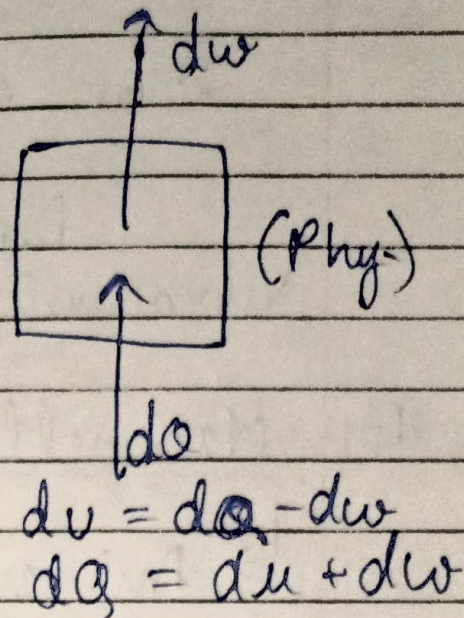
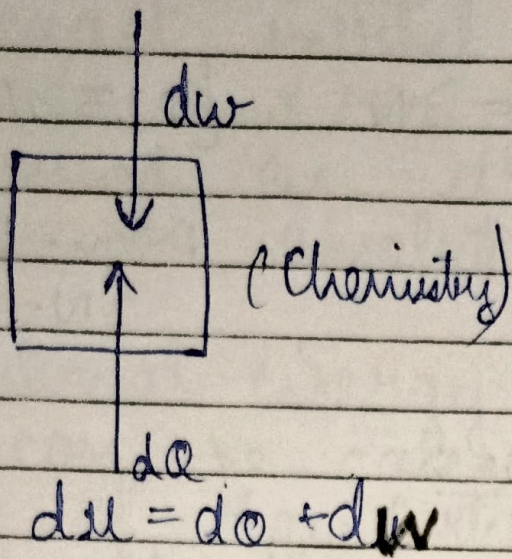


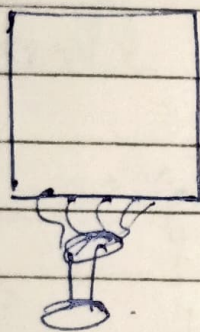
First Law of Thermodynamics

↳ Energy can neither be created nor destroyed, it ~~can~~ can only be converted from one form to another.



Applications of First law of Thermodynamics

* (A) Constant volume or Isochoric processes



(Internal energy)

$$du = dq + dw$$

$$= dq - PdV \rightarrow 0$$

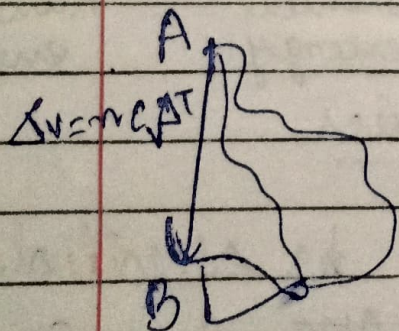
$$du = (dq)_v$$

Heat given at const volume is equal to change in Internal energy.

$$du = (nC dT)_v$$

$$du = n c_v dT$$

↳ molar heat capacity at const. volume



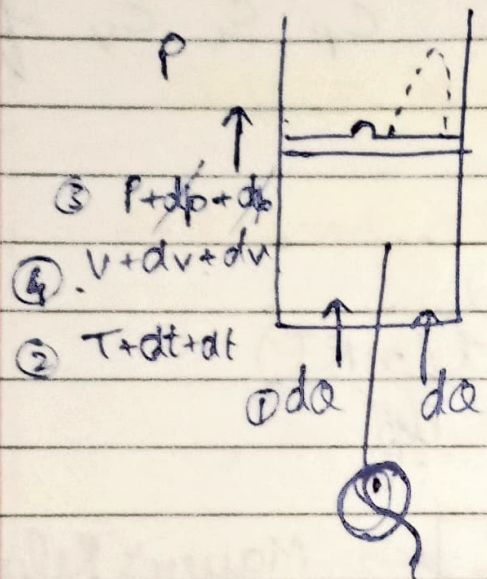
→ Intensive
→ State f^m.

For an ideal gas

$$du = n c_v dT = \frac{f}{2} n R dT$$

$$C_v = \frac{f}{2} R$$

b) Constant pressure processes (isobaric):



$$du = dq + dw$$

$$du = dq - P dv$$

$$\therefore dq = du + P dv \quad \text{--- (1)}$$

Defining

$$H = U + P V$$

$$H = U + P V$$

↳ enthalpy
 ↳ state func.
 ↳ extensive.

$$dH = du + P dv + v dp \quad \text{--- (2) (as pressure } \rightarrow \text{ const)}$$

from (1) & (2)

$$dH = (dq)_P \quad \text{--- means at const pressure.}$$

state func \leftarrow (dH) \rightarrow Heat content

Heat given at const pressure is equal to change in enthalpy of the system

$$dH = (nc dT)_p$$

$$\boxed{dH = n c_p dt} \rightarrow \text{always true.}$$

\rightarrow molar heat capacity at const 'p'

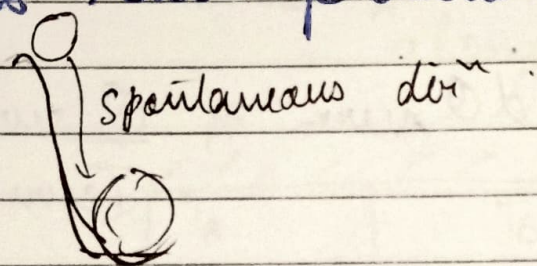
\rightarrow Intensive

\rightarrow state function.

IInd LAW OF THERMODYNAMICS

↳ Spontaneous, natural, ~~are~~ irreversible processes

↳ Processes which take place due to the natural interaction betⁿ a system & the surroundings are called spontaneous or natural processes.
* Such processes are all irreversible.



Ind Law of Thermodynamics

↳ Entropy (S) of universe is ~~not~~ continuously increasing.

$S \equiv$ Entropy

↳ State fⁿ.

↳ Extensive property.

$$\Delta S_{\text{UNIVERSE}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$$

for a spontaneous process.

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

$$\Delta S = \int \frac{dq_{rev}}{T}$$

It can only be calculated along a reversible path

Estimations of ΔS_{sys} & ΔS_{sur}

① ΔS_{sur} :

$$\Delta S_{sur} = \int \frac{dq_{rev, sur}}{T_{sur}} = \frac{1}{T_{sur}} \int dq_{rev, sur}$$

$$= \frac{1}{T_{sur}} \int dq_{sur} = \frac{Q_{sur}}{T_{sur}}$$

From FLOT (1st Law)
 $Q_{sur} = -Q_{sys}$

$$\Delta S_{sur} = \frac{-Q_{sys}}{T_{sur}}$$

E.g. For isochoric

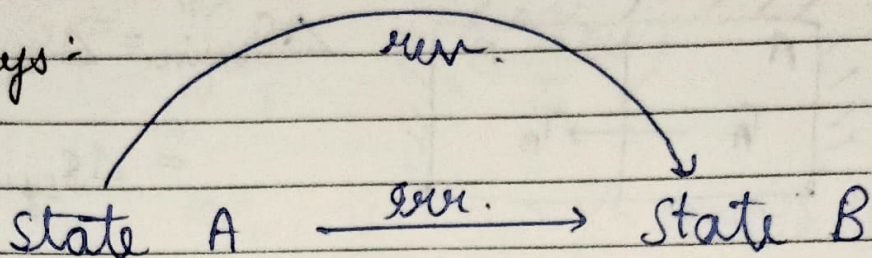
$$\Delta S_{sur} = \frac{-\Delta U_{sys}}{T_{sur}}$$

For isobaric

$$\Delta S_{sur} = \frac{-\Delta H_{sys}}{T_{sur}}$$

Estimation of ΔS_{sys} =

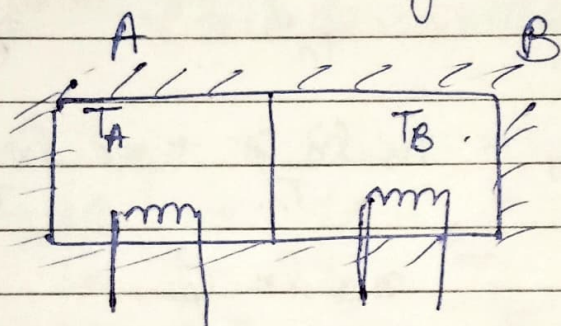
1. ΔS_{sys} =



$$\Delta S_{\text{sys}} \neq \int \frac{dQ_{\text{irr}}}{T}$$

$$\Delta S_{\text{sys}} = \int_A^B \frac{dQ_{\text{rev}}}{T}$$

along rev. path.



$$T_A > T_B$$

$$\Delta S_{\text{sys}} = \Delta S_A + \Delta S_B$$

$$= \int \frac{dQ_A}{T_A} + \int \frac{dQ_B}{T_B}$$

$$= \frac{Q_A}{T_A} + \frac{Q_B}{T_B}$$

From 1st Law.

$$Q_A = -Q_B$$

$$\therefore \Delta S_{\text{sys}} = \underbrace{-\frac{Q_B}{T_A}}_{\text{-ive}} + \underbrace{\frac{Q_B}{T_B}}_{\text{+ive}} > 0$$

Ist Method

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$= \int_{T_A}^{T_B} \frac{dq}{T} + \left(-\frac{q_{\text{sys}}}{T_B} \right)$$

$$= \int_{T_A}^{T_B} \frac{nc dT}{T} + \left(-\frac{nc(T_B - T_A)}{T_B} \right)$$

$$= \underbrace{nc \ln \frac{T_B}{T_A}}_{(-ive)} + \underbrace{nc \left(\frac{T_A - T_B}{T_B} \right)}_{(+ive)} > 0$$

IInd Method (Fundamentally)

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_{\text{UNIV}}$$

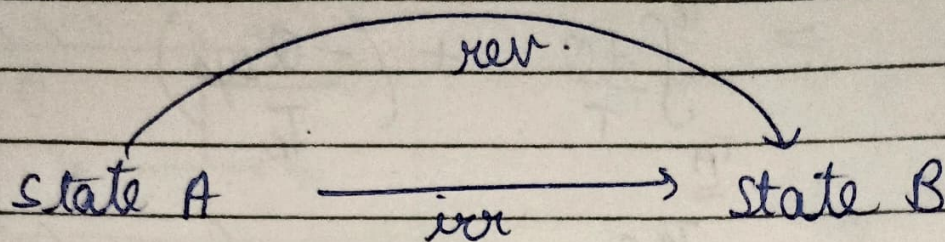
$$\frac{-dq}{T_A} + \frac{dq}{T_B} = +ive$$

$$\frac{-dq}{T_A - dt} + \frac{dq}{T_B} = +ive$$

$$\frac{-dq}{T_B + dt} + \frac{dq}{T_B} = +ive$$

$$\boxed{nc \ln \frac{T_B}{T_A} + nc \left(\frac{T_A - T_B}{T_B} \right) = +ive}$$

Entropy calculations for an ideal gas:



$$\Delta S_{\text{sys}} = \int_{T_A}^{T_B} \frac{dQ_{\text{rev}}}{T}$$

rev. path

$$du = dq + dw$$
$$du = dq_{\text{rev}} - P_g dv$$
$$\therefore dq_{\text{rev}} = du + P_g dv$$

$$= \int du + \int \frac{P_g dv}{T}$$

$$= \int \frac{du}{T} + \int \frac{P_g dv}{T}$$

$$= \int_{T_1}^{T_2} \frac{nC_v dT}{T} + \int_{V_1}^{V_2} \frac{nR dv}{v}$$

$$= nC_v \frac{\ln T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{sys}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Entropy

always applicable.