THERMODYNAMICS (T.D.)

"Entropy Change ΔS"

Isothermal

$$W_{system} \rightarrow U_{reservoir}$$

$$\Delta S_{system} = 0, \quad \Delta S_{surrounding} = \frac{Q}{T} = \frac{W}{T}$$

$$\Delta S_{universe} = 0 + \frac{W}{T} = \boxed{\frac{W}{T}}$$

Adiabatic

$$\Delta S_{system} = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_p\,dT}{T} = C_p \ln\frac{T_f}{T_i}$$

$$\Delta S_{surrounding} = 0, \quad \Delta S_{universe} = \boxed{C_p \ln\frac{T_f}{T_i}}$$

Free Expansion

$$\Delta S_{system} = \int_{V_i}^{V_f} \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{P\,dV}{T} = nR\ln\frac{V_f}{V_i}$$

$$\Delta S_{surrounding} = 0, \quad \Delta S_{universe} = \boxed{nR\ln\frac{V_f}{V_i}}$$

Conduction

$$\Delta S_{system} = 0, \quad \Delta S^{hot}_{reservoir} = -\frac{Q}{T_1},$$

$$\Delta S^{cold}_{reservoir} = +\frac{Q}{T_2}$$

$$\Delta S_{reservoir} = \boxed{\frac{Q}{T_2} - \frac{Q}{T_1}} = \Delta S_{universe}$$

Chemical reaction

Adiabatic wall

$\Delta S_{system1} = nR \ln V_f/V_i = \Delta S_{system2}$,

$\Delta S_{surrounding} = 0$, $\Delta S_{universe} = \boxed{2nR \ln V_f/V_i}$

LEGENDRE TRANSFORMATION IN T.D.

{ Extensive parameter = Independent variable
  Intensive parameter = Derived

NOT GOOD FOR EXPERIMENTS. X X X

Desired

{ Intensive parameter = Indepent variable
  Extensive parameter = Derived variable

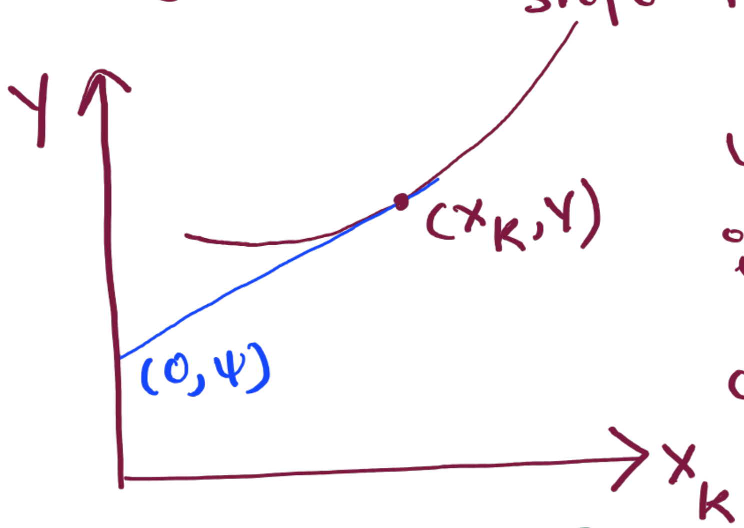
→ Fundamental relation in x representation

Given $Y = Y(X_0, X_1, X_2, \ldots, X_t)$, we want $\boxed{P_K = \frac{\partial Y}{\partial X_K}}$ as independent variable without losing any information ⇒ impossible to replace function with derivative!

→ Fundamental relation in P representation

So $\psi = \psi(P_0, P_1, P_2, \ldots, P_t)$ given 'slope' & 'intercept' (P_K, ψ) is equivalent to $Y = Y(X_0, X_1, X_2, \ldots, X_t)$

Legendre Transform



$$P_K = \frac{Y-\psi}{X_K - 0} \Rightarrow \boxed{\psi = Y - \sum_K P_K X_K}$$

ψ is the L.T. of Y and its reversible

$$d\psi = \cancel{dY} - \cancel{P\,dX} - X\,dP$$

$$= -X\,dP \quad \left(\because P = \frac{dY}{dX}\right)$$

$$\therefore \boxed{X_K = -\frac{\partial \psi}{\partial P_K}} \qquad d\psi = -\sum_K X_K\, dP_K$$

1-variable L.T.

$Y = Y(X)$	$\psi = \psi(P)$
$P = \frac{dY}{dX}$	$-X = \frac{d\psi}{dP}$
$\psi = -PX + Y$	$Y = XP + \psi$
Eliminating X, Y	Eliminating Y, ψ
$\psi = \psi(P)$.	$Y = Y(X)$

Example (Classical Mechanics):

$$\text{L.T.}\begin{cases} \mathcal{L} = \mathcal{L}(v_1, v_2, \dots, v_r, q_1, q_2, \dots, q_r) \\ \mathcal{H} = \mathcal{H}(p_1, p_2, \dots, p_r, q_1, q_2, \dots, q_r) \end{cases}$$

(Thermodynamics) : $dU < 0$, $dS > 0$

$U = U(S, V, N_1, N_2, \cdots N_t)$

derivative $T, -P, \mu_1, \mu_2 \cdots$ intensive parameters

$f = U - TS$ {L.T. of U replaces S by T as independent variable $F = U[T]$}

$U = U(S, V, N_1, N_2, \cdots)$ $-P = \dfrac{\partial U}{\partial V}$ $F = U - TS$ Eliminating U & S $F = F(T, V, N_1, N_2 \cdots)$	$F = F(T, V, N_1, N_2, \cdots)$ $-S = \dfrac{\partial F}{\partial T}$ $U = F + TS$ Eliminating F & T $U = U(S, V, N_1, N_2, \cdots)$

$H = U + PV$ {L.T. of U replaces V by P as independent variable $H = U[P]$}

$U = U(S, V, N_1, N_2, \cdots)$ $-P = \dfrac{\partial U}{\partial V}$, $H = U + PV$ Eliminating U & V $H = H(S, P, N_1, N_2, \cdots)$	$H = H(S, P, N_1, N_2, \cdots)$ $V = \dfrac{\partial H}{\partial P}$, $U = H - PV$ Eliminating H & P $U = U(S, V, N_1, N_2 \cdots)$

$G = U - TS + PV = F + PV$ {L.T. of U replaces S by T and V by P $\quad G = U[T,P]$}

$U = U(S, V, N_1, N_2, \cdots)$	$G = G(T, P, N_1, N_2, \cdots)$
$T = \frac{\partial U}{\partial S}, \; -P = \frac{\partial U}{\partial V}$	$-S = \frac{\partial G}{\partial T}, \; V = \frac{\partial G}{\partial P}$
$G = U - TS + PV$	$U = G + TS - PV$
Eliminating U, S, V	Eliminating G, T, P
$G = G(T, P, N_1, N_2, \cdots)$	$U = U(S, V, N_1, N_2 \cdots)$

Similarly more potentials canbe derived like Grand Canonical potential $U[T, \mu]$

$\boxed{\text{MASSIEU FUNCTIONS}}$

Fundamental relation
$S = S(U, V, N_1, N_2, \cdots)$

$$S\left[\frac{1}{T}\right] = S - \frac{U}{T} = -\frac{F}{T}$$

{L.T. of S replaces U by $\frac{1}{T}$ as independent variable}

$$S\left[\frac{P}{T}\right] = S - \frac{P}{T}V$$

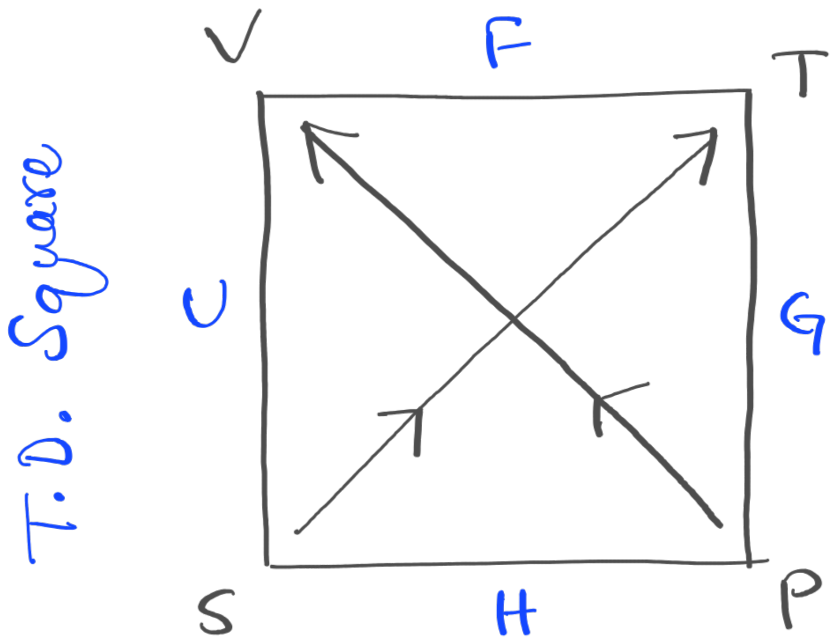
{L.T. of S replaces V by $\frac{P}{T}$ as independent variable}

$$S\left[\frac{1}{T}, \frac{P}{T}\right] = S - \frac{U}{T} - \frac{P}{T}V = -\frac{G}{T}$$ {L.T.

of S that replace U by $\frac{1}{T}$ and V by $\frac{P}{T}$ as independent variable?

$S = S(U, V, N_1, N_2, \dots)$	$S[\frac{P}{T}] = S[U, \frac{P}{T}, N_1, N_2, \dots]$
$\frac{P}{T} = \frac{\partial S}{\partial V}$	$-V = \frac{\partial S[P/T]}{\partial [P/T]}$
$S[\frac{P}{T}] = S - \frac{P}{T} V$	$S = S[\frac{P}{T}] + \frac{P}{T} V$
Eliminating S & V	Eliminating $S[\frac{P}{T}]$ & $\frac{P}{T}$
$S[\frac{P}{T}] = S[U, \frac{P}{T}, N_1, N_2, \dots)$	$S = S(U, V, N_1, N_2, \dots)$

THERMODYNAMIC MNEMONIC DIAGRAM



$$dU = T\,dS - P\,dV + \sum_K \mu_K \, dN_K$$

$$dF = -S\,dT - P\,dV + \sum_K \mu_K \, dN_K$$

$$dG = -S\,dT + V\,dP + \sum_K \mu_K \, dN_K$$

$$dH = TdS + VdP + \sum_K \mu_K dN_K$$