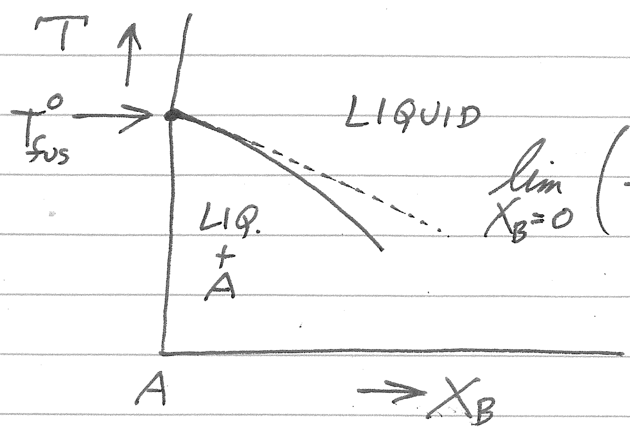
Limiting Slope Equation

(no solid solubility)
(model-independent)
(independent of excess terms)



$$\lim_{X_B=0}\left(\frac{dX_B}{dT}\right) = -\frac{\Delta h^o_{fusion(A)}}{\left(T^o_{fus(A)}\right)^2 \left(\Sigma\nu\right)}$$

Dilute Solution

$$\begin{cases} A = \text{solvent} & n_A \text{ moles} \\ B = \text{solute} & n_B \text{ moles} \end{cases}$$

$$N_A = n_A \cdot N_{Avogadro} \qquad N_B = n_B \cdot N_{Avogadro}$$

n_B moles of solute $\rightarrow$
- n_1 moles of "particles" 1 (atoms, molecules, ions, defects etc)
- n_2 moles of "particles" 2
- ⋮
- ⋮ which are NOT ALREADY IN THE SOLVENT

$$N_i = n_i \cdot N_{Avogadro}$$

and: $n_i = \nu_i \, n_B$

Example: (liquid) Solvent = $AgNO_3$, Solute = $CaCl_2$

$n_1 = n_{Ca} = 1 \cdot n_{CaCl_2}$ $\nu_1 = 1$
$n_2 = n_{Cl} = 2 \cdot n_{CaCl_2}$ $\nu_2 = 2$
$(\Sigma\nu = 3)$

Example: (liquid) Solvent = $AgCl$, Solute = $CaCl_2$

$n_1 = n_{Ca} = 1 \cdot n_{CaCl_2}$ $\nu_1 = 1$
$(\Sigma\nu = 1)$
(Cl^- is already in the solvent)

Example: (solid) Solvent = $NaCl$, Solute = $CaCl_2$

$n_1 = n_{Ca} = 1\, n_{CaCl_2}$ $\nu_1 = 1$
$n_2 = n_{Va} = 1\, n_{CaCl_2}$ $\nu_2 = 1$
$(\Sigma\nu = 2)$
(assuming Ca^{2+} and Va are not associated)
(if associated, then $\Sigma\nu = 1$)

Examples: $\begin{cases} O_2 \text{ in molten Fe} & \Sigma\nu = 2 \\ O_2 \text{ in } H_2O & \Sigma\nu = 1 \\ C\text{(interstitial) in steel} & \Sigma\nu = 1 \end{cases}$

Dilute Solution: (Henry's Law) (no interaction between B's)

$$\begin{cases} H = n_A H_A^\circ + n_B H_B^* & (H_B^* = \text{constant}) \\ S^{\text{non-config}} = n_A S_A^\circ + n_B S_B^* & (S_B^* = \text{constant}) \end{cases}$$

$$H_A = \frac{\partial H}{\partial n_A} = H_A^\circ \qquad \Delta H_A = H_A - H_A^\circ = 0$$

also: $\Delta S_A^{\text{non-config}} = 0$

(Number of ways of placing (new) particle i in solution) $= (\beta_i N_A)$

where β_i = constant

$$\text{Multiplicity} = \Omega = \frac{(\beta_1 N_A)^{N_1} (\beta_2 N_A)^{N_2} (\beta_3 N_A)^{N_3} \cdots\cdots}{(N_1!)(N_2!)(N_3!)\cdots\cdots}$$

Distributing the common (not new) particles provides only a relatively small increment to ΔS which can be ignored in the limit as $n_B \to 0$

$$\Delta S^{\text{config}} = k \ln \Omega$$

Stirling: $\ln(N!) \simeq N \ln N - N$

$$\begin{aligned} \Delta S/k &= \Sigma N_i \ln(N_A) + \Sigma N_i \ln \beta_i - \Sigma (N_i) \ln N_i + \Sigma N_i \\ &= \Sigma \nu_i N_B \ln N_A + \Sigma \nu_i N_B \ln \beta_i - \Sigma \nu_i N_B \ln(\nu_i N_B) + \Sigma(\nu_i N_B) \end{aligned}$$

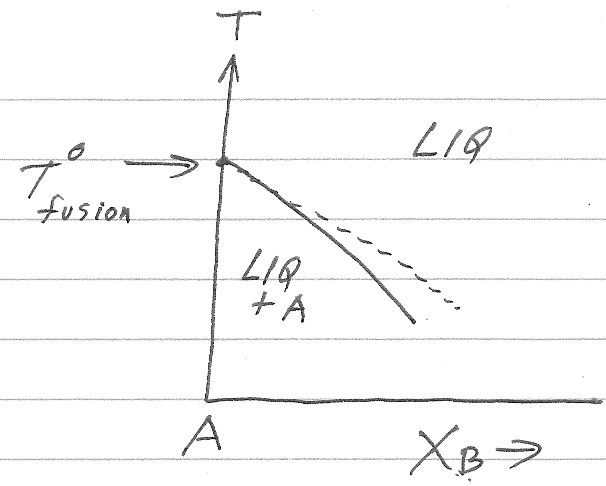
$$\Delta S_A^{\text{config}} = \left(\frac{\partial \Delta S}{\partial n_A}\right)_{n_B} = k N_{\text{Avogadro}} \left(\frac{n_B}{n_A}\right) \Sigma \nu_i = R \Sigma (X_B \nu_i)$$

$$\approx R \ln (1 - X_B \Sigma \nu_i)$$

(if $X_B \approx 0$)

Note: All β_i drop out (That is: model-independent)

$$(\mu_A - \mu_A^\circ) = \Delta H_A - T \Delta S_A^{\text{non-config}} - T \Delta S_A^{\text{config}} = -RT \ln (1 - X_B \Sigma \nu_i)$$



$$(\mu_A - \mu_A^{o})^{LIQUID} = -(\mu_A^{o\,LIQ} - \mu_A^{o\,Solid})$$

$$= -(\Delta h^{o}_{fusion} - T\Delta S^{o}_{fusion})$$

$$= -\Delta h^{o}_{fusion}\left(1 - T/T^{o}_{fusion}\right)$$

$$RT\ln(1 - X_B \Sigma \nu_i) = -\Delta h^{o}_{fusion}\left(\frac{T - T^{o}_{fusion}}{T^{o}_{fusion}}\right)$$

$X_B \rightarrow 0 \qquad T \rightarrow T^{o}_{fusion} \qquad X_B \rightarrow dX_B \qquad (T^{o}_{fusion} - T) \rightarrow dT$

$$\lim_{X_B \rightarrow 0}\left(\frac{dX_B}{dT}\right) = \frac{-\Delta h^{o}_{fusion(A)}}{(T^{o}_{fusion(A)})^2(\Sigma \nu_i)}$$

- independent of model
- independent of excess terms

$(\Sigma \nu_i)$ = number of moles of NEW particles in one mole of solute