

2-2. Enthalpy. $U[P] \equiv H$

$$dY_{\Psi} = - \sum_{k=0}^n x_k dP_k + \sum_{j=n+1}^t P_j dX_j$$

$$dH = TdS + (-V)d(-P) + \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

when in contact w/ P reservoir.

$$\rightarrow dH = TdS \quad (\text{Given } N = \text{const.})$$

$$\underline{Q_{i \rightarrow f}} = \int dQ_P = \int_i^f dH = H_f - H_i$$

knowing $H = H(S, P, N) \leftarrow U(S, V, N)$

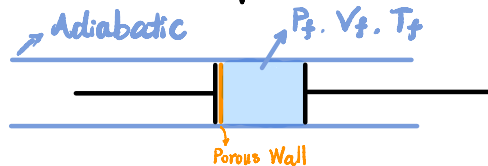
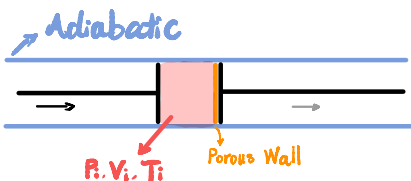
$$-x_k = \frac{\partial Y_{\Psi}}{\partial P_k} \rightarrow -V = \frac{\partial H}{\partial (-P)} \Rightarrow V = \underbrace{\left(\frac{\partial H}{\partial P} \right)}_{\rightarrow H(S, P, N)}_{S, N}$$

$$\rightarrow H = H(S, P, N) \quad \xrightarrow{\quad} \quad S = S(V, P, N) \leftarrow V = V(S, P, N)$$

$$= H(S(V, P, N), P, N) = H(V, P, N)$$

$$Q_{i \rightarrow f} = H_f - H_i = H(V_f, P_f, N) - H(V_i, P_i, N)$$

Joule - Thomson Process (Gas Liquefaction)



$$W_{\text{total}} = \int_{V_i}^0 -P_i dV + \int_0^{V_f} -P_f dV$$

$$\downarrow$$

$$\delta W = -P dV$$

$$= -P_i(0 - V_i) + (-P_f)(V_f - 0)$$

$$= P_i V_i - P_f V_f$$

$$\Delta U = \Delta U_L + \Delta U_R = (0 - U_i) + (U_f - 0)$$

$$= W_{\text{total}} = \underline{U_f - U_i = P_i V_i - P_f V_f}$$

$$\Rightarrow \frac{U_f + P_f V_f}{H_f} = \frac{U_i + P_i V_i}{H_i} \quad \left. \vphantom{\frac{U_f + P_f V_f}{H_f}} \right\} \text{ Isenthalpic process}$$

$\left(\frac{\partial T}{\partial P}\right)$ characterize the nature of the J-T process.

$$\Rightarrow \frac{\partial T}{\partial P} > 0 \Rightarrow P \downarrow \rightarrow T \downarrow$$

$$\Rightarrow \frac{\partial T}{\partial P} < 0 \Rightarrow P \downarrow \rightarrow T \uparrow$$

$$\Rightarrow \frac{\partial T}{\partial P} = 0 \Rightarrow P \downarrow \text{ or } \uparrow \rightarrow \text{const } T$$

what $\frac{\partial T}{\partial P}$ is equal to?

$$H = H(V, P, N) \quad \text{if } N = \text{const.}$$

$$\rightarrow H = H(V, P)$$

$$\downarrow$$

$$V(P, T)$$

$$\left. \begin{array}{l} \text{ideal gas: } PV = NRT \\ \text{vdW gas: } P = \frac{RT}{v-b} - \frac{a}{v^2} \end{array} \right\} (P, V, T)$$

$$\rightarrow H = H(P, T)$$

$$\Rightarrow \frac{\partial H}{\partial P} \cdot \boxed{\frac{\partial P}{\partial T}} \cdot \frac{\partial T}{\partial H} = -1 \Rightarrow \frac{\partial T}{\partial P} = - \left[\underbrace{\left(\frac{\partial H}{\partial P} \right)_T}_{\downarrow ?} / \underbrace{\left(\frac{\partial H}{\partial T} \right)_P}_{\downarrow ?} \right]$$

$$dY_f = - \sum_0^n X_k dP_k + \sum_{n+1}^{\ddagger} P_j dX_j$$

$$dH = -Vd(-P) + TdS = VdP + TdS$$

$$\frac{\partial H}{\partial P} = V + T \underbrace{\left(\frac{\partial S}{\partial P} \right)_T}_{\downarrow ?} \quad \frac{\partial H}{\partial T} = T \cdot \underbrace{\left(\frac{\partial S}{\partial T} \right)_P}_{\downarrow ?} \quad ?$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ thermal expansion coefficient.}$$

$$\Rightarrow \frac{\partial T}{\partial P} = f(\alpha)$$

$$P_k = \frac{\partial Y}{\partial X_k} \quad -X_k = \frac{\partial Y_f}{\partial P_k}$$

$$\downarrow$$

$$-S = \left(\frac{\partial G}{\partial T} \right)_P \Rightarrow \underbrace{\left(\frac{\partial S}{\partial P} \right)_T}_{\uparrow} = \left[\frac{\partial}{\partial P} \left(- \frac{\partial G}{\partial T} \right)_P \right]_T$$

$$\underbrace{\left(\frac{\partial S}{\partial T} \right)_P}_{\uparrow} = \left(\frac{T \partial S}{\partial T} \right)_P = \left(\frac{dQ}{dT} \right)_P = C_P$$

$$= \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial (-P)} \right)_T \right]_P \quad \downarrow -V$$

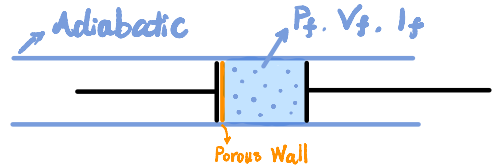
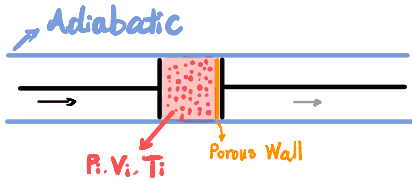
$$\Rightarrow - \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow \frac{\partial T}{\partial P} = \frac{V(T\alpha - 1)}{C_P} \Rightarrow \begin{cases} \text{if } T\alpha > 1 \Rightarrow P \downarrow \rightarrow T \downarrow \\ \text{if } T\alpha < 1 \Rightarrow P \downarrow \rightarrow T \uparrow \end{cases}$$

For ideal gas. $PV = NRT \Rightarrow \frac{1}{T} = \frac{NR}{PV}$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) = \frac{1}{V} \cdot \frac{\partial}{\partial T} \left(\frac{NRT}{P} \right) = \frac{1}{V} \cdot \frac{NR}{P} = \frac{1}{T}$$

$$\Rightarrow \frac{\partial T}{\partial P} = \frac{V}{C_P} (T\alpha - 1) = 0$$



$$\left(\frac{\partial T}{\partial P} \right)_H = \mu_{J-T}$$

$\mu_{J-T} > 0$ kinetic Energy \downarrow overcome attractive potential ($P \downarrow \rightarrow T \downarrow$)

$\mu_{J-T} < 0$ Repulsive potential \downarrow deposit into kinetic energy ($P \downarrow \rightarrow T \uparrow$)

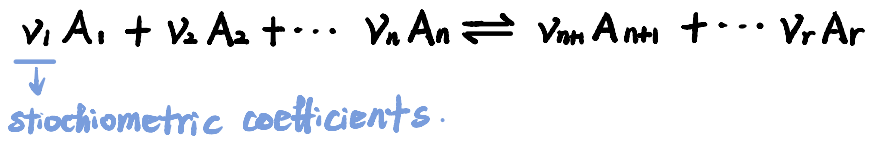
2-3. Gibbs potentials.

$$dG = -SdT + VdP + \sum_j \mu_j dN_j$$

if. $P = \text{const.}$ $T = \text{const.}$ $\Rightarrow dG = \sum_j \mu_j dN_j$

\downarrow
about matter flow

For General Reactions.



$$0 \rightleftharpoons \sum_j v_j A_j$$



$$\rightarrow 0 \rightleftharpoons -4H_2 - CO_2 + CH_4 + 2H_2O$$

then. $\frac{dN_j}{v_j} = d\tilde{N} \rightarrow$ Proportionality factor.

$$\Rightarrow dG = \sum_j \mu_j \cdot dN_j = d\tilde{N} \sum_j v_j \mu_j = 0$$

equilibrium condition.

$$* \cdot dG = 0$$

$$\Rightarrow \sum_j v_j \mu_j = 0$$

2> For evaluation of reaction:

should respect thermo. potential min. principle.

$\int dG = \Delta G_{total}$, if $\Delta G_{total} < 0 \Rightarrow$ reaction proceeds.