CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)
07 – ACTIVITY COEFFICIENTS AND MODIFIED RAOULT'S LAW

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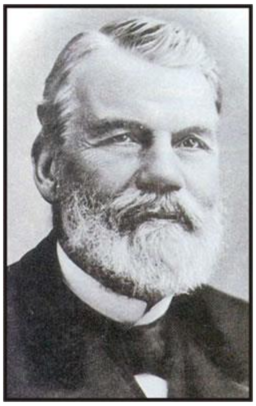
Outline

- Approaches to Phase equilibria
- Definition of Activity Coefficients
- Activity Coefficient Models
- Low Pressure VLE: Modified Raoult's Law
- Approaches to Activity Coefficient
  - Empirical
  - Local Composition
  - Group Contribution Models



François Marie Raoult
(10 May 1830 – 1 April 1901)

Approaches to Phase equilibria

- The starting point for all phase equilibria calculations is the equality of fugacity (isofugacity condition) of each species in every phase.
- For vapor-liquid equilibria (VLE) two approaches exist
  - Equation of state (ϕ-ϕ: phi-phi)

$$f_i^L(T,P,\mathbf{x}) = f_i^V(T,P,\mathbf{y})$$

$$x_i P\phi_i^L(T,P,\mathbf{x}) = y_i P\phi_i^V(T,P,\mathbf{y})$$

  - Equation of state-Activity Coefficient (γ-ϕ: gamma-phi)

$$f_i^L(T,P,\mathbf{x}) = f_i^V(T,P,\mathbf{y})$$

$$x_i\gamma_i(T,P,\mathbf{x})\phi_i^{L,sat}(T,P)P_i^{sat} = y_i P\phi_i^V(T,P,\mathbf{y})$$

Modified Raoult's law

$$\boxed{x_i\gamma_i P_i^{L,sat} = y_i P}$$

Definition of Activity Coefficients

- The activity coefficient for the liquid phase (L)

$$RT\ \ln \gamma_i (T,P,\mathbf{x}) = \bar{g}_i^{\text{ex}} = \left(\frac{\partial N g^{\text{ex}}}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

$$f_i^{L}(T,P,\mathbf{x}) = x_i \gamma_i (T,P,\mathbf{x}) f_i^{L}(T,P)$$

- Unity for an ideal mixture (IM) and for nonideal (real) mixtures is

$$\gamma_i (T,P,\mathbf{x}) = \exp\left(\frac{\bar{g}_i^{\text{ex}}}{RT}\right) = \exp\left(\frac{1}{RT}\int_0^P \left[\bar{v}_i (T,P,\mathbf{x}) - v_i (T,P)\right] dP\right)$$

Activity Coefficient Models

- Activity coefficient models are based on defining the excess partial molar Gibbs free energy as a function of composition at constant temperature and pressure.
- Activity coefficients are related directly to the excess partial molar Gibbs free energy which always is based on finding expressions for the activity coefficients from the g^{ex} expressions.

Situations

- When dealing with LLE or VLE, two main situations are encountered:
  - Experimental data are available
    - Find the "best" activity coefficients model to describe the data together with its parameters.
  - We have an activity coefficient model and its associated parameters
    - Carry out a certain type of VLE and/or LLE to determine the composition, temperature, and pressure of the coexisting phases.

Low Pressure VLE: Modified Raoult's Law

- Rigorous definition of the activity coefficient

$$\boxed{\gamma_i = \frac{f_i}{x_i f_i^\circ}}$$

- At low pressures, a good approximation is

$$\boxed{\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{sat}}}}$$

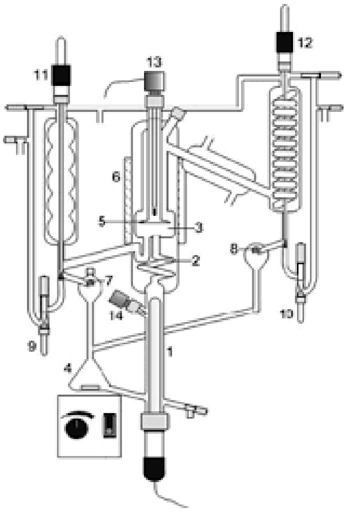
  - the fugacity coefficient for the reference state is essentially a unity.
  - Gas-phase corrections are neglected.

Limitations and Exceptions

- The simplified expression may not be applicable, even at low pressure
  - Mixtures of strongly polar and/or hydrogen-bonding components.
  - Mixtures of associating components e.g., acetic acid or hydrogen fluoride.
  - Mixtures at cryogenic temperatures since gas phase corrections are usually significant.

VLE Experimental Data

- VLE experimental data may be obtained in two distinct methods:
  - Isothermal Total-Pressure Data.
    - Run the VLE still at isothermal conditions, and measure the total pressure and composition (P,x,y).
  - Isobaric Boiling-Point data.
    - Run the VLE still at isobaric conditions, and measure the boiling point temperature and composition (T,x,y).



Approaches to Activity Coefficient

Approaches to Activity Coefficient

- Empirical expressions. Redlich-Kister & Wohl type expansion e.g., one-constant Margules, and van Laar modes.
- Local composition models. Assumes that on a molecular level there are local mole fractions, while on the macroscopic level there is the overall mole fractions e.g., nonrandom two liquids (NRTL) and Wilson.
- Group contribution models. Assumes materials are composed of functional groups that behave the same regardless of the compound they are in e.g., UNIQUAQ and UNIFAC.

Gibbs-Duhem Equation for γ

- Gibbs-Duhem equation for excess properties

$$s^{\text{ex}}dT - v^{\text{ex}}dP + \sum_{i=1}^{C} x_i d\bar{g}_i^{\text{ex}} = 0$$

- Use the definition of activity coefficients to obtain, at constant *T* and *P*,

$$s^{ex}dT - v^{ex}dP + \sum_{i=1}^{C} x_i d\ln\gamma_i\big|_{T,P} = 0$$

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$$

Pressure Effect on Activity Coefficients

- The pressure has some effect on the activity coefficient which can be shown to be given by

$$\gamma_i(T,P_2,\mathbf{x}) = \gamma_i(T,P_1,\mathbf{x})\exp\left[\int_{P_1}^{P_2}\frac{\bar{v}_i^{\text{ex}}(T,P,\mathbf{x})}{RT}\,dP\right]$$

$$\simeq \gamma_i(T,P_1,\mathbf{x})\exp\left[\frac{\bar{v}_i^{\text{ex}}(T,\mathbf{x})}{RT}(P_2-P_1)\right]$$

- The second approximate equation makes use of the fact that the excess partial molar volume is pressure independent (close to incompressible fluid concept)!

Temperature Effect on Activity Coefficients

- Temperature has a stronger effect on the activity coefficient compared to pressure

$$\gamma_i(T_2,P,\mathbf{x}) = \gamma_i(T_1,P,\mathbf{x})\exp\left[-\int_{T_1}^{T_2}\frac{\bar{h}_i^{\text{ex}}(T,P,\mathbf{x})}{RT^2}\,dT\right]$$

- For a **narrow temperature range**, or if the **excess partial molar enthalpy is temperature independent**,

$$\gamma_i(T_2,P,\mathbf{x}) = \gamma_i(T_1,P,\mathbf{x})\exp\left[\frac{\bar{h}_i^{\text{ex}}(\mathbf{x})}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

One-Constant (Two-Suffix) Margules Equation

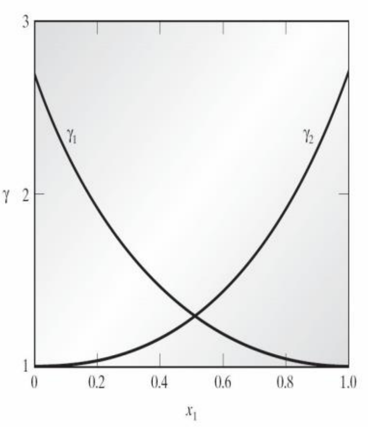
- Probably, the simplest model for γ

$$\frac{g^{ex}}{RT} = Ax_1x_2$$

$$\ln\gamma_1 = Ax_2^2, \quad \ln\gamma_2 = Ax_1^2$$

  - The two species activity coefficients are mirror images of each other.
  - In the limit of concentration approaching pure component; γ approaches unity.

$$\boxed{\lim_{x_i \to 1}\gamma_i \to 1} \Rightarrow \boxed{\lim_{x_i \to 1} f_i \to f_i^{\circ}}$$



- The parameter *A* can either be positive or negative
  - $A > 0$ leads to $\gamma > 1$;
  - $A < 0$ leads to $\gamma < 1$.
- satisfactory model for liquid mixtures containing constituents of **similar size, shape, and chemical nature**.
- Resort to more complicated models for dissimilar mixtures.

van Laar Model

- Used often to correlate vapor-liquid equilibrium (VLE) data.

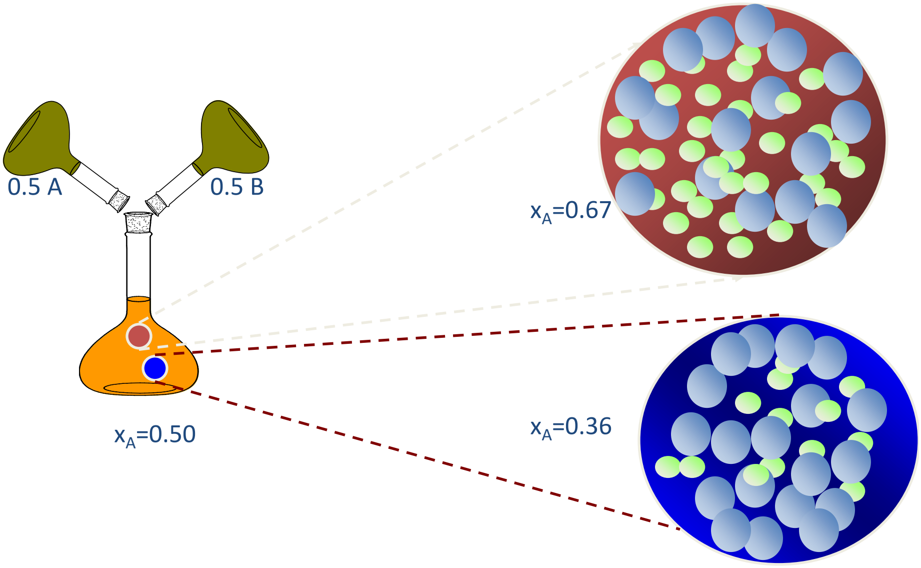
$$\frac{g^{\mathrm{ex}}}{RT} = x_1 x_2 \frac{\alpha\beta}{\alpha x_1 + \beta x_2} \Rightarrow \ln\gamma_1 = \frac{\alpha}{\left[1 + \dfrac{\alpha}{\beta}\dfrac{x_1}{x_2}\right]^2}, \quad \ln\gamma_2 = \frac{\beta}{\left[1 + \dfrac{\beta}{\alpha}\dfrac{x_2}{x_1}\right]^2}$$

- The parameters α, β are tabulated in Table 9.5-1 page 434 in Sandler. C.f., Perry's for detailed table.
- The values of the parameters in this model can be obtained from a single measurement.

$$\alpha = \left[1 + \frac{x_2}{x_1}\frac{\ln\gamma_2}{\ln\gamma_1}\right]^2 \ln\gamma_1 \quad + \quad \beta = \left[1 + \frac{x_1}{x_2}\frac{\ln\gamma_1}{\ln\gamma_2}\right]^2 \ln\gamma_2$$

Local Composition Models

- A certain overall mole fraction does not necessarily imply that on a microscopic scale the mole fraction is equal to the overall mole fraction.
- This idea of the difference between the overall and local mole fractions is used to find expressions for the activity coefficients of materials.



Overall macroscopic picture

Local microscopic picture

Wilson Model

- A local composition model; which is a two parameter model.

$$\frac{g^{\mathrm{ex}}}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12} x_2\right) - x_2 \ln\left(x_2 + \Lambda_{21} x_1\right)$$

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

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

- The two parameters Λ_{12} and Λ_{21} can be determined from infinite dilution activity coefficients

$$\ln\gamma_1^{\infty} = -\ln\Lambda_{12} + 1 - \Lambda_{21}$$

$$\ln\gamma_2^{\infty} = -\ln\Lambda_{21} + 1 - \Lambda_{12}$$

- Implies that at least two measurements are required to obtain these parameters.
- Reasonable accurate for vapor-liquid equilibria (VLE).
- *Unable to predict liquid-liquid equilibria.*

NRTL Model

- NRTL: Non-Random Two Liquid theory.
  - Local composition model which has three adjustable parameters

$$\frac{g^{\text{ex}}}{RT} = x_1 x_2 \left[\frac{G_{21}\tau_{21}}{x_1 + G_{21}x_2} + \frac{G_{12}\tau_{12}}{x_2 + G_{12}x_1} \right]$$

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

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

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

$$\tau_{12} = \frac{b_{12}}{RT}, \quad \tau_{21} = \frac{b_{21}}{RT}$$

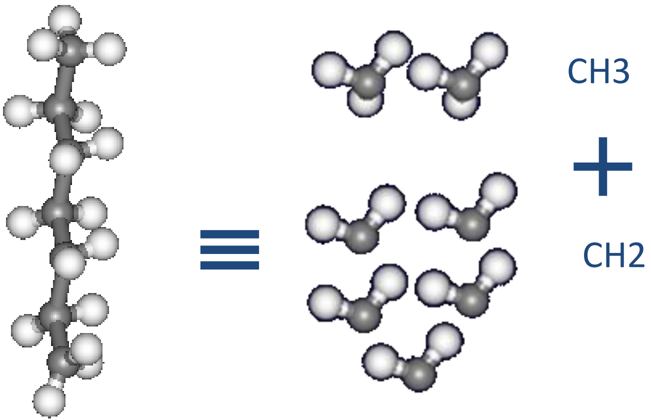
- The parameters are: α, b_{12}, and b_{21}.
- Infinite dilution activity coefficients

$$\ln\gamma_1^\infty = \tau_{21} + \tau_{12}\exp(-\alpha\tau_{12})$$

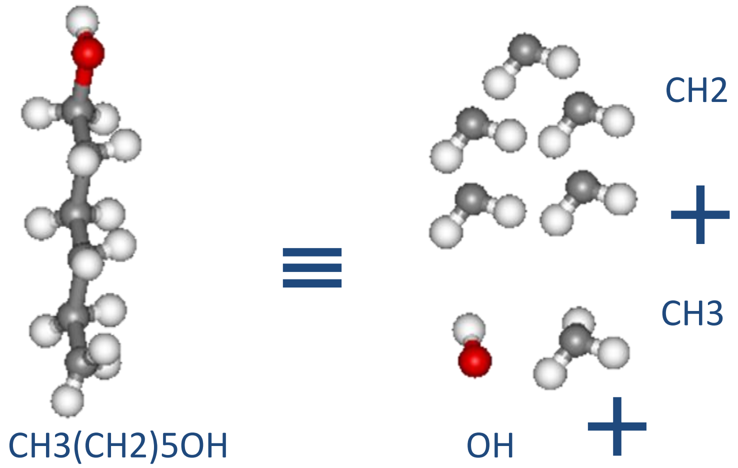
$$\ln\gamma_2^\infty = \tau_{12} + \tau_{21}\exp(-\alpha\tau_{21})$$

- At least three experimental measurements are needed to obtain these parameters.

UNIQUAC and UNIFAC



$CH_3(CH_2)_5CH_3$
n-Heptane



CH_2

+

CH_3

≡

$CH_3(CH_2)_5OH$
n-Hexanol

OH

+

Functional Group Concept

- Group contribution refers to the idea that we can consider any molecule as a collection of "functional groups" or building blocks.
  - The **surface area** and **volume** of any group will be approximately the same in any molecule in which that group occurs.
  - Advantage: use a relatively small number of functional groups to represent an almost infinite number of molecules.
- Analogous to the letters in any language and how words are constructed from a small number of letters.
  - There are 28 letters in the Arabic alphabet, many linguists estimate the words of Arabic language in the order of 20 million words!

UNIQUAQ Model

- UNIQUAQ stands for *Universal Quasi-Chemical.*
- Characterized by two adjustable parameters τ_{12} and τ_{21} or (u_{12}-u_{22}, and u_{21}-u_{11}).
- UNIQUAQ is based on splitting the excess Gibb free energy into two contributions:
  - Combinatorial. Accounts for **molecular size** and **shape** differences.
  - Residual. Accounts largely for **energy** differences.

G^{ex} for UNIQUAQ

$$\frac{g^{ex}}{RT} = \frac{g^{ex}(\text{combinatorial})}{RT} + \frac{g^{ex}(\text{residual})}{RT}$$

$$\frac{g^{ex}(\text{combinatorial})}{RT} = \sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_i x_i q_i \ln\frac{\theta_i}{\phi_i}$$

$$\frac{g^{ex}(\text{residual})}{RT} = -\sum_i x_i q_i \ln\left(\sum \theta_j \tau_{ji}\right)$$

$$\theta_i = \begin{pmatrix}\text{area fraction}\\ \text{of species } i\end{pmatrix} = \frac{x_i q_i}{\sum x_j q_j}$$

$$\phi_i = \begin{pmatrix}\text{segment or volume}\\ \text{fraction of species } i\end{pmatrix} = \frac{x_i r_i}{\sum x_j r_j}$$

$$\tau_{ij} = \frac{u_{ij} - u_{jj}}{RT}$$

r_i = volume parameter of species i

q_i = surface area parameter of species i

z = average coordination number $= 10$

u_{ij} = interaction energy for i - j species

Activity Coefficients for UNIQUAQ

$$\ln \gamma_i = \ln \gamma_i(\text{combinatorial}) + \ln \gamma_i(\text{residual})$$

$$\ln \gamma_i(\text{combinatorial}) = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

$$\ln \gamma_i(\text{residual}) = q_i \left[1 - \ln\left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right]$$

$$l_i = (r_i - q_i)\frac{z}{2} - (r_i - 1)$$

UNIFAC

- UNIFAC stands for ***UNI****quaq* ***F****unctional-group* ***A****ctivity* ***C****oefficient.*
  - The most successful activity coefficient model to-date.
  - Based on UNIQUAQ but both the combinatorial and residual terms are determined using group contribution.
  - The combinatorial part is evaluated from UNIQUAQ, while the residual part is evaluated using group contribution.

Combinatorial Contribution in UNIFAC

$$\ln\gamma_i = \ln\gamma_i(\text{combinatorial}) + \ln\gamma_i(\text{residual})$$

$$\ln\gamma_i(\text{combinatorial}) = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i + \frac{\phi_i}{x_i}\sum_j x_j l_j$$

$$l_i = (r_i - q_i)\frac{z}{2} - (r_i - 1)$$

Residual Contribution in UNIFAC

- The mixture is envisioned to be a mixture of functional groups, rather than of molecules.
- Residual part is calculated using group contribution similar in form to the residual part of UNIQUAQ

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m\Psi_{mk}\right) - \sum_m \frac{\Theta_m\Psi_{km}}{\sum_n \Theta_n\Psi_{nm}}\right]$$

$$\ln\gamma_i(\text{residual}) = \sum_k \nu_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right]$$

- $\nu_k^{(i)}$ is the number of k groups present in species i, and $\Gamma_k^{(i)}$ is the residual contribution to the activity coefficient of group k in a pure fluid of species i.

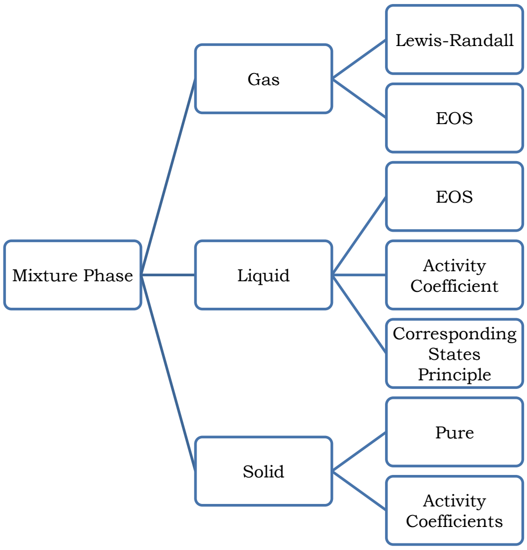
$$\Theta_m = \left(\begin{array}{l}\text{surface area}\\ \text{fraction of group m}\end{array}\right) = \frac{X_m Q_m}{\sum\limits_n X_n Q_n}$$

$$\Psi_{mk} = \exp\left[\frac{-(u_{mn} - u_{nn})}{RT}\right] = \exp\left[\frac{-a_{mn}}{T}\right]$$

$$X_m = \text{mole fraction of group } m \text{ in mixture}$$

- The binary interaction parameters (a_{mn}) are zero within the same subgroup and equal for interactions with other groups.

Fugacity in a Mixture



- Mixture Phase
  - Gas
    - Lewis-Randall
    - EOS
  - Liquid
    - EOS
    - Activity Coefficient
    - Corresponding States Principle
  - Solid
    - Pure
    - Activity Coefficients

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