

## - GIBBS-DUHEM EQ

DEF

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

AT CONSTANT T AND P

$$dG = \sum_i \mu_i dn_i$$

BUT

$$G = \sum_i n_i \mu_i$$

AND

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$\Rightarrow$

$$\boxed{\sum_i n_i d\mu_i = 0}$$

GIBBS-DUHEM  
EQ.

FOR BINARY SOLUTIONS

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

OR

$$\boxed{d\mu_2 = -\frac{n_1 d\mu_1}{n_2}}$$

# COLLIGATIVE PROPERTIES

COLLIGATIVE PROPERTIES DEPEND ON THE PROPERTIES OF THE SOLVENT!

BOILING POINT ELEVATION

FREEZING POINT DEPRESSION

CONSIDER EQUILIBRIUM BETWEEN A SOLUTION AND PURE SOLID SOLVENT

(SOLUTE DOES NOT SOLIDIFY)

$$\mu_{\text{sol}} = \mu_{\text{solid}}^*$$

$$\mu_{\text{sol}} = \mu_{\text{solvent}}^* + RT \ln X_{\text{solvent}}$$

$$= \mu_{\text{solid}}^*$$

$$\ln X_{\text{Solvent}} = \frac{\mu_{\text{Solid}} - \mu_{\text{Solvent}}}{RT}$$

$$= - \frac{\Delta \bar{G}_{\text{Fusion}}}{RT}$$

WE NEED  $T(X)$  OR

$$\left( \frac{\partial T}{\partial X_{\text{solvent}}} \right)_p$$

$$\left( \frac{\partial \ln X}{\partial X} \right)_p = - \frac{1}{R} \left( \frac{\partial \frac{\Delta \bar{G}_F}{T}}{\partial T} \right)_p \left( \frac{\partial T}{\partial X} \right)_p$$

$$\frac{1}{X} = \frac{\Delta \bar{H}_F}{RT^2} \left( \frac{\partial T}{\partial X} \right)_p$$

$$\int_1^X \frac{dX'}{X'} = \int_{T_F}^T \frac{\Delta \bar{H}_F}{R} \frac{dT}{T^2}$$

$$\ln X = + \frac{\Delta \bar{H}_f}{R} \left[ \frac{1}{T_f} - \frac{1}{T} \right]$$

$$\frac{1}{T} = \frac{1}{T_f} - \frac{R}{\Delta \bar{H}_f} \ln X$$

$$\frac{1}{T} - \frac{1}{T_f} = \frac{T_f - T}{T T_f} = \frac{\Delta T}{T T_f}$$

$$\approx \frac{\Delta T}{T_f^2}$$

$$\Delta T = - \frac{R T_f^2}{\Delta \bar{H}_f} \ln X$$

$$X = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{1}{1 + (n_{\text{solute}} / n_{\text{solvent}})}$$

$$\ln X = - \ln \left( 1 + \frac{n_{\text{solute}}}{n_{\text{solvent}}} \right) \approx - \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{n_{\text{solute}}}{m_{\text{solvent}}} \frac{M_{\text{solvent}}}{M_{\text{solvent}}} = M_{\text{solvent}} \frac{n_{\text{solute}}}{\text{mass solvent Kg}}$$

$$\Delta T_f = \left( \frac{R T_f^2}{\Delta H_f} M_{\text{solvent}} \right) M_{\text{solute}}$$

$M_{\text{solute}}$  = molality of solute

## Boiling Point Elevation

$$\Delta T_b = \left( \frac{R T_b^2}{\Delta H_{\text{vap}}} M_{\text{solvent}} \right) M_{\text{solute}}$$

$$K_f \gg K_b$$

# OSMOTIC PRESSURE

$$\mu_{\text{Solution}}(T, P+\pi, X_{\text{solu}}) = \mu_{\text{Solvent}}^*(T, P)$$

$$\mu_{\text{Solvent}}^*(T, P+\pi) + RT \ln X_{\text{solvent}}$$

$$d\mu = V_m dp \quad \text{AT CONST. } T$$

$$\mu_{\text{Solv}}^*(T, P+\pi, X) - \mu_{\text{Solv}}^*(T, P) = \int_P^{P+\pi} V_m^* dp'$$

$$-RT \ln X_{\text{solu}} = V_m^* \pi$$

$$\ln X_{\text{solu}} = - \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\boxed{\pi = \frac{RT}{V} n_{\text{solute}} = RT [\text{Solute}]}$$

# REAL SOLUTIONS

IDEAL  $V_m = X_A V_{m,A}^* + (1 - X_A) V_{m,B}^*$

ADDITIVE VOLUMES

DEVIATIONS FROM RAULT'S LAW

$$\bar{V}_1(P, T, n_1, n_2) = \left( \frac{\partial V}{\partial n_1} \right)_{P, T, n_2}$$

$$V = n_1 \bar{V}_1(P, T, n_1, n_2) + n_2 \bar{V}_2(P, T, n_1, n_2)$$

$$\Delta G_{mix} < 0$$

$$\Delta S_{mix} > 0$$

$$\Delta V_{mix} \neq 0$$

$$\Delta H_{mix} \neq 0$$

## THERMODYNAMICS

$$\mu_i^{\text{soln}} = \mu_i^* + RT \ln \left( \frac{P_i}{P_i^*} \right)$$

RAOULT'S LAW (IDEAL)

$$P_i = X_i P_i^*$$

## REAL SOLUTIONS

$$\text{Activity} \equiv a_i = \frac{P_i}{P_i^*} \quad \text{FOR THE SOLVENT}$$

$$a_i \equiv \gamma_i X_i$$

IDEAL BEHAVIOR

$$P \rightarrow 0$$

$$X_{\text{sol}} \rightarrow 0$$

$$\gamma_i \rightarrow 1$$

$$\mu_i^{\text{soln}} = \mu_i^* + RT \ln a_i$$



FOR THE SOLUTE ONE OBSERVES

A LINEAR RELATION AT LOW CONC.

$$p_{\text{solute}} = K_H^{\text{solute}} X_{\text{solute}} \quad \text{HENRY'S LAW}$$

AS  $X_{\text{solute}} \rightarrow 0$

### IDEAL SOLUTION

SOLVENT  $\rightarrow$  RAULT'S LAW

SOLUTE  $\rightarrow$  HENRY'S LAW

$$\mu_i^{\text{Soluto}} = \mu_i^{\text{*Soluto}} + RT \ln \left( \frac{k_H X_{\text{Soluto}}}{p_{\text{Soluto}}^*} \right)$$

$$= \mu_i^{\text{*H}} + RT \ln \left( \frac{X_{\text{Soluto}}}{p_{\text{Soluto}}^*} \right)$$

DEF

$$a_i = \frac{p_i}{p_i^H} = \gamma_i X_i$$

$$a_{\text{Soluto}} \rightarrow X_{\text{Soluto}}$$

$$\gamma_{\text{Soluto}} \rightarrow 1$$

$$X_{\text{Soluto}} \rightarrow 0$$

FOR THE SOLUTE

$$X_{ste} = \frac{n_{ste}}{n_{ste} + n_{sol}}$$

DIVIDE BY  $n_{sol} M_{sol} = \text{Solvent mass}$

$$X_{solute} = \frac{M_{solute}}{\frac{1}{M_{solvent}} + M_{solute}}$$

$$\cancel{X} = \frac{Mm}{1 + Mm}$$

$$X + Mxm = mm$$

$$\frac{X}{M} + Xm = m$$

$$m = \frac{X/M}{1 - X} \xrightarrow{x \rightarrow 0} \frac{X}{M}$$

## CHEMICAL POTENTIAL

$$\mu_i(P, T) = \mu_i^0(P^0, T) + RT \ln \left( \gamma_i \frac{P_i}{P^0} \right) \quad \text{GASES}$$

$$\lim_{P \rightarrow 0} \gamma_i = 1$$

$$\mu_i(P, T) = \mu_i^*(P^*, T) + RT \ln (\gamma_i X_i) \quad \text{solutes}$$

$$\lim_{X \rightarrow 1} \gamma_i = 1$$

$$\mu_i(P, T) = \mu_i^{\text{H}}(P^{\text{H}}, T) + RT \ln (\gamma_i M_i) \quad \text{Soluto}$$

$$\lim_{M \rightarrow 0} \gamma_i = 1$$

$$a = \frac{P}{k_{H1}} \xrightarrow{m \rightarrow 0} M$$

$$\gamma = \frac{a}{M} \xrightarrow{m \rightarrow 0} 1$$

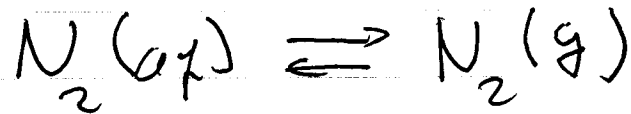
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### COLLIGATIVE PROP

$$\Delta T_f = -k_f \gamma M_{\text{solute}}$$

$$\Delta T_b = k_b \gamma M_{\text{solute}}$$

$$\Pi = \gamma C_{\text{solute}} RT$$

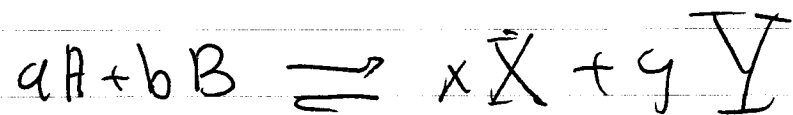


$$\mu_{\text{N}_2}^{\text{sol}} = \mu_{\text{N}_2}^{\text{H}} + RT \ln a_{\text{N}_2}$$

$$a_{\text{N}_2} \longrightarrow X_{\text{N}_2} = \frac{P_{\text{N}_2}}{k_{\text{H}}^{\text{N}_2}}$$

$$X_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}} \approx \frac{n_{\text{N}_2}}{n_{\text{H}_2\text{O}}}$$

$$n_{\text{N}_2} = n_{\text{H}_2\text{O}} \frac{P_{\text{N}_2}}{k_{\text{H}}^{\text{N}_2}}$$



$$K = \frac{(a_X)^x (a_Y)^y}{(a_A)^a (a_B)^b}$$

$$\sum_i \nu_i \mu_i = 0 \quad \text{AT EQUILIBRIUM}$$

$$\mu_i = \mu_i^{\text{H}\infty} + RT \ln a_i^{\text{eff}}$$

$$52 \text{ CARDS} \rightarrow 52! = 8 \times 10^{67}$$

$$\text{AGE OF THE U} = 13.6 \text{ BY}$$

$$13.6 \times 10^9 \times 365 \times 24 \times 60 \times 60 \text{ s} = 10^{17} \text{ sec.}$$