

1st Law of Thermodynamics

I^{st} Law For a Closed System:

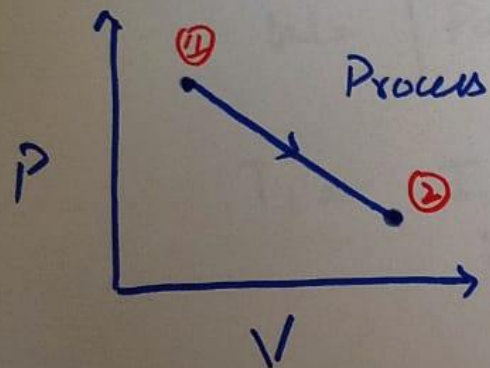
Examples: Sun, Piston Cylinder arrangement
without valves

Thermodynamic Cycle:

\Rightarrow Set of processes so arranged that initial and final state are the same

\rightarrow The change in a thermodynamic property is zero in a thermodynamic cycle

\Rightarrow Initial and Final state are same.



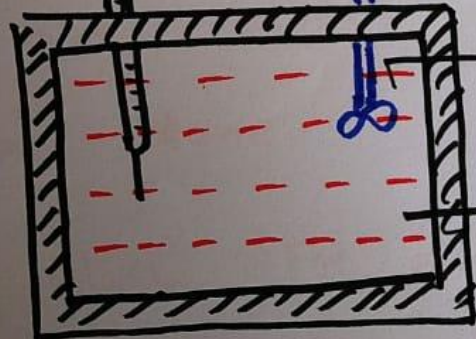
Thermodynamic Process

Ist Law For a closed system

Joule's Experiment
Conservation of Energy Proof

undergoing a cycle

Thermometer



Fluid = Mercury

$$Q = 0$$

①

h

②

P

Adiabatic Wall

Rigid
 $\Delta V = 0$
 $V = C$

$$W = \int P dV = 0$$

$T_1 =$ Initial temperature
of Hg

$$T_1 = T_{atm} \text{ (atmospheric temperature)}$$

Displacement work $\int P dV = 0$

But there are other forms of work
that can be done

Stirring work For e.g.

$$W = mgh$$

Shaft work

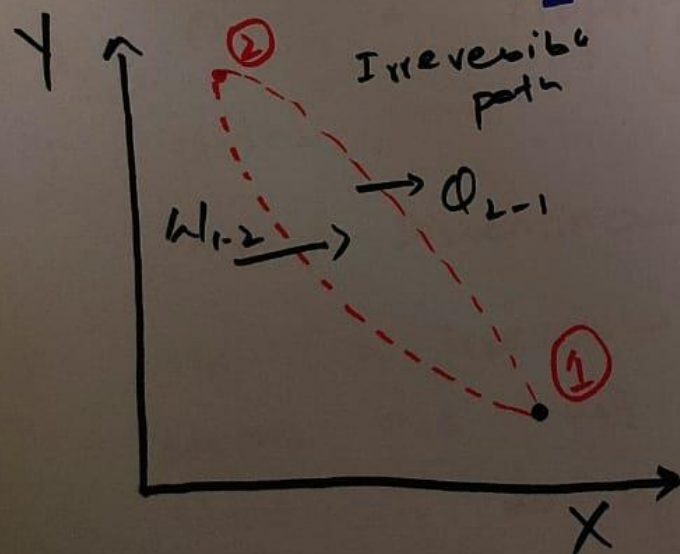
$$W = T\theta$$

$$W = mgh = T\theta$$

Work done on the system

Final temperature = T_2

$$T_2 > T_1$$



Mechanical work gave rise in K.E of the system which in turn has increased the temperature of the system. (4)

Remember:

- => Stirring Work is a rapid / spontaneous process.
- => That is why b/w Final and initial states are not in equilibrium.
- => Intermediate states are not in equilibrium
- => Irreversible Process
- => On a Property Diagram Irreversible paths are represented in dotted lines / Discontinuous lines
- => In an irreversible process intermediate states are not easily determined because there is no equilibrium.

Joule did this experiment with different setups. By changing fluids, Mechanical work setups, Electric work setups.

He found out the amount of work he puts into a system it is received back in the amount of heat. Irrespective of process either reversible & irreversible.

$$W_{1-2} \propto Q_{2-1} \quad \checkmark$$

$$Q_{1-2} \propto W_{2-1} \quad (\text{Not exact})$$

amount

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The concept of high grade energy & low grade energy was devised.

$$\sum W < \sum Q$$

$$\oint dW = \oint dQ$$

$$W_{\text{net}} = Q_{\text{net}}$$

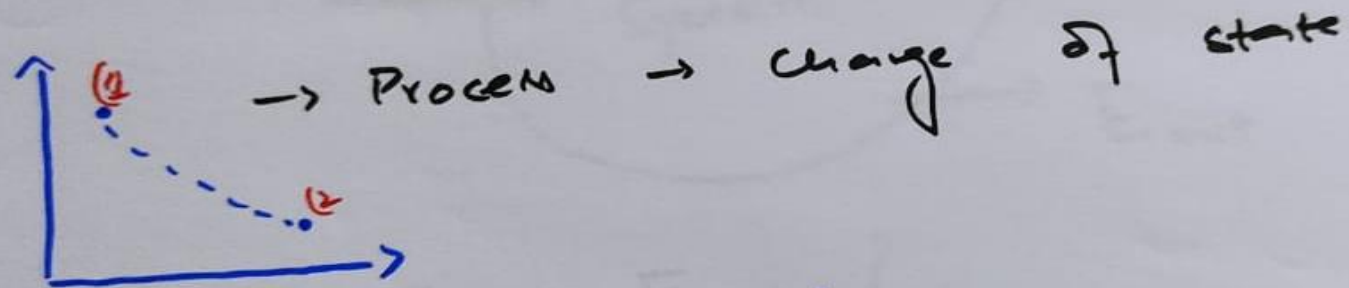
In a cycle.

$$\boxed{\oint dW = \oint dQ}$$

Only valid
for a cycle

First law of thermodynamics for a closed system undergoing a process.

$$\oint dW = \oint dQ \rightarrow \text{Cycle}$$

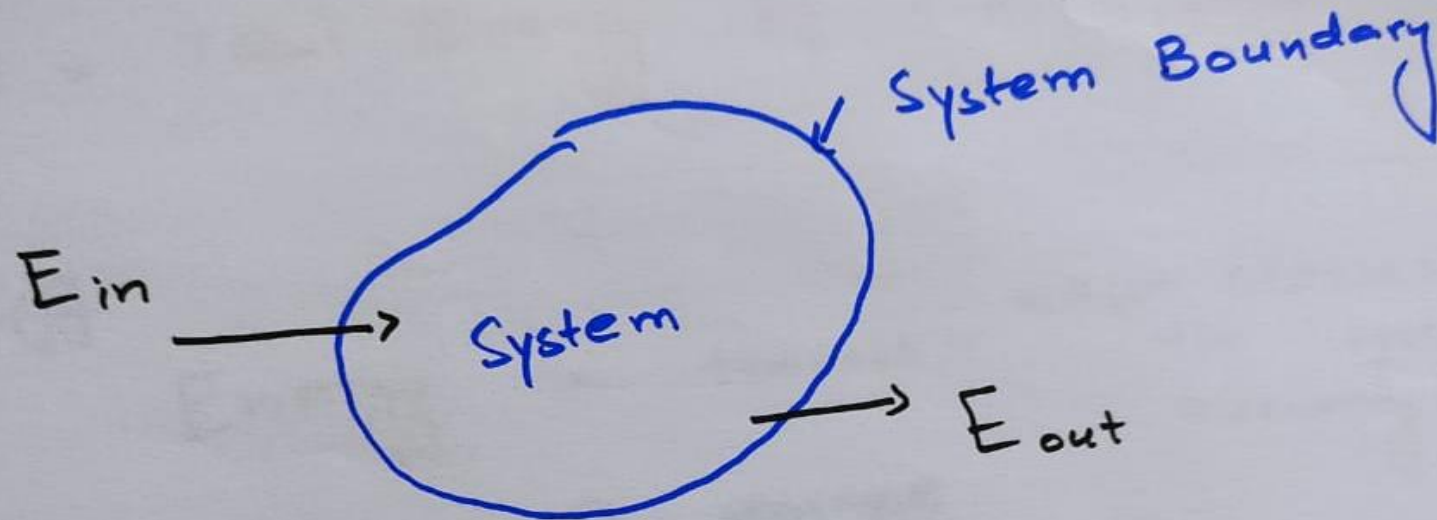


By Joule's Experiment: Conclusion

Work can ~~not~~ be completely converted to heat, but heat cannot be completely converted to work.

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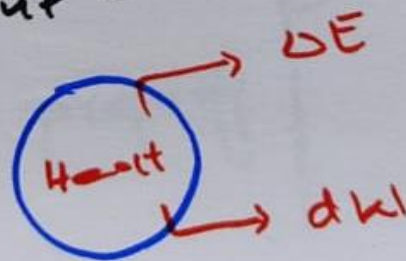
ENERGY BALANCE



$$E_{in} > E_{out} ?$$

$$E_{in} - E_{out} = \Delta E$$

← Stored Energy



$$\Phi_{1-2} = W_{1-2} + \Delta E$$

ΔE = Total Energy of the system : property

Energy:

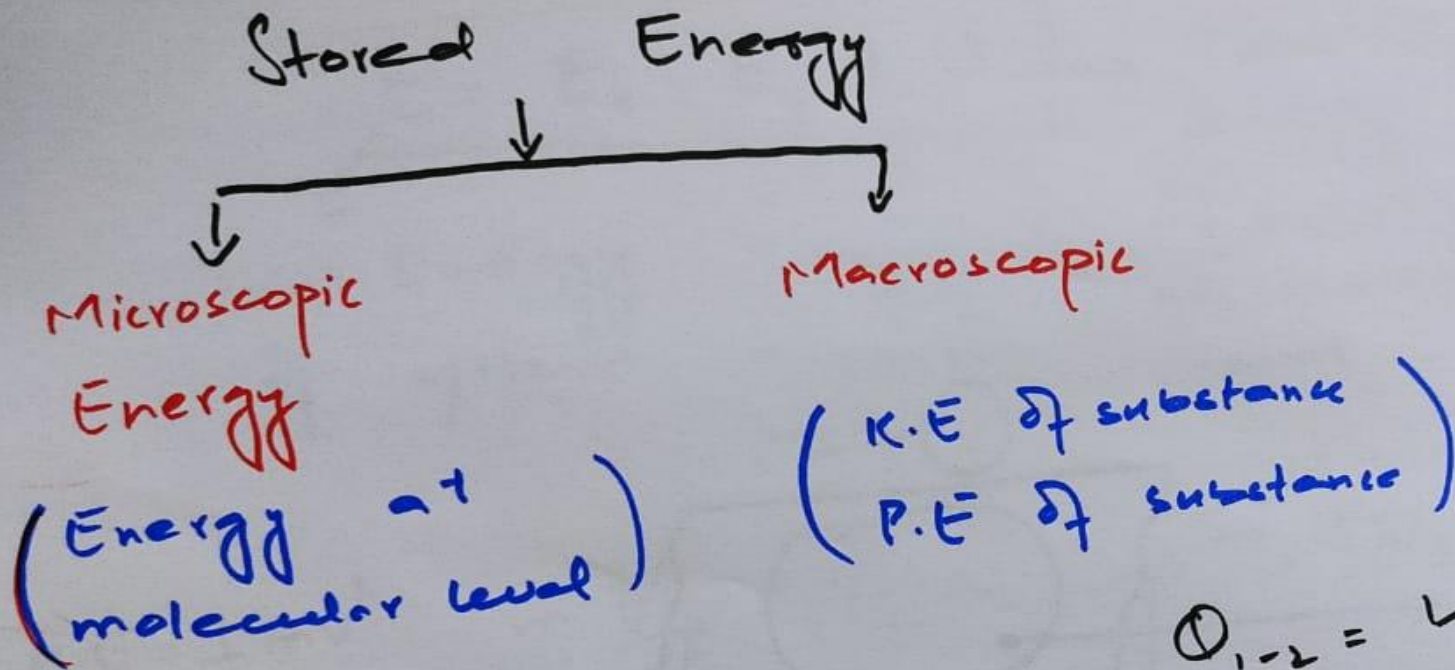
Energy in transit → which crosses the system's boundary
 Energy of storage

→ Path Function
 → Inexact Differential
 → They are not property of system

} Energies in transit

Heat

Work



* K.E exist in both in microscopic stored energies as well as macroscopic stored energies.

$$Q_{1-2} = W_{1-2} + \Delta E$$

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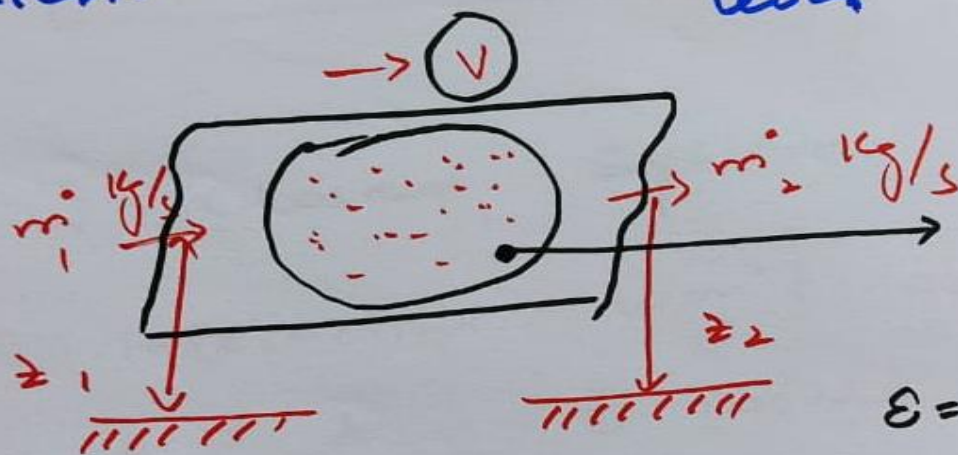
graph TD
    Q12["Q_{1-2} = W_{1-2} + ΔE"] --> ME1[Microscopic]
    Q12 --> M1[Macroscopic]
    ME1 --> IE[Internal Energy]
  
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$$E = E_k + E_p + U$$

Total Energy of system
 Total Energy of substance at molecular level

$$K.E = \frac{1}{2}mv^2$$

$$P.E = mg(z_2 - z_1)$$



E = Energy of one molecule

$$E = E_{\text{tran}} + E_{\text{rot}} + E_{\text{chem}} + E_{\text{electron}} + E_{\text{nuclear}}$$

neglected

if system's P.E & K.E are

$$\Delta E = \Delta U$$

$$Q_{1-2} = W_{1-2} + \Delta E$$

In differential form

Process $\boxed{dQ = dE + dW}$

→ This equation is valid for open as well as closed system.

For a closed system

Mass interaction won't exist

So K.E & P.E would be zero

So :-

$$\Rightarrow \Delta E = \Delta U$$

For a closed system

$$\boxed{dQ = \Delta U + dW}$$

if there are "N" number of molecules

$$U = N\varepsilon$$

Internal energy
of the substance

so

$$dQ = dE + dW$$

→ Open & closed ✓
system

↳ Reversible as well
as irreversible process

$$dQ = dU + dW$$

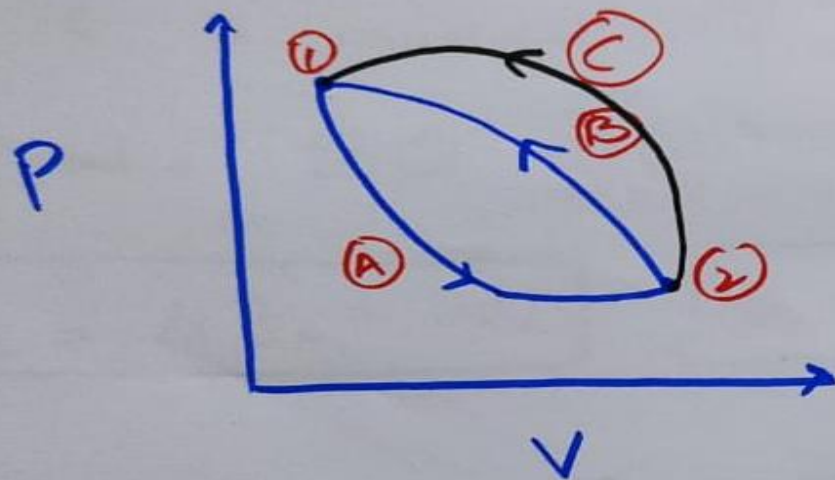
→ For a closed
system

U (For an Ideal gas)

Internal Energy of an Ideal gas

$$U = f(T)$$

Energy as property of system



A & B

$$\boxed{Q_A = \Delta E_A + W_A} \Rightarrow Q_A - W_A = \Delta E_A$$

$$Q_B - W_B = \Delta E_B \quad \boxed{Q_B = \Delta E_B + W_B} \quad \Sigma W = \Sigma Q$$

$$\boxed{W_A + W_B = Q_A + Q_B} \quad \boxed{Q_A - W_A = W_B - Q_B}$$

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$$\boxed{\Delta E_A = -\Delta E_B} \quad \text{--- (1)}$$

Process C is involved iff

A & C

$$\sum |w| = \sum Q$$

$$\boxed{Q_C = \Delta E_C + W_C}$$

$$\boxed{Q_C - W_C = \Delta E_C}$$

$$W_A + W_C = Q_A + Q_C$$

$$W_A - Q_A = Q_C - W_C$$

$$\boxed{\Delta E_A = -\Delta E_C} \quad \text{--- (2)}$$

$$\textcircled{1} \& \textcircled{2}$$

$$\boxed{+\Delta E_B = +\Delta E_C} \quad \text{--- (3)}$$

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$$\Delta E_A = \Delta E_B = \Delta E_C$$

it means whatever the path followed
b/w state ① & ②.
change in total energy is coming
out to be same.

$$\text{Stored Energy} = E_K + E_P + U$$

A point function
Exact Differential
That's why it is the property of
a system.

For a closed system

$$dQ = dU + dW$$

✓ it can be a sum of all type of works.

$$dW = dW_{Pdv} + dW_{shaft} + dW_{electric}.$$

$$dW = dW_{Pdv}$$

if all other types
of work are neglected
i.e. mechanical or electrical
work.

$$\boxed{dQ = dU + PdV}$$

Differential form of 1st Law for
a closed system involving only PdV
work.

For an Isochoric Process

1st Law analysis

$$dQ = dU + P dV = 0 \quad V = C$$

$$dQ = dU$$

$$Q_{1-2} = \Delta U$$

Heat transfer is equal to change in internal energy for an isochoric process.

Specific Internal Energy

Internal energy of 1 kg of substance

U/kg of substance

u → sp. Internal Energy

unit J/kg

$$\boxed{Q_{1-2} = \Delta U} \quad \text{KJ/kg or J/kg} \quad (\text{Isochoric Process})$$

Specific Heat at Constant Volume : C_v

Heat required to cause unit change in temperature in a unit quantity of substance at constant volume.

$$\boxed{C_p > C_v}$$

For constant volume process

$$\boxed{dQ = \Delta U}$$

Change in specific Internal energy

$$C_v = \left(\frac{dQ}{dT} \right)_v$$

$$\left(C_v = \frac{du}{dT} \right)_v$$

Heat required to cause a unit change in temperature.

$$dU = c_v dT$$

$$u_2 - u_1 = c_v (T_2 - T_1)$$

$$\boxed{\Delta u = c_v \Delta T}$$

Specific

Internal

Energy



For m kg of mass

$$\boxed{\Delta U = m c_v \Delta T}$$

$$\therefore \boxed{Q = \Delta U}$$

$$\boxed{Q = m c_v \Delta T}$$

For an Isochoric process

The formula for heat transfer

ENTHALPY "H" (Property of a system)

Total Heat content of a system at a particular state.

Unit KJ, J

For one kg of matter

Specific Enthalpy "h" J/kg, KJ/kg

$$H = U + PV \rightarrow \text{Flow Work}$$

For 1 kg of substance

$$h = u + Pv \rightarrow \text{Flow Work per kg}$$

Heat transfer for an Isobaric process
For a closed system

$$dQ = dU + dW$$

$$dW = dW_{pdu} + dW_{mech} + dW_{electr} \dots \dots$$

if no work other than PdV work

$$dQ = dU + PdV$$

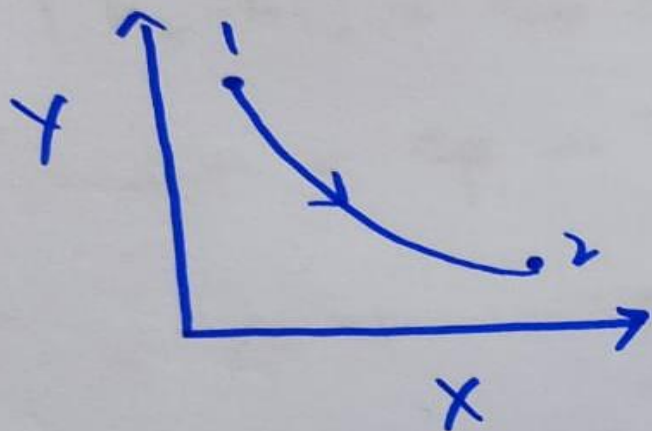
Isobaric
Process

$$P = C$$

$$dQ = dU + d(PV)$$

$$\frac{dQ}{1} = d(u + Pv)$$
$$\boxed{dQ = dh}$$

For one kg of
substance undergoing
an isobaric process
in a closed
system.



$$Q_{12} = \Delta h$$

Heat transfer is equal to change in enthalpy for an isobaric process in a closed system

Specific heat at constant pressure: C_p

Heat required to cause a unit change in temperature for a unit quantity of substance through a constant pressure process.

$$C_p = \left(\frac{dQ}{dT} \right)_P \rightarrow J/kg$$

$$C_p = \left(\frac{dh}{dT} \right)_P$$

$$dh = C_p dT \quad \int_1^2 dh = \int_1^2 C_p dT \quad (24)$$

$$(h_2 - h_1) = c_p \Delta T$$

$$\Delta h = c_p \Delta T$$

$$\boxed{\Delta H = m c_p \Delta T}$$

$$\delta Q = \Delta H$$

For a closed system
undergoing a constant pressure
process.

$$\boxed{\delta Q = m c_p \Delta T}$$



Heat transfer formulas :-

Isobaric Process

$$Q = m c_p \Delta T$$

Isochoric Process

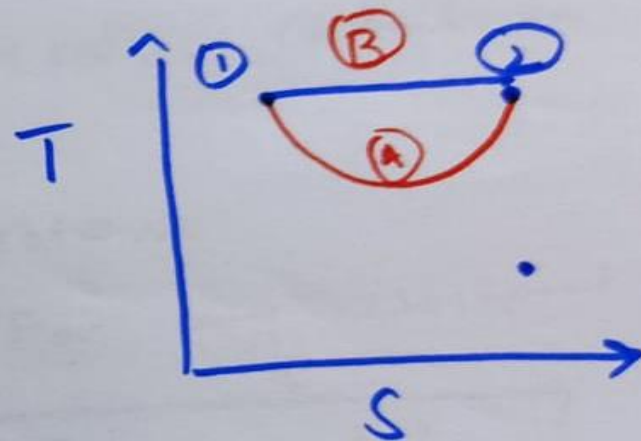
$$Q = m c_v \Delta T$$

Isothermal Process :-

$$T = C$$

For an Ideal gas

$PV = C$ \rightarrow Hyperbolic equation/relationship



B is isothermal
A is not isothermal
path

$$PV = C$$

→ For ideal gas this relation only represents an Isothermal process.

→ But for pure substances or real gases this $PV = C$ is a hyperbolic relation.

$$\boxed{Q_{12} = \Delta U + W_{12}}$$

closed system

For any isothermal process

$$\boxed{\Delta U = m c_v \Delta T}$$

Hence,

$$\boxed{Q_{12} = W_{12}}$$

$$T = C$$

$$\Delta T = 0$$

$$\Delta U = 0$$

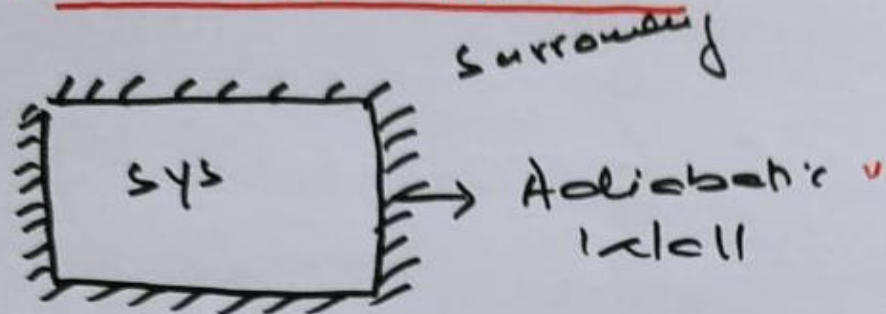
$$W_{1-2} = P_1 V_1 \ln V_2/V_1 = Q_{1-2}$$

$$\text{or } P_1 V_1 \ln P_1/P_2$$

$$\boxed{\text{Same formula}}$$

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Adiabatic Process



$$Q_{1-2} = \Delta U + W_{1-2}$$

$$Q_{1-2} = 0 \quad \text{Adiabatic}$$

$$0 = \Delta U + W_{1-2}$$

$$\boxed{\Delta U = -W_{1-2}}$$

In an adiabatic process if work transfer is taking place it will change the internal energy of the system only!!

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

$$\gamma = C_p / C_v$$

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