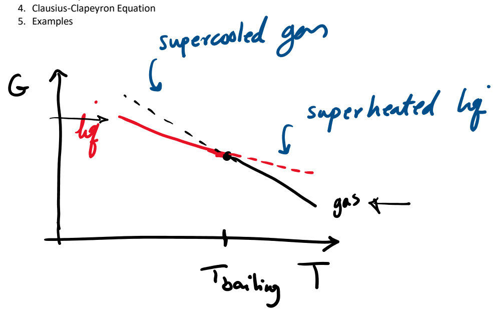
CHEM3321-CH 23, March 6th, 2023

Monday, March 6, 2023 12:32 PM

1. Phase Equilibria==> Only consider one substance at different phases
2. G-T and P-T phase diagrams
3. Clausius Equation
4. Clausius-Clapeyron Equation
5. Examples

Fig 23.10



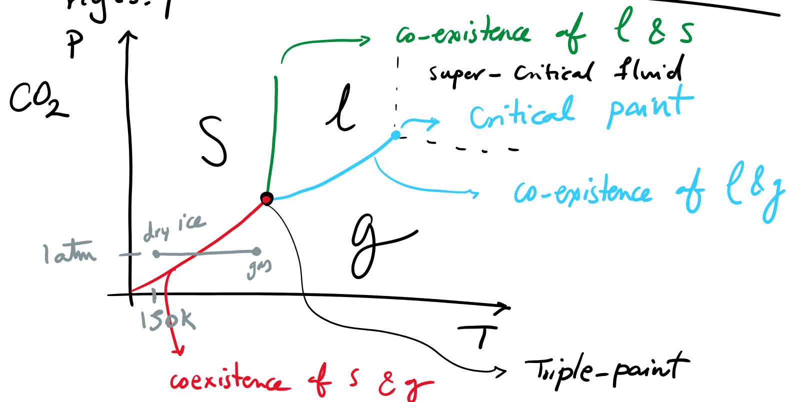
$T_{boiling} = 100°C = 373K$ at 1 atm

$$slope = \frac{dG}{dT} = -S \qquad dG = \cancel{VdP} - SdT$$

0

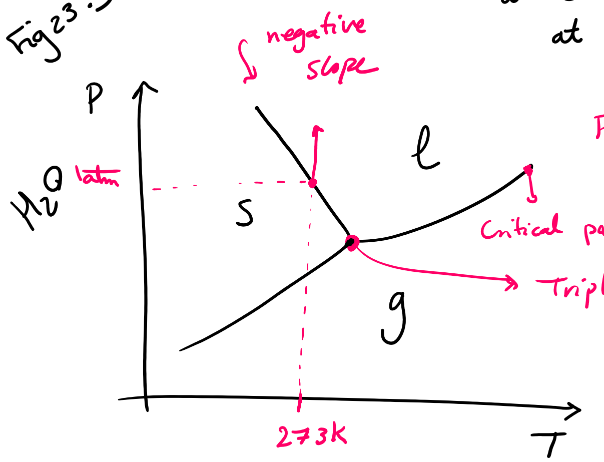
$$S^{gas} >>> S^{liq}$$

Fig 23.4



Triple-point = all 3 phases are at eq.

Fig 23.5



For water, by increasing $P \rightarrow$ freezing point drops

$$H_2O(l) \rightleftharpoons H_2O(g) \text{ at const } T, P$$

$$G(T, P, n^l, n^g)$$

$$\frac{\partial G}{\partial n^l} \quad dn^l \quad \frac{\partial G}{\partial n^g} \quad dn^g$$

$$G(T, p, n^{\ell}, n^{g})$$

$$dG = \underbrace{\left.\frac{\partial G}{\partial n^{\ell}}\right)_{p,T}} \cdot dn^{\ell} + \underbrace{\left.\frac{\partial G}{\partial n^{g}}\right)_{p,T}} \cdot dn^{g}$$

$$dG = \mu^{\ell} \cdot dn^{\ell} + \mu^{g} \cdot dn^{g}$$

$$dn^{\ell} = -dn^{g}$$ Conservation of matter

$$dG = \mu^{\ell} \cdot (-dn^{g}) + \mu^{g} \cdot dn^{g}$$

$$dG = (\mu^{g} - \mu^{\ell}) \cdot dn^{g}$$

at eq: $dG = 0 \rightsquigarrow \mu^{g} - \mu^{\ell} = 0$

$$\Downarrow$$

$$\boxed{\mu^{g} = \mu^{\ell}}$$

$\alpha \rightleftharpoons \beta$ $\qquad G(T, p, n^{\alpha}, n^{\beta})$

$$dG = \left.\frac{\partial G}{\partial n^{\alpha}}\right)_{T,p} \cdot dn^{\alpha} + \left.\frac{\partial G}{\partial n^{\beta}}\right)_{T,p} \cdot dn^{\beta}$$

$$dG = \mu^{\alpha} \cdot dn^{\alpha} + \mu^{\beta} \cdot dn^{\beta}$$

$$dn^{\alpha} = -dn^{\beta}$$

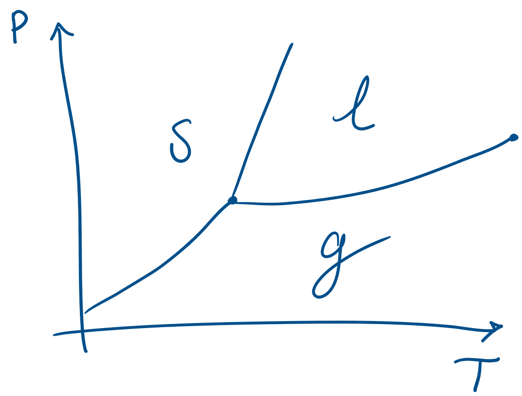
$$dG = \mu^{\alpha}(-dn^{\beta}) + \mu^{\beta} \cdot dn^{\beta}$$

$$dG = (\mu^{\beta} - \mu^{\alpha}) \cdot dn^{\beta}$$

$\beta \quad \alpha$

$dG = (\mu^{\beta} - \mu^{\alpha}) \cdot dn'$

at eq $dG = 0 \longrightarrow \boxed{\mu^{\beta} = \mu^{\alpha}}$



slope $= \dfrac{dP}{dT}$

At eq: $dG = 0 \qquad \mu^{\alpha} = \mu^{\beta}$

$$\mu^{\alpha}(T,p) = \mu^{\beta}(T,p)$$

$\downarrow$ Take derivative w/ T, P

$$d\mu^{\alpha}(T,p) = d\mu^{\beta}(T,p)$$

$$\underbrace{\left(\frac{\partial\mu^{\alpha}}{\partial p}\right)_T}_{\bar{V}^{\alpha}} \cdot dp + \underbrace{\left(\frac{\partial\mu^{\alpha}}{\partial T}\right)_p}_{\bar{S}^{\alpha}} \cdot dT = \underbrace{\left(\frac{\partial\mu^{\beta}}{\partial p}\right)_T}_{\bar{V}^{\beta}} \cdot dp + \underbrace{\left(\frac{\partial\mu^{\beta}}{\partial T}\right)_p}_{\bar{S}^{\beta}} \cdot dT$$

$$\left(\frac{\partial\mu}{\partial p}\right)_T = \frac{\partial}{\partial p}\left(\left(\frac{\partial G}{\partial n}\right)\right)_T = \frac{\partial}{\partial n}\left(\underbrace{\left(\frac{\partial G}{\partial p}\right)}_{V}\right)_T = \frac{\partial V}{\partial n} = \bar{V}$$

$$dG = V\,dp - S\,\cancel{dT}^{\,0}$$

$$\left(\frac{\partial\mu}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\left(\frac{\partial G}{\partial n}\right)\right)_p = \frac{\partial}{\partial n}\left(\underbrace{\left(\frac{\partial G}{\partial T}\right)}_{-S}\right)_p$$

$$\left.\frac{\partial\mu}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n}\right)\Bigg)_p = \frac{\partial}{\partial n}\left(\frac{\partial G}{\partial T}\right)\Bigg)_p$$

$$= -\frac{\partial S}{\partial n} = -\bar{S}$$

$$\bar{V}^{\alpha}dp - \bar{S}^{\alpha}dT = \underbrace{\bar{V}^{\beta}dp} - \bar{S}^{\beta}dT$$

$$\bar{V}^{\alpha}\,\underbrace{dp} - \bar{V}^{\beta}\underbrace{dp} = \bar{S}^{\alpha}\underbrace{dT} - \bar{S}^{\beta}\underbrace{dT}$$

$$\underbrace{(\bar{V}^{\alpha} - \bar{V}^{\beta})}_{\Delta\bar{V}_{trans}} dp = \underbrace{(\bar{S}^{\alpha} - \bar{S}^{\beta})}_{\Delta\bar{S}_{trans.}} \cdot dT$$

$$\Delta\bar{V}_{trans} \cdot dp = \Delta\bar{S}_{trans} \cdot dT$$

$$\frac{dp}{dT} = \frac{\Delta\bar{S}_{trans}}{\Delta\bar{V}_{trans}}$$

at eq: rev. process

$$\Delta\bar{S}_{trans} = \frac{\Delta\bar{H}_{trans}}{T}$$

$$\frac{dp}{} \qquad \Delta\bar{H}_{trans}$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_{trans}}{T \Delta \bar{V}_{trans}}}$$ clapeyron_ eq

$$s \rightleftharpoons l$$

$$\Delta \bar{V}_{trans} = \bar{V}_l - \bar{V}_s > 0 \longrightarrow \frac{dp}{dT} > 0$$

water $\Delta \bar{V}_{trans} = \bar{V}_l - \bar{V}_s < 0 \longrightarrow \frac{dp}{dT} < 0$
