Faculty of Engineering and Technology
Department of Chemical Engineering
University Of Jordan

Thermodynamics II

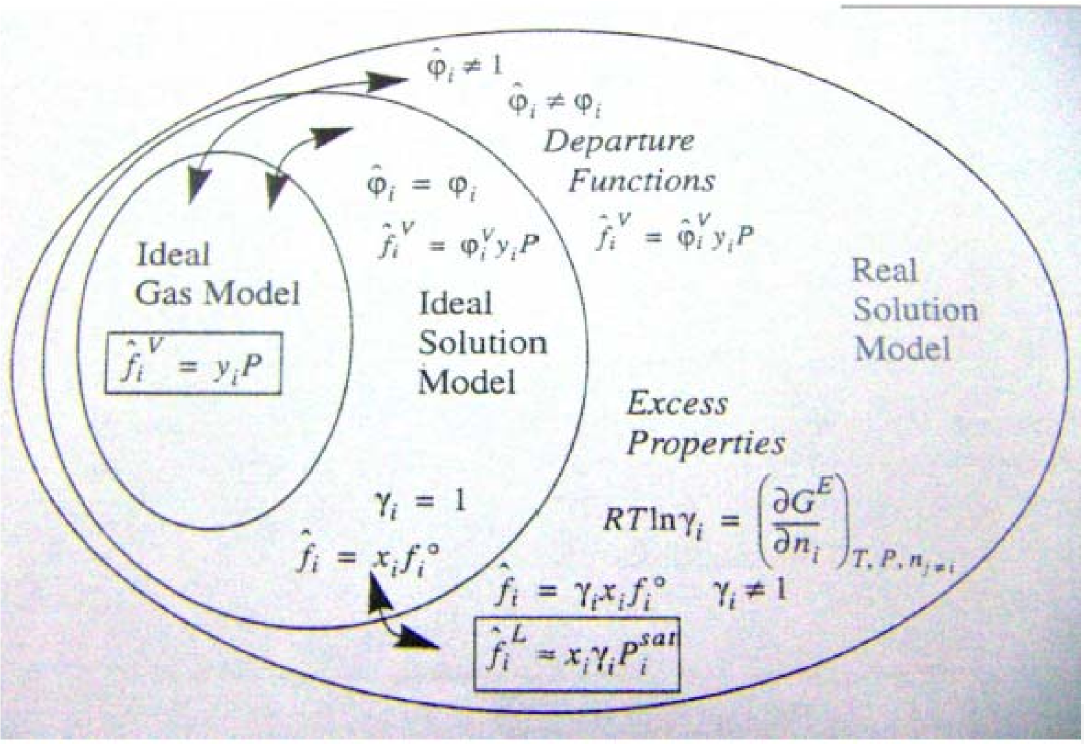
G^E models and VLE data

Dr.-Eng. Zayed Al-Hamamre

Review

- Excess Gibbs free energy: $G^E=G-G^{is}$
- dst diperoleh: $G^E=RT\sum_i x_i\ln(\gamma_i)$
- Activity Coefficient and excess Gibbs free energy are coupled.
- Excess Gibbs energy is zero for an ideal solution
- Activity Coefficients as derivatives:
- $$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_{j\neq i}}=RT\ln(\gamma_i)$$

Review

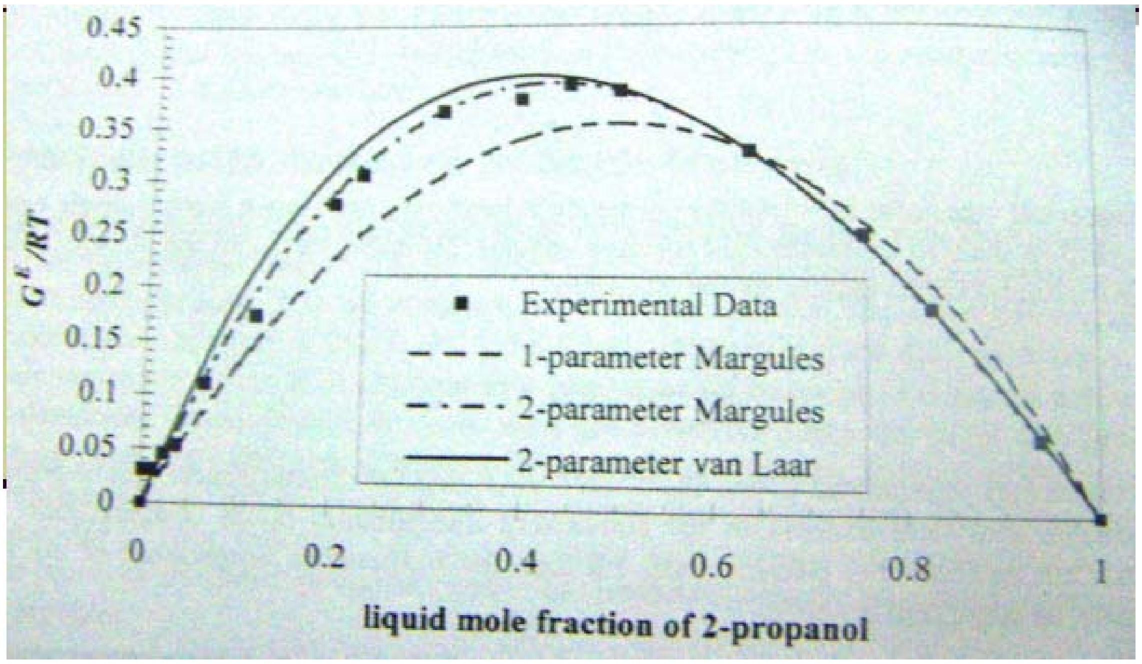


Determination of G^E from Experimental Data

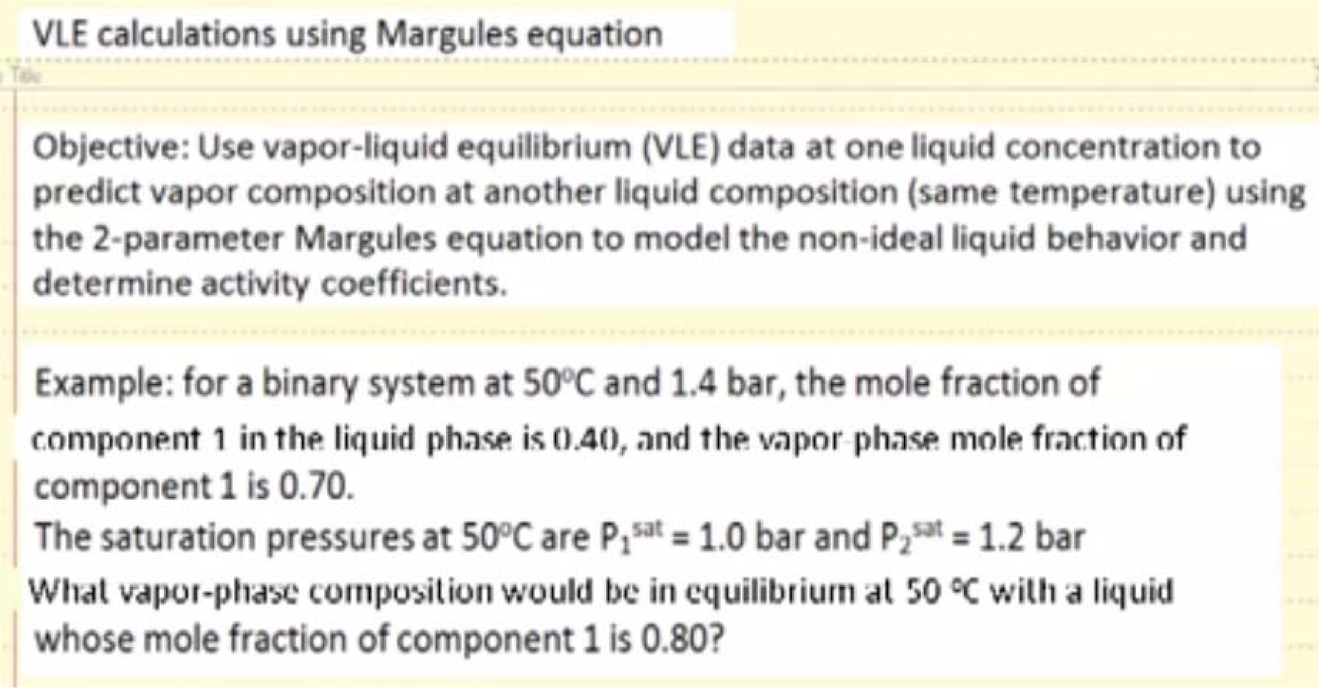
- Modified Raoult's Law: $\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$
- Excess Gibbs energy from activity coefficient (for binary system):
- $$\frac{G^E}{RT} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2)$$
- plot G^E/RT vs x_1
  - Example (1): system of 2-propanol (1) + water (2)
  - from citation data: T=30 °C, P_1^{sat} = 60.7 mmHg, P_2^{sat} = 32.1 mmHg, y_1 = 0.6462, when x_1 = 0.6369 at P=66.9 mmHg
  - ==> determine activity coefficient and relate to excess Gibbs energy
  - $\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{(0.6462)(66.9)}{(0.6369)(60.7)} = 1.118 \quad \gamma_2 = \frac{y_2 P}{x_2 P_2^{sat}} = \frac{(0.3538)(66.9)}{(0.3631)(32.1)} = 2.031$

$$\frac{G^E}{RT} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2) = 0.6369 \ln(1.118) + 0.3631 \ln(2.031) = 0.328$$

Determination of G^E from Experimental Data



Example



VLE calculations using Margules equation

Objective: Use vapor-liquid equilibrium (VLE) data at one liquid concentration to predict vapor composition at another liquid composition (same temperature) using the 2-parameter Margules equation to model the non-ideal liquid behavior and determine activity coefficients.

Example: for a binary system at 50°C and 1.4 bar, the mole fraction of component 1 in the liquid phase is 0.40, and the vapor-phase mole fraction of component 1 is 0.70.

The saturation pressures at 50°C are $P_1^{sat} = 1.0$ bar and $P_2^{sat} = 1.2$ bar

What vapor-phase composition would be in equilibrium at 50 °C with a liquid whose mole fraction of component 1 is 0.80?

Example cont.

Example

Example cont.

Example cont.

Example cont.

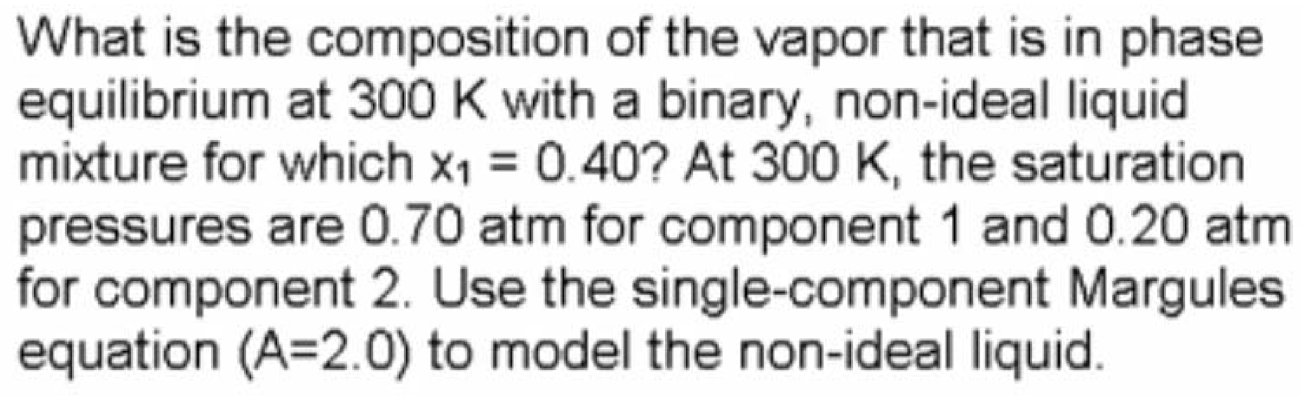
Example cont.

Example cont.

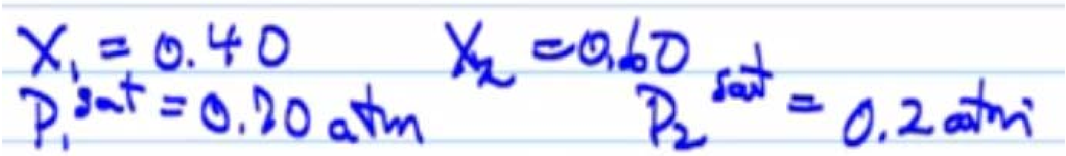
Example cont.

Example cont.

Example



What is the composition of the vapor that is in phase equilibrium at 300 K with a binary, non-ideal liquid mixture for which $x_1 = 0.40$? At 300 K, the saturation pressures are 0.70 atm for component 1 and 0.20 atm for component 2. Use the single-component Margules equation (A=2.0) to model the non-ideal liquid.



$X_1 = 0.40$ $X_2 = 0.60$

$P_1^{sat} = 0.70$ atm $P_2^{sat} = 0.2$ atm

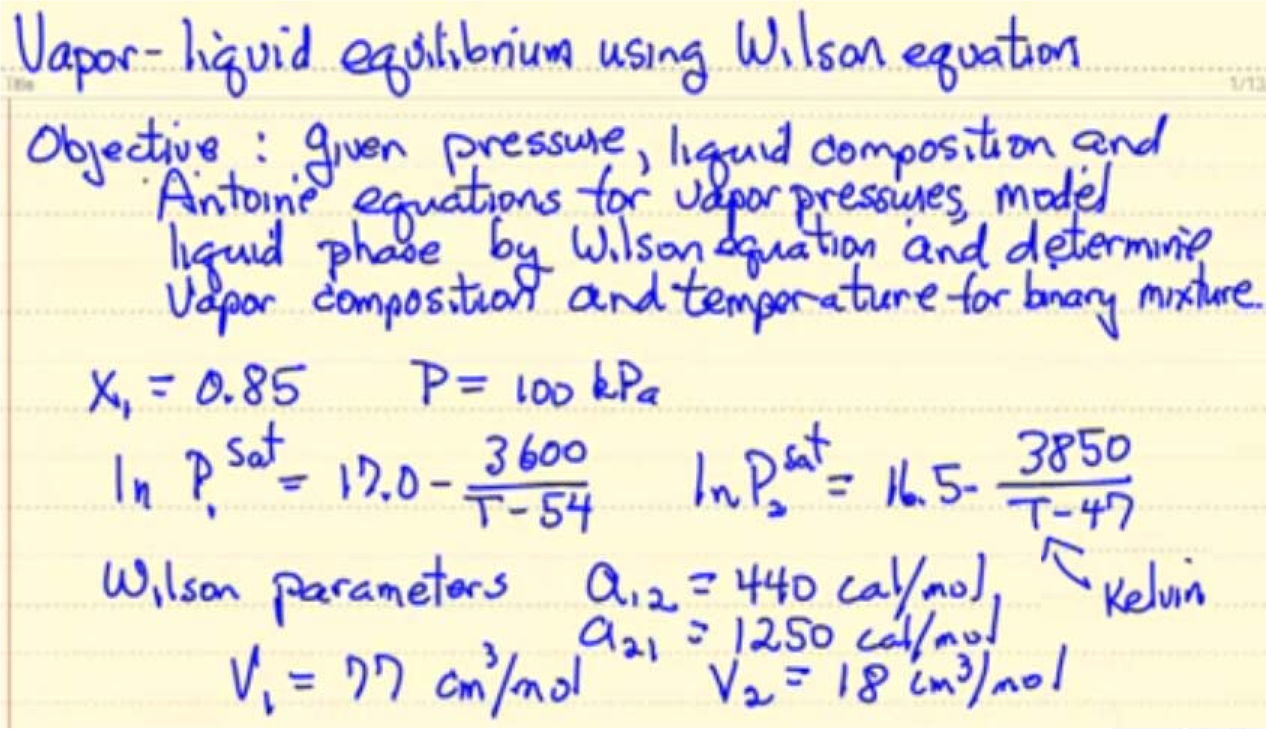
One-parameter Margules equation

$$\frac{G^E}{x_1 x_2 RT} = A$$

Example cont.

Example cont.

Example



Vapor-liquid equilibrium using Wilson equation

Objective: given pressure, liquid composition and Antoine equations for vapor pressures, model liquid phase by Wilson equation and determine vapor composition and temperature for binary mixture.

$x_1 = 0.85$ $P = 100$ kPa

$\ln P_1^{sat} = 17.0 - \frac{3600}{T-54}$ $\ln P_2^{sat} = 16.5 - \frac{3850}{T-47}$

Kelvin

Wilson parameters $a_{12} = 440$ cal/mol, $a_{21} = 1250$ cal/mol

$V_1 = 77$ cm^3/mol $V_2 = 18$ cm^3/mol

Wilson's Equation

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$$

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

$$\ln \gamma_2 = -\ln(x_1 \Lambda_{21} + x_2) + x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right)$$

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-A_{12}}{RT} \right) \quad \textit{and.} \quad \Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-A_{21}}{RT} \right)$$

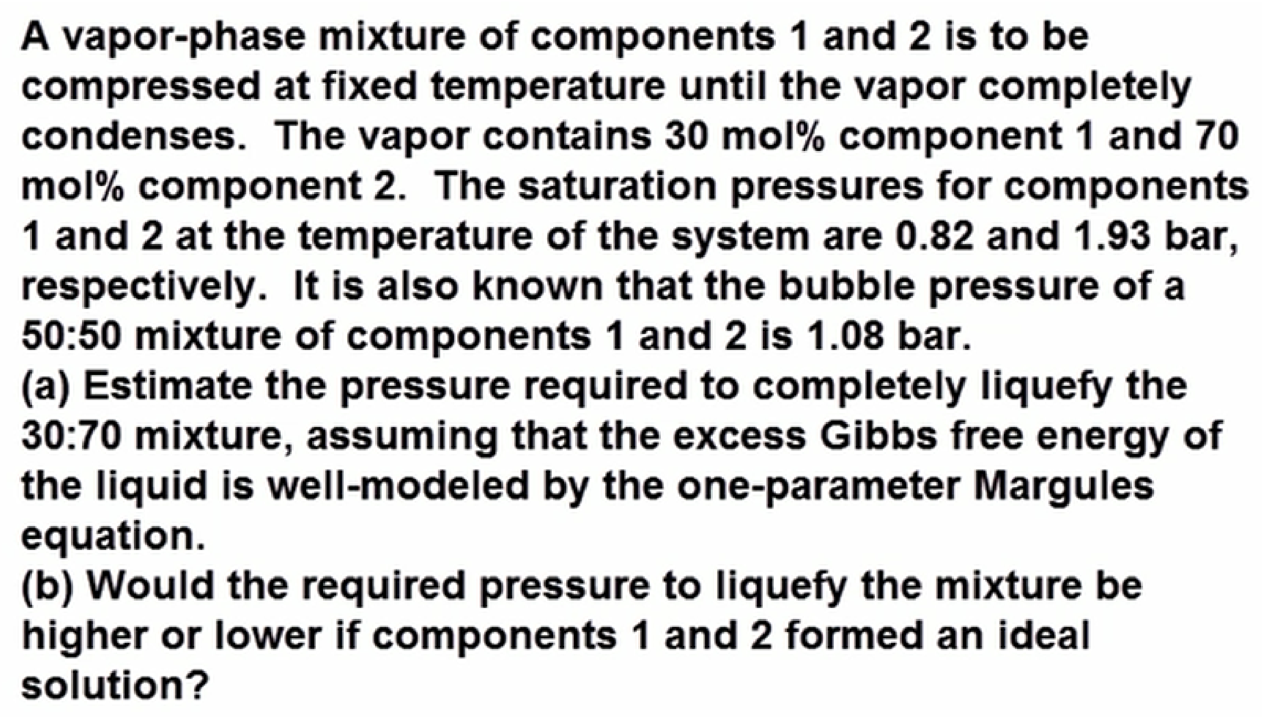
V_i, V_j : molar volume of pure liquid i, j, at temperature T

Example cont.

Example cont.

Example cont.

Example



A vapor-phase mixture of components 1 and 2 is to be compressed at fixed temperature until the vapor completely condenses. The vapor contains 30 mol% component 1 and 70 mol% component 2. The saturation pressures for components 1 and 2 at the temperature of the system are 0.82 and 1.93 bar, respectively. It is also known that the bubble pressure of a 50:50 mixture of components 1 and 2 is 1.08 bar.

(a) Estimate the pressure required to completely liquefy the 30:70 mixture, assuming that the excess Gibbs free energy of the liquid is well-modeled by the one-parameter Margules equation.

(b) Would the required pressure to liquefy the mixture be higher or lower if components 1 and 2 formed an ideal solution?

Example cont.

Example cont.

Example cont.

---

how to select these models properly for a specific system.

Table 2.9 Empirical and Semitheoretical Equations for Correlating Liquid-Phase Activity Coefficients of Binary Pairs

Name	Equation for Species 1	Equation for Species 2
(1) Margules	$\log\ \gamma_1 = Ax_2^2$	$\log\ \gamma_2 = Ax_1^2$
(2) Margules (two-constant)	$\log\ \gamma_1 = x_2^2[\bar{A}_{12} + 2x_1(\bar{A}_{21} - \bar{A}_{12})]$	$\log\ \gamma_2 = x_1^2[\bar{A}_{21} + 2x_2(\bar{A}_{12} - \bar{A}_{21})]$
(3) van Laar (two-constant)	$\ln \gamma_1 = \dfrac{A_{12}}{[1 + (x_1 A_{12})/(x_2 A_{21})]^2}$	$\ln \gamma_2 = \dfrac{A_{21}}{[1 + (x_2 A_{21})/(x_1 A_{12})]^2}$
(4) Wilson (two-constant)	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$	$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$
(5) NRTL (three-constant)	$\ln \gamma_1 = \dfrac{x_2^2 \tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \dfrac{x_1^2 \tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$	$\ln \gamma_2 = \dfrac{x_1^2 \tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \dfrac{x_2^2 \tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$
(6) UNIQUAC (two-constant)	$\ln \gamma_1 = \ln \dfrac{\Psi_1}{x_1} + \dfrac{\bar{Z}}{2} q_1 \ln \dfrac{\theta_1}{\Psi_1} + \Psi_2\left(l_1 - \dfrac{r_1}{r_2} l_2\right) - q_1 \ln(\theta_1 + \theta_2 T_{21}) + \theta_2 q_1 \left(\dfrac{T_{21}}{\theta_1 + \theta_2 T_{21}} - \dfrac{T_{12}}{\theta_2 + \theta_1 T_{12}}\right)$	$\ln \gamma_2 = \ln \dfrac{\Psi_2}{x_2} + \dfrac{\bar{Z}}{2} q_2 \ln \dfrac{\theta_2}{\Psi_2} + \Psi_1\left(l_2 - \dfrac{r_2}{r_1} l_1\right) - q_2 \ln(\theta_2 + \theta_1 T_{12}) + \theta_1 q_2 \left(\dfrac{T_{12}}{\theta_2 + \theta_1 T_{12}} - \dfrac{T_{21}}{\theta_1 + \theta_2 T_{21}}\right)$

Margules equations

- Margules equations result from power-series expansions of partial excess molar free energy.

- They are the simplest equations to calculate activity coefficients from Gibbs free energy models, discovered in 1895.

- The one-constant form of Margules equation is rarely used now because it is not observed experimentally.

- The second-constant form of Margules equation is still occasionally used but significantly limited by its simplicity.

Van Laar equation

The van Laar equation was derived from the van der Waals equation of state. It's widely used because of its flexibility, simplicity, and ability to fit many systems.

CAN: fit activity coefficient-composition curves corresponding to both positive and negative deviations from Raoult's Law, especially, mixtures of self-associated polar molecules (class II) with nonpolar molecules such as hydrocarbons (class V).

CANNOT: fit curves that exhibit minima or maxima. For example, in the dilute regions, the predicted activity coefficients are inaccurate. Moreover, the van Laar equation may erroneously predict formation of two liquid phases when activity coefficients are larger than 7.

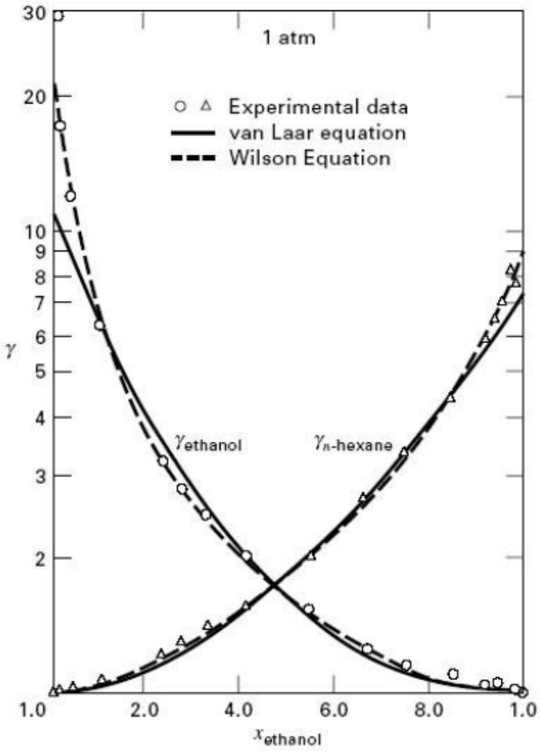
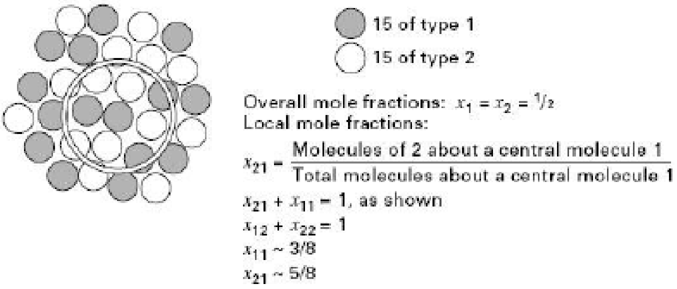


Figure 2.16 Liquid-phase activity coefficients for ethanol/*n*-hexane system.

Wilson model

The Wilson equation (in 1964) accounts for effects of differences both in molecular size and intermolecular forces.

In this model, the overall solution-volume fractions are replaced by local-volume fraction. The local-volume fraction is related to local-molecule segregations caused by differing energies of interaction between pairs of molecules.



Overall mole fractions: $x_1 = x_2 = 1/2$

Local mole fractions:

$$x_{21} = \frac{\text{Molecules of 2 about a central molecule 1}}{\text{Total molecules about a central molecule 1}}$$

$x_{21} + x_{11} = 1$, as shown

$x_{12} + x_{22} = 1$

$x_{11} \sim 3/8$

$x_{21} \sim 5/8$

Figure 2.17 The concept of local compositions.

[From P.M. Cukor and J.M. Prausnitz, *Int. Chem. Eng. Symp. Ser. No.* 32, 3, 88 (1969).]

Wilson model

CAN: apply to strongly nonideal but miscible systems; be very effective for dilute compositions where entropy effects dominate enthalpy effects; be readily extended to multicomponent mixtures by neglecting ternary and higher molecular interactions.

CANNOT: apply to mulitcompoent liquid-liquid systems of three or more species, in which the third binary pair constants are not the same for all constituent binary pairs. In other words, the multicomponent system can not be assumed as a pseudo-binary mixture.

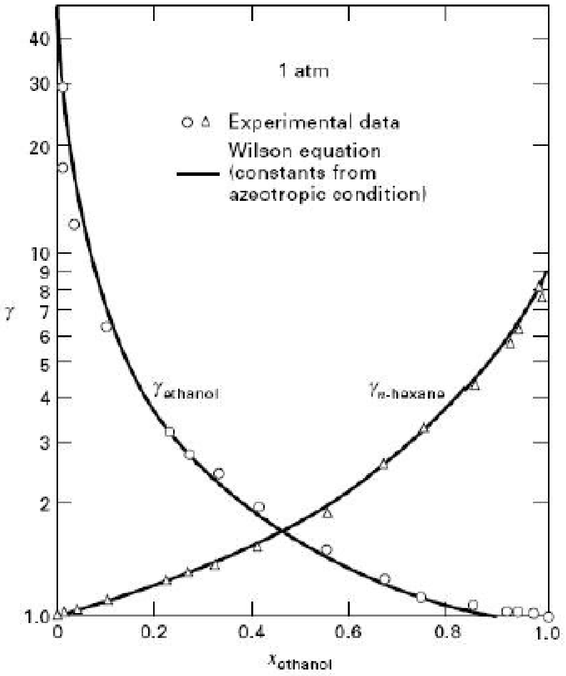
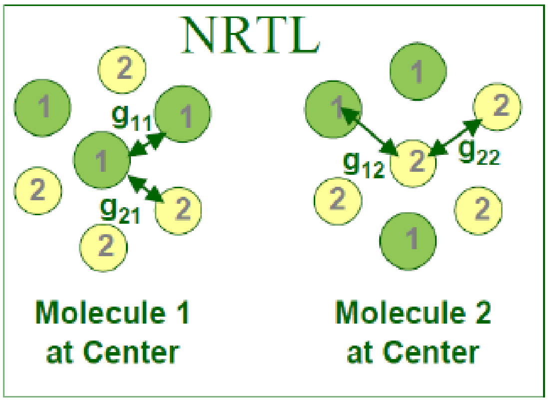


Figure 2.19 Liquid-phase activity coefficients for ethanol/*n*-hexane system.

NRTL model

The **Non-Random Two Liquid** model (**NRTL** equation) represents an accepted extension of Wilson model. It is based on the hypothesis of Wilson that the local concentration around a molecule will be different from the bulk concentration when there is a difference between the interaction energy of the central molecule with the molecules of its own kind g_{ii} and that with the molecules of the other kind g_{ij}. This difference introduces a non-randomness at the molecular level. The NRTL model is a so-called local composition model.

CAN: apply to multicomponent vapor-liquid, liquid-liquid, and vapor-liquid-liquid systems. For multicomponent vapor-liquid systems, only binary-pair constants from the corresponding binary-pair experimental data are required.



NRTL model

NRTL Equation

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

$$G_{12} = \exp(-\alpha \tau_{12}) \qquad G_{21} = \exp(-\alpha \tau_{21})$$

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

- α, b_{12}, and b_{21} are parameters specific to a particular pair of species, and are independent of composition and temperature
- NRTL: Non Random Two Liquid

NRTL model

- For the infinite-dilution values of the activity coefficient:
- $$\ln \gamma_1^{\infty} = \tau_{21} + \tau_{12} \exp(-\alpha \tau_{12})$$

  $$\ln \gamma_2^{\infty} = \tau_{12} + \tau_{21} \exp(-\alpha \tau_{21})$$

UNIQUAC model

UNIQUAC (*UN*iversal *QUA*si*C*hemical) is a so-called lattice model and this one has been derived from a first order approximation of interacting molecule surfaces in statistical thermodynamics.

CAN: apply to mixtures of molecules that differ appreciably in size and shape. The activity coefficients can be achieved by interpolation from only a few known parameters, without requiring experimental data from all desired points.

UNIQUAC requires two basic underlying parameters:
Local area fraction consisting of relative number of segments per molecule (volume parameter) and relative surface area of the molecule (surface parameter) must be known for all chemicals. These parameters are all chemical constants, which can be computed from bond angles and bond distances.

Empirical parameter between components that describes the intermolecular behavior. This parameter must be known for all binary pairs in the mixture. The empirical parameters are derived from experimental activity coefficients or from phase diagrams.

UNIQUAC model

- For multicomponent solution:

$$\frac{G^E}{RT}=\sum_j x_j \ln(\Phi_j/x_j)-5\sum_j q_j x_j \ln(\Phi_j/\theta_j)-\sum_j q_j x_j \ln\left(\sum_i \theta_i \tau_{ij}\right)$$

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

$$\ln\gamma_k^{COMB}=\ln(\Phi_k/x_k)+(1-\Phi_k/x_k)-5\mathrm{q}_k[\ln(\Phi_k/\theta_k)+(1-\Phi_k/\theta_k)]$$

$$\ln\gamma_k^{RES}=q_k\left[1-\ln\left(\sum_i \theta_i \tau_{ik}\right)-\sum_j \frac{\theta_j \tau_{kj}}{\sum_i \theta_i \tau_{ij}}\right]$$

- UNIQUAC equation requires two adjustable parameters characterized from experimental data for each binary system ==>

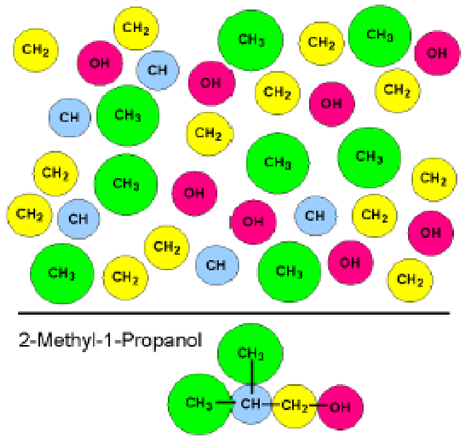
UNIQUAC model

- R_k parameter ==> group volume
- Q_k parameter ==> group surface area
- Molecule size (r_j) and molecule shape (q_j) may be calculated by multiplying the group parameters by the number of times each group appears in the molecule,
- and summing all the groups in the molecule
- where $v_k^{(j)}$ is the number of groups of the kth type in the jth molecule.

Group contribution methods

A group contribution method is a technique to estimate and predict thermodynamic and other properties from molecular structures. It uses the principle that some simple aspects of the structures of chemical components are always the same in many different molecules. The smallest common constituents are the atoms and the bonds. All organic component for example are built of carbon, hydrogen, oxygen, nitrogen, halogens, and maybe sulfur. Together with a single, a double, and a triple bond there are only ten atom types and three bond types to build thousands of components. The next slightly more complex building blocks of components are functional groups which are themselves built of few atoms and bonds.

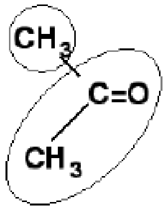
A group contribution method is used to predict properties of pure components and mixtures by using group or atom properties. This reduces the number of needed data dramatically. Instead of needing to know the properties of thousands or millions components only data for a few dozens or few hundreds groups have to be known.



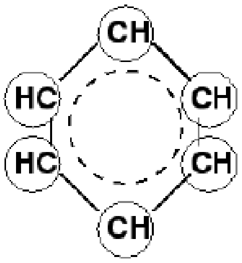
UNIFAC model

UNIFAC (*UNI*versal *F*unctional *A*ctivity *C*oefficient) method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures. It is developed as a combination of the UNIQUAC model and the *solution of functional groups* concept.

UNIFAC uses the functional groups present on the molecules that make up the liquid mixture to calculate activity coefficients. By utilizing interactions for each of the functional groups present on the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated.



ACETONE



BENZENE

The division of the components acetone and benzene into functional groups defined by the UNIFAC model. Acetone consists of the subgroups CH_3 and $CH_3C=O$ and benzene consists of 6 CH subgroups.

UNIFAC model

There are three types of **parameters** needed for the UNIFAC model:

- Group volume parameters
- Group surface area parameters
- Group interaction parameters

There are some **limitations** in the use of the UNIFAC model:

- Pressure should not be greater than a few bar (limit of about 5 bar).
- Temperature should be below 150C.
- Calculations are only applicable to condensable non-electrolytes.
- Components must not contain more than 10 functional group.

UNIFAC (Dortmund) Model: to correlate data for mixtures having a wide range of molecular size.

Models for difficult mixtures

The EoS models describe mixtures of nonpolar and slightly polar compounds.
Gibbs free-energy activity-coefficient models describe subcritical nonpolar and polar compounds.

Predictive Soave-Redlich-Kwong (PSRK) Model:
A combination of modified S-R-K equation-of-state and the UNIFAC model to describe mixtures of both polar compounds and supercritical (light gas) components (e.g. a mixture of hydrogen, carbon monoxide, methane, methyl acetate, and ethanol).

Electrolyte Solution Models:
Models of Pitzer and Chen and associates to describe dilute to concentrated solutions containing multicomponent of electrolytes.

Polymer Solution Model:
Modified NRTL model of Chen to describe polymer solutions in which polymer generally is nonvolatile but the solvent and monomer are volatile. Chen represents the polymer with segments.

Selection of models

To solve a particular separation problem, it is necessary to select an appropriate model.

Step 1: Characterize the mixture by chemical types

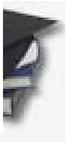
- **LG:** Light gas
- **HC:** Hydrocarbons
- **PC:** Polar organic compounds
- **A:** Aqueous solution
- **E:** Electrolye

Step 2: Select a proper model

HC±LG: If covering a wide boiling range: Lee-Kesler-Plocker (L-K-P) model
If not wide boiling range, the selection depends on P and T
- all T and P: Peng-Robinson (P-R) equation
- all P and noncryogenic T: Soave-Redlich-Kwong (S-R-K) equation
- all T and not critical P: Benedict-Webb-Rubin-Starling model

PC+LG: PSRK model

PC-LG: Select a suitable activity coefficient model
- If binary interaction coefficients are available:
  - Not split into two liquid phases: Wilson or NRTL equations
  - Split into two liquid phases: UNIQUAC equation
- If binary interaction coefficients are not available: UNIFAC method



A+E: Modified NRTL

Note: ‘+”: with; ‘-’: without.