Excess Gibbs free Energy Models

$$\overline{G}_i^{Ex} = RT\ln\gamma_i \qquad \underline{G}^{Ex} = \underline{G}(\text{mixture}, T, P) - \underline{G}^{IM}(T, P, \{x\})$$

Solution non-idealities important in

   * separations   * biophysics

Simple (empirical) models — Margules

$$\underline{G}^{Ex} = C x_1 x_2 \qquad \text{for 2-component system}$$

     $\hookrightarrow$ constant from data

$$\gamma_1, \gamma_2 = ? \qquad \overline{G}_1^{Ex} = \left.\frac{\partial G^{Ex}}{\partial N_1}\right)_{T,P,N_2} = \frac{\partial}{\partial N_1}\left(\frac{C N_1 N_2}{N_1 + N_2}\right)$$

$$= C\,\frac{N_2(N_1+N_2) - N_1 N_2}{(N_1+N_2)^2} = C x_2^2 \Rightarrow RT\ln\gamma_1 = C x_2^2$$

Same way, $\qquad RT\ln\gamma_2 = C x_1^2$

van Laar

$$\underline{G}^{Ex} = \frac{C_1 C_2 x_1 x_2}{C_1 x_1 + C_2 x_2}$$

$$RT\ln\gamma_1 = C_1\left(1 + \frac{C_1 x_1}{C_2 x_2}\right)^{-2} \qquad RT\ln\gamma_2 = C_2\left(1 + \frac{C_2 x_2}{C_1 x_1}\right)^{-2}$$

Proof? See Practice Problems II

Note correct limits: $\underline{G}^{Ex} \to 0$ for $x_1 \to 0$ or $x_1 \to 1$

         $\ln\gamma_1 \to 1$ for $x_1 \to 1$, $x_2 \to 0$

         $\ln\gamma_2 \to 1$ for $x_1 \to 0$, $x_2 \to 1$

Semitheoretical Models — "Regular" solutions

Excess Entropy of mixing $= 0$ $\Delta V^{Ex} = 0$

Regular Solution theory gives (no proof)

$$\ln \gamma_1 = \frac{\underline{V}_1 \, \phi_2^2 \, (\delta_1 - \delta_2)^2}{RT} \qquad \ln \gamma_2 = \frac{\underline{V}_2 \, \phi_1^2 \, (\delta_1 - \delta_2)^2}{RT}$$

where ϕ_1 = volume fraction = $\dfrac{x_1 \underline{V}_1}{x_1 \underline{V}_1 + x_2 \underline{V}_2}$

δ = "solubility parameter" = $\sqrt{\dfrac{\underline{u} - u_L}{\underline{V}_L}}$

Solubility parameters can be obtained for many liquids, listed in Table 8.2 for a few.

<u>Flory-Huggins model</u> : good for polymers, still in use.

→ monomeric solvent + chains ←

$$\frac{\Delta S_{mix}}{R} = - N_s \ln \phi_s - N_p \ln \phi_p \qquad \begin{array}{l} m: \text{ beads} \\ \quad \text{per chain} \end{array}$$

$$\phi_s = \frac{N_s}{N_s + m N_p} \qquad \phi_p = \frac{m N_p}{N_s + m N_p}$$

Much lower ΔS_{mix} than of monomeric components

$$\frac{H^{Ex}}{RT} = \chi \, N_s \, \phi_p \qquad \longrightarrow \text{ counts polymer-solvent interaction pairs}$$

$\;\;\;\;\;\; \hookrightarrow$ "χ" (chi) parameter, a measure of interactions between polymer + solvent segments

UNIQUAC + UNIFAC

Abrams + Prausnitz (1975); UNIFAC is group contribution version of UNIQUAC

$$\underline{G}^{EX} = \underline{G}^{EX}(\text{combinatorial}) + \underline{G}^{EX}(\text{interactions})$$

$\underbrace{\qquad\qquad}_{\text{size + shape}}$

$$= RT \sum_i x_i \ln \Phi_i/x_i + \ldots \qquad\qquad - RT \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ij}\right)$$

$$+ \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\Phi_i}$$

→ τ_{ij}: binary parameters

θ_j: area fractions

→ q_i: surface parameter

→ fitted to experimental data on activity coeffs., phase equilibrium (VLE, LLE) data.

Infinite-dilution properties

"Standard" definition of activity

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \underline{\text{pure } i \text{ liq. or solid}})$$

$\underbrace{\qquad\qquad}_{\text{same state as solution}}$

Runs into difficulties if pure component state does not exist or is hard to obtain —

e.g. proteins in solution, electrolytes, gases above their critical points

"Infinite Dilution" reference state for comp 1

$$RT \ln a_1^\infty = RT \ln(\gamma_1^\infty x_1) = \mu_1(T, P, x_1) - [\mu_1^o(T, P, x_1^o) - RT \ln x_1^o]$$

in same solvent, temp. and pressure ⤴ $x_1^o \to 0$

By construction, $\gamma_i^\infty \rightarrow 1$ as $x_i \rightarrow 0$

For dissolved gases the main quantity of interest is the partial pressure above a solution of certain concentration.

Recall $a_i = \gamma_i x_i = \dfrac{f_i(T, P, \{x\})}{f_i(T, P, \text{pure } i)} \leftarrow$ constant

We can rewrite this as $f_i = \gamma_i x_i \cdot$ Const.

Even if pure comp. (reference) fugacity is not directly measurable, at low concentrations the activity coefficients are independent of concentration,

so $f_i \simeq y_i P$ (for gas) $= x_i \cdot H$

$\qquad\qquad\qquad\qquad\qquad\qquad\uparrow \qquad \uparrow$

$\qquad\qquad\qquad\qquad\qquad\quad$ liq. mole   "Henry's
$\qquad\qquad\qquad\qquad\qquad\quad$ fraction   Constant"

The higher the Henry's Constant, the <u>lower</u> the solubility of a gas in a liquid –

E.g. O_2 in H_2O @ $25^\circ C$ $H \simeq 4 \cdot 10^4$ bar

$\qquad N_2$ "   " $H \simeq 9 \cdot 10^4$ bar

H is a <u>strong</u> function of T.