Lecture 14

Tuesday, October 29, 2024 10:02

The Solid-Liquid Boundary

$$\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}$$

$$\int_{p^*}^{p} dp' = \underbrace{\frac{\Delta_{fus} H}{\Delta_{fus} V}}_{\text{assume constant in small range of T and p}} \int_{T^*}^{T} \frac{1}{T'} dT'$$

$$p - p^* = \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \boxed{\frac{T}{T^*}}$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \cdots$$

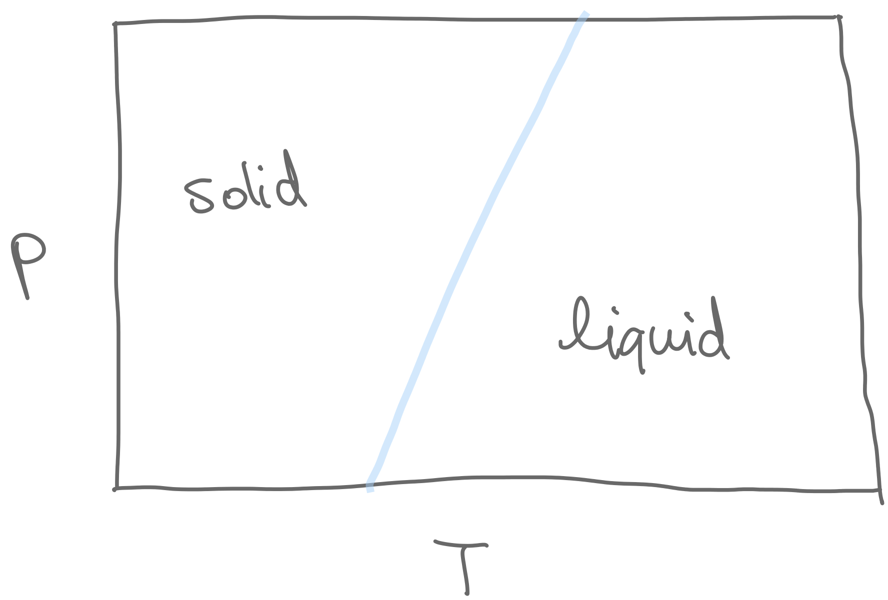
$$\ln \frac{T}{T^*} = \ln \frac{T + T^* - T^*}{T^*}$$

$$= \ln\left(1 + \frac{T - T^*}{T^*}\right)$$

$$\approx \boxed{\frac{T - T^*}{T^*}}$$

cut off after first term in series

$$\boxed{p = p^* + \frac{\Delta_{fus}H}{T^* \Delta_{fus}V}(T - T^*)}$$



The Liquid-Vapour Boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

← positive

← large and positive

$$\Delta_{vap}V = V_m(g) - V_m(l)$$

if $V_m(g) \gg V_m(l)$, then

$$\Delta_{vap}V \approx V_m(g)$$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\,V_m(g)}$$

assume perfect behaviour

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T \cdot RT/p} = \frac{p\,\Delta_{vap}H}{RT^2}$$

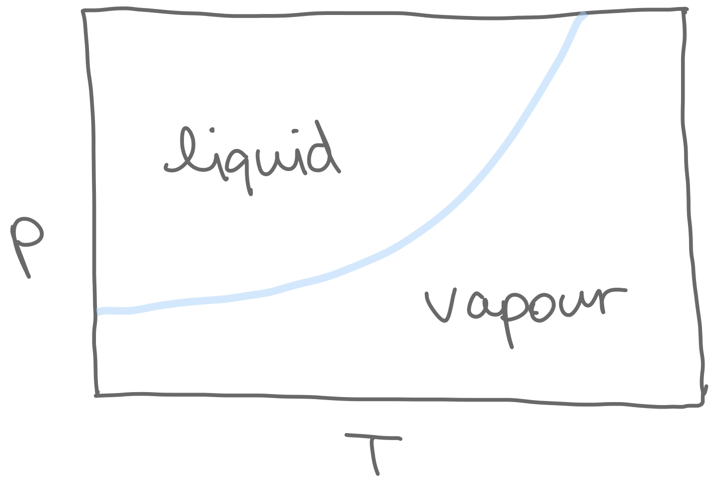
$$\int_{p^*}^{p} \frac{1}{p'}\,dp' = \frac{\Delta_{vap}H}{R} \int_{T^*}^{T} \frac{1}{T'^2}\,dT'$$

$$\ln \frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* e^{-\chi}$$

$\Delta_{vap}H$ ...

$$\boxed{x = \frac{\Delta_{vap} H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)}$$

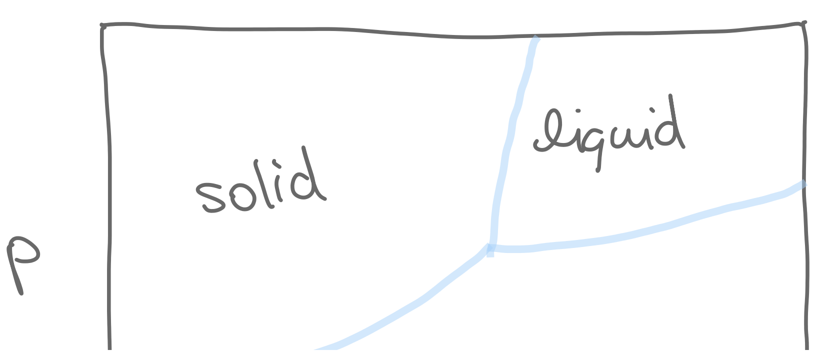


The Solid-Vapour Boundary

Similar to the liquid-vapour boundary, replace $\Delta_{vap} H$ and $\Delta_{vap} V$ with $\Delta_{sub} H$ and $\Delta_{sub} V$.

$$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$$

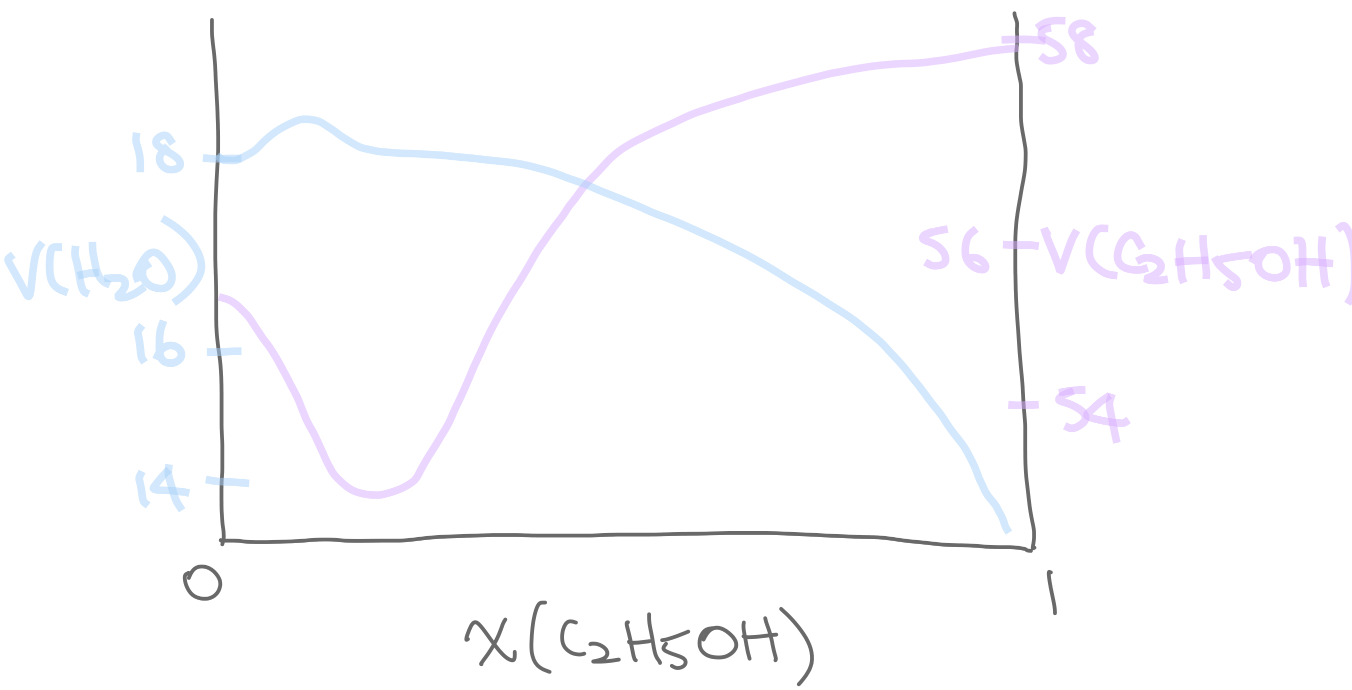
steeper slope

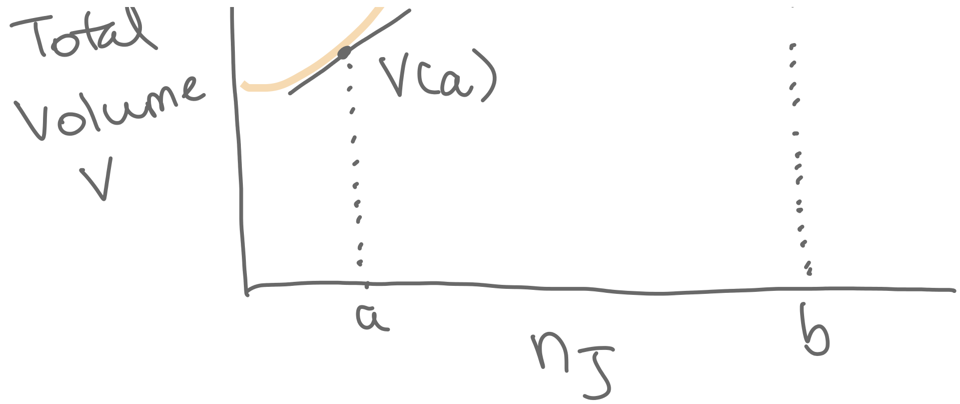


Topic 5A : The Thermodynamic Description of Mixtures

Partial molar volume

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$





Binary mixture,

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

$$dV = V_A dn_A + V_B dn_B$$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B$$

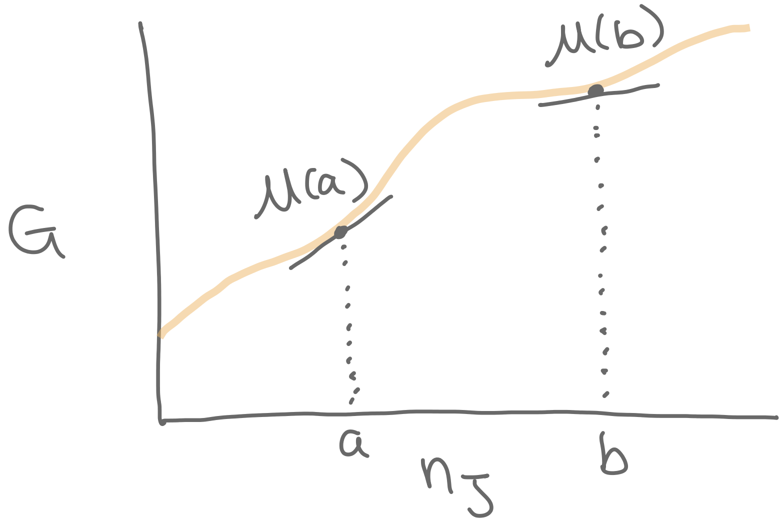
$$\boxed{V = V_A n_A + V_B n_B}$$

Partial Molar Gibbs Energies

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$ mixture

$\mu_J = G_{J,m}$ pure substance

$G = n_A\mu_A + n_B\mu_B$ binary mixture



$$\boxed{dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \ldots}$$

fundamental equation of chemical thermodynamics

At constant pressure and temperature,

$$dG = \mu_A dn_A + \mu_B dn_B + \ldots$$

Under certain other conditions,

$$dU = \mu_A dn_A + \mu_B dn_B + \ldots$$

$$dH = \mu_A dn_A + \mu_B dn_B + \ldots$$

$$dH = \mu_A dn_A + \mu_B dn_B + \ldots$$

$$dA = \mu_A dn_A + \mu_B dn_B + \ldots$$

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$$

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}$$

$$\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{T,V,n'}$$

Gibbs-Duhem Equation

$$G = n_A\mu_A + n_B\mu_B$$

$$dG = d(n_A\mu_A) + d(n_B\mu_B)$$

0

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B$$

From fundamental equation,

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\boxed{\sum_J n_J \, d\mu_J = 0}$$

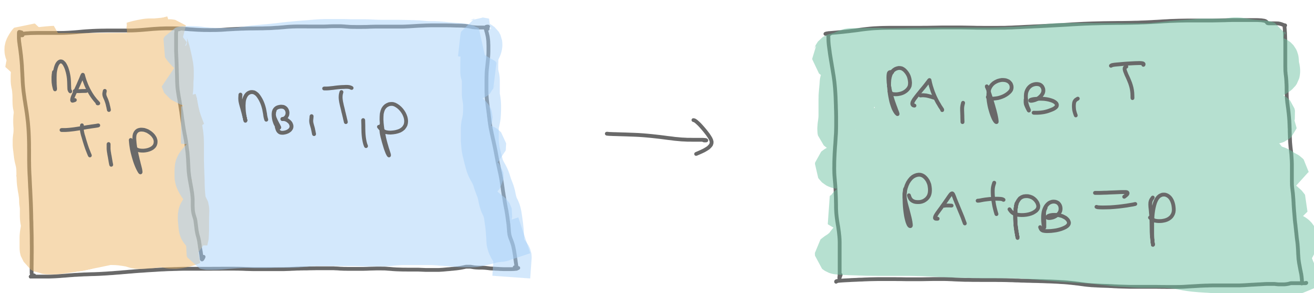
Gibbs – Duhem equation

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

$$\sum_J n_J \, dV_J = 0$$

$$dV_B = -\frac{n_A}{n_B} dV_A$$

The Gibbs Energy of Mixing for Perfect Gases



$$G_m(p) = G_m^{\ominus} + RT \ln \frac{p}{p^{\ominus}}$$

$$\mu = \underbrace{\mu^\ominus}_{} + RT \ln \frac{p}{p^\ominus}$$

standard chemical potential, chemical potential of the pure gas at 1 bar

$$\mu = \mu^\ominus + RT \ln p$$

$$G_i = n_A \mu_A + n_B \mu_B$$

$$G_i = n_A(\mu_A^\ominus + RT \ln p) + n_B(\mu_B^\ominus + RT \ln p$$

$$G_f = n_A(\mu_A^\ominus + RT \ln p_A) + n_B(\mu_B^\ominus + RT \ln p_B$$

$$\Delta_{mix} G = \cancel{n_A \mu_A^\ominus} + n_A RT \ln p_A$$

$$+ \cancel{n_B \mu_B^\ominus} + n_B RT \ln p_B$$

$$-(\cancel{n_A \mu_A^\ominus} + n_A RT \ln p$$

$$+ \cancel{n_B \mu_B^\ominus} + n_B RT \ln p)$$

$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

$$n_J = x_J n, \quad p_J = x_J p$$

$$\frac{p_A}{p} = \frac{x_A p}{p} = x_A$$

$$\boxed{\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)}$$

Gibbs energy of mixing for a perfect gas