Outline

- o Bubble/Dew Calculations using MRL

Making the function for G^E realistic:

- o 12.1-2 Van der Waals perspective
  - Van Laar
  - Scatchard/Hildebrand
  - Flory, Flory-Huggins
- o 12.5 Theory - Skip
- o 13.1 Local Composition Theory
  - Wilson
  - UNIQUAC
  - UNIFAC

12.1-2 Van der Waals perspective

Regular Solutions ($V^E = 0$, $S^E = 0$)
energetics of mixing are described by the same energy equation for mixtures that we previously developed in discussing the simple basis for mixing rules.

$$U - U^{ig} = -\rho \sum\sum x_i x_j a_{ij}$$

Noting that $1/\rho = V = \Sigma x_i V_i$ according to "regular solution theory",

$$(U - U^{ig}) = \frac{-\sum\sum x_i x_j a_{ij}}{\sum x_i V_i}$$

For the pure fluid, taking the limit as $x_i \rightarrow 1$,

$$(U - U^{ig})_i = -\frac{a_{ii}}{V_i} \Rightarrow (U^{is} - U^{ig}) = -\sum \frac{x_i a_{ii}}{V_i}$$

For a binary mixture, subtracting the ideal solution result to get the excess energy gives,

$$U^E = x_1 \frac{a_{11}}{V_1} + x_2 \frac{a_{22}}{V_2} - \left(\frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 V_1 + x_2 V_2} \right)$$

van Laar

$$Q \equiv \left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2} \right)^2 \Rightarrow U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q$$

$$\boxed{\frac{G^E}{RT} = \frac{U^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})}}$$

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2} \right]^2}$$

Fitting Van Laar to a single experiment:

$$A_{12} = \ln\gamma_1\left[1 + \frac{x_2\ln\gamma_2}{x_1\ln\gamma_1}\right]^2$$

$$A_{21} = \ln\gamma_2\left[1 + \frac{x_1\ln\gamma_1}{x_2\ln\gamma_2}\right]^2$$

Azeotrope point can be used. See example 11.5

Infinite dilution can be used. See example 11.6

Scatchard Hildebrand

$a_{12} = \sqrt{a_{11}a_{22}}$

$$U^E = \frac{x_1x_2V_1V_2}{x_1V_1 + x_2V_2}\left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2\sqrt{\frac{a_{11}}{V_1^2}\frac{a_{22}}{V_2^2}}\right)$$

$$U^E = \frac{x_1x_2V_1V_2}{x_1V_1 + x_2V_2}\left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2}\right)^2$$

$$\boxed{G^E = U^E = \Phi_1\Phi_2(\delta_1 - \delta_2)^2(x_1V_1 + x_2V_2)}$$

$\Phi_i \equiv x_iV_i / \sum x_iV_i$ is known as the "volume fraction"

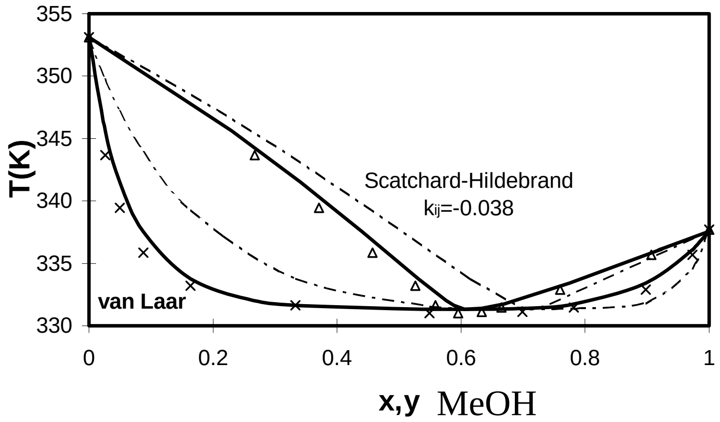
$\delta_i = (\sqrt{a_{ii}})/V$ is known as the “solubility parameter”

$$\delta_i \equiv \sqrt{\frac{\Delta U^{vap}}{V_i}} = \sqrt{\frac{\Delta H^{vap} - RT}{V_i}}$$

This is a predictive technique valid for nonpolar substances. See table 11.1 for parameters.

Also can make adjustable.

Van Laar and Scatchard-Hildebrand



MeOH

methanol + benzene

Flory’s Equation

Recall Ideal Solution result (pg 109)

$$\Delta\underline{S}_1 = n_1 R \ln \frac{\underline{V}_T}{\underline{V}_1^i} = n_{tot} x_1 R \ln \frac{\underline{V}_T}{\underline{V}_1^i}$$

$$\Delta\underline{S}_2 = n_2 R \ln \frac{\underline{V}_T}{\underline{V}_2^i} = n_{tot} x_2 R \ln \frac{\underline{V}_T}{\underline{V}_2^i}$$

$$\Delta\underline{S} = \Delta\underline{S}_1 + \Delta\underline{S}_2 = n_{tot} R \left(x_1 \ln \frac{\underline{V}_T}{\underline{V}_1^i} + x_2 \ln \frac{\underline{V}_T}{\underline{V}_2^i} \right)$$

Refine by recognizing volume taken by molecules:

$$\Delta\underline{S} = nR \left(x_1 \ln \left(\frac{(x_1 V_1 + x_2 V_2)\lambda}{x_1 V_1 \lambda} \right) + x_2 \ln \frac{(x_1 V_1 + x_2 V_2)\lambda}{x_2 V_2 \lambda} \right)$$

$$G^E = H^E - TS^E = RT(x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2})$$

Flory-Huggins Model

$$G^E = RT\left(x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2}\right) + \Phi_1\Phi_2(x_1 + x_2\mathrm{R})\chi RT$$

Flory

$$\mathrm{R} = \frac{V_2}{V_1}$$

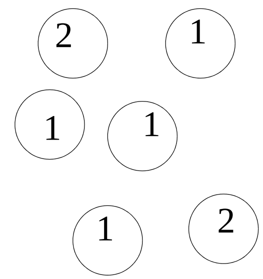
Scatchard-Hildebrand

$$\chi = \frac{V_1(\delta_1 - \delta_2)^2}{RT}$$

13.1 Local composition models (nonrandom)

Common Features

- o Lattice Model - Fixed number of neighbors = 10
- o Uses $G^E = A^E$ approximation (good)
- o Local Composition



$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2}\Omega_{12} \qquad \frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\Omega_{21}$$

- o Two-fluid Theory

$$(U - U^{ig}) = x_1(U - U^{ig})^{(1)} + x_2(U - U^{ig})^{(2)}$$

$$(U - U^{ig})^{(1)} = (N_A/2)z(x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21})$$

$$(U - U^{ig})_{pure1} = (N_A/2)z\varepsilon_{11}$$

$$U^E = \frac{N_A z}{2}\left[\frac{x_1 x_2\Omega_{21}(\varepsilon_{21} - \varepsilon_{11})}{x_1 + x_2\Omega_{21}} + \frac{x_2 x_1\Omega_{12}(\varepsilon_{12} - \varepsilon_{22})}{x_1\Omega_{12} + x_2}\right]$$

$$\frac{A^E}{RT} = \int\frac{-U^E}{RT}\frac{dT}{T} + C$$

Wilson's equation

$$\Omega_{12} = \Lambda_{21} = \frac{V_1}{V_2}\exp\left(\frac{-A_{21}}{RT}\right)$$

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right)$$

UNIQUAC

$$\Omega_{ij} = \frac{q_i}{q_j}\exp\left(\frac{-N_A z(\varepsilon_{ij}-\varepsilon_{jj})}{2RT}\right) = \frac{q_i}{q_j}\exp\left(\frac{-a_{ij}}{T}\right) = \frac{q_i}{q_j}\tau_{ij}$$

r_i volume (look up)

q_i surface area (look up)

θ_i surface area fractions

$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right)$ parameter

$$\frac{G^E}{RT} = x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2)$$
$$-5\left[q_1x_1\ln(\Phi_1/\theta_1) + q_2x_2\ln(\Phi_2/\theta_2)\right]$$
$$-q_1x_1\ln(\theta_1+\theta_2\tau_{21}) - q_2x_2\ln(\theta_1\tau_{12}+\theta_2)$$

$$\ln\gamma_1 = \ln\frac{\Phi_1}{x_1} + \left(1-\frac{\Phi_1}{x_1}\right) - 5q_1\left[\ln\frac{\Phi_1}{\theta_1} + \left(1-\frac{\Phi_1}{\theta_1}\right)\right]$$
$$+ q_1\left[1-\ln(\theta_1+\theta_2\tau_{21}) - \frac{\theta_1}{\theta_1+\theta_2\tau_{21}} - \frac{\theta_2\tau_{12}}{\theta_1\tau_{12}+\theta_2}\right]$$

$$\ln\gamma_2 = \ln\frac{\Phi_2}{x_2} + \left(1-\frac{\Phi_2}{x_2}\right) - 5q_2\left[\ln\frac{\Phi_2}{\theta_2} + \left(1-\frac{\Phi_2}{\theta_2}\right)\right]$$
$$+ q_2\left[1-\ln(\theta_1\tau_{12}+\theta_2) - \frac{\theta_1\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\theta_2}{\theta_1\tau_{12}+\theta_2}\right]$$

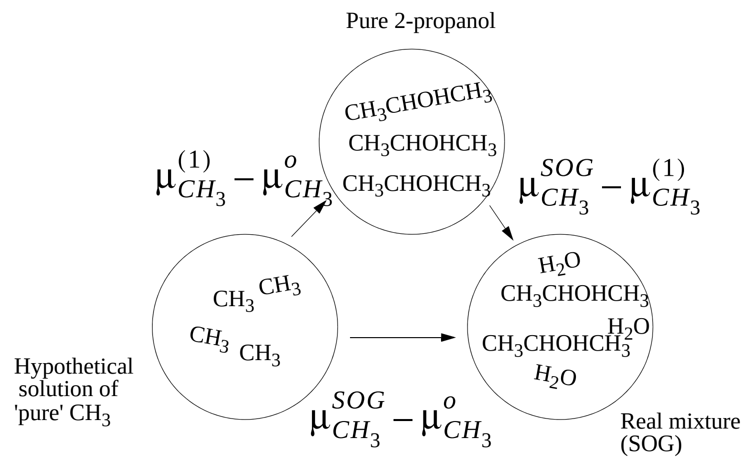
$$\ln\gamma_i^{res} = q_m\left[1-\ln\sum_i\theta_i\tau_{im} - \sum_j\frac{\theta_j\tau_{mj}}{\sum_i\theta_i\tau_{ij}}\right]$$

Group parameters for Uniquac and UNIFAC (Selected)

Main Group	**Sub-group**	***R*(rel.vol.)**	***Q*(rel.area)**	**Example**
CH2	CH3	0.9011	0.8480	
	CH2	0.6744	0.5400	*n*-hexane: 4 CH2 + 2 CH3
	CH	0.4469	0.2280	isobutane: 1CH + 3 CH3
	C	0.2195	0	neopentane: 1C + 4 CH3
C=C	CH2=CH	1.3454	1.1760	1-hexene: 1 CH2=CH + 3 CH2 + 1 CH3
	CH=CH	1.1167	0.8670	2-hexene: 1 CH=CH + 2 CH2 + 2 CH3
	CH2=C	1.1173	0.9880	
	CH=C	0.8886	0.6760	
	C=C	0.6605	0.4850	
ACH	ACH	0.5313	0.4000	benzene: 6 ACH
	AC	0.3652	0.1200	benzoic acid: 5 ACH + 1 AC + 1 COOH
ACCH2	ACCH3	1.2663	0.9680	toluene: 5 ACH + 1 ACCH3

	ACCH2	1.0396	0.6600	ethylbenzene: 5 ACH + 1 ACCH2 + 1 CH2
	ACCH	0.8121	0.3480	
OH	OH	1.0000	1.2000	*n*-propanol: 1 OH + 1 CH3 + 2 CH2
CH3OH	CH3OH	1.4311	1.4320	methanol is an independent group
water	H2O	0.9200	1.4000	water is an independent group
ACOH	ACOH	0.8952	0.6800	phenol: 1 ACOH + 5 ACH
CH2CO	CH3CO	1.6724	1.4880	dimethylketone: 1 CH3CO + 1 CH3
				methylethylketone: 1 CH3CO + 1 CH2 + 1 CH3
	CH2CO	1.4457	1.1800	diethylketone: 1 CH2CO + 2 CH3 + 1 CH2
CHO	CHO	0.9980	0.9480	acetaldehyde: 1 CHO+1 CH3
CCOO	CH3COO	1.9031	1.7280	methyl acetate: 1 CH3COO + 1 CH3
COOH	COOH	1.3013	1.2240	benzoic acid: 5 ACH + 1 AC + 1 COOH

UNIFAC



$$\ln\gamma_k = \ln\gamma_k^{COMB} + \ln\gamma_k^{RES}$$

$$\frac{\mu^{SOG}_{CH_3} - \mu^{(1)}_{CH_3}}{RT} = \frac{\mu^{SOG}_{CH_3} - \mu^{o}_{CH_3}}{RT} - \frac{\mu^{(1)}_{CH_3} - \mu^{o}_{CH_3}}{RT}$$

IPA

$$\mu_1 = 2\mu^{SOG}_{CH_3} + \mu^{SOG}_{CH} + \mu^{SOG}_{OH}$$

$$\mu_1^o = 2\mu^{(1)}_{CH_3} + \mu^{(1)}_{CH} + \mu^{(1)}_{OH}$$

$$\ln\gamma_1^{resid} = \frac{\mu_1 - \mu_1^o}{RT} = \sum_m \nu_m^{(1)}[\ln\Gamma_m - \ln\Gamma_m^{(1)}]$$

	Group Variable	Molecular Variable
volume	R	r
surface area	Q	q
activity coefficient	Γ	γ
surface fraction	Θ	θ
energy variable	Ψ_{ij}	τ_{ij}
energy parameter	a_{ij}	a_{ij}
mole fraction	X	x

$$\ln \Gamma_m = Q_m \left[1 - \ln \sum_i \Theta_i \Psi_{im} - \sum_j \frac{\Theta_j \Psi_{mj}}{\sum_i \Theta_i \Psi_{ij}} \right]$$

$$\Theta_j = (\text{surface area fraction of group } j) \equiv \frac{X_j Q_j}{\sum_i X_i Q_i}$$

$$\Psi_{mj} = \exp\left(\frac{-a_{mj}}{T} \right)$$

$$X_j = \frac{\sum_{molecules \text{ i}} \nu_j^{(i)} x_i}{\sum_{molecules \text{ i}} \sum_{groups \text{ k}} \nu_k^{(i)} x_i}$$