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Thermodynamic derivation of colligative properties using Chemical Potential.

All the colligative properties arises from the reduction of the chemical potential of the liquid solvent as a result of the presence of solute. The reduction is from μ_A^* for the pure solvent to $\mu = \mu_A^* + RT \ln X_A$, when a solute is present.

($\ln X_A$ is negative because $X_A < 1$). The reduction in chemical potential of the solvent implies that the liquid vapour equilibrium occurs at a higher temperature (the b. Pt is raised or elevated) and the solid-liquid equilibrium occurs at a lower temperature (the freezing point is lowered).

For a non-ideal solution $\mu = \mu_A^* + RT \ln a_A$ where a_A is the activity of A in the solution or $\mu = \mu_A^* + RT \ln \gamma_A X_A$, where γ_A is the activity coefficient of A.

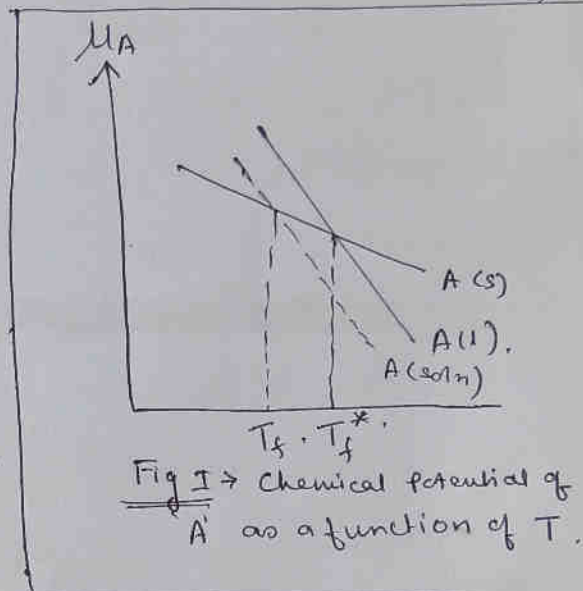
Freezing point Depression and boiling point elevation:

The normal boiling point of a pure liquid or solution is the temperature at which the vapour pressure equals 1 atm. A non volatile liquid lowers the vapour pressure. Hence it requires a higher temperature for the solution's vapour pressure to reach 1 atm., and the normal boiling point of the solution is elevated above that of the pure solvent. Similarly addition of a non volatile solute usually lowers the freezing point of the solution, since ~~at~~

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The freezing point of a solution is the temperature at which the vapour pressure of liquid and the solid become equal. Fig ① shows the plot of chemical potential μ_A , for pure solid A, pure liquid A and A in solution (A_{soln}) versus temperature at a fixed pressure of 1 atm.

At the normal freezing point T_f^* of pure A, the phases $A(s)$ and $A(l)$ are in equilibrium and their chemical potentials are equal $\mu_{A(s)}^* = \mu_{A(l)}^*$. Below T_f^* , pure solid A is more stable than pure liquid A, and $\mu_{A(s)}^* < \mu_{A(l)}^*$.



Since the most stable phase is the one with the lowest μ . Above T_f^* , $A(l)$ is more stable than $A(s)$ and $\mu_{A(l)}^* < \mu_{A(s)}^*$. Addition of solute to $A(l)$ at constant temp^r and pressure always lowers μ_A , so $\mu_{A(soln)}^* < \mu_{A(l)}^*$ at any given T.

Let us now calculate the freezing point depression due to the solute B in solvent A. The equilibrium is established at a temperature for which.

$$\mu_{A(s)}^* = \mu_{A(l)}^* + RT_f \ln \chi_A \quad \rightarrow \textcircled{1}$$

Where $\mu_{A(l)}^*$ is the chemical potential of pure liquid and χ_A is the mole fraction of A in the solution.

The chemical potential μ^* of pure substance equals to molar Gibbs energy G_m^* $\left[\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P} = G_{m,i}^* \right]$

$$\text{Then } \ln \chi_A = \frac{G_{m,A(s)}^* - G_{m,A(l)}^*}{RT_f} \quad \left[\text{From equ}^n \textcircled{1} \right]$$

$$= - \frac{\Delta_{fus} G_{m,A}}{RT} \quad \rightarrow \textcircled{2}$$

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$$\text{or } \ln(1-x_B) = -\frac{\Delta_{\text{fus}} G_{m,A}}{RT_f} \rightarrow (3) \text{ since } (x_A + x_B = 1)$$

$$\text{where } \Delta_{\text{fus}} G_{m,A} = G_{m,A(l)}^* - G_{m,A(s)}^*$$

We have .

$$\frac{d}{dT_f} \left(\frac{-\Delta_{\text{fus}} G_{m,A}}{RT_f} \right) = \frac{\Delta_{\text{fus}} H_{m,A}}{RT_f^2} \quad [\text{van't Hoff equation}]$$

Putting the value of $\frac{\Delta_{\text{fus}} G_{m,A}}{RT_f}$ in eqnⁿ. (3)

$$\frac{d}{dT_f} [\ln(1-x_B)] = \frac{\Delta_{\text{fus}} H_{m,A}}{RT_f^2}$$

$$d \ln(1-x_B) = \frac{\Delta_{\text{fus}} H_{m,A}}{RT_f^2} dT_f \rightarrow (4)$$

Integrating within the limit of freezing point of pure A T_f^* and T_f (freezing point of the solution).

$$\int d \ln(1-x_B) = \int_{T_f^*}^{T_f} \frac{\Delta_{\text{fus}} H_{m,A}}{RT_f^2} dT_f$$

$$\ln(1-x_B) = \frac{\Delta_{\text{fus}} H_{m,A}}{R} \int_{T_f^*}^{T_f} \frac{1}{T^2} dT_f \quad (5)$$

Now, if we suppose that the amount of solute present is so small that $x_B \ll 1$, we can write $\ln(1-x_B) \approx -x_B$

$$-x_B = \frac{\Delta_{\text{fus}} H_{m,A}}{R} \left(\frac{1}{T_f} - \frac{1}{T_f^*} \right) \quad \left[\text{Since } \int \frac{1}{T^2} dT = -\frac{1}{T} \right]$$

$$-x_B = \frac{\Delta_{\text{fus}} H_{m,A}}{R} \left(\frac{T_f - T_f^*}{T_f^* T_f} \right) \rightarrow (6)$$

Since T_f is close to T_f^* , the quantity $T_f^* T_f$ can be replaced by $(T_f^*)^2$.

$$-x_B = \frac{\Delta_{\text{fus}} H_{m,A}}{R} \left(\frac{T_f - T_f^*}{(T_f^*)^2} \right) \rightarrow (7)$$

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The quantity $T_f - T_f^*$ is the freezing point depression
 ΔT_f $\Delta T_f = T_f - T_f^*$

From equⁿ (7)

$$\Delta T_f = \frac{-x_B R (T_f^*)^2}{\Delta_{\text{fus}} H_{m,A}} \rightarrow (8)$$

If n_B is the number of moles of solute and n_A is the number of moles of pure solvent A.

$$x_B = \frac{n_B}{(n_A + n_B)}$$

Since the solution is very dilute $n_B \ll n_A$.

$$x_B = \frac{n_B}{n_A}$$

The molality of the solute $m_B = \frac{n_B}{n_A M_A}$.

where M_A is the molar mass of the solvent.

$$\text{or } \frac{n_B}{n_A} = m_B M_A$$

$$\text{or } x_B = m_B M_A$$

Putting the value of x_B in equⁿ (8)

$$\Delta T_f = \frac{-M_A R (T_f^*)^2 m_B}{\Delta_{\text{fus}} H_{m,A}} \rightarrow (9)$$

$$\text{or } \Delta T_f = -K_f m_B \rightarrow (10)$$

where $-K_f$ is the solvent's molal freezing point depression constant.
 K_f is defined as

$$K_f = \frac{M_A R (T_f^*)^2}{\Delta_{\text{fus}} H_{m,A}}$$

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