- 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

$$G = \sum n_i \mu_i$$

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

COLLIGAIVE PROPERTIES DEPEND ON THE PROPERTIES OF THE SOLVENT!

BOILING POINT ELEVATION

FREEZING POINT DEPRESSION

CONSIDER EQUILIBRIUM BETWEEN A SOLUTION AND PURE SOLID SOLVENT

(SOLUTE DONOT SOLIDIFIES)

$$\mu_{SOL} = \mu^*_{SOLID}$$

$$\mu_{Sol} = \mu^*_{Solvent} + RT \ln X_{Solvent}$$

$$= \mu^*_{Solid}$$

$$\ln X_{Solvent} = \frac{\mu_{solid}^{*} - \mu_{SOLVENT}^{*}}{R\,T}$$

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

WE NEED $T(X)$ OR

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

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

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

$$\boxed{\int_1^X \frac{dX'}{X'} = \int_{T_f}^{T} \frac{\Delta \bar{H}_f}{R}\frac{dT}{T^2}}$$

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

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

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

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

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

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

$$\ln X = -\ln\left(1 + \frac{n_{solute}}{n_{solve}}\right) \simeq -\frac{n_{solute}}{m_{solvent}}$$

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

$$\boxed{\Delta T_f = \left(\frac{R T_f^2}{\Delta \bar{H}_f} M_{solvent}\right) m_{solute}}$$

m_{solut} = molality of solute

Boling Point Elevation

$$\boxed{\Delta T_b = \left(\frac{R T_b^2}{\Delta \bar{H}_{vap}} M_{solvent}\right) m_{solute}}$$

$K_f >> K_b$

OSMOTIC PRESSURE

$$\mu_{\text{Solution}}(T, P+\Pi, X_{\text{solv}}) = \mu^*_{\text{Solvent}}(T, P)$$

$$\mu^*_{\text{Solvent}}(T, P+\Pi) + RT \ln X_{\text{solvent}}$$

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

$$\mu^*_{\text{Solv}}(T, P+\Pi, X) - \mu^*_{\text{Solv}}(T, P) = \int_P^{P+\Pi} V_m^* \, dP'$$

$$-RT \ln X_{\text{solv}} = V_m^* \Pi$$

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

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

REAL SOLUTIONS

IDEAL $V_m = X_1 V^*_{mA} + (1-X_1) V^*_{mB}$

ADDITIVE VOLUMES

DEVIATIONS FROM RAOULT'S LAW

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

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

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

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

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

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

THERMODYNAMICS

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

RAOULT'S LAW (IDEAL)

$$P_i = X_i P_i^{*}$$

Real Solutions

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

$$a_i \equiv \gamma_i X_i$$

IDEAL BEHAVIOR $p \to 0$

$X_{Sol} \to 0$

$\gamma_i \to 1$

$$\boxed{\mu_i^{Solo} = \mu_i^{*} + RT \ln a_i}$$

FOR THE SOLUTE ONE OBSERVES

A LINEAR RELATION AT LOW CONC.

$$\boxed{p_{solute} = k_H^{solute} X_{solute}}$$ HENRY'S LAW

AS $X_{solute} \rightarrow 0$

IDEAL SOLUTION

SOLVENT $\longrightarrow$ RAOULT'S LAW

SOLUTE $\longrightarrow$ HENRY'S LAW

$$\mu_i^{solute} = \mu_i^{*solute} + RT \ln\left(\frac{k_H^{solute} X^{solute}}{P^*_{solute}}\right)$$

$$= \mu_i^{*H} + RT \ln\left(\frac{\cancel{k_H}^{solute}}{pa}\right)$$

DEF

$$a_i = \frac{P_i}{k_i^H} = \gamma_i X_i$$

$$a_{solute} \longrightarrow X_{solute}$$

$$\gamma_{solute} \longrightarrow 1$$

$$X_{solute} \longrightarrow 0$$

FOR THE SOLUTE

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

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

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

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

$$X + MXm = Mm$$

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

$$m = \frac{X/M}{1 - X} \xrightarrow[X \to 0]{} \frac{X}{M}$$

CHEMICAL POTENTIAL

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

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

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

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

$$\mu_i(P,T) = \mu^{H}_{(P^o,T)} + RT \ln(\gamma_i m_i) \quad \text{Solute}$$

$$\lim_{m\to 0} \gamma_i = 1$$

$$a = \frac{P}{k_{H}} \xrightarrow[m \to 0]{} m$$

$$\gamma = \frac{a}{m} \xrightarrow[m \to 0]{} 1$$

Colligative Prop

$$\Delta T_f = -K_f \, \gamma \, m_{solute}$$

$$\Delta T_b = K_b \, \gamma \, m_{solute}$$

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

$$N_2(aq) \rightleftharpoons N_2(g)$$

$$\mu^{sol}_{N_2} = \mu^{\infty H}_{N_2\,(g)} + RT \ln a_{N_2}$$

$$a_{N_2} \longrightarrow X_{N_2} = \frac{P_{N_2}}{k^{H}_{N_2}}$$

$$X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} \simeq \frac{n_{N_2}}{n_{H_2O}}$$

$$\boxed{n_{N_2} = n_{H_2O} \frac{P_{N_2}}{K^{H}_{N_2}}}$$

$$aA + bB \rightleftharpoons xX + yY$$

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

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

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

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

AGE OF THE U = 13.6 BY

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