

Review

$$Q(N, V, T) = \frac{q_{\text{trans}}^N}{N!} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} V^N$$

• internal energy $U = \frac{3}{2} RT$

• pressure (new!):

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T}$$

$$\ln Q = \ln[V^N \dots] = N \ln V + \dots$$

$$P = k_B T \frac{N}{V}$$

$$PV = N k_B T = n N_A k_B T$$

• atomically:

$$PV = nRT \quad \text{ideal gas law}$$

$$\hookrightarrow \text{molar form } P\bar{V} = RT$$

• this holds for polyatomic ideal gases

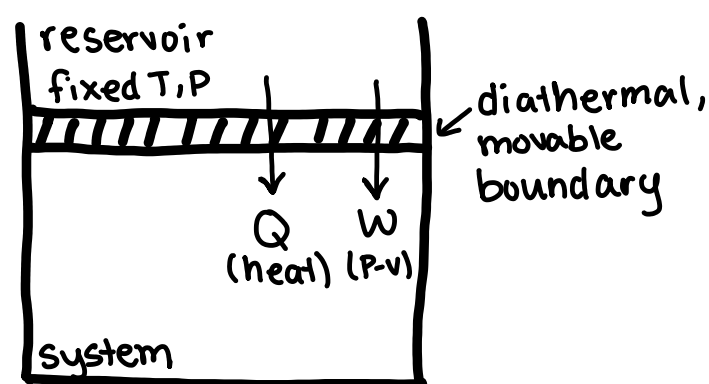
\hookrightarrow add terms to Q , but no V dependence,

so $\left. \frac{\partial \ln Q}{\partial V} \right|_{N, T}$ is the same

• primer: enthalpy and Gibbs energy

• useful properties for processes:

$$\left\{ \begin{array}{l} \text{@ const. } P : H = U + PV \\ \text{@ const. } T, P : G = H - TS \end{array} \right.$$



• 1st law:

$$\Delta U = Q + W \quad W = P \Delta V$$

$$Q = \Delta U + P \Delta V$$

$$Q = \Delta(U + PV)$$

$$Q = \Delta H \quad \text{isobaric}$$

• 2nd law:

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T \quad \Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{Q}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S - \frac{\Delta H}{T} \geq 0$$

$$\Delta(TS - H) \geq 0$$

$$\Delta G \leq 0 \quad \text{spontaneity}$$

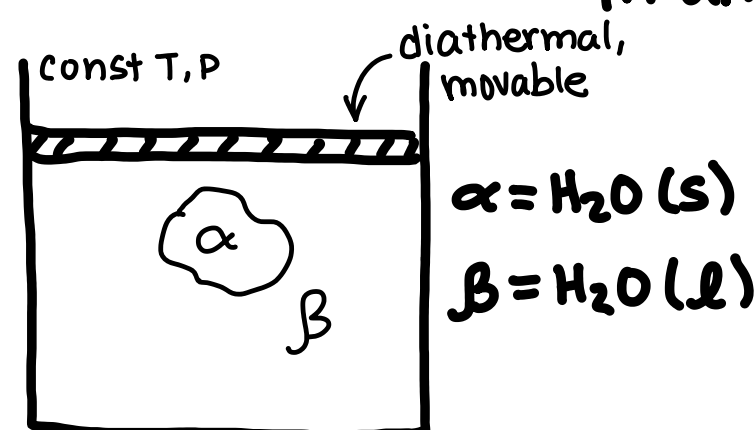
• these are only for isobaric + isothermal

• G is minimized at equilibrium

Phase Equilibria

• phase: region of homogeneous properties

• phase equilibrium: stable coexistence of phases in any proportions



• phase boundaries are diathermal, movable, open!

$$\Rightarrow \left\{ \begin{array}{l} \text{thermal eq. } T^\alpha = T^\beta \\ \text{mechanical eq. } P^\alpha = P^\beta \\ \text{chemical eq. } \mu_i^\alpha = \mu_i^\beta \Rightarrow \bar{g}_i^\alpha = \bar{g}_i^\beta \quad (\text{pure species only}) \end{array} \right.$$

$$\text{recall: } \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$\text{pure species } i: G = n_i \bar{g}_i$$

• Gibbs Phase Rule

nonreactive system contains m chemical species and π -phases

$$\text{"degrees of freedom": } F = m - \pi + 2$$

\hookrightarrow # of intensive properties

to constrain system

• ex: pure species ($m=1$)

$$F = 3 - \pi$$

$$\rightarrow \pi = 1: F = 2$$

e.g. liquid H_2O , specify T, P

$$\rightarrow \pi = 2: F = 1$$

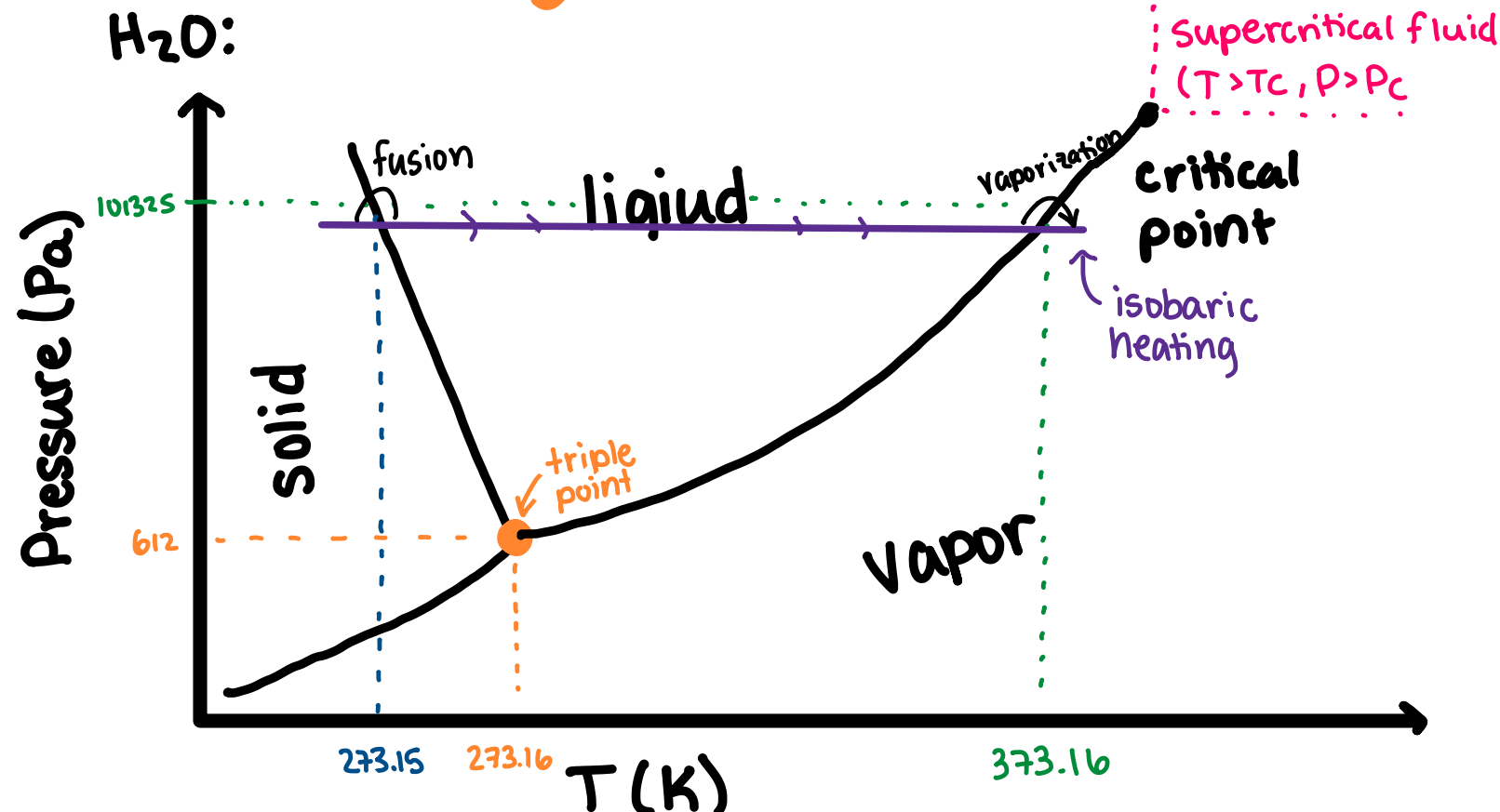
e.g. liquid H_2O + steam, specify P/T

$$\rightarrow \pi = 3: F = 0$$

this is **triple point**

Phase Diagram

H_2O :



isobaric, $P = 101325 \text{ Pa}$

