

HEAT AND THERMODYNAMICS

Thermometry

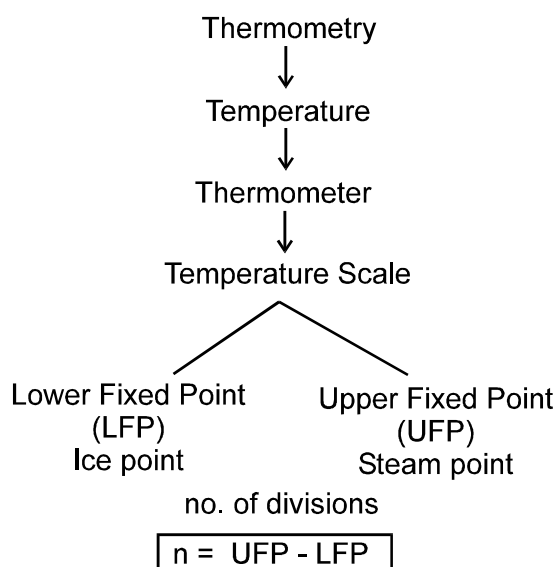
Heat

Heat is the form of energy which gives the sensation of hotness or coldness of a body. It is the physical cause of sensation of hotness or coldness.

Temperature

Degree of hotness or coldness of a body is temperature. It determines the direction of heat flow.

Thermometry is the technique for the quantitative determination of thermodynamic temperature



Different temperature Scale

Scale	LFP	UFP	n	Representation
Celsius	0°C	100°C	100	1°C
Fahrenheit	32°F	212°F	180	1°F
Reaumer	0°R	80°R	180	1°R
Kelvin	273 K	373 K	100	1 K

Conversion of temperature Scales

Let x be a facility / Reference Scale

$$\frac{x - x_{LFP}}{x_{UFP} - x_{LFP}} = \frac{C - 0}{100 - 0} = \frac{F - 32}{212 - 32} = \frac{R - 0}{80 - 0} = \frac{K - 273}{373 - 273}$$

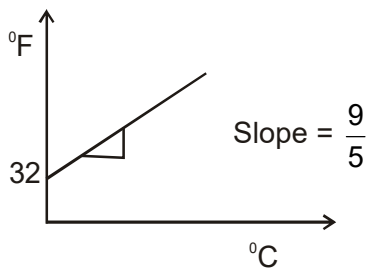
$\frac{x - x_{LFP}}{x_{UFP} - x_{LFP}} = \frac{C}{100} = \frac{F - 32}{180} = \frac{R}{80} = \frac{K - 273}{180}$

Relation between temperature scales**Celsius and Fahrenheit**

$$\frac{C}{100} = \frac{F - 32}{180}$$

$$\frac{C}{5} = \frac{F - 32}{9}$$

$F = \frac{9}{5} C + 32$



$$F_1 = \frac{9}{5} C_1 + 32$$

$$F_2 = \frac{9}{5} C_2 + 32$$

$$[F_2 - F_1] = \frac{9}{5} [C_2 - C_1]$$

$\Delta F = \frac{9}{5} \Delta C$ $\Delta C = \frac{5}{9} \Delta F$

Common Reading in celsius and Fahrenheit is -40°

Celsius and Kelvin

$$\frac{C}{100} = \frac{K - 273}{100}$$

$C = K - 273$

$K = C + 273$

No common Reading in Celsius and Kelvin

Since the no. of divisions in both the scales are same

Change in temperature in Celsius is equivalent to change in temperature Fahrenheit

Fahrenheit and Kelvin

$$\frac{F - 32}{180} = \frac{K - 273}{100}$$

$$\frac{F - 32}{9} = \frac{K - 273}{5}$$

Common Reading in Fahrenheit and kelvin is 574.25

Note :-

As the no. of divisions in a temperature scale increases “size of the degree” decreases.

The zero value in Kelvin scale is known as “the absolute zero”. It is 0 Kelvin or -273.15°C .

In modern temperature scales absolute zero and triple point of water are taken as fixed reference points.

Triple point of water 0.01°C or 273.16 K @ 4.58 mm Hg pressure or at pressure $6.11 \times 10^2\text{ Pa}$ or $6 \times 10^{-3}\text{ atm}$

Thermometers

Devices used for the measurement of temperature

Principle : Linear variation of thermometric property with temperature

Eg : Pressure of a gas

Volume of a liquid

Resistance of metal

Light Intensity

Thermo emf, magnetic properties

Liquid Thermometers

Mercury and alcohol are thermometric liquids advantages of Hg

High conductivity, high boiling point, low specific heat, high visibility, high sensitivity to heat, high angle of contact

Gas Thermometers (Most Sensitive)

Constant Volume Gas Thermometers

$P \propto T$ Based on Gaylussac's law

Constant Pressure Gas Thermometers

$V \propto T$ Based on Charles law

Resistance Thermometers

Eg : Platinum Resistance Thermometer

Germanium Resistance Thermometer

To find unknown temp

Let α be a thermometric property

x_0 = thermometric property at 0°C

x_{100} = thermometric property at 100°C

x_t = thermometric property at $t^{\circ}\text{C}$

then unknown temp

$$t = \frac{x_t - x_0}{x_{100} - x_0} \times 100$$

for pressure

$$t = \frac{P_t - P_0}{P_{100} - P_0} \times 100$$

for resistance

$$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

Thermal Expansion

Expansion of Solids

Three types of Expansion is possible in solids

- 1) Linear Expansion (in length)
- 2) Areal Expansion (in area)
- 3) Volume Expansion (in volume)

	Linear Expansion	Areal Expansion	Cubical Expansion
	$\alpha \rightarrow$ linear Expansivity	$\beta \rightarrow$ superficial Expansivity	$\gamma \rightarrow$ cubical Expansivity
Co-efficient	$\alpha = \frac{\Delta L}{L \Delta t}$	$\beta = \frac{\Delta A}{A \Delta t}$	$\gamma = \frac{\Delta V}{V \Delta t}$
Change in value	$\Delta L = L \alpha \Delta t$	$\Delta A = A \beta \Delta t$	$\Delta V = V \gamma \Delta t$
Fractional change	$\frac{\Delta L}{L} = \alpha \Delta t$	$\frac{\Delta A}{A} = \beta \Delta t$	$\frac{\Delta V}{V} = \gamma \Delta t$
% change	$\frac{\Delta L}{L} \times 100 = \alpha \Delta t \times 100$	$\frac{\Delta A}{A} \times 100 = \beta \Delta t \times 100$	$\frac{\Delta V}{V} \times 100 = \gamma \Delta t \times 100$
Final Value	$L' = L [1 + \alpha \Delta t]$	$A' = A [1 + \beta \Delta t]$	$V' = V [1 + \gamma \Delta t]$

Application of Linear Expansion

Time loss/gain of a pendulum clock

we have time period

$$T = 2\pi \sqrt{\ell / g}$$

$$T = \frac{2\pi}{\sqrt{g}} \ell^{1/2} \quad T = k \ell^{1/2}$$

Fractional change

$$\frac{\Delta T}{T} = \frac{1}{2} \frac{\Delta \ell}{\ell}$$

Fractional change in T

$$\frac{\Delta T}{T} = \frac{1}{2} \alpha \Delta \theta$$

Change in time period $\frac{\Delta T}{T} = \frac{1}{2} \alpha \Delta \theta \times T$

Time loss/gain in a day $T = 1 \text{ day} = 24 \text{ hrs} = 86400 \text{ s}$

$$\Delta T = \frac{1}{2} \alpha \Delta \theta \times 86400$$

In summer Temperature \uparrow length \uparrow time period \uparrow

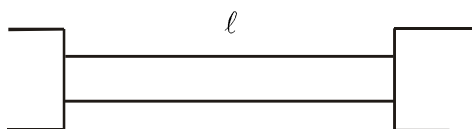
Time loss clock will become slow

In winter Temperature \downarrow length \downarrow time period \downarrow

Time gain clock will become fast

Thermal Stress

When a metal rod is rigidly fixed at its both ends so that it is prevented from expansion or contraction. On heating stress will be developed due to thermal strain it is called thermal stress



$$\text{Thermal strain} = \frac{\Delta l}{l} = \alpha \Delta t$$

$$Y = \frac{\text{Thermal stress}}{\text{Thermal strain}}$$

$$\begin{aligned} \text{Thermal stress} &= Y \times \text{Thermal strain} \\ &= Y \alpha \Delta t \\ \text{Tension or force} &= \text{Thermal stress} \times \text{Area} \\ &= Y A \alpha \Delta t \end{aligned}$$

Note : Thermal stress developed in a rod is depending on the material of rod and rise in temperature and is independent of length of the rod.

Expansion of Liquids

For heating a liquid, it has to be kept in a container. On heating the container will also expand.

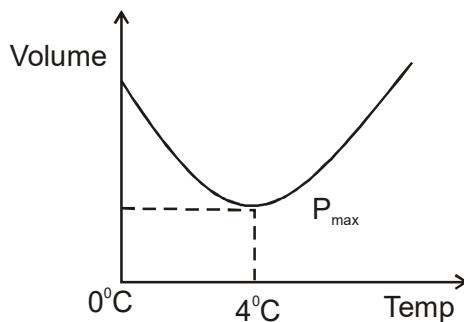
Real Expansion of Liquid = Apparent Expansion of Liquid + Expansion of the container

$$\gamma_{\text{Real}} = \gamma_{\text{apparent}} + \gamma_{\text{container}}$$

$$\gamma_{\text{Real}} = \gamma_{\text{apparent}} + 3\alpha_{\text{vessel}}$$

Anomalous Expansion Water

Volume of given amount of water decreases with increase in temperature from 0 to 4°C. But beyond 4°C water will normally expand. Water has the least volume and maximum density at 4°C



It plays an important role in the survival of aquatic life in cold winter season in polar regions.

There is expansion of water above and below 4°C

Condition for two metal rods of different length and α to have same difference in length at all temperature

For difference in length independent of temperature $\Delta l = \text{constant}$ $\Delta l_1 = \Delta l_2$

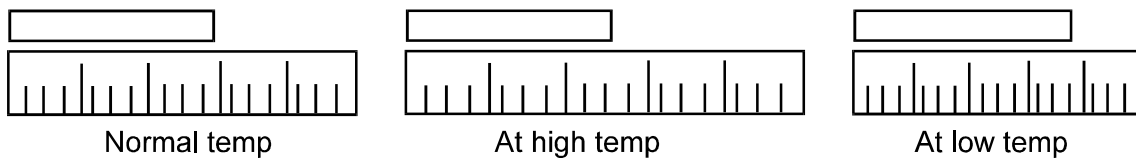
$$l_1 \alpha_1 \Delta t = l_2 \alpha_2 \Delta t$$

$$l_1 \alpha_1 = l_2 \alpha_2$$

$$\frac{l_1}{l_2} = \frac{\alpha_2}{\alpha_1}$$

The correct the reading of a metallic scale

Case 1 : When scale is expanding



$$\text{True reading} = \text{Scale reading}(1 + \alpha \Delta t)$$

$\Delta t \rightarrow$ temp diff (temp at which measurement is taken and temperature at which scale is calibrated)

Variation of density with temperature

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\rho = \frac{m}{V}$$

as temp increases volume increases and density decreases

$$\rho' = \frac{m}{V'}$$

$$\rho' = \frac{m}{V[1 + \gamma \Delta t]}$$

$$\rho' = \frac{\rho}{1 + \gamma \Delta t}$$

$$\rho' = \rho (1 - \gamma \Delta t) \quad \text{expanding binomially}$$

Variation of upthrust with temperature

Apparent weight = Actual weight – Upthrust

At normal temperature

$$\text{Upthrust } F_B = V \rho_L g$$

When temperature increases by Δt

$$\text{Upthrust } F'_B = V' \rho'_L g$$

$$F'_B = V[1 + \gamma_s \Delta t] \times \frac{\rho_L}{[1 + \gamma_L \Delta t]} g$$

$$F'_B = V \rho_L g \left[\frac{1 + \gamma_s \Delta t}{1 + \gamma_L \Delta t} \right]$$

$$F'_B = F_B \left[\frac{1 + \gamma_s \Delta t}{1 + \gamma_L \Delta t} \right]$$

$$\frac{F'_B}{F_B} = \frac{1 + \gamma_s \Delta t}{1 + \gamma_L \Delta t}$$

In other way

$$F'_B = F_B [1 + (\gamma_s - \gamma_L) \Delta t]$$

Special Cases

1. When a metallic disc with an inner hole is heated the diameter of the hole will also increase.
2. When a metallic sphere with a cavity is heated size and volume of cavity increase.
3. When a broken ring with gap between ends is heated the gap will also increase.

4. **For an anisotropic solids** (shows different properties in different directions)

$$\gamma = \alpha_x + \alpha_y + \alpha_z$$

Calorimetry

Calorimetry deals with two types of heats

Specific heat and latent heat

Joules mechanical equivalent of heat (J)

Joule found that when mechanical work is converted into heat (Q) the ratio of W and Q is always a constant

$$\frac{W}{Q} = J \text{ or } W = JQ$$

J → joules mechanical equivalent of heat (It is a conversion factor)

$$J = 4.186 \text{ Joule/ Calorie}$$

Calorie

It is the amount of heat energy required to rise the temperature of 1 g water by 1°C (14.5°C to 15.5°C)

$$1 \text{ Calorie} = 4.2 \text{ J}$$

Principle of Calorimetry

Law of mixtures

Heat lost by hot body = heat gained by cold body

[when no heat is lost to the surroundings]

Specific heat capacity (C)

It is the amount of heat energy required to rise the temperature of unit mass (1 g or 1 kg) of any substance by 1°C or 1 K

for a given mass m

heat required is H = m

H is called heat capacity or thermal capacity for a given mass m and Δt rise in temperature

Amount of heat required

$$Q = mc\Delta t$$

Unit of specific heat capacity

$$C = \frac{Q}{m\Delta t} = \frac{\text{Joule}}{\text{kg} \times \text{K}}$$

SI unit : J Kg⁻¹K⁻¹

$$C = \frac{Q}{m\Delta t} = \frac{\text{Calorie}}{\text{g} \times ^\circ\text{C}}$$

CGS unit : Calg⁻¹ °C⁻¹

for water C = 4200 J Kg⁻¹K⁻¹

C = 1 Calg⁻¹ °C⁻¹

for ice C = 2100 J Kg⁻¹K⁻¹

C = 0.5 Calg⁻¹ °C⁻¹

Latent Heat

It is the amount of heat energy exclusively utilized for phase transition at certain fixed temperatures like melting point or boiling point etc

Latent heat of fusion (L_f)

For solid \longrightarrow Liquid Transition @ melting point

Eg : 1 g ice @ 0°C $\xrightarrow{L_f}$ 1 g water @ 0°C

L_f of ice = 80 cal/g

For a given mass m $Q = mL_f$

Latent heat of Vapourisation (L_v)

For liquid \longrightarrow Gas transition @ boiling point

Eg : 1 g water @ 100°C $\xrightarrow{L_v}$ 1 g steam @ 100°C

L_v of water = 540 Cal/g

For a given mass m $Q = mL_v$

Unit of Latent Heat Capacity

$Q = mL$ S.I. Unit : Joule/kilogram

$L = Q/m$ CGS Unit : Calorie/gram

Water Equivalent

It is the amount of water which has got the same heat capacity as that of a given substance

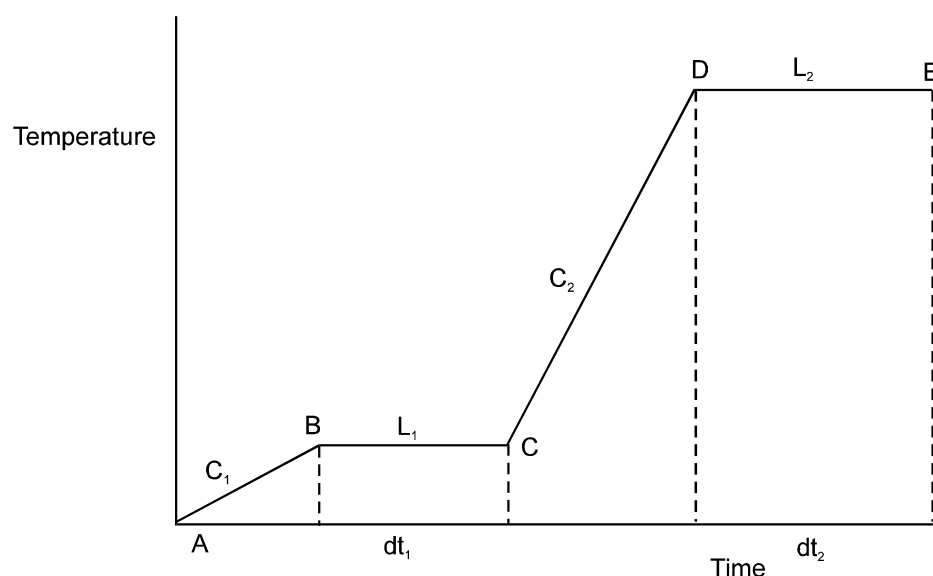
$H = mC$ $mC = m_w C_w$

for water

$$H = m_w C_w \quad \boxed{m_w = \frac{mC}{C_w}}$$

Water equivalent is numerically equal to heat capacity of the substance in CGS system

Temperature - Time Graph



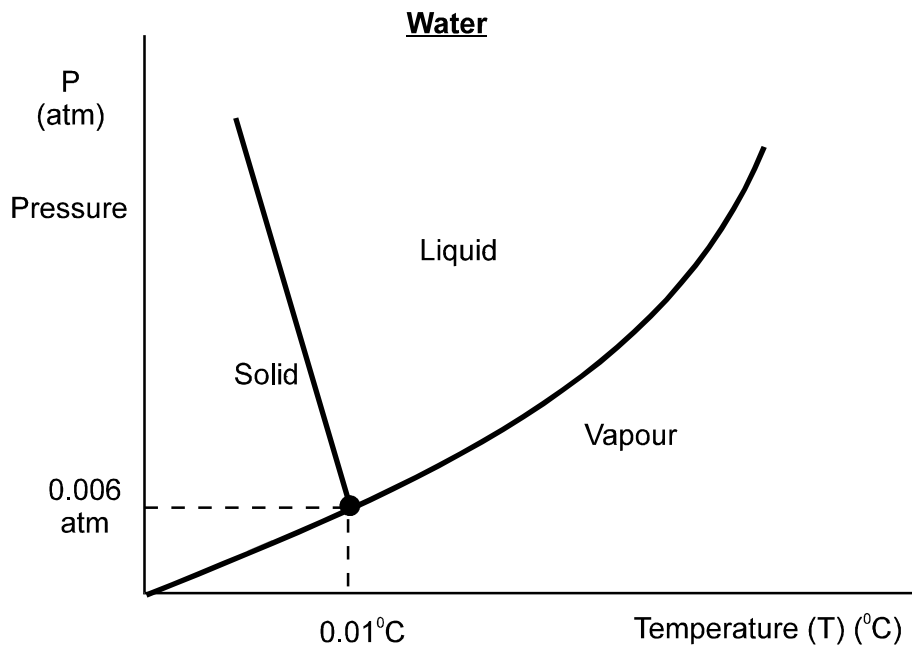
Graph plotted with time along x axis and temperature along y axis

Phase Change	Increase in temperature
$dQ = mL$ $p = \frac{dQ}{dt} = \frac{mL}{dt}$ $L = \left[\frac{P}{m} \right] dt$ $L = \text{a constant} \times dt$ $L \propto dt$ $L \propto \text{time interval}$ $L \propto \text{change in } x \text{ value}$	$dQ = mcdT$ $p = \frac{dQ}{dt} = \frac{mcdT}{dt}$ $\frac{dT}{dt} = \left[\frac{P}{m} \right] \times \frac{1}{C}$ $\frac{dT}{dt} = \text{a constant} \times \frac{1}{C}$ $\text{Slope} \propto \frac{1}{C}$ $C \propto \frac{1}{\text{Slope}}$

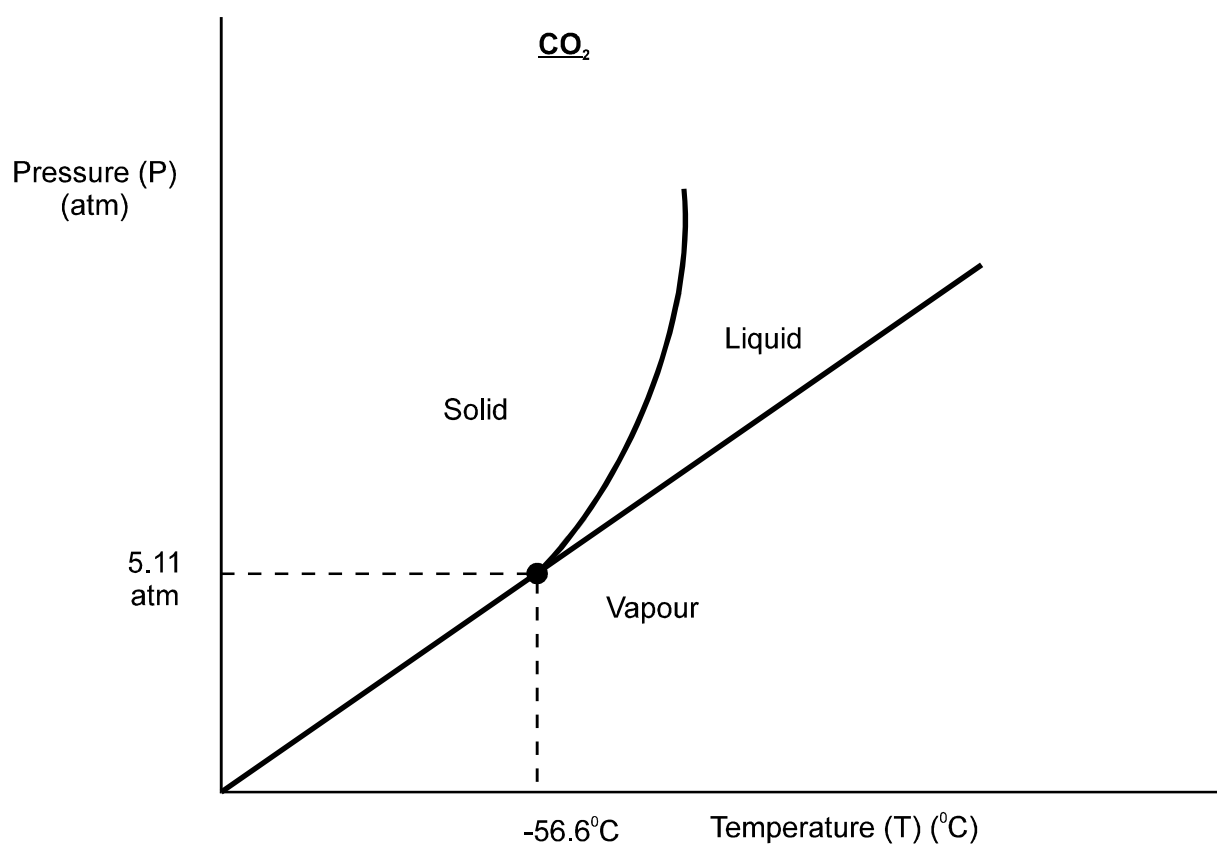
P-T diagram

A graph between the temperature T and pressure P of the substance is called phase diagram or P-T diagram.

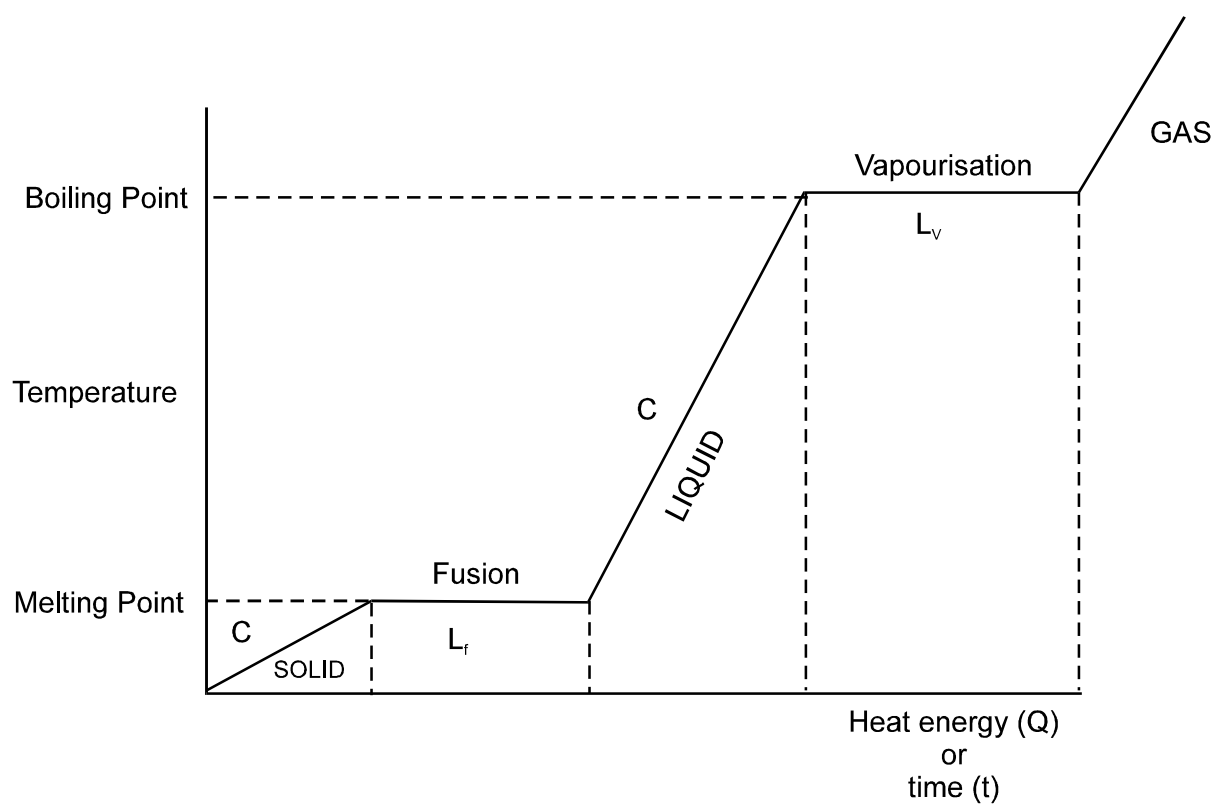
Phase Diagram



Note : for water melting point decreases with increase in pressure



Heating Curve



Regelation

Melting of ice at lower temperature due to increase in pressure and refreezing when pressure is withdrawn is regelation

Heat Transfer

Transport of heat energy from one point to another can be done in 3 ways

Conduction

Convection

Radiation

Conduction

Particle to particle heat transfer without actual transport of matter.

It is common to solids and mercury

Gravity has no effect in conduction

Metals are good conductors of heat

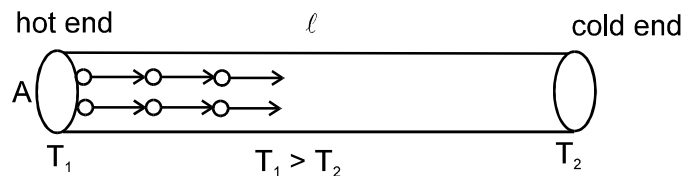
Heat Current (H)

Rate of flow of heat energy through a conductor

$$H = \frac{Q}{t} \quad \text{unit : Watt}$$

Thermal Conductivity

The ability of a conductor to allow the passage of heat energy through it

Expression for Thermal conductivity

Consider a metallic rod with length ℓ , uniform cross sectional area A . Its both ends are maintained at two different temperatures T_1 and T_2 ($T_1 > T_2$).

Steady State is a condition in which heat current through every cross section of the conductor becomes a constant. There is no further absorption of heat energy by molecules. Only effective method of heat transfer is conduction in steady state.

At Steady State

Rate of heat flow

$$H = \frac{Q}{t} \propto \text{area of cross section}$$

$$\frac{Q}{t} \propto \text{temperature gradient}$$

$$\frac{Q}{t} \propto A \quad \frac{Q}{t} \propto \frac{T_1 - T_2}{\ell}$$

$\begin{aligned} \text{Temperature gradient} &= \frac{\text{Temp diff}}{\text{length}} \\ &= \frac{T_1 - T_2}{\ell} \end{aligned}$
--

$\frac{Q}{t} = KA \frac{(T_1 - T_2)}{\ell}$	$\frac{Q}{t} = \frac{KA \Delta T}{\ell}$
---	--

Unit of thermal conductivity

$$H = \frac{KA \Delta T}{\ell}$$

$$K = \frac{H \ell}{A \Delta T} = \frac{\text{Watt} \times \text{m}}{\text{m}^2 \times \text{Kelvin}}$$

$$\text{Unit of } K \rightarrow \text{Watt m}^{-1}\text{K}^{-1}$$

Thermal Resistance (R_T)

It is the ability to oppose the flow of heat energy through a conduction

$$\text{Heat Current} = \frac{\text{Temperature difference}}{\text{Thermal Resistance}}$$

$$H = \frac{\Delta T}{R_T} \quad (1)$$

$$\text{We have } H = \frac{KA \Delta T}{\ell}$$

$$H = \frac{\Delta T}{[\ell / KA]} \quad (2)$$

Thermal Resistance $R_T = \ell / KA$

Unit of Thermal Resistance

$$H = \frac{\Delta T}{R_T}; R_T = \frac{\Delta T}{H} = \frac{\text{Kelvin}}{\text{Watt}}$$

Convection

It is the transfer of heat energy along with actual transport of matter. Gravity plays an important role in natural convection.

Natural Convection

With the help of gravity.

In upward direction only

Eg : Sea breeze

Land breeze

Trade winds

Boiling water

Forced Convection

With some mechanical support

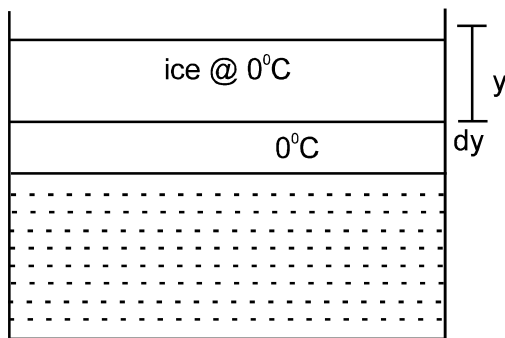
Possible in all directions

Eg : Human circulatory system

Automobile cooling system

House hold heating system

furnaces

Growth of ice ponds

Ice starts forming in a pond at sub zero temperature $-\theta^{\circ}\text{C}$ in winter season. To find time taken for growth of ice upto a thickness y , we will consider a small thickness dy

The heat energy released when ice of thickness dy is formed is dQ . Heat energy is transferred to the environment

$$dQ = \frac{KA[0 - (-\theta)]dt}{y}$$

For melting $dQ = mL = \rho \times A \times dy \times L$

$$\frac{KA\theta}{y} dt = \rho A dy L$$

$$dt = \frac{\rho L}{K\theta} y dy$$

for total time taken to grow from 0 to y

$$t = \int_0^y \frac{\rho L}{K\theta} y dy$$

$$t = \frac{\rho L}{K\theta} \int_0^y y dy$$

$$t = \frac{\rho L}{K \theta} \left[\frac{y^2}{2} \right]_0^y$$

$\rho \rightarrow$ density of ice

$$t = \frac{1}{2} \frac{\rho L}{K \theta} y^2$$

$L \rightarrow$ Latent heat of fusion

$\theta \rightarrow$ Atmospheric temperature

$K \rightarrow$ Thermal conductivity of ice

$y \rightarrow$ Thickness of ice

Time taken by ice to grow up to thickness y , $2y$ and $3y$ from O is given by

$$t_1 : t_2 : t_3 = 1 : 4 : 9$$

$$t \propto y^2$$

t_1, t_2, t_3 are time taken by

$$0 \rightarrow y \quad t_1 \propto y^2$$

ice to grow upto $y, 2y$ and

$$0 \rightarrow 2y \quad t_2 \propto (2y)^2$$

$3y$ respectively

$$0 \rightarrow 3y \quad t_3 \propto (3y)^2$$

$$t_1 \propto y^2$$

$$t_2 \propto 4y^2$$

$$t_3 \propto 9y^2$$

Time taken by ice ice to grow from o to y to $2y$ and $2y$ to $3y$ is

$$0 \rightarrow y \quad \Delta t_1 = t_1 - 0 = y^2 - 0 = y^2$$

$$y \rightarrow 2y \quad \Delta t_2 = t_2 - t_1 = 4y^2 - y^2 = 3y^2$$

$$2y \rightarrow 3y \quad \Delta t_3 = t_3 - t_2 = 9y^2 - 4y^2 = 5y^2$$

$$\Delta t_1 : \Delta t_2 : \Delta t_3 = 1 : 3 : 5$$

Radiation

Radiation is the fastest mode of heat transfer

Properties of heat radiations

It travels in straight lines

It is universal, invisible

All bodies above zero kelvin will emit radiations

It belongs to IR Region

It shows reflection, refraction, interference, diffraction and polarisation

They are em waves with speed 3×10^8 m/s

Let Q be total incident energy, then part of it may absorbed. Some part will be reflected and the rest is transmitted

$$Q = A + R + T$$

$$\div \text{ing by } Q \quad a = \frac{A}{Q} = \text{absorptance}$$

$$\frac{Q}{Q} = \frac{A}{Q} + \frac{R}{Q} + \frac{T}{Q} \quad r = \frac{R}{Q} = \text{reflectance}$$

$$\boxed{a + r + t = 1} \quad t = \frac{I}{Q} = \text{transmittance}$$

Absorptive Power (absorptance) [a]

$$a = \frac{\text{Radiant energy absorbed}}{\text{Total incident energy}}$$

$$a = \frac{A}{Q} \quad \text{No units and dimensions}$$

for a perfect black body $a = 1$

for a non black body $a < 1$

Emissive Power [E]

Radiant energy emitted per unit area per unit time

$$E = \frac{Q}{At} = \frac{\text{Energy}}{\text{area} \times \text{time}} \quad E = \frac{\text{Power}}{\text{area}} \quad \text{unit : Watt / m}^2$$

$$\text{Emissive power} \times \text{area} = \text{Power}$$

Spectral Emissive Power (E_λ)

Emissive power per unit

Wave length range at wavelength λ

$$E = \int_0^\alpha E_\lambda d\lambda; \quad \frac{dE}{d\lambda} = E_\lambda$$

area of $E_\lambda - \lambda$ graph = Emissive Power

Kirchoff's Law

for a given wavelength and temperature

$$\frac{\text{Emissive power}}{\text{Absorptive power}} = \text{Constant}$$

$$\frac{E}{a} = \text{Constant}$$

$$E \propto a$$

\therefore A good absorber is a good emitter

A bad absorber is a bad emitter

Emissivity / Relative Emittance (e)

$$e = \frac{\text{Emissive power of a body}}{\text{Emissive power of black body}}$$

$$e = \frac{E}{E_B} \quad E = e \times E_B$$

for a perfect black body $e = 1$

for a non black body $e < 1$

Stefan's Law

Emissive power of a black body

$$E_B \propto T^4 \quad T \rightarrow \text{absolute temperature}$$

$$E_B = \sigma T^4 \quad \sigma \rightarrow \text{Stefan's constant}$$

$$\sigma = 5.68 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$

$$\text{Power } P = \frac{Q}{t} = \sigma A T^4$$

for a non black body

$$E = e \sigma T^4 \quad e \rightarrow \text{emissivity} \quad P = e \sigma A T^4$$

When temperature difference between body and surrounding is very large

Stefan - Boltzmann's Law

$$\text{for black body } E_B = \sigma (T^4 - T_0^4)$$

$$\text{for non black body } E = e \sigma (T^4 - T_0^4)$$

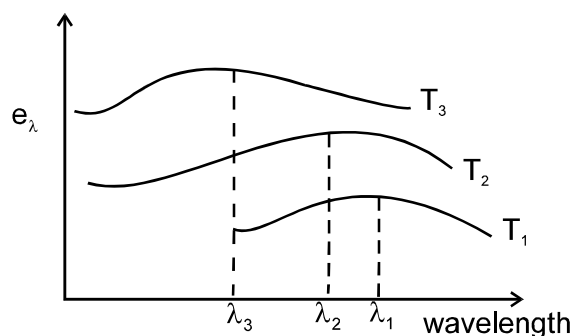
Wiens Displacement Law

"Wavelength corresponding to maximum spectral intensity is inversely proportional to absolute temperature"

$$\lambda_m \propto \frac{1}{T} \quad \lambda T = b \text{ a constant}$$

$$b = \text{Wien's constant} \quad b = 0.29 \text{ cm K}$$

$$\lambda_1 T_1 = \lambda_2 T_2$$



$T_3 > T_2 > T_1$
 $\lambda_3 < \lambda_2 < \lambda_1$
 area of the graph
 = Emissive power

As wavelength is inversely related to temperature a Blue Star is more hotter than a Red Star

Newton's Law of Cooling

When temperature difference between the surrounding is not very large, rate of cooling is proportional to temperature difference between body and surroundings

$$R \propto \theta_{\text{Body}} - \theta_{\text{Surroundings}}$$

$$\frac{Q}{t} \propto \left[\frac{\theta_1 + \theta_2}{2} \right] - \theta_0$$

$\theta_1 \rightarrow$ Initial temperature of body

$$\frac{mcd\theta}{t} \propto \left[\frac{\theta_1 + \theta_2}{2} \right] - \theta_0$$

$\theta_2 \rightarrow$ Final temperature of body

$$\frac{mc(\theta_1 - \theta_2)}{t} \propto \left[\frac{\theta_1 + \theta_2}{2} \right] - \theta_0$$

$\theta_0 \rightarrow$ Surrounding temperature

$$\boxed{\frac{mc(\theta_1 - \theta_2)}{t} = K \left[\frac{\theta_1 + \theta_2}{2} \right] - \theta_0}$$

$t \rightarrow$ time of cooling

To find time of cooling (t)

Newton's law of cooling

$$\boxed{\frac{dT}{dt} = -k [T - T_0]}$$

$$\frac{dT}{T - T_0} = -K dt$$

$$\int_{T_1}^{T_2} \frac{dT}{T - T_0} = -K \int dt$$

$$[\ell n [T - T_0]]_{T_1}^{T_2} = -Kt$$

$$\ell n [T_2 - T_0] - \ell n [T_1 - T_0] = -Kt$$

$$\ell n \left[\frac{T_2 - T_0}{T_1 - T_0} \right] = -Kt$$

$$t = -\frac{1}{K} \ell n \left[\frac{T_2 - T_0}{T_1 - T_0} \right]$$

$$t = \frac{1}{K} \ln \left[\frac{T_1 - T_0}{T_2 - T_0} \right]$$

$$t = \frac{1}{K} \ln \left[\frac{\text{Initial temperature difference}}{\text{Final temperature difference}} \right]$$

Solar Constant

It is the amount of solar radiant energy received by unit area of earth surface in unit time

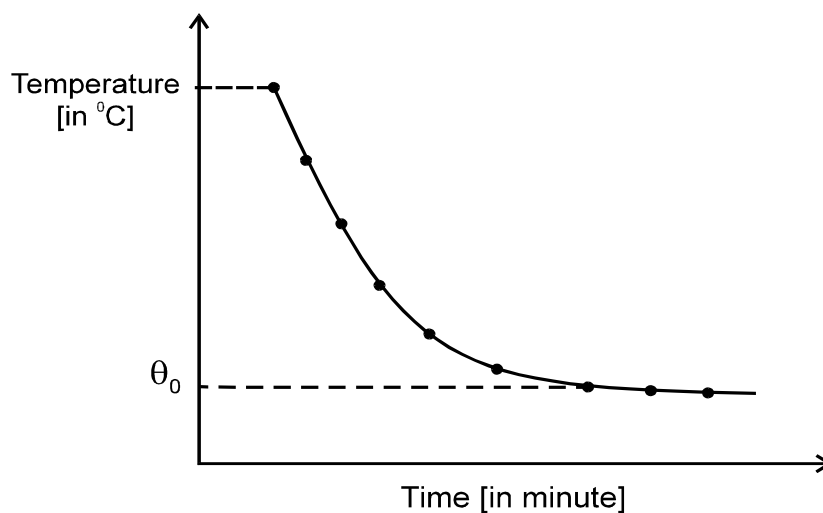
Solar constant

$$S = 1400 \text{ W/m}^2$$

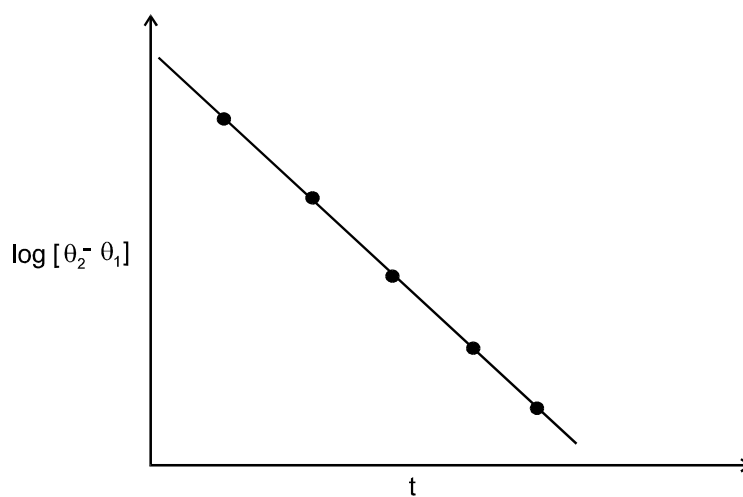
Graph of Newton's Law of Cooling

temp along y axis

time along x axis



Graph connecting $\log_e [\theta_2 - \theta_1]$ and time taken (t)



We have $-\frac{d\theta}{dt} = K[\theta_2 - \theta_1]$

$$-mc \frac{d\theta}{dt} = K[\theta_2 - \theta_1]$$

$$\frac{d\theta}{\theta_2 - \theta_1} = -K dt$$

Integrating

$$\log_e[\theta_2 - \theta_1] = -Kt + C$$

$$y = mx + c$$

Graph : Straight line

Kinetic Theory of Gases

Postulates

1. Molecules in a gas are in a random irregular motion.
2. During the motion they collide with each other and also with the walls of the container.
3. These collisions are perfectly elastic in nature.
4. Size of the molecules is negligible compared to average separation between the molecules.
5. Molecules behave like perfect spheres.
6. Molecular dynamics is governed by Newton's Laws of motion

Pressure exerted by an ideal gas on the walls of the container is given by

$$P = \frac{1}{3} \rho C_{\text{RMS}}^2$$

$\rho \rightarrow$ density of the gas

$C_{\text{RMS}} \rightarrow$ Root mean square velocity

Root mean Square Velocity (C_{RMS})

$$C_{\text{RMS}} = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2}{n}}$$

We have $P = \frac{1}{3} \rho C_{\text{RMS}}^2$

$R / N_A = K$ Boltzmann's constant

$$K = 1.38 \times 10^{-23}$$

$$C_{\text{RMS}}^2 = \frac{3P}{\rho}$$

$M / N_A = m$, mass of molecule

$$C_{\text{RMS}} = \sqrt{3P / \rho}$$

$$C_{\text{RMS}} = \sqrt{\frac{3P}{M/V}}$$

$$C_{\text{RMS}} = \sqrt{\frac{3PV}{M}}$$

$$C_{\text{RMS}} = \sqrt{\frac{3RT}{M}}$$

$$C_{\text{RMS}} = \sqrt{\frac{3R / N_A}{M / N_A}}$$

$$C_{\text{RMS}} = \sqrt{\frac{3KT}{m}}$$

$$C_{\text{RMS}} \propto \sqrt{T}$$

Average Speed (C_{avg})

$$C_{avg} = \frac{C_1 + C_2 + C_3 + C_4 + \dots + C_n}{n}$$

$$C_{avg} = \sqrt{\frac{8RT}{\pi M}} \quad C_{avg} \propto \sqrt{T}$$

$$C_{avg} = \sqrt{\frac{8KT}{\pi m}}$$

Most Probable Velocity (C_{mp})

Velocity possessed by maximum fraction of molecules

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

$$C_{mp} = \sqrt{\frac{2KT}{m}} \quad C_{mp} \propto \sqrt{T}$$

$C_{RMS} : C_{avg} : C_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$ $C_{RMS} > C_{avg} > C_{mp}$
--

Average Translational KE of an ideal gas

We have $P = \frac{1}{3} \rho C_{RMS}^2$

$$P = \frac{1}{3} \frac{M}{V} C_{RMS}^2$$

$$PV = \frac{1}{3} M C_{RMS}^2$$

$$3PV = \frac{1}{2} \times 2M C_{RMS}^2$$

$$\frac{1}{2} \times M C_{RMS}^2 = \frac{3}{2} PV$$

$KE = \frac{3}{2} PV = \frac{3}{2} RT$
--

$KE = \frac{3}{2} KT$

for a molecule

$KE \propto T$

Mean free path (λ)

It is average distance travelled by molecules between two successive collisions

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

$$\lambda = \frac{KT}{\sqrt{2} \pi d^2 P}$$

$n \rightarrow$ no. of molecules / volume (no density)

$P \rightarrow$ Pressure

$K \rightarrow$ Boltzmann's constant

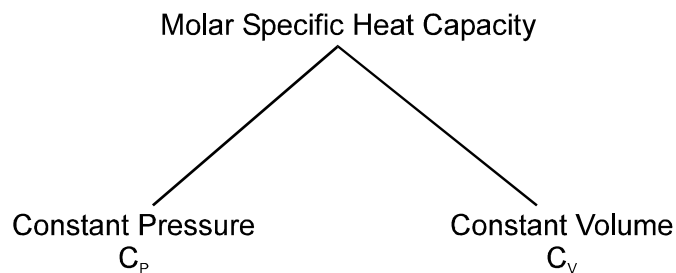
$T \rightarrow$ Temperature

Collision frequency (f)

$$f = \frac{C_{RMS}}{\lambda}$$

Specific Heat of Gases**Molar Specific Heat Capacity**

It is the amount of heat energy required to rise the temperature of 1 mole of an ideal gas by 1°C . It can be supplied by two ways.



$$C_P - C_V = R \quad \text{Mayers Relation}$$

for n moles and dt rise in temperature

$$dQ = nC_V dt \quad \text{at constant volume}$$

$$dQ = nC_P dt \quad \text{at constant pressure}$$

Ratio of Specific Heats (γ)

$$\gamma = \frac{C_P}{C_V}$$

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

Monoatomic molecule

$$n = 1 \quad \bullet$$

$$r = 0$$

$$f = 3n - r = 3 \times 1 - 0 = 3 \text{ (translational)}$$

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = \frac{5}{3}$$

$$\gamma = 1.67$$

$$C_p - C_v = R$$

dividing by C_v

$$\frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$$

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

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

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

$$C_p = \gamma C_v$$

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

for monoatomic gas

$$C_v = \frac{R}{\frac{5}{3} - 1} = \frac{R}{\frac{2}{3}} = \frac{3}{2} R$$

$$C_p = \gamma \times C_v = \frac{5}{3} \times \frac{3}{2} R = \frac{5}{2} R$$

Diatomic molecule

$$n = 2 \quad \bullet \text{---} \bullet$$

$$r = 1$$

$$f = 3n - r = 3 \times 2 - 1 = 5$$

3 translational + 2 rotational

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5} = \frac{7}{5}$$

$$\gamma = 1.4$$

for diatomic gas

$$C_v = \frac{R}{\frac{7}{5} - 1} = \frac{R}{\frac{2}{5}} = \frac{5}{2} R$$

$$C_p = \gamma \times C_v = \frac{7}{5} \times \frac{5}{2} R = \frac{7}{2} R$$

molecule	n	r	f	γ	C_v	C_p
monoatomic	1	0	3	$5/3$	$3/2 R$	$5/2 R$
diatomic gas	2	1	5	$7/5$	$5/2 R$	$7/2 R$

Law of Equipartition of Energy

An ideal gas divides its total energy equally among all degrees of freedom

$$\begin{aligned}
 \text{KE of a molecule / degree of freedom} &= \frac{1}{2} KT \\
 \text{Total KE of a molecule} &= f \times \frac{1}{2} KT \\
 \text{KE of } n \text{ molecules} &= n \times f \times \frac{1}{2} KT \\
 \text{KE of 1 mole / degree of freedom} &= \frac{1}{2} RT \\
 \text{Total KE of 1 mole} &= f \times \frac{1}{2} RT \\
 \text{Total KE of } n \text{ moles} &= n \times f \times \frac{1}{2} RT
 \end{aligned}$$

Specific Heat of Solids

Consider 1 gram mole of a solid containing N_A (Avogadro No.)

Average energy associated with an atom due to its oscillation in one dimension = $2 \times \frac{1}{2} KT = KT$

in 3 dimensions

$$U = 3 \times KT$$

for 1 gram mole of solid

$$U = 3KT \times N_A = 3RT$$

According to first law of thermodynamics

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

for solid ΔV is negligible

$$\Delta Q = \Delta U$$

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = \frac{3RT}{T} = 3R$$

$$\boxed{C = 3R} \quad C = 3 \times 8.314 = 24.93 \text{ Jmol}^{-1} \text{K}^{-1}$$

Specific Heat Capacity of Water

We treat water like a solid made up of 3 atoms [2 Hydrogen + 1 Oxygen]

Total energy of 1 mole of water

$$U = 3 \times 3 KT \times N_A = 9 RT$$

$$C = \frac{\Delta U}{\Delta T} = \frac{9RT}{T} = 9R \quad \left[\begin{array}{l} \because \Delta V = 0 \\ \Delta Q = \Delta U \end{array} \right]$$

$$\boxed{C = 9R} \quad C = 9 \times 8.314$$

$$C = 75.22 \text{ Jmol}^{-1} \text{K}^{-1}$$

when n_1 molecules of an ideal gas is mixed with n_2 molecules of another gas

$$M_{\text{mixture}} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$T_{\text{mixture}} = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

$$C_{V_{\text{mixture}}} = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}$$

$$C_{P_{\text{mixture}}} = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$$

$$\gamma_{\text{mixture}} = \frac{C_{P_{\text{mixture}}}}{C_{V_{\text{mixture}}}}$$

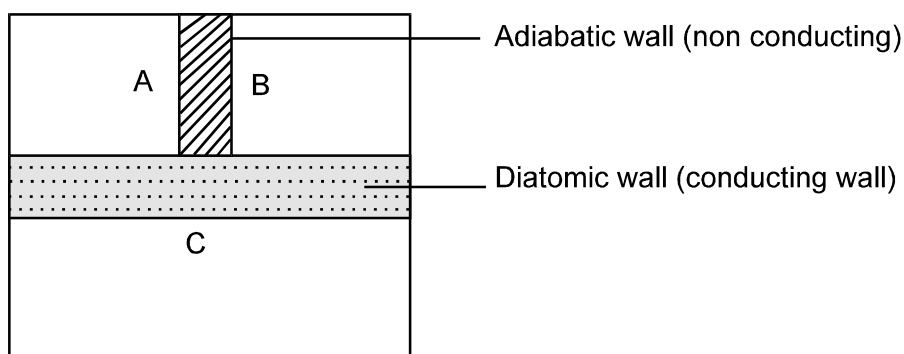
Thermodynamics

Zero'th Law of Thermodynamics

It defined the existence of thermodynamic temperature. It states that “when two systems A and B are separately in thermal equilibrium with a third system C then the systems A and B will also be in thermal equilibrium with each other”.

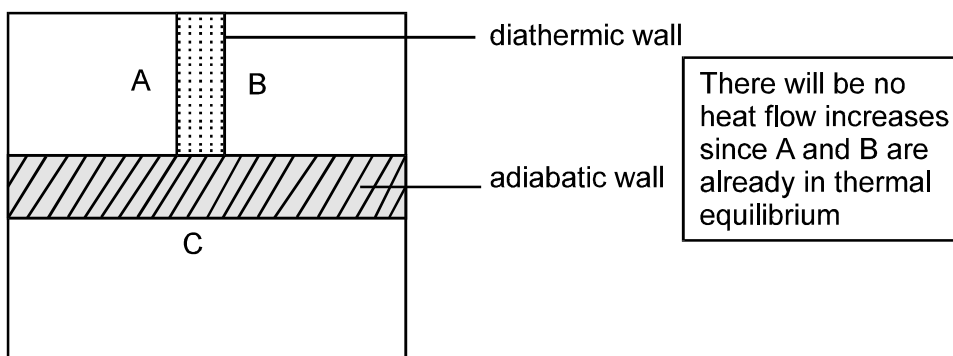
Consider 3 systems A, B and C

Case 1



Now walls are interchanged

Case 2



First Law of Thermodynamics

It is another form of “Law of conservation of Energy”

It states that

Heat supplied to a system	=	change in internal energy	+	work done
---------------------------	---	---------------------------	---	-----------

$\Delta Q = \Delta U + \Delta W$
$dQ = dU + dw$
$dQ = dU + pdV$

$$d\omega = pdV$$

$$dW = F \times dx$$

$$d\omega = p \times A dx$$

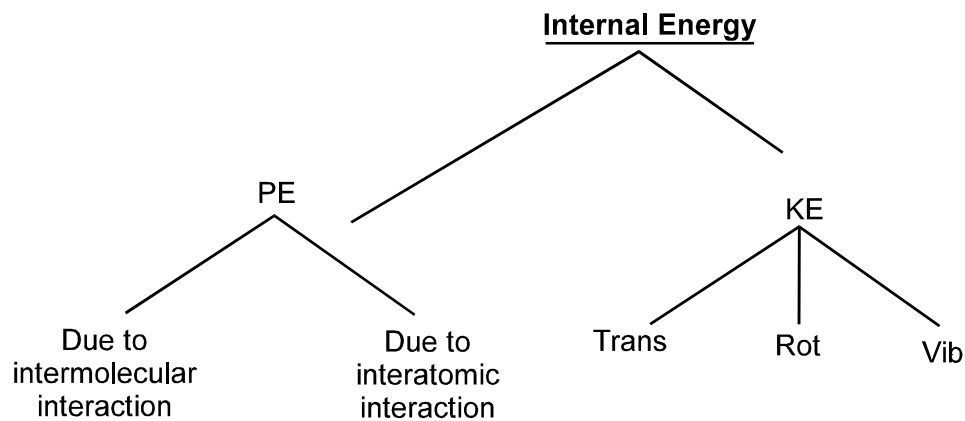
$$d\omega = pdV$$

$$P = \frac{F}{A}$$

Heat Energy (dQ)

When heat is added to a system $dQ = +ve$

When heat is removed from a system $dQ = -ve$

Internal Energy (du)

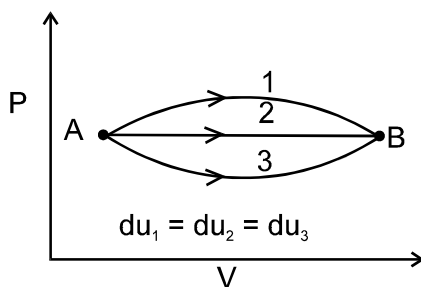
Internal energy is a state variable. It is independent of the path.

If initial and final points are same $\Delta U = 0$
--

In a cyclic process when a system returns to its initial status $du = 0$
--

If initial and final points are same / in a cyclic process when a system returns to its initial state $du = 0$

Eg :



at constant volume $dV = 0$ $pdV = 0$ $dW = 0$

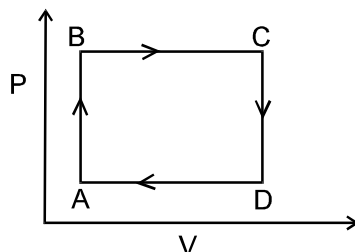
$du = nC_v dT$

Work done (W)

$$dW = pdV \quad W = \int_{V_1}^{V_2} pdV$$

W = area of P-V diagram
In a cyclic process

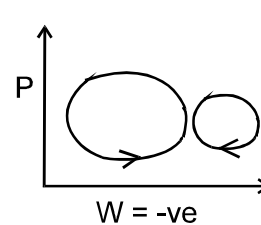
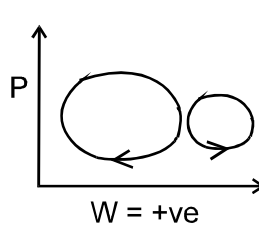
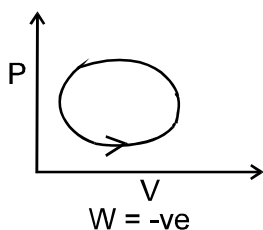
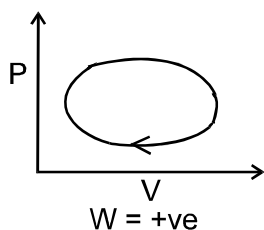
Work done = area of the cyclic loop
= area of ABCDA



On cyclic process

Work done in clockwise direction = +ve

Work done in anticlockwise direction = -ve



Expansion

Volume increases

Work done by the system

$W = +ve$

Compression

Volume decreases

Work done on the system

$W = -ve$

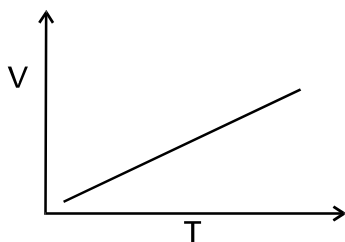
Thermodynamic Process

Isobaric Process

Constant Pressure

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

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



fraction of energy for internal energy change

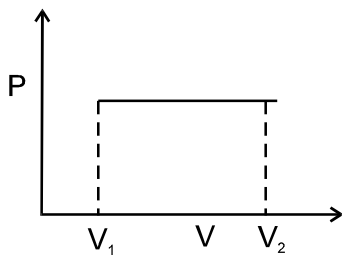
$$\frac{du}{d\theta} = \frac{nC_v dT}{nC_p dT} = \frac{C_v}{C_p} = \frac{1}{\gamma}$$

fraction of energy for work done

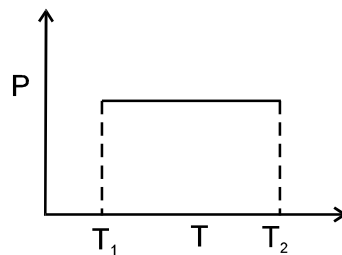
$$\frac{d\omega}{d\theta} = 1 - \frac{1}{\gamma}$$

$$\begin{aligned} dQ &= nC_p dT \\ dU &= nC_v dT \\ dW &= p dV \end{aligned}$$

P-V graph



P-T graph

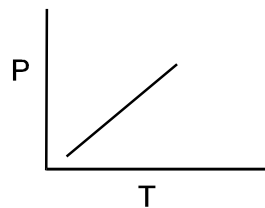
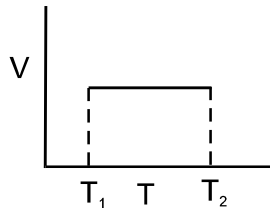
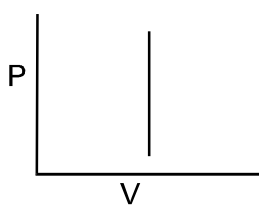


Work done

$$\begin{aligned} W &= P(V_2 - V_1) \\ W &= nR(T_2 - T_1) \end{aligned}$$

Isochoric Process

Constant volume



$$P \propto T$$

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

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\begin{aligned} dQ &= nC_v dT \\ du &= nC_v dT \\ dw &= 0 \end{aligned}$$

$$dQ = du$$

$$dV = 0$$

$$PdV = 0$$

Isothermal Process

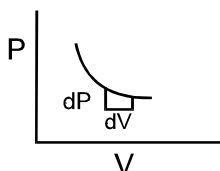
Constant temperature $dT = 0$

$$PV = \text{a constant} \quad du = nC_v dT \quad p \propto \frac{1}{V}$$

$$\therefore du = 0$$

$$P_1 V_1 = P_2 V_2$$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$



Slope of isothermal graph

$$PV = \text{a constant} \quad du = 0$$

$$PdV + VdP = 0 \quad dw = nRT \ln \frac{V_2}{V_1}$$

Work done

$$PdV = -VdP$$

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

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

$$\text{Specific heat capacity} = \alpha$$

$$\text{Slope} = -\frac{P}{V}$$

Adiabatic Process

$$dQ = 0 \quad PV^\gamma = \text{constant} \quad \text{Work done}$$

$$du = -dw \quad TV^\gamma = \text{constant}$$

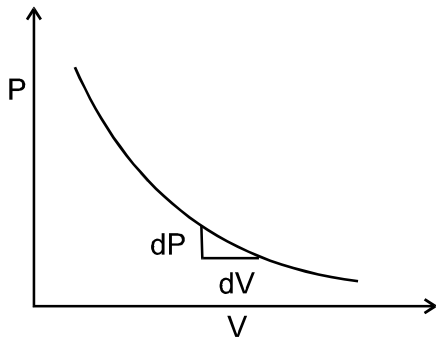
$$W = \frac{nR}{\gamma - 1} [T_1 - T_2]$$

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

$$dw = -du \quad PV^{1-\gamma} T^\gamma = \text{constant}$$

Slope of Adiabatic Graph

$$\frac{dP}{dV} = \gamma \times -\frac{P}{V}$$



Specific heat capacity $C = 0$

Slope of adiabatic $= \gamma \times \text{slope of isothermal}$
--

To find general equation for adiabatic process

In adiabatic process $Q = 0$

$$\Delta U = -W$$

$$W = -\Delta U$$

$$W = -nC_V dT \quad (1)$$

$$dU = -dw = -PdV$$

$$nC_V \Delta T = -pdV \quad (2)$$

$$d(PV) = d[nRT] \quad \because PV = nRT$$

$$PdV + VdP = nRdT$$

$$ndT = \frac{PdV + VdP}{R} \quad (3)$$

Sub (3) in (1)

$$C_V \frac{[PdV + VdP]}{R} = -PdV$$

$$\frac{[C_V + R]dV}{V} + C_V \frac{dP}{P} = 0$$

$$\left[\frac{C_P}{C_V} \right] \frac{dV}{V} + \frac{dP}{P} = 0$$

Integrating

$$\frac{C_p}{C_v} \ln [V] + \ln [P] = \ln [C]$$

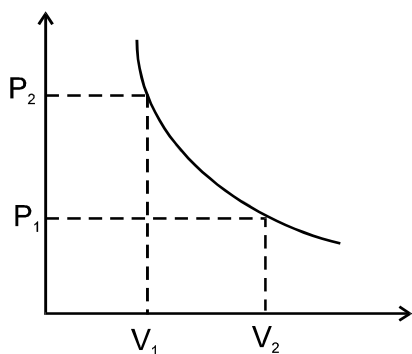
The ratio $\frac{C_p}{C_v} = \gamma$

$$\ln V^\gamma + \ln P = \text{a constant}$$

$$\ln PV^\gamma = \text{a constant} \quad \boxed{PV^\gamma = \text{a constant}}$$

Work done in Isothermal process

$$P = \frac{nRT}{V} \quad P_1 V_1 = P_2 V_2$$



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

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

$$= nRT [\ln V]_{V_1}^{V_2} \quad PV = \text{a constant}$$

$$= nRT \ln \frac{V_2}{V_1} \quad P_1 V_1 = P_2 V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{W = 2.303 nRT \log \frac{V_2}{V_1}}$$

$$\boxed{W = 2.303 nRT \log \frac{P_1}{P_2}}$$

Work done in Adiabatic Process

In adiabatic process

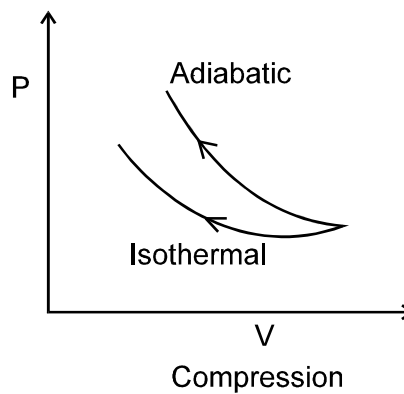
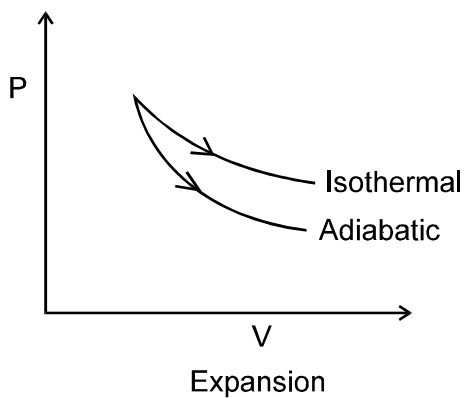
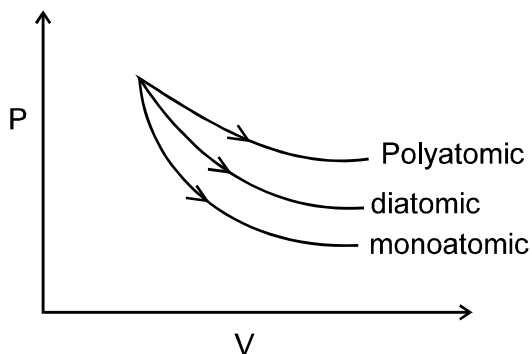
$$d\theta = 0 \quad dW = -dU$$

$$dW = -nC_v dT$$

$$W = -n \frac{R}{\gamma - 1} [T_2 - T_1]$$

$$W = \frac{nR}{\gamma - 1} [T_1 - T_2]$$

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

Comparison between Isothermal and Adiabatic**Adiabatic Curves of Different Gases**

Slope of
adiabatic $\propto \gamma$

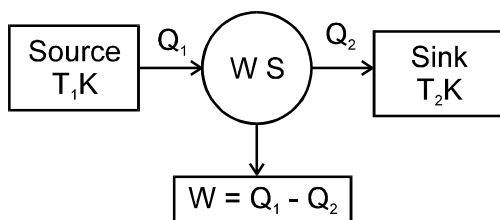
$$\gamma_{\text{mono}} > \gamma_{\text{di}} > \gamma_{\text{poly}}$$

Heat Engines

Heat Engines are the devices that convert heat energy to mechanical work.

Essential Parts

1. Source - A high temperature reservoir (T_1 Kelvin)
2. Sink - A low temperature reservoir (T_2 Kelvin)
3. A working substance



Working substance absorbs an amount of heat energy Q_1 from the source and will undergoes a series of changes and will release an amount of heat energy Q_2 to sink.

Useful work is transferred to external environment. Since working substance undergo cyclic process.

$$du = 0$$

$$dQ = dW$$

$$W = Q_1 - Q_2$$

Thermal Efficiency (η)

$$\eta = \frac{\text{net work done / cycle}}{\text{heat absorbed from source / cycle}}$$

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

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

Carnot's Heat Engine

It is an ideal heat engine designed by Zadi Carnot. According to Carnot's theorem "no reversible heat engine can claim more efficiency than a reversible Carnot's heat engine" working in the same temperature range.

From Carnot's theorem

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

Substitution in (1)

$$\eta = 1 - \frac{T_2}{T_1}$$

For $\eta = 1$ % of $\eta = 100\%$ $T_2 = 0$ Kelvin

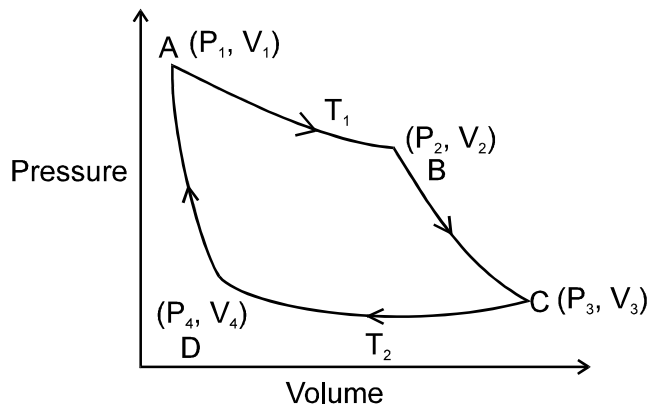
It is practically unattainable

The value of α can never be unity

Carnot's Cycle

A Carnot's cycle involves 4 stages

1. Isothermal expansion
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression



AB (Isothermal Expansion)

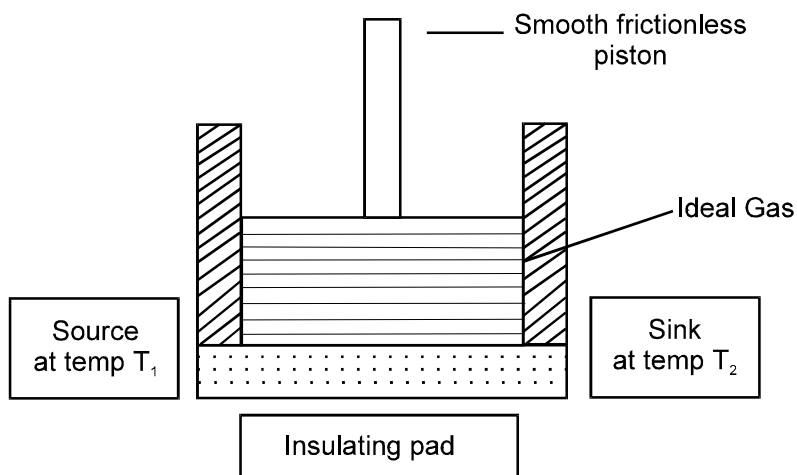
Cylinder is placed on source. Gas expands slowly. Q_1 heat is absorbed. Temperature is kept constant (T_1)

BC (Adiabatic Expansion)

Cylinder is placed on insulating pad. Gas expands further. No heat is absorbed. Temperature falls to T_2

CD (Isothermal Compression)

Cylinder is placed on the sink. Gas is compressed slowly. Q_2 heat is rejected to the sink.



From Carnots we obtain a result

From Carnots we obtain
a result

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

Efficiency

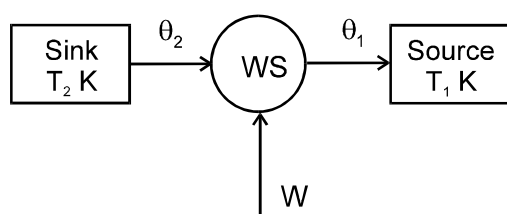
$$\eta = 1 - \frac{T_2}{T_1}$$

DA (Adiabatic Compression)

Cylinder is again placed on insulating pad. Gas is compressed further. Reaches initial pressure and volume. Temperature of Gas raises to T_1

Refrigerator

It is an ideal heat engine working in reverse order. It is used for cooling



Second Law of Thermodynamics

It states that “It is impossible to design a self acting machine unaided by an external agency to transfer heat energy from a low temperature reservoir to a high temperature reservoir”.

In refrigerator working substance absorbs an amount of heat energy Q_2 from sink and will release an energy Q_1 to the source. It is aided by an external work W .

Co-efficient of performance (β)

$$\beta = \frac{\text{heat removed from sink / cycle}}{\text{Energy spent / cycle}}$$

$$\beta = \frac{Q_2}{W}$$

$$\beta = \frac{Q_2}{Q_1 - Q_2}$$

$$\beta = \frac{T_2}{T_1 - T_2}$$

The value β can be α

Relation between η and β

$$\beta = \frac{1 - \eta}{\eta}$$