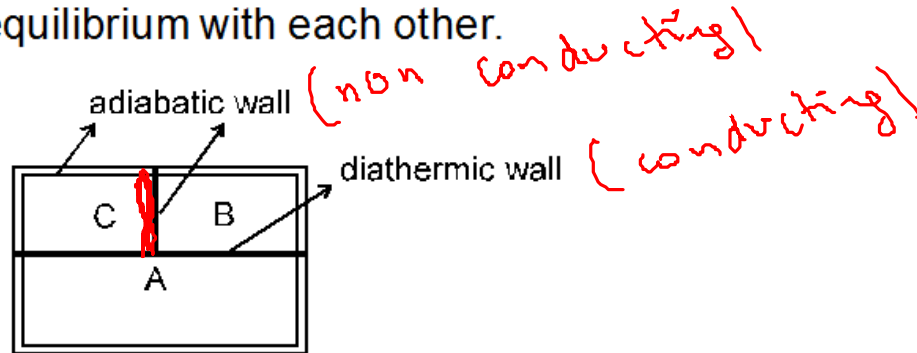
Thermodynamic System

Collection of an extremely large number of atoms or molecules confined within certain boundaries such that it has a certain value of pressure (P), volume (V) and temperature (T) is called a **thermodynamic system**. Anything outside the thermodynamic system to which energy or matter is exchanged is called its surroundings. Taking into consideration the interaction between a system and its surroundings thermodynamic system is divided into three classes :

- (a) **Open system** : A system is said to be an open system if it can exchange both energy and matter with its surroundings.
- (b) **Closed system** : A system is said to be closed system if it can exchange only energy (not matter with its surroundings).
- (c) **Isolated system** : A system is said to be isolated if it can neither exchange energy nor matter with its surroundings.

Zeroth law of Thermodynamics

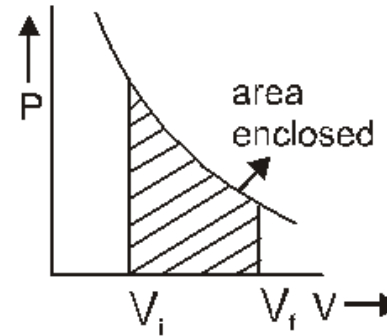
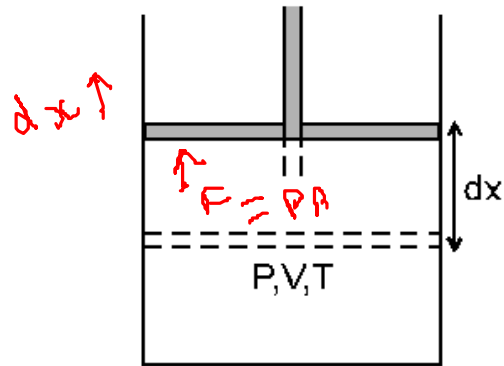
If two systems (B and C) are separately in thermal equilibrium with a third one (A), then they themselves are in thermal equilibrium with each other.



Work Done by a Gas

$$W = \int dW = \int P dV$$

Area enclosed under P-V curve gives work done during process.



$$\begin{aligned} W &= \int F dx \\ &= \int P A dx \\ &= \int P dV \end{aligned}$$

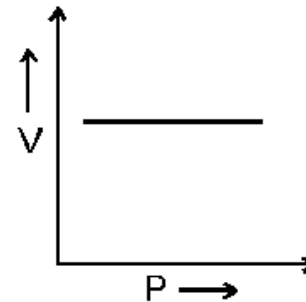
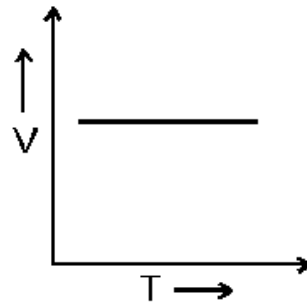
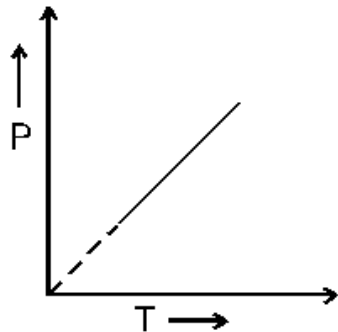
$V \uparrow$ $w = +ve$
 $V \downarrow$ $w = -ve$

Isochoric Process (Isometric Process)

$$PV = nRT$$

$V = \text{constant} \Rightarrow \frac{P}{T}$ is constant (Gay lussac's law)

Indicator diagram of isochoric process :



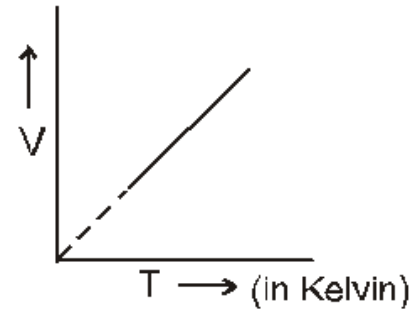
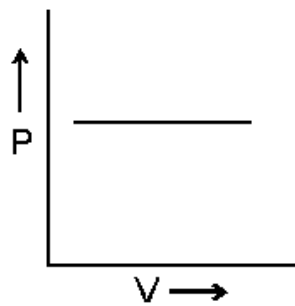
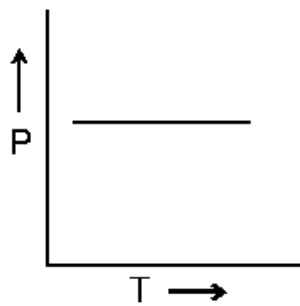
Work done in isochoric process : $W = 0$

Change in internal energy in isochoric process : $\Delta U = n \frac{f}{2} R \Delta T$

Isobaric Process

$$P = \text{constant} \Rightarrow \frac{V}{T} = \text{constant}$$

Indicator diagram of isobaric process :



Work done in isobaric process :

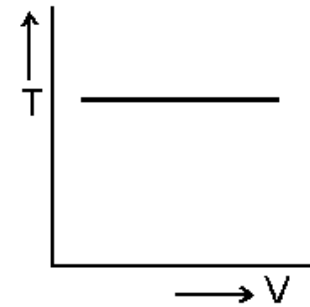
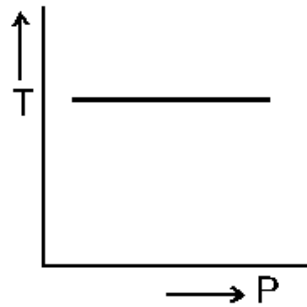
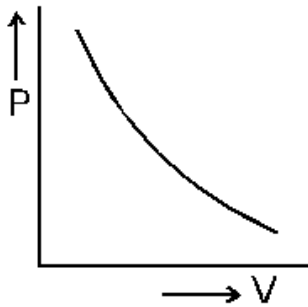
$$W = P \Delta V = P (V_{\text{final}} - V_{\text{initial}}) = nR (T_{\text{final}} - T_{\text{initial}}) = nR \Delta T$$

Change in internal energy in isobaric process :
$$\Delta U = n \frac{f}{2} R \Delta T = \frac{f}{2} W$$

Isothermal Process

$T = \text{constant}$ [Boyle's law applicable] $PV = \text{constant}$

$$P \propto \frac{1}{V}$$



$$P_i V_i = P_f V_f$$
$$W = nRT \ln \frac{P_i}{P_f}$$

Work done in isothermal process:

$$W = nRT \ln \frac{V_f}{V_i} \quad W = \left[2.303 nRT \log_{10} \frac{V_f}{V_i} \right]$$

Internal energy in isothermal process :

$$\Delta U = 0$$

Cyclic Process

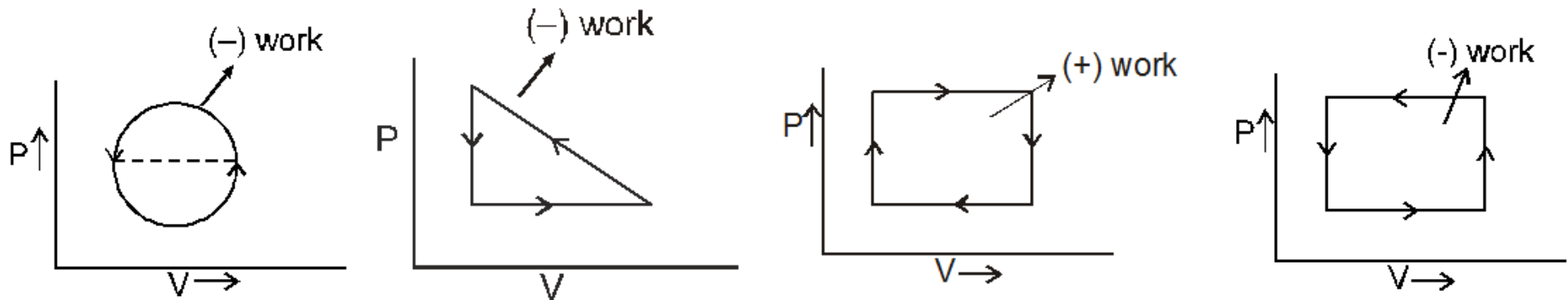
$P-V$	$+w$	$-w$
$V-P$	$A.C.W$	$C.W$

In the cyclic process initial and final states are same therefore; initial state = final state
 Work done = Area enclosed under P-V diagram.

Change in internal Energy $\Delta U = 0$



If the process on P-V curve is clockwise, then net work done is (+ve) and vice-versa.
 The graphs shown below explains when work is positive and when it is negative



First Law of Thermodynamics

$$\Delta U = Q + W$$

The first law of thermodynamics is the law of conservation of energy. It states that if a system absorbs heat dQ and as a result the internal energy of the system changes by dU and the system does a work dW , then **$dQ = dU + W$** .

Heat gained by a system, work done by a system and increase in internal energy are taken as positive.

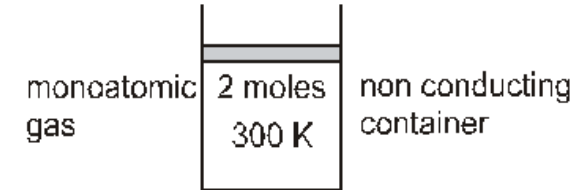
Heat lost by a system, work done on a system and decrease in internal energy are taken as negative.

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

Example

Two moles of a monoatomic gas at 300 K are kept in a non conducting container enclosed by a piston. Gas is now compressed to increase the temperature from 300 K to 400 K. Find work done by

the gas ($R = \frac{25}{3}$ J/mol-K)



Sol.

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

Since container is non conducting therefore

$$\Delta Q = 0 = \Delta U + W$$

$$\Rightarrow W = -\Delta U = -n \frac{f}{2} R \Delta T$$

$$= -2 \times \frac{3}{2} R (400 - 300)$$

$$= -3 \times \frac{25}{3} \times 100 \text{ J} = -2500 \text{ J}$$

Efficiency of a Cycle (η)

$$\eta = \frac{\text{total Mechanical work done by the gas in the whole process}}{\text{Heat absorbed by the gas (only +ve)}}$$

$$= \frac{\text{area under the cycle in P-V curve}}{\text{Heat injected into the system}}$$

$$\eta = \left(1 - \frac{Q_2}{Q_1}\right) \text{ for Heat Engine}$$

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \text{ for Carnot cycle}$$

$Q_1 = \text{Heat injected}$
 $Q_2 = \text{Heat rejected}$
 $\Delta Q = Q_1 - Q_2$
 $\Delta U = 0$
 $w = Q_1 - Q_2$
 $\eta = \frac{w}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$

Molar Heat Capacity

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

Molar Heat Capacity at constant volume

$$C_v = \left(\frac{\Delta Q}{n\Delta T} \right)_{\text{constant volume}} = \frac{f}{2} R$$

Molar Heat Capacity at constant pressure

$$C_p = \left(\frac{\Delta Q}{n\Delta T} \right)_{\text{constant pressure}} = \left(\frac{f}{2} + 1 \right) R$$

MOLAR HEAT CAPACITY OF IDEAL GAS IN TERMS OF R

(i) For a monoatomic gas $f = 3$

$$C_v = \frac{3}{2} R, \quad C_p = \frac{5}{2} R \quad \rightarrow \gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67$$

(ii) For a diatomic gas $f = 5$

$$C_v = \frac{5}{2} R, \quad C_p = \frac{7}{2} R \quad \rightarrow \gamma = \frac{C_p}{C_v} = 1.4$$

(iii) For a Triatomic non-linear gas $f = 6$

$$C_v = 3R, \quad C_p = 4R \quad \Rightarrow \gamma = \frac{C_p}{C_v} = \frac{4}{3} = 1.33$$

$$C_p = C_v + R$$

Adiabatic Process

$$PV^\gamma = \text{const} \quad PV = nRT$$

$$V \propto \frac{T}{P}$$

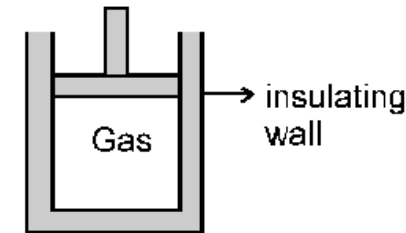
When no heat is supplied or extracted from the system the process is called adiabatic. Process is sudden so that there is no time for exchange of heat. If walls of a container are thermally insulated no heat can cross the boundary of the system and process is adiabatic.

Equation of adiabatic process is given by
 $PV^\gamma = \text{constant}$ [Poisson Law]

$$T^\gamma P^{1-\gamma} = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

$$\Delta U = \frac{f}{2} nR \Delta T = nC_v \Delta T$$



$$C_v = \frac{R}{\gamma - 1}$$

$$C_p = \frac{\gamma R}{\gamma - 1}$$

$$\gamma = 1 + \frac{2}{f}$$

$$W = \frac{nR \Delta T}{\gamma - 1}$$

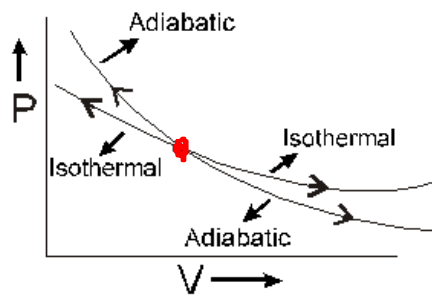
Work done in adiabatic Process

$$\Delta W = -\Delta U = nC_v(T_i - T_f) = \frac{P_i V_i - P_f V_f}{(\gamma - 1)} = \frac{nR(T_i - T_f)}{\gamma - 1}$$

work done by system is (+ve) , if $T_i > T_f$ (For expansion)

work done on the system is (-ve) if $T_i < T_f$ (For compression)

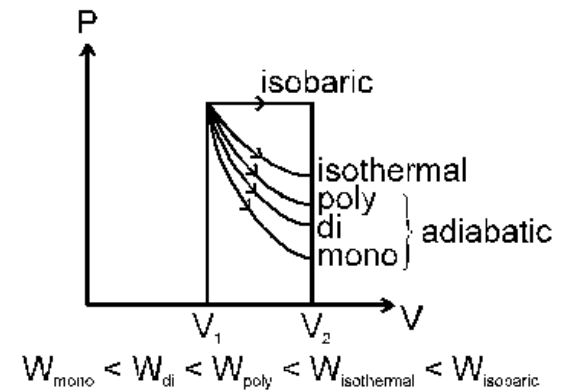
Comparison of Slopes of an Isothermal and Adiabatic Curve



$$PV^m = \text{const}$$

$$\frac{dP}{dV} = -m \frac{P}{V}$$

$$\left| \frac{dP}{dV} \right|_{\text{adia}} > \left| \frac{dP}{dV} \right|_{\text{isothermal}}$$



In compression up to same final volume: $|W_{\text{adia}}| > |W_{\text{isothermal}}|$
 In Expansion up to same final volume: $W_{\text{isothermal}} > W_{\text{adia}}$

Mixture of non-reacting Gases

(a) Molecular weight = $\frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$,

M_1 & M_2 are molar masses.

(b) Specific heat $C_V = \frac{n_1 C_{V1} + n_2 C_{V2}}{n_1 + n_2}$,

$$C_P = \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 + n_2}$$

(c) for mixture, $\gamma = \frac{C_{P_{\text{mix}}}}{C_{V_{\text{mix}}}} = \frac{n_1 C_{P1} + n_2 C_{P2} + \dots}{n_1 C_{V1} + n_2 C_{V2} + \dots}$

Heat Engine

Heat engine is a device which converts heat into work.

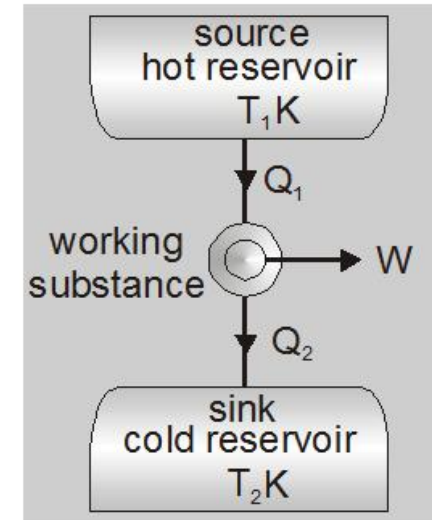
Three parts of a heat engine:

- (i) Source of high temperature reservoir at temperature T_1
- (ii) Sink or low temperature reservoir at temperature T_2
- (iii) Working substance.

In a cycle of heat engine the working substance extracts heat Q_1 from source, does some work W and rejects remaining heat Q_2 to the sink.

Efficiency of heat engine $\eta = \frac{\text{work done (W)}}{\text{heat taken from source (} Q_1 \text{)}}$

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{Q_1 - Q_2}{Q_1}$$



$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Refrigerator

It is inverse of heat engine. It extracts heat (Q_2) from a cold reservoir, same external work W is done on it and rejects heat (Q_1) to hot reservoir.

The coefficient of performance of a refrigerator.

$$\beta = \frac{\text{heat extracted from cold reservoir}}{\text{work done on refrigerator}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

For Carnot reversible refrigerator $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

$$\therefore \beta = \frac{Q_2}{W} = \frac{1}{\left[\frac{Q_1}{Q_2} - 1\right]} = \frac{1}{\left[\frac{T_1}{T_2} - 1\right]} \Rightarrow \beta = \frac{T_2}{T_1 - T_2}$$

