Thermodynamics processes

Note : This PPT will NOT help you learn physics concepts. It is intended only as a <u>quick revision</u> of formulas, definitions, theorems and concepts before examinations. No physics can be learnt just by watching a few videos or going through a few slides of PPT.

V Vijaykiran
M.Sc., B.Ed., NET
SIGMA Physics Resource Centre
http://www.sigmaprc.in

Thermodynamics

Thermodynamic variables or state variables

Macroscopic variables which are used to characterize the state of a system.
Eg : Temperature (T) , volume (V), mass (m), pressure (P) etc.

Extensive variables :

Variables that indicate the 'size' of the system. They change with the size of the system. Eg : Volume, mass, internal energy etc.

Intensive variables :

Variables that do not depend on 'size' of the system. They remain constant when the system is 'halved'. Eg : Temperature, Pressure

Equation of state

It is a relation between the thermodynamic parameters or variables characterizing the state of a system.

Example : The ideal gas equation $PV = nRT$

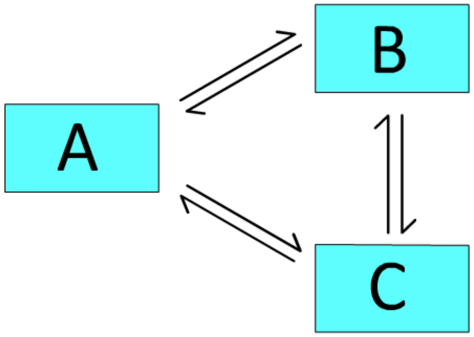
Thermodynamic equilibrium

The state of a system in which its thermodynamics parameters (or variables) do not change with time.

Thermodynamics

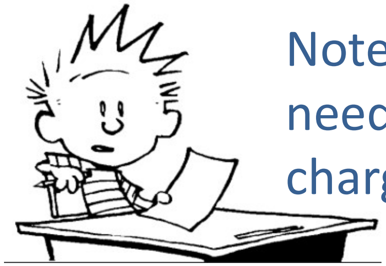
Zeroeth law of thermodynamics

When two bodies (A and B) are in thermal equilibrium with a third body (C) separately, then they (A and B) are in thermal equilibrium with each other.



Zeroeth law introduces the concept of temperature (T) .

Thermal equilibrium : A state where two or more systems are at the same temperature, resulting in no net flow of heat between them.



Note that for bodies to be in thermal equilibrium *ONLY TEMPERATURE* needs to be the same. Anything else (size, shape, volume, density, mass, charge, …may be different !

Heat (Q)

- Heat is a form of energy in transit
- Heat flows from a region of higher temperature to a region of lower temperature
- SI unit of heat energy is joule (J)
- Heat is a path function i.e. it depends of the path of evolution of the system

Diathermic wall	: Allows flow of heat through it
Adiabatic wall	: Does not allow flow of heat through it

Specific calorie

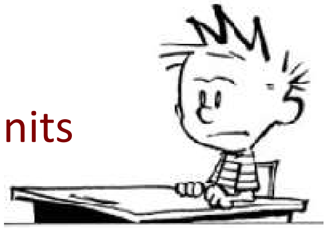
It is the amount of heat required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C.

Mechanical equivalent of heat

It is the amount of work done to produce 1 calorie of heat.

1 calorie = 4.186 joules

Since heat and work are now known to be equivalent, they have same units in SI and mechanical equivalent of heat is redundant.



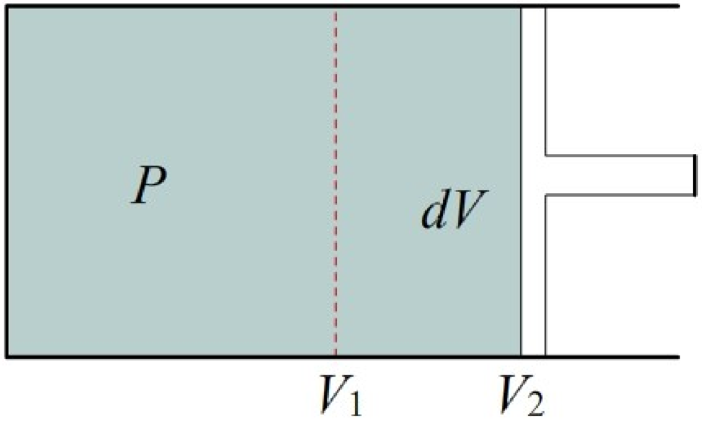
Internal energy (U)

- It is the sum of kinetic energies and potential energies of ALL the constituent particles (atoms/molecules) of the system.
- The above mentioned energy is from the frame of reference in which the centre of mass of the system is at rest.
- Internal energy is a state function i.e. its value depends on the initial and final states of the system and not on path of evolution of the system.

$$\mathrm{d}U = nC_{\mathrm{V}}\,\mathrm{d}T$$

Work done in a thermodynamic process

Consider a certain volume of an ideal gas enclosed in a cylinder fitted with a movable piston. Let A be the area of cross-section of the piston and P be the pressure. All surfaces in contact are assumed to be of negligible friction.



Work done by a force causing a displacement is given by

$$\mathrm{d}W = F \bullet \mathrm{d}s$$

As the piston moves only along the x-direction, we get

$$\mathrm{d}W = F\,\mathrm{d}x \quad \text{— i}$$

Pressure and force are related as

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

$$\Rightarrow F = PA \quad \text{— ii}$$

Substituting this in equation (i) we get

$$\mathrm{d}W = PA\,\mathrm{d}x$$

$A\mathrm{d}x$ is change in volume of the gas therefore

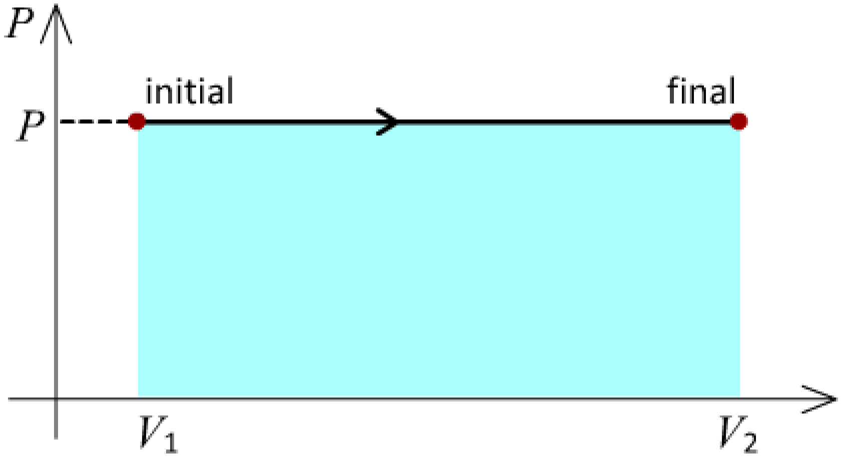
$$\boxed{\mathrm{d}W = P\,\mathrm{d}V}$$

Work done in a thermodynamic process

If pressure remains constant during change in volume then the work done is given by

$$dW = P\,dV$$

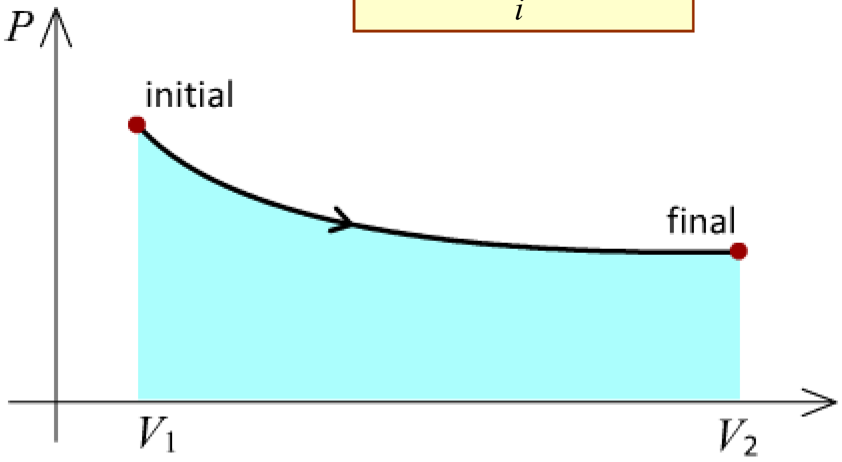
$$\boxed{W = P(V_f - V_i)}$$



If pressure does not remain constant during the change in volume then the work done is give by

$$dW = P\,dV$$

$$\boxed{W = \int_i^f P\,dV}$$



Work done in a thermodynamic process is given by area under (or the area enclosed by) the PV graph

Work done (dW)

d$W = P$dV

dW may be +ve, zero or -ve

dW is a path function i.e. it depends on the path of evolution of the system

Heat exchanged (dQ)

d$Q = n\ C$ dT

dQ may be +ve, zero or -ve

dQ is a path function i.e. it depends on the path of evolution of the system .

Internal energy (dU)

d$U = n\ C_V$ dT

dU : may be +ve, zero or -ve.

dU is a state function and does not depend on path of evolution .

First law of thermodynamics

Heat energy (dQ) supplied to a system equal to the sum of change in internal energy (dU) and work done (dW) by the system .

$$\boxed{\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W}$$

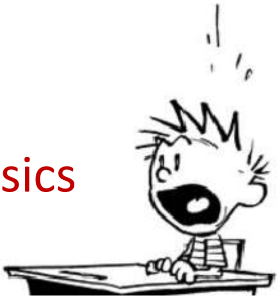
- First law of thermodynamics is based on the law of conservation of energy
- First law is used to define internal energy in terms of heat supplied and the work done

First law of thermodynamics

Sign convention

- Heat given to a system is considered positive and heat given out by system is considered negative
- Work done on the system is considered negative and work done by the system is considered positive
- Change in internal energy depends on change in temperature of the system

Sign convention in Physics is ***different*** from that in chemistry. In physics remember that the entire idea is to make a **better heat engine.**



Work done in an isothermal process

Consider n moles of an ideal gas at absolute temperature T. Let initial pressure and volume of the gas be P_1 and V_1 respectively and let V_2 and P_2 be its final volume and pressure as it undergoes isothermal expansion.

Work done in a thermodynamic process is given by the relation

$$\mathrm{d}W = P\,\mathrm{d}V \qquad \text{i}$$

Using ideal gas equation we get

$$PV = nRT$$

$$\Rightarrow \quad P = \frac{nRT}{V} \qquad \text{ii}$$

Substituting this in equation (i) we get

$$\mathrm{d}W = \frac{nRT}{V}\mathrm{d}V$$

Total work done by the gas as it expands from V_1 to V_2, is obtained by integrating $\mathrm{d}W$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V$$

$$W = nRT\int_{V_1}^{V_2} \frac{1}{V}\mathrm{d}V$$

$$W = nRT\left[\log_e V\right]_{V_1}^{V_2}$$

$$\boxed{W = 2.3026\, nRT \log_{10}\left[\frac{V_2}{V_1}\right]}$$

or

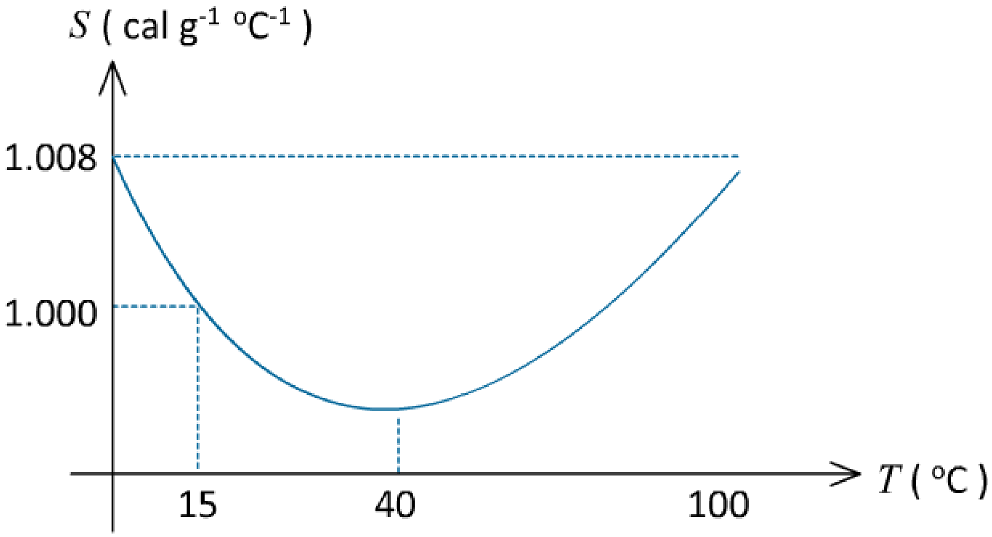
$$\boxed{W = 2.3026\, nRT \log_{10}\left[\frac{P_1}{P_2}\right]}$$

Specific heat (C)

The amount of heat required to raise the temperature of unit mass of a substance by 1 degree.

Specific heat capacity depends on the nature of material and the scale of temperature used.

Specific heat of a material may not be constant over a range of temperature.
Graph of specific heat of water, as a function of temperature, indicates that the specific heat of a material is not constant.



Application of specific heat : Coolant in a nuclear reactor should have high specific heat capacity. Such a coolant absorbs large amount of heat for a given change in temperature and is thus useful in draining out the heat from the reactor.

Molar specific heat at constant pressure (C_P)

The amount of heat required to raise the temperature of 1 mole of a substance by 1 degree at constant pressure.

Molar specific heat at constant volume (C_V)

The amount of heat required to raise the temperature of 1 mole of a substance by 1 degree at constant volume.

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

Specific heat capacities depend on the nature of the material.

Type of gas	C_V	C_P	γ
Monoatomic	3R/2	5R/2	5/3
Diatomic	5R/2	7R/2	7/5
Polyatomic*	3R	4	4/3

Relation between C_P and C_V

Consider a system of n moles of an ideal gas.
When heat is supplied to the system at constant volume there is no work done by the system (as $\mathrm{d}V = 0$). All the heat supplied causes an increase in the internal energy and thereby results in increase in temperature.

$$\mathrm{d}Q = \mathrm{d}U$$

$$nC_V\,\mathrm{d}T = \mathrm{d}U$$

When heat is supplied to the system at constant pressure, there is work done by the system (as $\mathrm{d}V \neq 0$). Only a part of the heat supplied causes an increase in the internal energy and hence more heat energy is required to cause the same increase in temperature.

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W$$

$$nC_P\,\mathrm{d}T = \mathrm{d}U + \mathrm{d}W$$

Therefore to cause the same temperature change in a system, heat required at constant pressure is more than the heat required at constant volume.
Hence $C_P > C_V$.

Relation between C_P and C_V

Consider a system of n moles of an ideal gas. Let heat be supplied to it at constant volume resulting a change in temperature ($\mathrm{d}T$). Using 1st law of thermodynamics

$$\mathrm{d}Q = \mathrm{d}U + 0 \longrightarrow \boxed{\text{i}}$$

Heat required for this process is given by

$$\mathrm{d}Q = nC_V\mathrm{d}T$$

Therefore

$$\mathrm{d}U = nC_V\mathrm{d}T \longrightarrow \boxed{\text{ii}}$$

Let the heat be now supplied to the same system at constant pressure resulting same change in temperature.

$$\mathrm{d}Q = \mathrm{d}U + P\mathrm{d}V$$

Heat required for this process is given by

$$\mathrm{d}Q = nC_P\mathrm{d}T$$

Therefore

$$nC_P\mathrm{d}T = \mathrm{d}U + P\mathrm{d}V$$

Using equation (ii) for internal energy

$$nC_P\mathrm{d}T = nC_V\mathrm{d}T + P\mathrm{d}V$$

$$n\mathrm{d}T\,(C_P - C_V) = P\mathrm{d}V \longrightarrow \boxed{\text{iii}}$$

Using ideal gas equation

$$PV = nRT$$

$$P\mathrm{d}V = nR\,\mathrm{d}T$$

Substituting this in equation (iii) we get

$$n\mathrm{d}T\,(C_P - C_V) = nR\mathrm{d}T$$

$$\boxed{C_P - C_V = R}$$

Work done in an adiabatic process

Consider n moles of an ideal gas in a state characterized (T_1, P_1, V_1). As it undergoes adiabatic expansion let its final state be characterized by (T_2, P_2, V_2).

Work done in a thermodynamic process is given by

$$\mathrm{d}W = P\,\mathrm{d}V \quad \text{— i}$$

In an adiabatic process P and V are related as

$$PV^{\gamma} = K \text{ (constant)}$$

$$P = \frac{K}{V^{\gamma}}$$

Substituting this in eq(i) we get

$$\mathrm{d}W = \frac{K}{V^{\gamma}}\,\mathrm{d}V$$

Total work done by the gas is obtained by integration

$$W = \int_{V_1}^{V_2} \frac{K}{V^{\gamma}}\,\mathrm{d}V$$

$$W = K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$W = \frac{K}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$W = \frac{1}{1-\gamma}\left[P_2 V^{\gamma}{}_2 V_2^{1-\gamma} - P_1 V^{\gamma}{}_1 V_1^{1-\gamma}\right]$$

$$\boxed{W = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]}$$

Using ideal gas equation

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

Comparison of slopes in isothermal and adiabatic processes

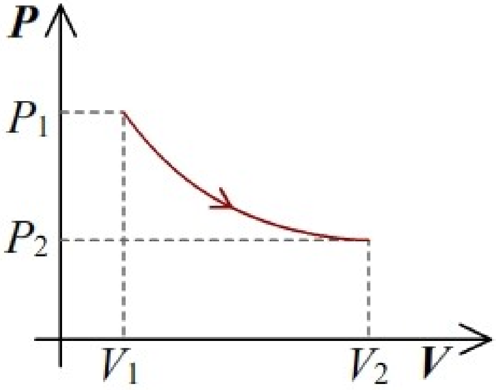
For an isothermal process

$$PV = \text{constant}$$

$$\frac{\mathrm{d}}{\mathrm{d}V}[PV] = 0$$

$$P\frac{\mathrm{d}V}{\mathrm{d}V} + V\frac{\mathrm{d}P}{\mathrm{d}V} = 0$$

$$\frac{\mathrm{d}P}{\mathrm{d}V} = -\frac{P}{V}$$



For an adiabatic process

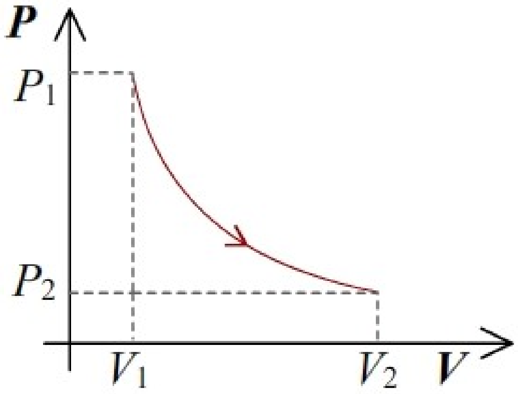
$$PV^{\gamma} = K\ (\text{constant})$$

$$\frac{\mathrm{d}}{\mathrm{d}V}\left[PV^{\gamma}\right] = 0$$

$$P\gamma V^{\gamma\text{-}1} + V^{\gamma}\frac{\mathrm{d}P}{\mathrm{d}V} = 0$$

$$\frac{\mathrm{d}P}{\mathrm{d}V} = -\frac{P\gamma V^{\gamma\text{-}1}}{V^{\gamma}}$$

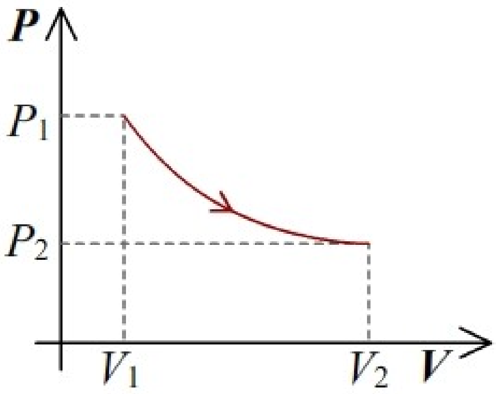
$$\frac{\mathrm{d}P}{\mathrm{d}V} = -\gamma\frac{P}{V}$$



Thermodynamics

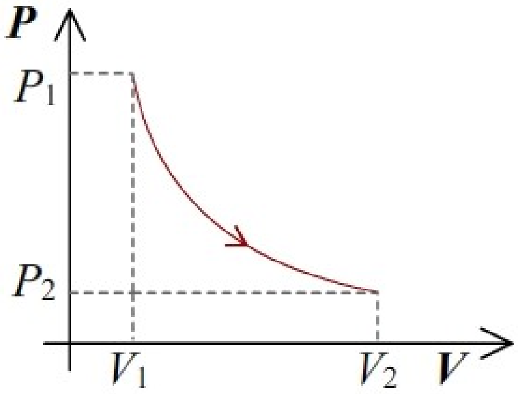
Isothermal process

- No change in temperature ($dT = 0$)
- $dU = 0$
- $dQ = dW$
- PV = constant
- Specific heat is undefined
- Generally a slow process
- $W = 2.3026\, nRT \log_{10}\left[\frac{V_2}{V_1}\right]$
- Slope is $-P/V$



Adiabatic process

- No heat exchanged ($dQ = 0$)
- $dU = -dW$
- $PV^{\gamma} = TV^{\gamma-1} = P^{1-\gamma}T^{\gamma}$ = constant
- Specific heat is zero
- Generally a rapid process
- $W = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$
- Slope is $-\gamma P/V$



Application

Pressure of a system is reduced to 50% using (i) adiabatic process (ii) isothermal process. Which of these result in greater increase in pressure of the system?

In adiabatic process

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

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

$$P_1V_1^{\gamma} = P_2\,{\frac{V_1}{2}}^{\gamma}$$

$$P_2 = 2^{\gamma}P_1$$

In isothermal process

$$PV = \text{constant}$$

$$P_1V_1 = P_2V_2$$

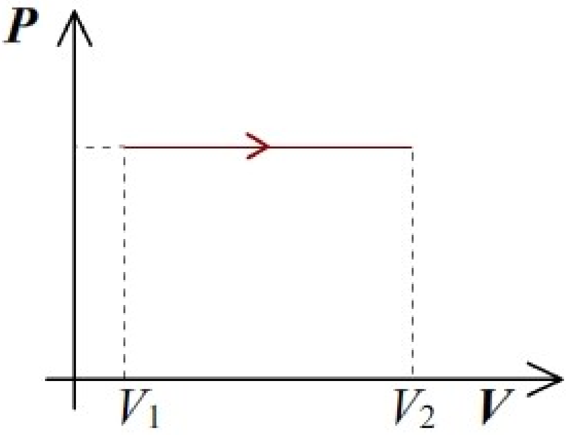
$$P_1V_1 = P_2\,\frac{V_1}{2}$$

$$P_2 = 2P_1$$

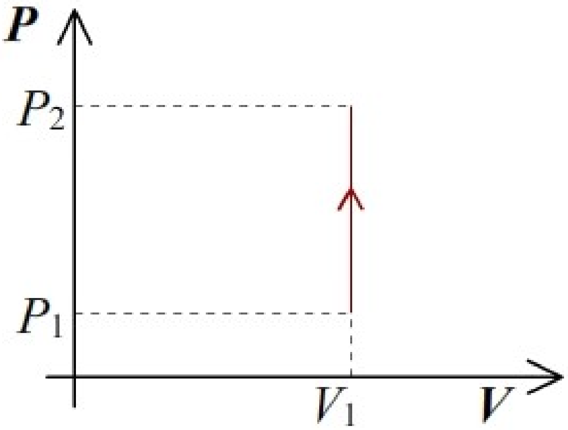
Since γ is always greater than 1 , increase in pressure in adiabatic process is more than that in the isothermal process

Thermodynamics

- **Isobaric process** : A process in which pressure of the system remains constant.
- dW by system is the maximum
- dU is the minimum

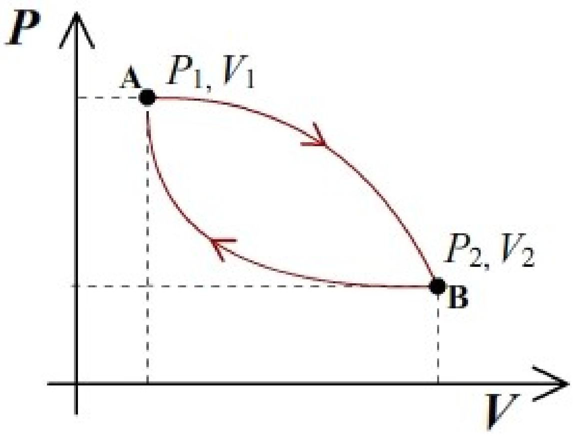


- **Isochoric process** : A process in which volume of the system remains constant.
- dW by the system is zero
- dU is the maximum



Thermodynamics

- **Cyclic process** : A process in which the system returns to its initial state.
- dU = 0
- dW may be 0, +ve or –ve



- **Non-cyclic process** : A process in which the system retraces its path of evolution
- dU may not be zero
- dW may not be zero

A process is reversible if it can be reversed such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. Spontaneous processes of nature are irreversible. An idealized reversible process is a quasi-static process with no dissipative factors such as friction, viscosity, etc.

- **Irreversible process** :

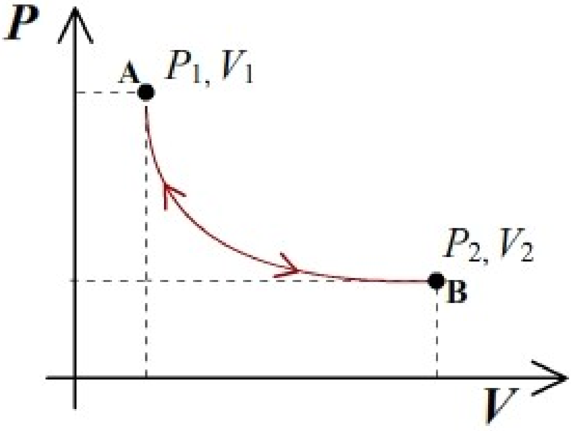
  Irreversible processes involve finite gradients (rapid expansion), generating entropy and cannot be perfectly reversed.

- **Reversible process** :

  Reversible processes occur infinitely slowly through equilibrium states, allowing exact reversal without net changes to system or surroundings.

  Reversible are idealized

  $dU = 0, \quad dW = 0$



- **Quasi-static process**

  It is a thermodynamic process that occurs infinitesimally slowly, allowing the system to remain in internal equilibrium at every stage. This ensures state variables like pressure, volume, and temperature are well-defined throughout, as the system passes through a continuous succession of equilibrium states.

  In quasi-static process the first law of thermodynamic process is applicable without any changes .

Day to day applications

In summer, when the valve of a bicycle tube is opened, the escaping air appears cold.

Escaping air from a tube feels cold due to adiabatic expansion. Inside the tube, warm summer air suddenly expands into lower pressure, performing work on surroundings. No heat enters the system, so internal energy drops, cooling the air significantly.

Why does the brake drum of an automobile get heated up while moving down at constant speed?

The brake drum of an automobile heats up while moving downhill at constant speed because friction between the brake shoes and drum. Due to the incline, the speed of the vehicle tends to increase due to gravity. Breaks are applied to counter this force. Continuous friction from breaks generates heat temperature to rise.

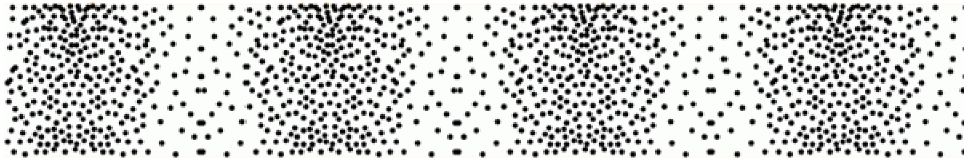
Day to day applications

A thermos flask containing a liquid is shaken vigorously. What happens to its temperature?

The liquid's temperature increases slightly because mechanical work done during shaking converts to internal energy in the thermally insulated system, raising molecular kinetic energy. The change is small but positive.

A sound wave is sent into a gas pipe. Does its internal energy change?

Yes. Sound wave is generated by a source that generates vibrations in the air column. These produce small, rapid changes of pressure and density. As these changes are adiabatic, they cause a increase in temperature hence its internal energy.



Concept, design and development by

Sigma

Physics resource centre

sigmaprc@gmail.com

sigmaprc.in