

# Thermodynamics

## Introduction

Thermodynamics: Interaction of one body with another in terms of the quantities of heat and work.

↳ Boltz change the internal energy of the system.

(K.E. + P.E.) of all the constituent particles of a system.

$$U = f(T, P/V) \text{ in general.}$$

$$= f(T) \text{ only for ideal gas}$$

Heat is best understood in terms of increase and decrease in temperature of a system, when it is added or removed, respectively, from the system.

Convenient (non-SI unit) unit of Heat: Calorie  $\Rightarrow$  Amount of heat required to raise the temperature of 1 g of water at  $15^\circ\text{C}$  by  $1^\circ\text{C}$ .

Work  $\Rightarrow$  It is best understood in terms of lifting up or lowering down a mass (say,  $m$ ) through a distance (say,  $h$ ) in the surrounding. The magnitude of work involved  $\Rightarrow mgh$ .

## Mechanical equivalent of heat:

Joule's exp<sup>t</sup> establishes that expenditure of a given amount of work, no matter whatever is its origin, always produces the same quantity of heat  $\Rightarrow$

$$4.184 \text{ Joule of work} \equiv 1 \text{ cal of heat.}$$

(+) sign  $\left\{ \begin{array}{l} \text{Heat given to a system} \\ \text{Work done on a system} \end{array} \right\} \rightarrow$  increase  $U$  of this system.

Now, Time is not a thermodynamic variable and hence, thermodynamics cannot give any information regarding time taken for any real process.

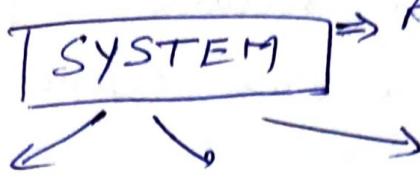
$\Rightarrow$  Combination of  $T & P$  thermodynamically feasible  $\Rightarrow$  but requires infinite time without any external excitation.

$\Rightarrow$  If water at  $-10^\circ C$  and  $0.1 \text{ MPa}$  pressure is unstable with respect to ice at that  $T & P$ . Still, water can be supercooled to  $-10^\circ C$  and  $0.1 \text{ MPa}$  pressure and be maintained at that  $T & P$  for a long time.

$$\boxed{\begin{aligned} 1 \text{ atm} &\equiv 0.1013 \text{ MPa} = 101.3 \text{ kPa} \\ 1 \text{ atm} &\equiv 1.013 \text{ bar} \quad || \quad 1 \text{ bar} = 0.1 \text{ MPa.} \\ 1 \text{ atm} &\equiv 14.69 \text{ psi} [\text{Pound per sq inch}] \end{aligned}}$$

(3)

## Basic Definitions:



A region in space under investigation

Closed System

(No exchange of matter)

[Earth or a frying pan on a stove with a closed lid]  
Simple water bottle.

piston cylinder arrangement without valve

Open System

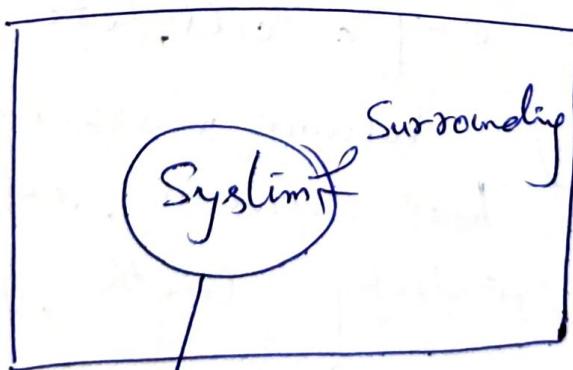
(Both matter & energy can be exchanged b/w sys. & surr.)

[Living organism  
Turbine, Compressor, pump, Boiler]

Isolated system

No exchange of matter nor energy.

[Thermos Flask, (approximate approach)]



System + surr.  
+ Universe  
which has nothing outside it & interact  $\Rightarrow$   
Isolated system.

Imaginary

Boundary  
Real  
Diathermal      Adiabatic

## State Variables / properties

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By specifying the values of only a few state variables, we can define the state of the system.

e.g. To define an ideal gas system we need to define only  $T, P, V$ . Other variables like amount of gas, density etc. will automatically be defined and need not be stated.

Intensive property :  $T, P, \text{concentration}$ , density, dipole-moment, viscosity, surface tension, molar volume, molar entropy, dielectric constant, specific heat capacity, emf of a cell, etc.

Extensive property : Volume, mass, entropy, heat capacity, enthalpy, entropy, length, free energy.

State function or point function  $\Rightarrow$  change in state function does not depend on the path by which state change has occurred.

Path function or process function  $\Rightarrow$  work ( $w$ ), heat ( $q$ ) and arc length.

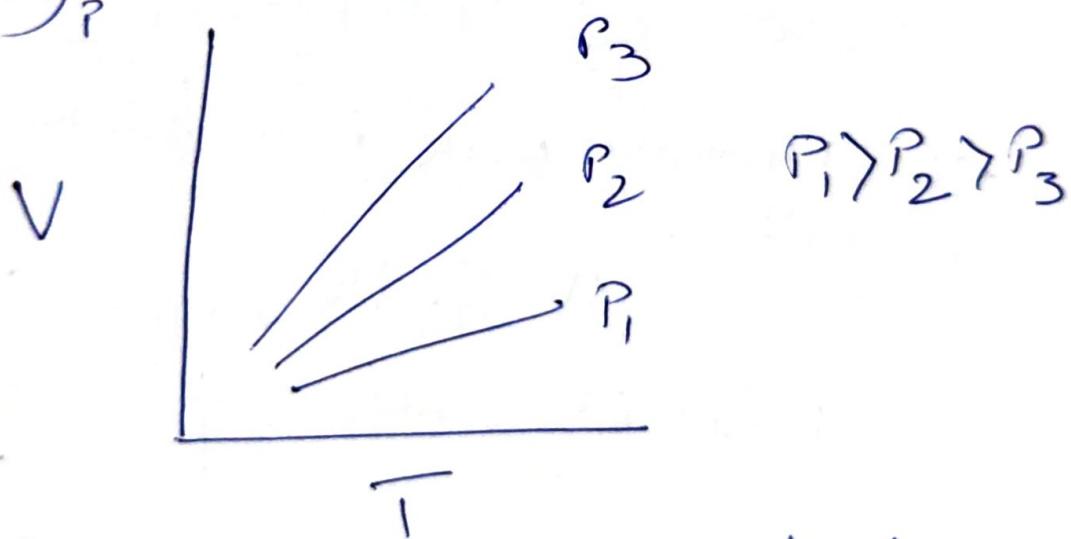
## Properties of thermody fns.

Functions are  $\Rightarrow$  Single valued } well-behaved  
 continuous }  
 differentiable } fns.  
 ↓

1st derivative is also continuous,  
 i.e. fns of the other variable, and  
 thus can be differentiable.

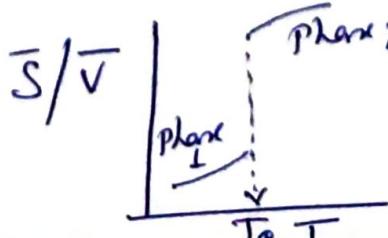
$$\text{e.g., } V = f(T, P)$$

$\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow$  slope  $\rightarrow$  which is a fn of P.



$\left(\frac{\partial^2 V}{\partial T \cdot \partial P}\right) \Rightarrow$  called fluctuation.

In case of 1st order phase transition,  
 thermody fns are like (V, S, H, U) are  
 double valued at the vicinity of phase  
 transition.

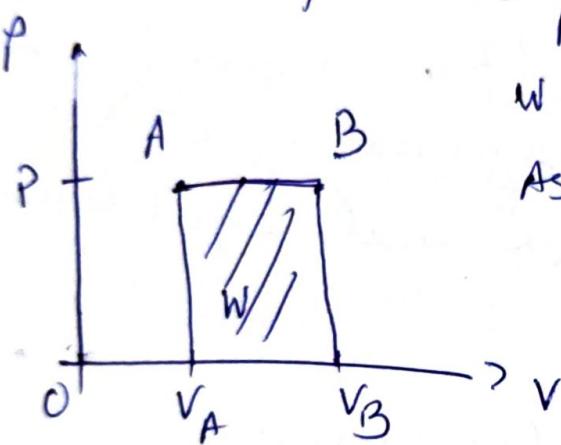


Each phase has  
 a different value  
 of these fns.

Process: By which state of a system is changed. (7)

- i) Isothermal process  $\Rightarrow$  using diathermal wall.  
( $T \text{ const}$ )
- ii) Adiabatic process . using adiabatic wall.  
(Ad. expansion  
for closed system  $\Rightarrow T$  falls)  
Ad. compression  $\Rightarrow T$  increases.  
(for closed system)

- iii) Isobaric process ( $P \text{ const}$ ):



P-V work in a closed system

$$W = \int P \cdot dV$$

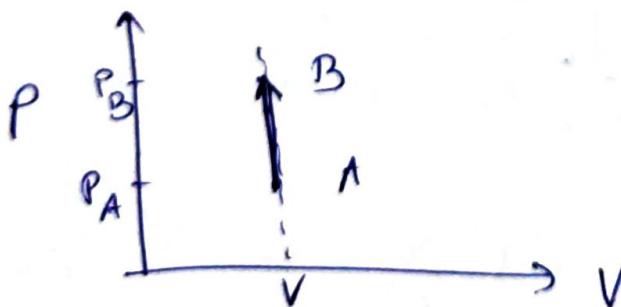
As  $P$  is const here,

$$W = P \Delta V$$

For ideal gr.

$$\frac{W}{P} = nR\Delta T$$

- iv) Isochoric process ( $V \text{ const}$ )



$$dW = P \cdot dV = 0.$$

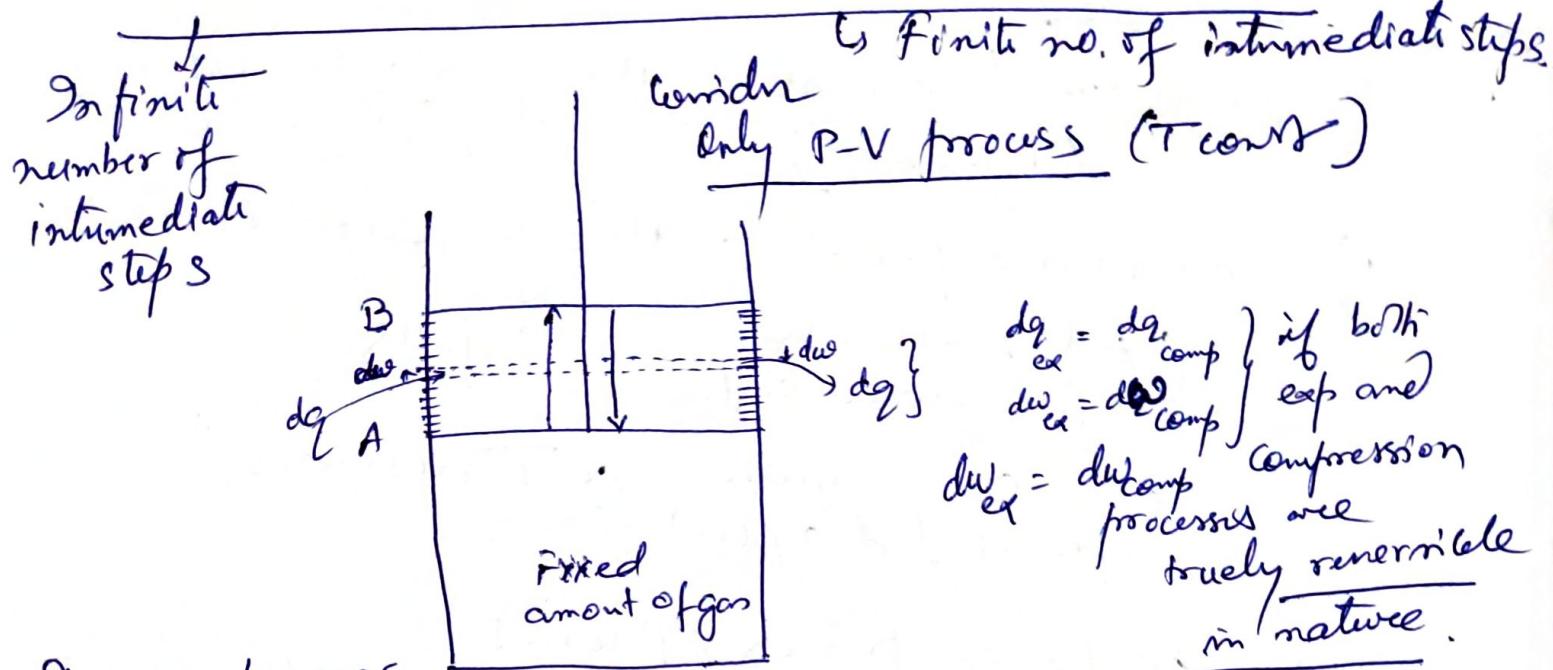
$$\therefore \underline{dQ = dU}$$

e.g. ideal Otto cycle

where, gasoline-air mixture is burnt in a car's engine . The  $P$  of the gas inside the engine increases while maintaining the volume of the gas exactly the same.

- ⑤ Cyclic Process:  $\oint dx = 0$ ;  $x$  is a state func

# Reversible Vs. IRREVERSIBLE process



## Reversible process

Each intermediate step is sufficiently slow that the system gets sufficient time to maintain thermal and mechanical equilibrium with the surrounding.

For an irreversible process :

Work done on compression & bring back the system in original state is more than the work done by the system during expansion.

$\therefore$  For Rev P-V process:  $\oint \frac{W}{\text{Total}} = 0$   
(exp. + comp)

$$q_{\text{total}} = 0$$

For irrev P-V process:

$$\frac{W}{\text{total}} \Rightarrow (+)$$

$$q_{\text{total}} \Rightarrow (-)$$

## Some mathematical properties of State funs:

Let  $z = f(x, y)$

when  $z$  is a state fun,  $dz \Rightarrow$  exact differential.

Exactness is tested by the following relation :

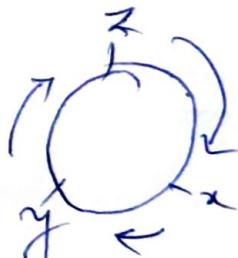
$$\frac{\partial^2 z}{\partial x \cdot \partial y} = \frac{\partial^2 z}{\partial y \cdot \partial x}$$

e.g. For an ideal gas:

$$\frac{\partial}{\partial T} \left( \frac{\partial \bar{V}}{\partial P} \right)_T = \frac{\partial}{\partial P} \left( \frac{\partial \bar{V}}{\partial T} \right)_P = - \frac{R}{P^2}$$

Cyclic Rule:

$$\# \quad \left( \frac{\partial z}{\partial x} \right)_y \cdot \left( \frac{\partial x}{\partial y} \right)_z \cdot \left( \frac{\partial y}{\partial z} \right)_x = -1$$



$$\# \quad \left( \frac{\partial z}{\partial y} \right)_x = \frac{1}{\left( \frac{\partial y}{\partial z} \right)_x}$$

$$\# \quad \left( \frac{\partial x}{\partial y} \right)_z = - \frac{\left( \frac{\partial z}{\partial y} \right)_x}{\left( \frac{\partial z}{\partial x} \right)_y}$$

$$\# \quad \left( \frac{\partial z}{\partial x} \right)_y = \left( \frac{\partial z}{\partial y} \right)_x \cdot \left( \frac{\partial y}{\partial x} \right)_z$$

## Some Applications:

$$\text{Isothermal Compressibility } (\kappa) = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

[ $\kappa = \frac{1}{P}$  for an ideal gas]

$$\text{Coefficient of cubic expansion } (\alpha) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

[ $\alpha = \frac{1}{T}$  for an ideal gas]

$$\text{Pressure coefficient } (\beta) = \left( \frac{\partial P}{\partial T} \right)_V$$

Now: Show that  $\beta = \frac{\alpha}{\kappa}$

Soln:  $V = f(P, T)$

$$\therefore dV = \left( \frac{\partial V}{\partial T} \right)_P \cdot dT + \left( \frac{\partial V}{\partial P} \right)_T \cdot dP$$

Dividing by  $dT$  and specifying const  $V$ ,

$$\Rightarrow 0 = \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial V}{\partial P} \right)_T \cdot \left( \frac{\partial P}{\partial T} \right)_V$$

$$\therefore \left( \frac{\partial P}{\partial T} \right)_V = - \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial V}{\partial P} \right)_T} = - \frac{\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P}{\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T}$$

$$\therefore \boxed{\beta = \frac{\alpha}{\kappa}}$$

HW show that  $P$  is a state func for a gas

bying  $(P + \frac{a}{V^2})V = RT$

## 1st law of Thermodynamics:

Mathematical form:

$$dU = dq + dw$$

$dq \rightarrow (+) \Rightarrow$  Heat absorbed by the system  $\Rightarrow dU \rightarrow (+)$   
(i.e. increases)

$dw \rightarrow (+) \Rightarrow$  Work done by the surrounding on the system  
(compression work)  $\Rightarrow dU \rightarrow (+)$ .

$dw \rightarrow (-) \Rightarrow$  Work done by the system on the surrounding  $\Rightarrow dU \rightarrow (-)$   
(expansion work) (i.e. decreases)

For an isolated system,  $dq = 0$ ;  $dw = 0$ .

[As no interaction b/w the system and surrounding]

Hence, for an isolated system (like Universe)  
 Internal energy  $\downarrow$  is conserved.

$\Rightarrow$  Statement of 1st law of thermodynamics.

## Expression of P-V work done :

Case I Irreversible / spontaneous process:

$$W_{irrev} = -P_{\text{ext}} \cdot \Delta V = -P_f (V_f - V_i)$$

Here, (-) sign denotes work done by the system.

Case II Reversible / Equilibrium process:

Here, opposing pressure is reduced by an infinitesimal small quantity, and hence volume is also increasing by infinitesimal small quantity.

$$dW = - (P - dP) \cdot dV = - P_{\text{int}} dV + \underbrace{dP \cdot dV}_{\text{negligible}}$$

$$\therefore W_{rev} = - \int_{V_1}^{V_2} P_{\text{int}} dV$$

Now, for an ideal gas

$$W_{rev} = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

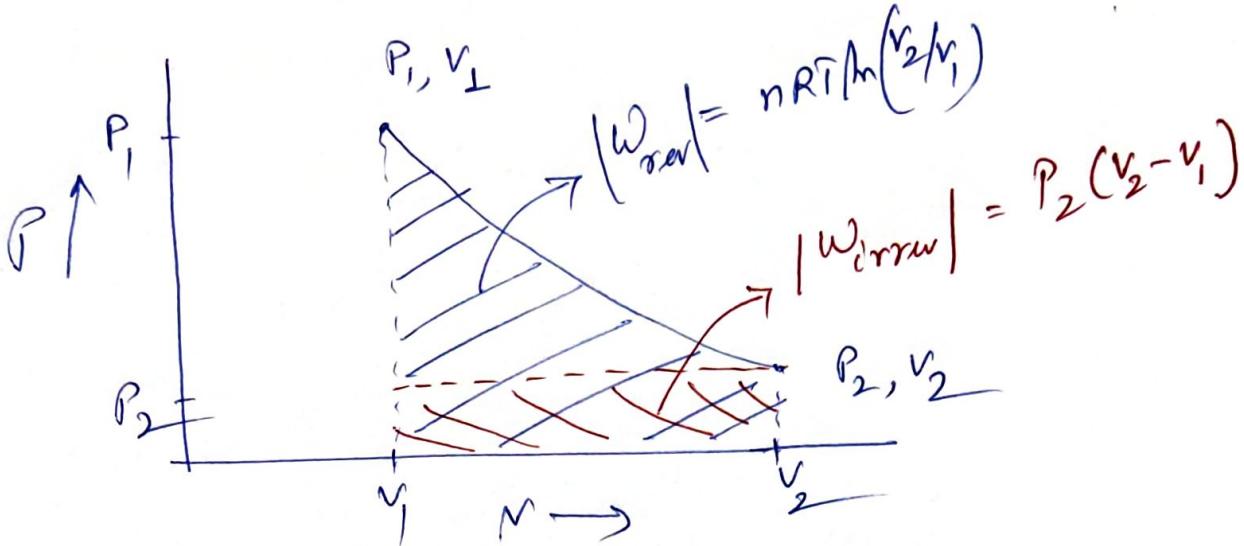
Under isothermal condn:

$$W_{rev, T, \text{ideal gas}} = - nRT \int_{V_1}^{V_2} \frac{dV}{V} = - nRT \ln \left( \frac{V_2}{V_1} \right)$$

H.W Expression of  $W_{rev, T}$  for an van der Waals gas??

$$\left( P + \frac{nra}{V^2} \right) (V - nb) = nRT$$

Show that  $\left(\omega_{\text{rw}, T}\right)_{\text{exp}} > \left(\omega_{\text{irrw}, T}\right)_{\text{exp}}$ . (14)



$$|W_{\text{rw}}| = nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left[1 + \left(\frac{V_2}{V_1} - 1\right)\right]$$

$$\begin{aligned} \ln(1+x) &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} \approx nRT \left(\frac{V_2}{V_1} - 1\right) = \frac{nRT}{V_1} (V_2 - V_1) \\ &= P_1 (V_2 - V_1) \end{aligned}$$

$$|W_{\text{irrw}}| = P_2 (V_2 - V_1)$$

$$\begin{aligned} \therefore |W_{\text{rw}}| - |W_{\text{irrw}}| &= P_1 (V_2 - V_1) - P_2 (V_2 - V_1) \\ &= (V_2 - V_1) (P_1 - P_2) \\ &\Rightarrow (+) \end{aligned}$$

$\therefore |W_{\text{rw}}| > |W_{\text{irrw}}| \text{ on expansion.}$

H.W Only compression  $|W_{\text{irrw}}| > |W_{\text{rw}}|$ .

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Now, consider a <sup>isothermal</sup> cyclic change, i.e. expansion + compression

Both steps are  
Irreversible:

$$(P_1, V_1) \xrightleftharpoons{T \text{ const}} (P_2, V_2)$$

$$W_{\text{exp}} = -P_2(V_2 - V_1) \Rightarrow (-) \quad (V_2 > V_1 \\ P_2 < P_1)$$

$$W_{\text{comp}} = -P_1(V_1 - V_2) \Rightarrow (+)$$

$$\therefore W_{\text{Total}} = (W_{\text{exp}} + W_{\text{comp}}) = -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ = (V_2 - V_1)(P_1 - P_2) \Rightarrow (+).$$

i.e. Surrounding has to do more work to bring back the system to its original state than the work done by the system during expansion.

Case II Reversible change:

$$W_{\text{exp}} = -nRT/m \left( \frac{V_2}{V_1} \right)$$

$$W_{\text{comp}} = -nRT/m \left( \frac{V_1}{V_2} \right)$$

$$\therefore W_{\text{Total}} = 0.$$

## Enthalpy for (H)

1st law:  $dU = dq + dw$ .

Consider P-V work done by the system at const P:  $dw = -P_{\text{ext}} \cdot dV$

For rev. process  $dw = -(P_{\text{int}} - P) dV \approx -P_{\text{int}} \cdot dV$

Hence, for rev P-V work done by the system  $\approx -P_{\text{int}} \cdot dV$   
 $\therefore dU = dq - P \cdot dV$

or,  $dq = dU + P_{\text{int}} \cdot dV$

Integrating betw. two states at const P:

$$\int_{q_1}^{q_2} dq = \int_{V_1}^{V_2} dU + P \int_{V_1}^{V_2} dV$$

$$\begin{aligned} \therefore (q_2 - q_1) &= (U_2 - U_1) + P(V_2 - V_1) \\ &= (U_2 + PV_2) - (U_1 + PV_1) \end{aligned}$$

U, P, V all are state frms.

Hence,  $(U + PV)$  is also a state frm.

Enthalpy,  $H = U + PV$

$$\therefore q_2 - q_1 = H_2 - H_1 ; \quad dH = (dq_{\text{rev}}) \text{ across P.}$$

H.W. All adiabatic processes are not isoenthalpic.

## Isothermal change vs Adiabatic change:

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Consider state change of an ideal gas from state 1 ( $P_1, V_1$ ) to state 2 ( $P_2, V_2$ )

$\Rightarrow$  Isothermal change:  $PV = \text{const}$  at const  $T$

$$\text{i.e. } P_1 V_1 = P_2 V_2$$

$\Rightarrow$  Adiabatic change:  $PV^\gamma = \text{const}$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\begin{aligned} \gamma &= \frac{\bar{C}_P}{\bar{C}_V} \\ \gamma &> 1. \\ \text{As, } \bar{C}_P &> \bar{C}_V \end{aligned}$$

$$\Rightarrow \frac{nRT_1}{V_1} \cdot V_1^\gamma = \frac{nRT_2}{V_2} \cdot V_2^\gamma$$

$$\therefore \frac{T_1 V_1^{\gamma-1}}{T_2 V_2^{\gamma-1}} = \frac{V_2}{V_1}$$

$$TV^{\gamma-1} = \text{const.}$$

QHW What will be relation involving  $P$  and  $T$ ?

Adiabatic change

Now Isothermal change

$$PV = \text{const}$$

$$\therefore P = \frac{\text{const}}{V}$$

$$\therefore \left( \frac{\partial P}{\partial V} \right)_T = - \left( \frac{\text{const}}{V^2} \right) = - \left( \frac{PV}{V^2} \right) = - \left( \frac{P}{V} \right)$$

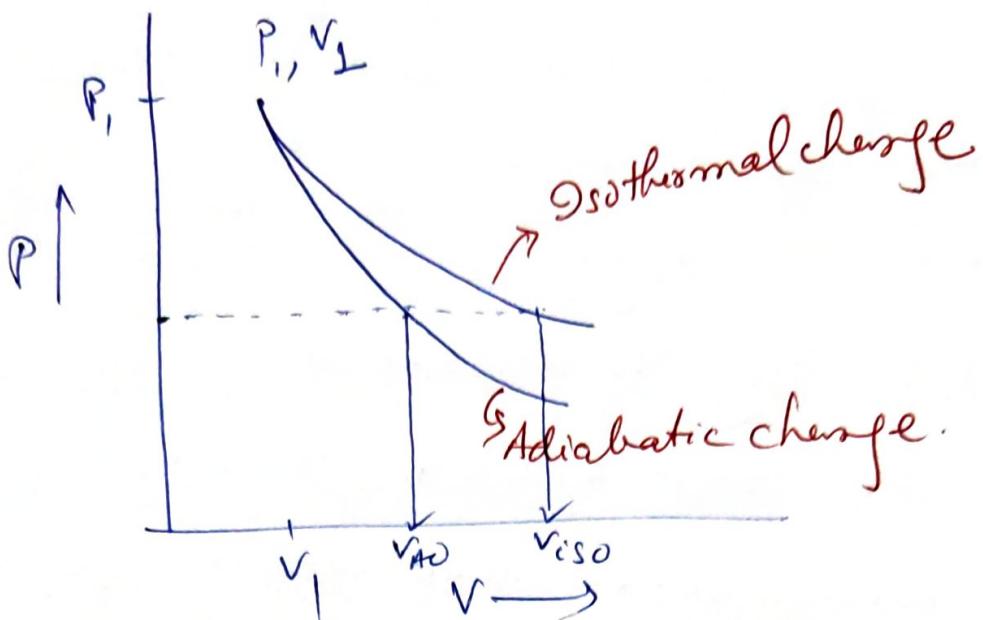
$$PV^{\gamma-1} = \text{const}$$

$$\therefore P = \frac{\text{const}}{V^{\gamma-1}}$$

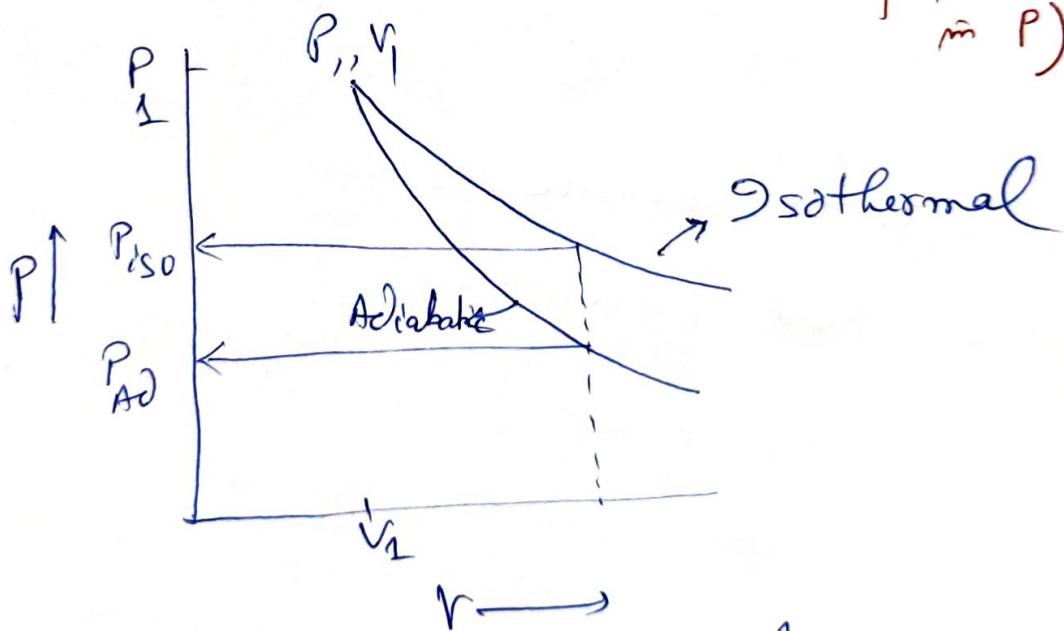
$$\therefore \left( \frac{\partial P}{\partial V} \right)_{AD} = -\gamma \left( \frac{PV^\gamma}{V^{\gamma+1}} \right) = -\gamma \left( \frac{P}{V} \right)$$

Hence, slope of P-V curve

is more negative for Adiabatic change than Isothermal change.



⇒ For same  $P \xrightarrow{\text{decrease}}$ , final volume in isothermal change will be more than that for Adiabatic change. ( $V_{\text{iso}} > V_{\text{Ad}}$  for same decrease in  $P$ )



⇒ For same increase in volume,  
 $P_{\text{iso}} > P_{\text{Ad}}$ .

T.H.W For both the above cases, explain the results in terms of molecular interaction happening within the system

[Hint: For Ad. expansion temp drops, while for isothermal process, no change in T]

## Concept of heat capacity:

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Amount of heat required to increase the temperature of a system by unity is known as heat capacity.

Temp may be increased in two ways:

Case I : At const volume process.

$$\text{Corresponding heat capacity} \Rightarrow C_V = \left( \frac{\partial Q}{\partial T} \right)_V$$

Case II By constant pressure process:

$$\text{Corresponding heat capacity} \Rightarrow C_P = \left( \frac{\partial Q}{\partial T} \right)_P \cdot \left( \frac{\text{unit}}{\text{JK}^{-1}} \right)$$

$C_P / C_V \Rightarrow$  Extensive property

$$\text{Molar heat capacity} \Rightarrow \frac{C_P}{\text{no of mol}} \quad (= \bar{C}_P) \quad \left. \begin{array}{l} \text{Intensive} \\ \text{property} \end{array} \right\}$$

$$\text{or, specific heat capacity} \Rightarrow \frac{C_P / C_V}{\text{mass of the material}} \quad \left. \begin{array}{l} \Rightarrow \\ \text{Intensive} \\ \text{property} \end{array} \right\}$$

$$(\text{JK}^{-1} \text{kg}^{-1})$$

$$\boxed{\text{HW: Why } \bar{C}_P > \bar{C}_V}$$

$$Q = \left( \frac{\partial q}{\partial T} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P$$

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$$\left| \begin{array}{l} \left( \frac{\partial q}{\partial T} \right)_{\text{const } P} = dH \\ \hline \end{array} \right.$$

$$G = \left( \frac{\partial q}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$\left| \begin{array}{l} dU = dq - P \cdot dV \\ \text{At const } V, \\ \underline{dq = dU} \end{array} \right.$$

General Expression of  $(Q - G)$ :

$$Q - G = \left( \frac{\partial H}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V$$

$$= \left[ \frac{\partial \{ U + PV \}}{\partial T} \right]_P - \left( \frac{\partial U}{\partial T} \right)_V$$

$$= \left( \frac{\partial U}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V + P \left( \frac{\partial V}{\partial T} \right)_P \quad \text{--- (1)}$$

Now,  $U = f(T, V)$

$$\therefore dU = \left( \frac{\partial U}{\partial T} \right)_V \cdot dT + \left( \frac{\partial U}{\partial V} \right)_T \cdot dV$$

Dividing by  $dT$  and maintaining  $\text{const } P$ :

$$\left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \cdot \left( \frac{\partial V}{\partial T} \right)_P$$

$$\therefore \left( \frac{\partial U}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial V} \right)_T \cdot \left( \frac{\partial V}{\partial T} \right)_P \quad \text{--- (2)}$$

Comparing eqns ① & ② :

$$G_p - G_v = \left( \frac{\partial U}{\partial V} \right)_T \cdot \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

$$\boxed{G_p - G_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P}$$

Now, for ideal gas:  $\left( \frac{\partial U}{\partial V} \right)_T = 0$  | As no intramolecular interaction among ideal gas molecules.  
 ( Joule's law )  $V = f(T)$  only for ideal gas.

Hence, for ideal gas:

$$\begin{aligned} G_p - G_v &= P \left( \frac{\partial V}{\partial T} \right)_P \\ &= P \cdot \frac{nR}{P} \end{aligned}$$

or,  $\boxed{G_p - G_v = nR}$  for ideal gas.

$$\bar{G}_p - \bar{G}_v = R.$$

Except ideal gas,  $\left( \frac{\partial U}{\partial V} \right)_T \neq 0$

$$\boxed{\left( \frac{\partial U}{\partial V} \right)_T = -T \left( \frac{\partial P}{\partial T} \right)_V - P}$$

$$\boxed{\left( \frac{\partial H}{\partial P} \right)_T = -T \left( \frac{\partial V}{\partial T} \right)_P + V}$$

$$\begin{cases} P = \frac{nRT}{V} \\ \bar{V} = \frac{nRT}{P} \\ \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \end{cases}$$

Thermodynamic  
Eqn. of States.

HW

Show that for van der Waals gas,

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$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2} \Rightarrow \text{known as Internal pressure.}$$

$$\left[ \left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \right]$$

Work involved in Adiabatic process:

$$W_{Ad, \text{irrev}} = -P_p \cdot (V_2 - V_1)$$

$$W_{Ad, \text{rev}} = ?$$

Adiabatic process:  $Q = 0$ .

$$\Delta U = Q + W \rightarrow \text{1st law}$$

$$\therefore \text{For adiabatic process: } W = \Delta U = \bar{C}_V (T_2 - T_1)$$

$$\left[ \text{As, } \bar{C}_V = \left(\frac{\partial U}{\partial T}\right)_V \right] \\ \therefore dU = \bar{C}_V \cdot dT$$

$$\therefore \boxed{W_{rev, ad} = n \bar{C}_V (T_2 - T_1)}$$

For Ad expansion temp drops:  $T_2 < T_1$ ;  $W < 0$ .  
 $(W \rightarrow -)$

$$\boxed{W_{rev, Ad} = n \bar{C}_V \left( \frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right)}$$

$$:\left(\dot{W}_{rev, Ad}\right)_{ideal\ gas} = \frac{\bar{Q}}{R} (P_2 V_2 - P_1 V_1)$$

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$$\begin{aligned} \bar{Q} - \bar{W} &= R \\ \Rightarrow \frac{\bar{Q}}{\bar{W}} &= \gamma \end{aligned}$$

QW (1) Isothermal expansion of ideal gas —  
Is it isenthalpic? [ <sup>that:</sup> Apply Joule's law ]

(2) Isothermal free expansion of ideal gas — is it adiabatic?

[ For free expansion,  $P_{ext} = 0$ , ]  
Hence,  $\dot{W} = -P_{ext} \cdot \Delta V = 0$ . ]

# Relation betw.  $q_p$  (as SH) and  $q_v$  (as SU) :

$$H = U + PV$$

$$\text{or, } \Delta H_p = \Delta U + P \Delta V$$

$$\text{For gas, } P \Delta V = P(V_2 - V_1) = n_2 RT - n_1 RT = \Delta n_g \cdot RT$$

$$\therefore \Delta H = \Delta U + \Delta n_g \cdot RT$$

$$\therefore \boxed{q_p = q_v + \Delta n_g \cdot RT}$$

$\Delta n_g$  : change in  
number of moles  
of gaseous molecules  
in the process