B. Sc (H) – III Paper – VI, Gp-A, 07-02-24
Dr. SKY

STATISTICAL MECHANICS (3rd CLASS):

We were discussing the reviews of thermodynamics.

First law: $dU = dQ - dW$, $dU \rightarrow$ change in internal energy of the system
$dQ \rightarrow$ Amount of heat added to the system
$dW \rightarrow$ amount of work done by the system during an infinitesimal process

Second law: $dQ_{rev} = TdS$

$dQ_{irr} \leq TdS$

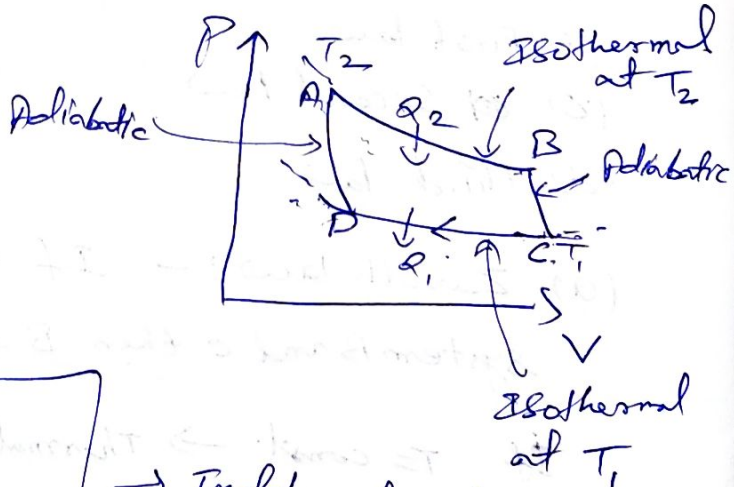
$S \rightarrow$ entropy
$T \rightarrow$ temperature
$rev \rightarrow$ Reversible
$irr \rightarrow$ Irreversible

Two equivalent statements of the second law →

Kelvin statement: There exists no thermodynamic process whose sole effect is to extract a quantity of heat from a system and to convert it entirely to work.

Clausius Statement: No process exists in which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at a higher temperature.

Carnot engine:



Efficiency $\eta = \frac{\Delta W}{Q_2}$

$$\eta = 1 - \frac{T_1}{T_2}$$

→ Independent of working substance

Thermodynamic potentials

Term is derived from an analogy with mechanical potential energy. Taking an example of PVT system the internal energy is $E(S, V)$.

From the first law combined with the second law of thermodynamics (for a reversible process)

$$\boxed{dE = TdS - PdV + \mu dN}$$

Helmholtz free energy A is related to E via a Legendre transformation.

$$A = E - TS$$

$$dA = dE - TdS - SdT$$

$$\boxed{dA = -SdT - PdV + \mu dN}$$

Similarly, Gibbs free energy G for a PVT system is obtained as

$$G = A + PV$$

$$dG = dA + PdV + VdP$$

$$\text{or } \boxed{dG = -SdT + VdP}$$

Gibbs-Duhem Relation

For a single component PVT system

$$E = TS - PV + \mu N$$

$$X = E - TS + PV - \mu N = 0$$

$$X = G - \mu N = 0$$

$$\boxed{dX = -SdT + VdP - Nd\mu = 0}$$

Gibbs Duhem relation.