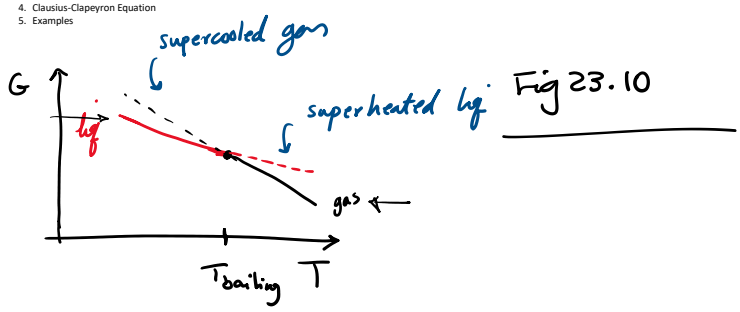
CHEM3321-CH 23, March 6th, 2023

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



$100°C = 373K$ at 1 atm

$$\text{slope} = \frac{dG}{dT} = -S \qquad dG = \cancel{V\,dP}^{\,0} - S\,dT$$

$$S^{gas} \gg S^{liq}$$

Fig 23.4

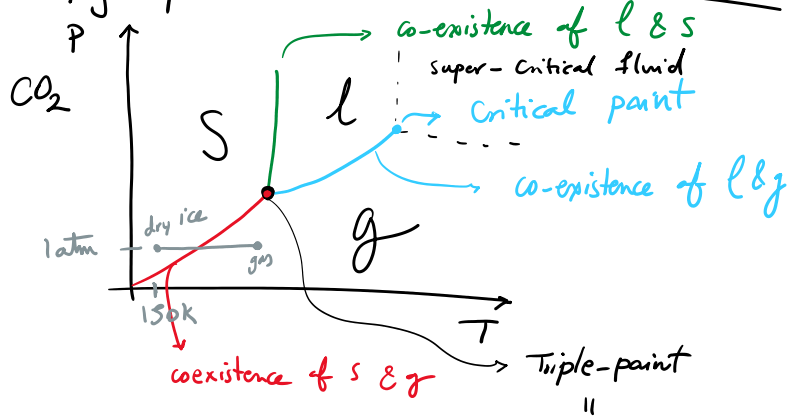
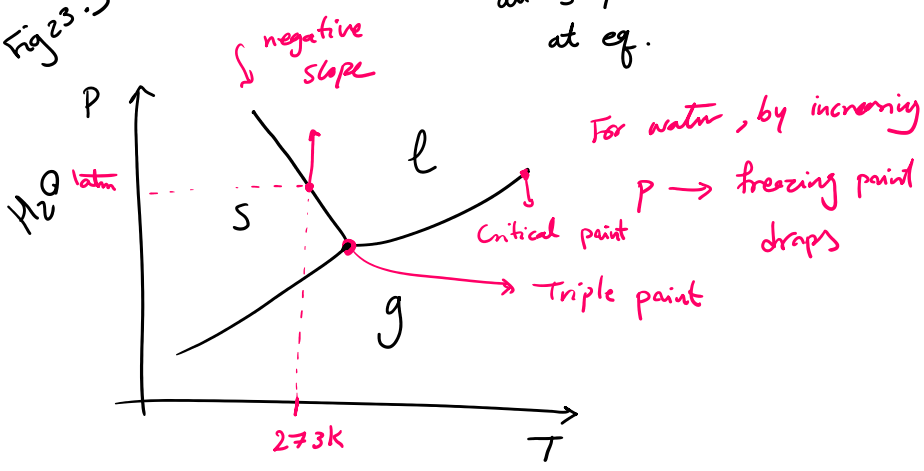


Fig 23.5



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

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

$$\left(\frac{\partial G}{\partial n^l}\right) dn^l \quad \left(\frac{\partial G}{\partial n^g}\right) dn^g$$

$G(T, p, \ldots, \ldots)$

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

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

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

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

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

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

$$\Downarrow$$

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

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

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

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

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

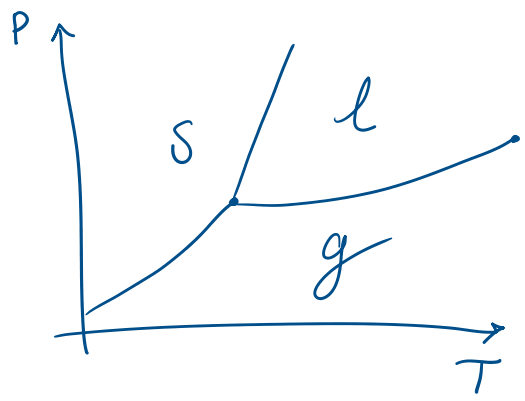
$$dG = \mu^{\alpha}(-dn^{\beta}) + \mu^{\beta} \cdot dn^{\beta}$$

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

$\beta \quad \alpha$

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

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



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

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

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

$\downarrow$ Take derivatives w/ T, P

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

$$\overbrace{\left.\frac{\partial \mu^{\alpha}}{\partial P}\right)_T}^{\bar{V}^{\alpha}} \cdot dP + \underbrace{\left.\frac{\partial \mu^{\alpha}}{\partial T}\right)_P}_{\bar{S}^{\alpha}} \cdot dT = \underbrace{\left.\frac{\partial \mu^{\beta}}{\partial P}\right)_T}_{\bar{V}^{\beta}} \cdot dP + \overbrace{\left.\frac{\partial \mu^{\beta}}{\partial T}\right)_P}^{\bar{S}^{\beta}} \cdot dT$$

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

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

$$\left.\frac{\partial \mu}{\partial}\right) \quad \frac{\partial}{\partial}\left(\frac{\partial G}{\partial}\right)\Bigg) = \frac{\partial}{\partial}\overbrace{\left(\frac{\partial G}{\partial T}\right)}^{-S}\Bigg)_P$$

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

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

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

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

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

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

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

at eq: rev. process

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

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

$$\frac{dP}{dT} = \frac{\Delta H_{trans}}{T\,\Delta \bar{V}_{trans}}$$ clapeyron_eq

$$s \rightleftharpoons l$$

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

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