

## Thermodynamics -

①

### 2nd law of thermodynamics:

Main limitation of 1st law: though it deals with interconversion of different forms of energy and equivalency of energy during such transformation main limitation is it cannot predict whether any particular transformation in energy is at all feasible / spontaneous, or not.

Mechanical clock  $\rightarrow$  Heat : Spontaneous.

(Ex. But reverse is not.  $\rightarrow$  Heat engine (some other external agency) is required for such a transformation to be effective.

This human experience can also be interpreted in terms of change in randomness / disorderliness of the system & surroundings.

Work  $\Rightarrow$  max displacement along the direction of applied force  $\Rightarrow$  directionality.

Manifested in terms of lifting of weights / or a piston  $\Rightarrow$  all occurs at a particular direction.

But, heat generated is dispersed in all directions  $\Rightarrow$  more random.

(2)

Thm: Work  $\rightarrow$  heat  $\Rightarrow$  loss of directionality  $\Rightarrow$   
 more random state of matter  $\Rightarrow$  Natural spontaneous.  
 Heat  $\rightarrow$  work  $\Rightarrow$  random state to ordered state  $\Rightarrow$   
Non-spontaneous.

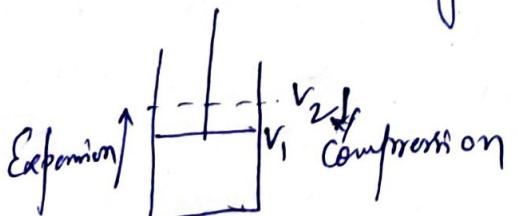
This is domain of 2nd law of thermodynamics.

$\rightarrow$  Any spontaneous transformation is associated  
 with increase in randomness of the system and  
 surroundings taken together. ( $S_{\text{universe}} > 0$ ).

Now: Heat  $\rightarrow$  Work: Not spontaneous.  
 Then how to achieve this transformation?

In isothermal cyclic process: Heat can not be  
 converted into work.

e.g. Consider reversible isothermal process involving  
 ideal gas:



During expansion:

$$\text{Heat absorbed} \Rightarrow nRT/m \left( \frac{V_2}{V_1} \right)$$

$$\text{2 work done by the system} = -nRT/m \left( \frac{V_2}{V_1} \right) \\ = -nRT/m \left( \frac{V_2}{V_1} \right)$$

During compression:

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

$$\text{Work done} = nRT/m \left( \frac{V_2}{V_1} \right)$$

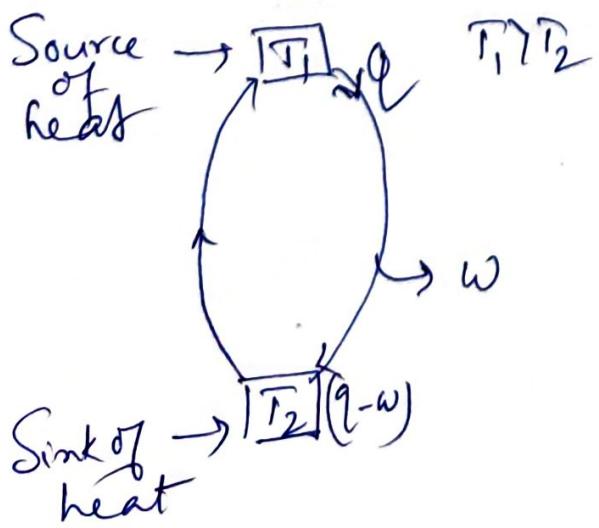
$$\therefore \oint \left[ Q_{\text{total}} = 0 ; W_{\text{total}} = 0 \right]$$

## ③ Two statements of the 2nd law of thermodynamics.

i) Kelvin-Planck Statement: It is impossible for a system working in a cycle and connected to a single heat reservoir to produce positive amount of work by absorbing equivalent amount of heat from the single thermal reservoir.

ii) ~~Claudius~~ ~~Planck~~ Statement: It is impossible for heat to move by itself from a low-temperature medium to a high-temperature medium. i.e. heat transfer spontaneously ~~from~~ in the direction of temperature drop.

From K.P. statement, minimum requirement for conversion of Heat into work is two temperature regions/reservoir. A cyclic system will take up heat from



high temp reservoir and will ~~not~~ utilize a part of that heat & do some work on the surroundings and will discard the rest amount of

heat to the lower temp sink.

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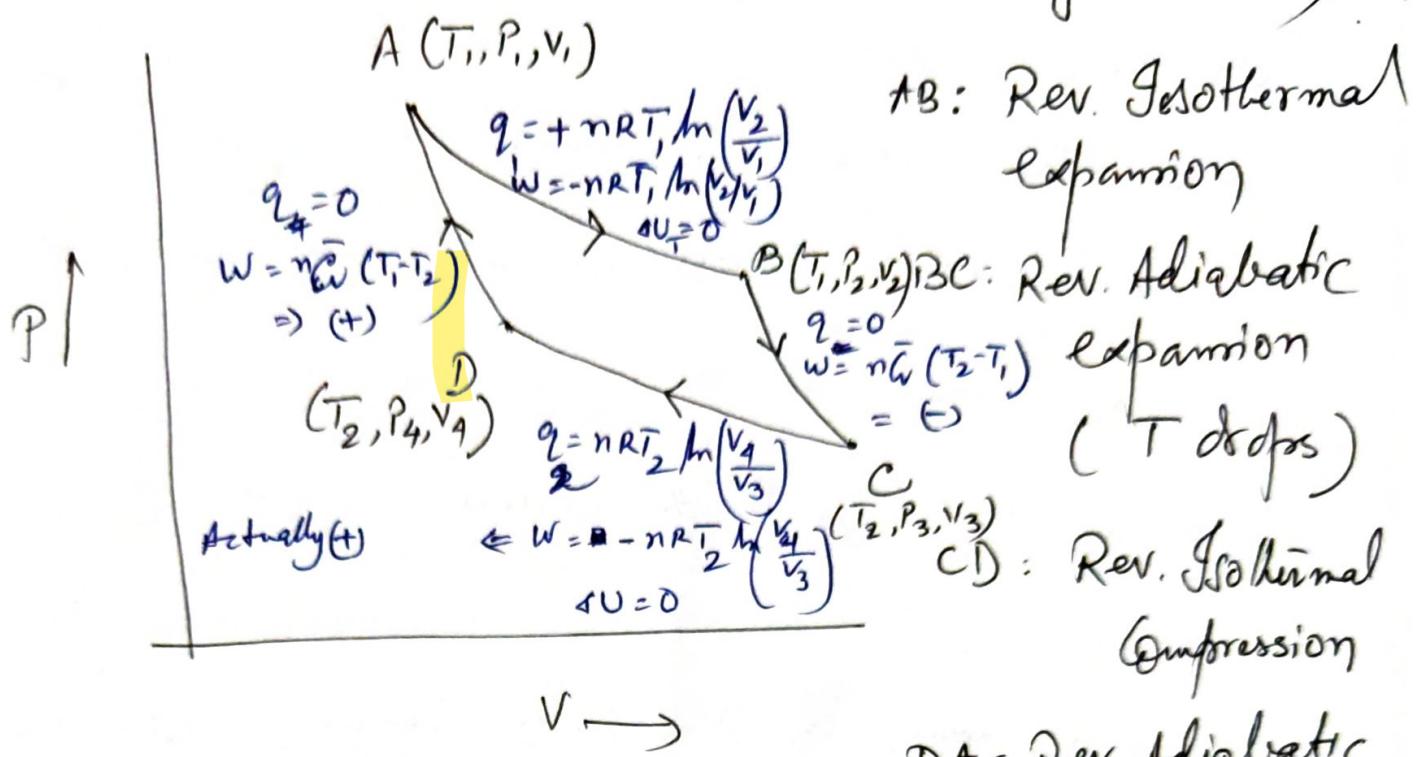
Now, it is of human experience that even such transformation all the heat absorbed from higher temp. source will never be completely converted into work. Always there will

be some loss of heat into the lower temp sink.

e.g. efficiency of heat to work transformation can never be  $\underline{100\%}$  =

$\uparrow$   
Another form of K.P statement.

# Ideal Carnot Cycle (First considering ideal gas as working substance) ⑥



Temp. of source = T<sub>1</sub>  
from where the system absorbs heat

DA: Rev. Adiabatic Compression (T increases)

Temp of sink = T<sub>2</sub>  
where system releases the remaining amount of heat after utilizing a part of heat absorbed from higher temp source.

$$w_{\text{total}} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) + nRT_2 \ln\left(\frac{V_3}{V_4}\right) = -nR(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)$$

$$\frac{P_2 V_2^{\gamma-1}}{P_1 V_1^{\gamma-1}} = P_3 V_3^{\gamma-1} \quad (\text{from step 2})$$

$$\frac{P_1 V_1^{\gamma-1}}{P_4 V_4^{\gamma-1}} = P_3 V_3^{\gamma-1} \quad (\text{from step 4})$$

$$\frac{\left(\frac{V_2}{V_1}\right)^{\gamma-1}}{\left(\frac{V_4}{V_3}\right)^{\gamma-1}} = \frac{(V_3/V_4)^{\gamma-1}}{(V_2/V_1)^{\gamma-1}}$$

Efficiency  $\eta = \frac{\text{Total work done}}{\text{Work that would be done if all the heat absorbed from higher temp source be fully converted into work}}$

$$\begin{aligned}\therefore \eta &= \frac{W_{\text{total}}}{Q_1} \\ &= \frac{-nR(T_1 - T_2) \ln \left( \frac{V_2}{V_1} \right)}{-nRT_1 \ln \left( \frac{V_2}{V_1} \right)} \\ &= \frac{T_1 - T_2}{T_1} = \left( 1 - \frac{T_2}{T_1} \right) = \frac{\Delta T}{T_1}\end{aligned}\quad (7)$$

Conclusions:

- i)  $\eta$  is independent of the nature of working substance.
- ii)  $\eta$  depends on the temp of the source and that of the sink.
- iii) Higher temp of source and lower temp of sink will result into more efficiency.  
Out of these two, second process is more efficient.

$$\eta = 1 - \left( \frac{T_2}{T_1} \right); \quad \left( \frac{\partial \eta}{\partial T_1} \right)_2 = \frac{T_2}{T_1^2} = \frac{(1-\eta)}{T_1}$$

$$\left( \frac{1-\eta}{T_1} \right) < \frac{1}{T_1}$$

$$-\left( \frac{\partial \eta}{\partial T_2} \right)_{T_1} = \frac{1}{T_1}$$

Hence, decrease in  $T_2$  to increase  $\eta$  is more efficient than increase in  $T_1$  to increase  $\eta$ .

- iv) If  $T_1 = T_2$ ;  $\eta = 0$ ; if isothermal cyclic process heat cannot be converted into work.

v) If  $T_2 = 0K$ ,  $\eta = 1$  cl. 100% conversion of heat into work. (8)  
Conclusion of 2nd law of thermodynamics:  $0K$  is unattainable.  
Hence,  $\eta$  is always less than 100% (always some heat will be lost during heat to work conversion).

vi) If any of the intermediate steps becomes irreversible,  $\eta$  will be lower than the ideal reversible Carnot cycle.

[ In irreversible isothermal expansion, less work is done by the system than that in rev. isoth. expn.  
In irrev. isothermal compression, surrounding will do more work than rev. isothermal compression]

$\Rightarrow$  We get concept of a new thermodynamic func., called entropy  $f(S)$ :

$$(q_1/T_1) + (q_2/T_2) = \frac{nRT_1/m\left(\frac{V_2}{V_1}\right)}{T_1} + \frac{nRT_2/m\left(\frac{V_3}{V_2}\right)}{T_2}$$

$$= nR\ln\left(\frac{V_2/V_1}{V_3/V_2}\right) = 0.$$

$\therefore \oint \frac{dq_{rev}}{T} = 0$ ;  $\frac{dq_{rev}}{T}$  = differential quantity of a state function  $S$ .

$$\therefore \boxed{TdS = dq_{rev}/T}$$

$$dS = q_{rev}/T \quad (\text{JK}^{-1}\text{mol}^{-1})$$

If  $q_{rev} \Rightarrow (+)$  (if system absorbs heat),  $dS \Rightarrow (+)$   
 $\Rightarrow$  measure of randomness of the system

$$\boxed{S = k/\ln W}$$

$$k \Rightarrow \text{Boltzmann constant} = \boxed{(R/N_A)}$$

$W$  = Thermodynamic Probability

Ideal Carnot cycle  $\Rightarrow$  Basic THERMODYNAMIC CYCLE.

# ⑨

## Entropy Change during Reversible Phase Transition:

$$\Delta S_{\text{fusion}} = \frac{q_{\text{fusion}}}{T_m} = \frac{\text{Latent heat of fusion}}{\text{Melting temp}}$$

$$\Delta S_{\text{evaporation}} = \frac{q_{\text{evap}}}{T_B} = \frac{\text{Latent heat of evaporation}}{\text{Corresponding Boiling point}}$$

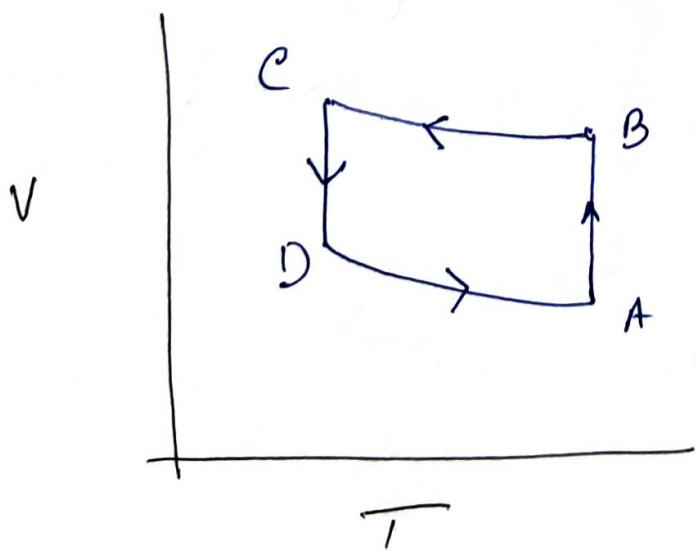
$\Delta S_{\text{fusion}}$  or  $\Delta S_{\text{evaporation}} \Rightarrow (+) \text{ ex. entropy}$   
 increases  $\Rightarrow$  Randomness increased.

T.H.W

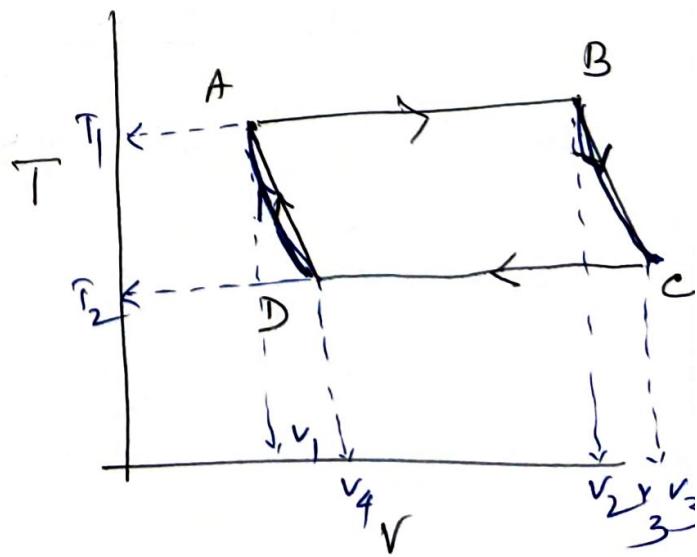
Derive the efficiency of the Ideal Carnot Cycle  
 Considering van der Waals gas the working substance:  
 (Consult: K.L Kapoor's Book pg. 2)

$\eta$  will be the same as  $(T_1 - T_2)/T_1$

V-T diagram

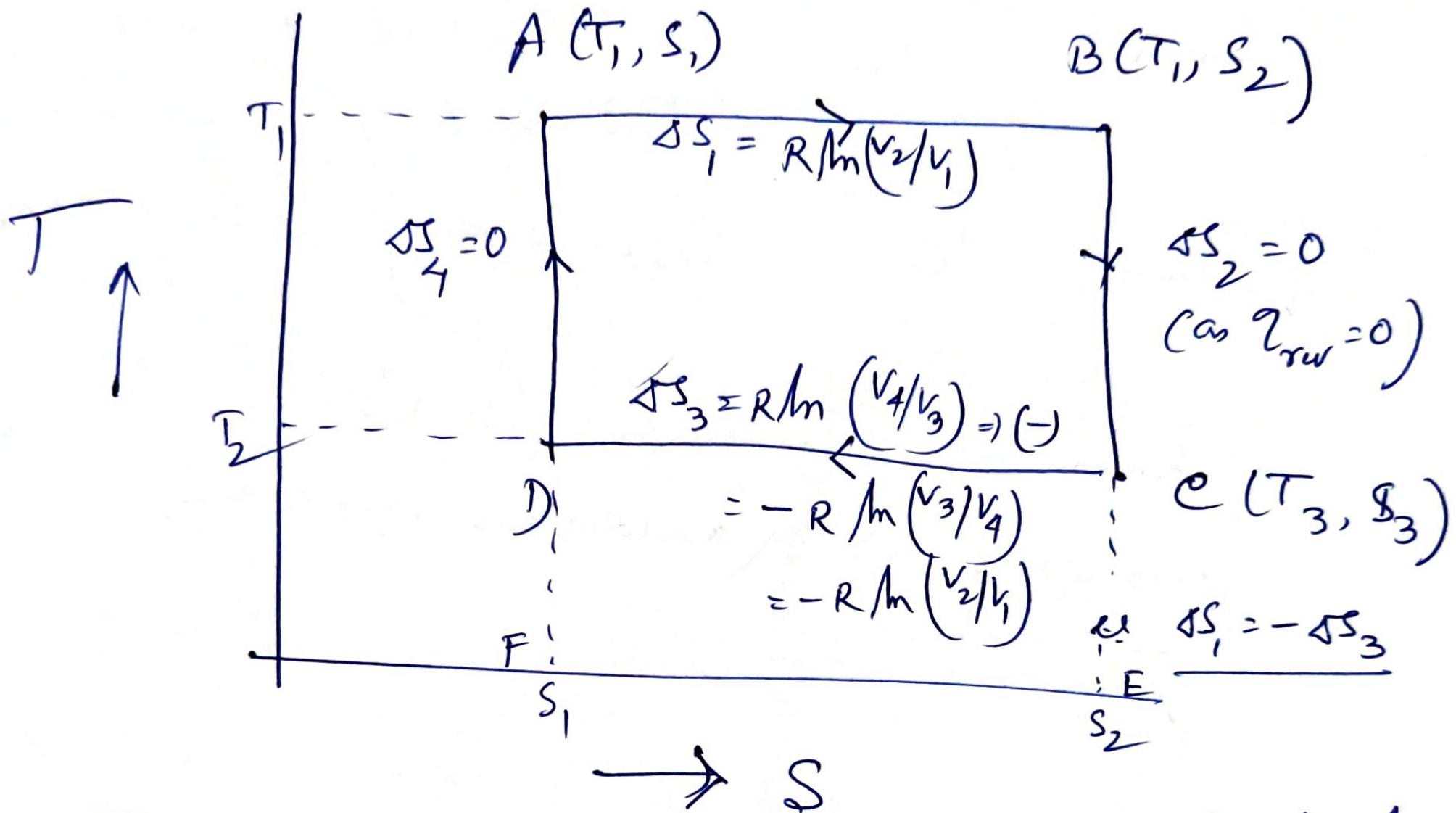


T-V diagram



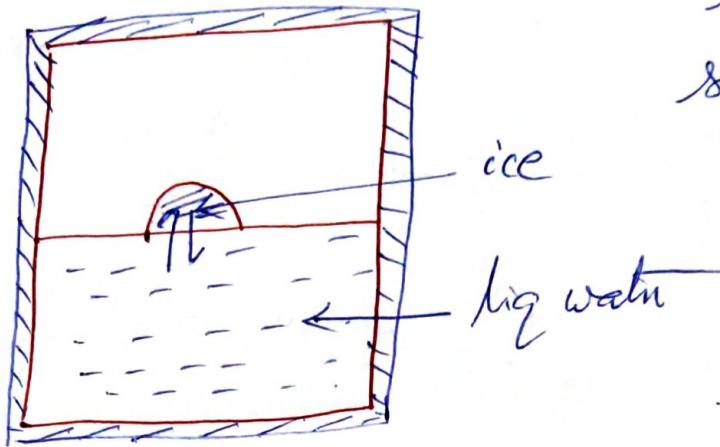
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Carnot Cycle ( $T-S$ ) diagram  
 (Considering ideal gas)



Variation of entropy for reversible and irreversible processes in an isolated system :  
Clausius inequality.

Case I: Reversible/Equilibrium change :



In an isolated system, let ice and liq. water are under equilibrium at melting point ( $T_m$ )

Solid ice  $\rightleftharpoons$  liq. water

Now, for solid ice to liq. water transition :

$$\Delta S_{\text{fusion}} = \frac{+Q_{\text{fusion}}}{T_m} \Rightarrow (+)$$

Again, for liq. water to solid ice transition :

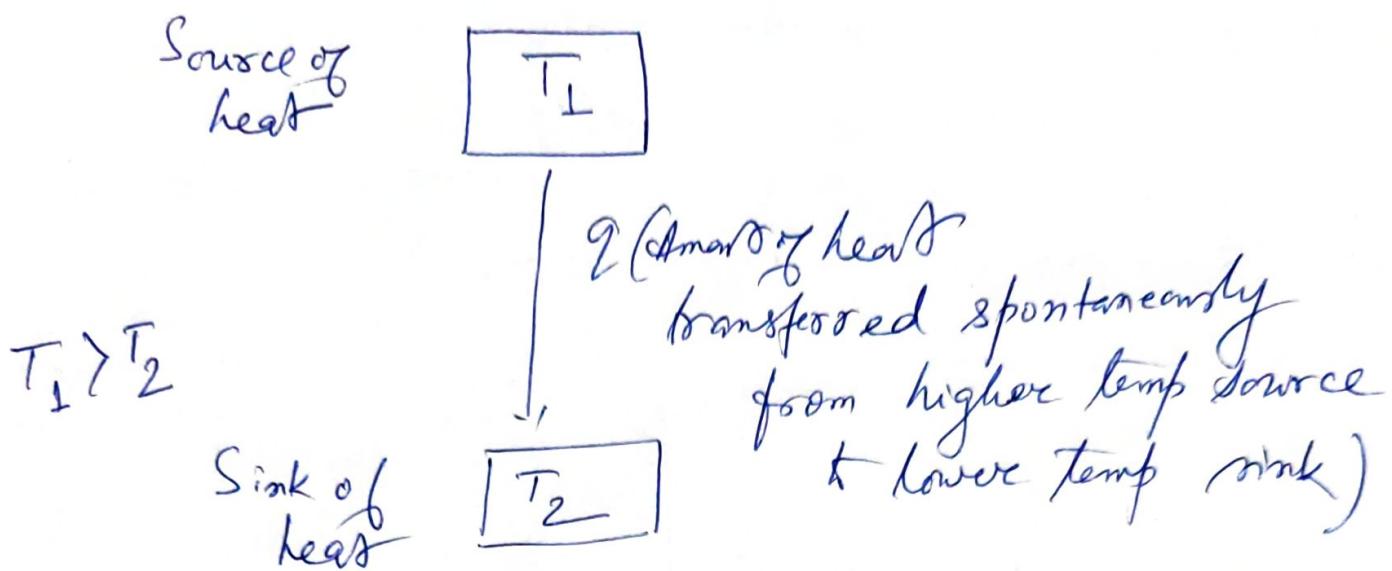
$$\Delta S_{\text{solidification}} = \frac{-Q_{\text{fusion}}}{T_m} = \frac{Q_{\text{solidification}}}{T_m} \Rightarrow (-)$$

Hence, for the whole cycle :

$$\Delta S_{\text{total}} = (\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}) = 0$$

$$\Rightarrow \boxed{\Delta S_{\text{universe}} = 0} \text{ for a reversible change.}$$

## Case II For irreversible / spontaneous process:



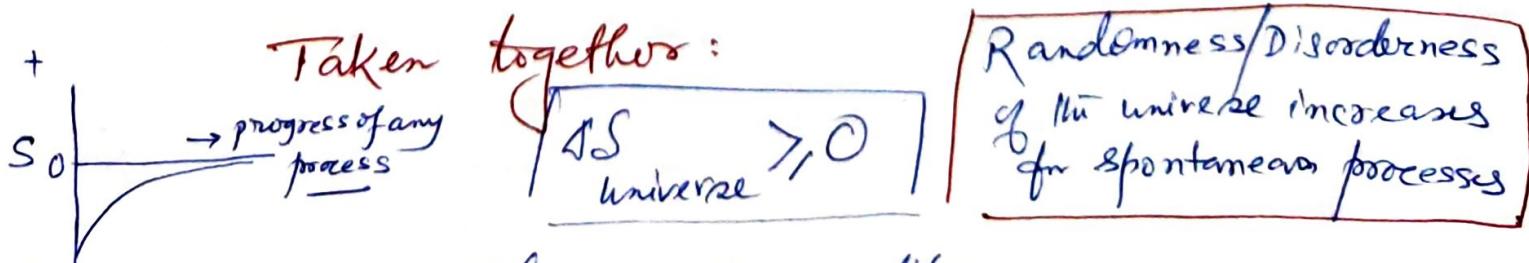
$$\text{Entropy change of source} = \frac{-Q}{T_1} \quad \left[ \begin{array}{l} \text{As heat is released} \\ \text{from source} \end{array} \right]$$

$$\text{Entropy change of the sink} = \frac{+Q}{T_2}$$

$$\Delta S_{\text{total}} = (\Delta S_{\text{source}} + \Delta S_{\text{sink}}) = \left( \frac{Q}{T_2} - \frac{Q}{T_1} \right) \\ = Q \left( \frac{T_1 - T_2}{T_1 T_2} \right) \Rightarrow (+)$$

$$\therefore (\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}) = \boxed{\Delta S_{\text{universe}} > 0}$$

for irreversible process.



Clausius Inequality  
# Increase in entropy is the net unavailable Work.

Change of entropy for an ideal gas with change in volume/pressure and temperature:

$$dS = \frac{dq_{rev}}{T}$$

Case I: Isothermal process:

For isothermal process of an ideal gas:  $\Delta U_T = 0$ .

$$\text{Hence, } q_{rev} = -w = nRT/m\left(\frac{V_2}{V_1}\right) = nRT/m\left(\frac{P_1}{P_2}\right)$$

$$\text{Hence, } \frac{dS}{T} = \frac{q_{rev}}{T} = nR/m\left(\frac{V_2}{V_1}\right) = nR/m\left(\frac{P_1}{P_2}\right).$$

Case II When temp varies at constant volume/pressure:

$$\left. \begin{aligned} C_V &= \left(\frac{\partial Q}{\partial T}\right)_V \\ C_P &= \left(\frac{\partial Q}{\partial T}\right)_P \end{aligned} \right] \quad dS = \frac{dq_{rev}}{T} = \frac{C_V dT}{T} \text{ for const V process} \\ &\quad = \frac{C_P dT}{T} \text{ for const P process.}$$

Hence, integrating:

$$\begin{aligned} dS &= n\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) \text{ for Const. V process} \\ &= n\bar{C}_P \ln\left(\frac{T_2}{T_1}\right) \text{ for Const. P process} \end{aligned}$$

$n\bar{C}_P / n\bar{C}_V \Rightarrow$  Total heat capacity of the system.

Combining both the cases:

$$\begin{aligned} dS &= n\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad \left| \left( \frac{V_2}{V_1} = \frac{P_1}{P_2} \right) \right. \\ dS &= n\bar{C}_P \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

## Concept of Gibbs free energy ( $G$ ):

$$\boxed{G = H - TS}$$

For any spontaneous/irreversible process:

$$\Delta G_{T,P} < 0 \quad \begin{array}{l} \text{[i.e. free energy at} \\ \text{constant T and P} \end{array}$$

$$\Rightarrow -\Delta G_{T,P} > 0 \quad \text{decreases]$$

When the process reaches the equilibrium state:

$$\Delta G_{T,P} = 0$$

Taken together:

$$\boxed{\Delta G_{T,P} \leq 0}$$

for the system only

If for any process/reaction  $\Delta G_{T,P} > 0$ ; then the reverse process is spontaneous.

Example:



At lower temp, forward red<sup>n</sup> is spontaneous.

But, at higher temp, reverse, i.e. dissociation

of water is spontaneous.  $\Rightarrow$  Explain how?

$\Delta S \Rightarrow (-)$  (Randomness decreases)

$\Delta H \rightarrow (-)$  (Exothermic Red<sup>n</sup>).

For forward process:  $\Delta G = \Delta H - T \Delta S$

At lower temp

$$|T\Delta S| < |\Delta H|$$

$$\therefore \Delta G_{T,P} < 0 \text{ at lower } T.$$

At higher temp:

$$|T\Delta S| > |\Delta H|$$

$$\Rightarrow \Delta G_{T,P} > 0 \text{ at high } T.$$

What is the significance of decrease in free energy at constant T and P?

$$G = H - TS$$

$$\text{or, } G = U + PV - TS.$$

$$H = (U + PV)$$

$$\therefore dG = dU + P.dV + VdP - TdS - SdT$$

$$\text{or, } dG_{T,P} = dU + P.dV - TdS \quad || \quad dS = \frac{dq_{rev}}{T}$$

$$\begin{aligned} dG_{T,P} &= dU + P.dV - dq \\ &= P.dV - dw. \end{aligned}$$

$$\begin{aligned} \text{1st law:} \\ dU &= dq - dw \\ \downarrow \\ \text{Work done by the system} \\ \therefore dU - dq &= -dw. \end{aligned}$$

Hence, decrease in free energy at constant T & P:

$$-dG_{T,P} = dw - P.dV$$

$$\text{Integrating: } \int -\frac{dG}{T,P} = w - P.dV$$

(Total work done by the system - mechanical P-V work done by the system)

,  $-\Delta G_{T,P}$  = Net available work which can be utilised for some other purpose.

For example: In an galvanic cell:

$$-\Delta G_{T,P} = \text{Net electrical work available} = nFE_{cell}$$

$$\therefore \Delta G_{T,P} = -nFE_{cell}$$

## Variation of G with T and P

$$G = H - TS$$

$$[H = U + PV]$$

$$\therefore dG = dH - TdS - SdT$$

$$= dU + \underbrace{P_dV}_{dq} + VdP - \underbrace{TdS}_{q} - SdT$$

$$\therefore \boxed{dG = - SdT + VdP}$$

$$\therefore \left( \frac{\partial G}{\partial T} \right)_P = -S.$$

Suppose: State 1  $\rightarrow$  State 2

$$\text{change in free energy} = \Delta G$$

$$\text{change in entropy} = \Delta S.$$

$$\boxed{\left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = -\Delta S}$$

Now, at any temp T,

$$\Delta G = \Delta H - T\Delta S$$

$$\therefore -\Delta S = \frac{\Delta G - \Delta H}{T}$$

$$\text{or, } \boxed{\left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = \frac{\Delta G}{T} - \frac{\Delta H}{T}}$$

$$\text{or, } \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P - \frac{\Delta G}{T} = -\frac{\Delta H}{T}$$

$$\text{Hence, } T \left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T}$$

$$\text{or, } \boxed{\left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}}$$

$$\text{Now, } \left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = \frac{1}{T} \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P - \frac{\Delta G}{T^2}$$

$$\therefore \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P - \frac{\Delta G}{T} = T \left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P$$

Gibbs-Helmholtz Eqn.