# Vapor Liquid Equilibrium

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- **Phase equilibria**
  - **VLE, VLLE**
  - **Thermodynamic models**
    - $\gamma$–$\phi$ **(Activity coefficient models)**
    - $\phi$–$\phi$ **(Equations of state)**
- **At phase equilibria:**
  - $T^{I} = T^{II} = T^{III} = \ldots = T$
  - $p^{I} = p^{II} = p^{III} = \ldots = p$
  - $f_i^{I}\,(T, p, x_i^{I}) = f_i^{II}\,(T, p, x_i^{II}) = f_i^{III}\,(T, p, x_i^{Iii}) = ..$ *for* $i = 1, 2,.., c$

- **Criteria for systems at VLE:**
  - $f_i^V = f_i^L$ **for** $i = 1, 2, \ldots, c$
  - **One-model method:**

$$f_i^V = \boxed{\phi_i^V y_i p} = f_i^L = \boxed{\phi_i^L x_i p}$$

**Both the vapor phase and liquid phase fugacities are calculated from an equation of state.**

- **Two-model method:**

$$f_i^V = \boxed{\phi_i^V y_i p} = f_i^L = \boxed{\gamma_i x_i f_i^{oL}}$$

**Vapor phase fugacity is calculated from an equation of state and liquid phase fugacity from an activity coefficient model.**

# The Partial Molar Gibbs Free Energy and Fugacity—Revisit

- **Recall** $dG = -SdT + Vdp + \sum_{i=1}^{C} \overline{G}_i dN_i$
- **Then** $\frac{\partial}{\partial N_i}\left[\left(\frac{\partial G}{\partial T}\right)_{p,N_j}\right]_{T,p,N_{j\neq i}} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,p,N_{j\neq i}} \boxed{= -\overline{S}_i =} \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}\right]_{p,N_j} = \boxed{\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{p,N_j}}$

  $\frac{\partial}{\partial N_i}\left[\left(\frac{\partial G}{\partial p}\right)_{T,N_j}\right]_{T,p,N_{j\neq i}} = \left(\frac{\partial V}{\partial N_i}\right)_{T,p,N_{j\neq i}} \boxed{= \overline{V}_i =} \frac{\partial}{\partial p}\left[\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}\right]_{T,N_j} = \boxed{\left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,N_j}}$
- **So** $\boxed{\overline{S}_i = -\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{p,N_j}}$ and $\boxed{\overline{V}_i = \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,N_j}}$ ← Why?
- **Therefore** $\overline{G}_i(T_1, p_2, \underline{x}) - \overline{G}_i(T_1, p_1, \underline{x}) = \int_{p_1}^{p_2} \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,N_j} dp = \int_{p_1}^{p_2} \overline{V}_i dp$

for isothermal change at $T=T_1$

# The Partial Molar Gibbs Free Energy and Fugacity—Revisit

- **Define the fugacity of species *i* in a mixture**

$$\hat{f}_i(T,p,x) = p_i \exp\left\{\frac{\overline{G}_i(T,p,x) - \overline{G}_i^{IG}(T,p,x)}{RT}\right\}$$

$$\boxed{\overline{G}_i^R = RT\ln\hat{\phi}_i}$$

$$= x_i p \exp\left\{\frac{\overline{G}_i(T,p,x) - \overline{G}_i^{IG}(T,p,x)}{RT}\right\} = x_i p \exp\left\{\frac{1}{RT}\int_0^p \left(\overline{V}_i - \overline{V}_i^{IG}\right)dp\right\}$$

- **so that as** $p \to 0, \quad \hat{f}_i \to x_i p = p_i$
- **The fugacity coefficient for a component in a mixture**

$$\hat{\phi}_i = \frac{\hat{f}_i}{x_i p} = \exp\left\{\frac{\overline{G}_i(T,p,x) - \overline{G}_i^{IG}(T,p,x)}{RT}\right\}$$

$$\boxed{\hat{\phi}_i = \frac{\hat{f}_i}{y_i p}}$$

$$= \exp\left\{\frac{1}{RT}\int_0^p \left(\overline{V}_i - \overline{V}_i^{IG}\right)dp\right\}$$

# The Partial Molar Gibbs Free Energy and Fugacity—Revisit

$$\overline{V}_i = \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,N_j}$$

$$\mu_i \equiv \Gamma_i(T) + RT\ln \hat{f}_i$$

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial p}\right)_{T,x} = \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,x} = \overline{V}_i$$

$$RT\left(\frac{\partial \ln f}{\partial p}\right)_{T} = \left(\frac{\partial \underline{G}}{\partial p}\right)_{T} = \underline{V}$$

for pure component

- **To relate the fugacity of pure component *i* to the fugacity of component *i* in a mixture**

$$RT\left\{\int_0^p \left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,\underline{x}} dp - \int_0^p \left(\frac{\partial \ln f_i}{\partial P}\right)_{T} dp\right\}$$

$$= RT\left\{\int_0^p d\ln \hat{f}_i - \int_0^p d\ln f_i\right\} = RT\left\{\ln\frac{\hat{f}_i(T,p,\underline{x})}{\hat{f}_i(T,0,\underline{x})}\right\} - RT\left\{\ln\frac{f_i(T,p)}{f_i(T,0)}\right\}$$

$$= \int_0^p (\overline{V}_i - \underline{V}_i)\,dp$$

$\boxed{p_i}$ $\boxed{p}$

- **As** $p \to 0,\ \hat{f}_i \to p_i = px_i$ **and** $f_i \to p$
- **thus** $RT\left\{\ln\frac{\hat{f}_i(T,p,x)}{x_i f_i(T,p)}\right\} = \int_0^p \left(\overline{V}_i - \underline{V}_i\right)dp$

# The Partial Molar Gibbs Free Energy and Fugacity—Revisit

- **Therefore, for a mixture in which** $\bar{V}_i = \underline{V}_i$ **same as earlier,**
- $\boxed{\hat{f}_i = f_i x_i}$ **true for ideal gas mixtures and ideal solutions.**
- **Therefore,**

$$\hat{\phi}_i = \frac{\hat{f}_i}{x_i p} = \exp\left\{\frac{\bar{G}_i(T,p,x) - \bar{G}_i^{IG}(T,p,x)}{RT}\right\}$$

$$\left[\frac{\partial \ln(\hat{f}_i / x_i p)}{\partial T}\right]_{p,\underline{x}} = \frac{\partial}{\partial T}\bigg|_{p,\underline{x}}\left\{\frac{\bar{G}_i(T,p,\underline{x}) - \bar{G}_i^{IG}(T,p,\underline{x})}{RT}\right\}$$

$$= -\frac{\bar{G}_i - \bar{G}_i^{IG}}{RT^2} + \frac{1}{RT}\left\{\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{p,\underline{x}} - \left(\frac{\partial \bar{G}_i^{IG}}{\partial T}\right)_{p,\underline{x}}\right\}$$

$$= -\frac{1}{RT^2}\left[\bar{G}_i - \bar{G}_i^{IG} - T\left(\bar{S}_i - \bar{S}_i^{IG}\right)\right] = \boxed{-\frac{\bar{H}_i - \bar{H}_i^{IG}}{RT^2} = \left[\frac{\partial \ln \phi_i}{\partial T}\right]_{p,\underline{x}}}$$

$$\boxed{dG = -SdT - Vdp + \sum_{i=1}^{r} \mu_i dn_i}$$

$$\boxed{\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}}$$

# Phase equilibrium criteria in terms of fugacity

- **Let** $\Delta \bar{G}_i = \bar{G}_i(T, p, \underline{x}^{II}) - \bar{G}_i(T, p, \underline{x}^{I})$
- **with** $\bar{G}_i(T, p, \underline{x}) = \bar{G}_i^{IG}(T, p, \underline{x}) + RT \ln \phi_i(T, p, \underline{x})$ $\boxed{\bar{G}_i^{R} = RT \ln \hat{\phi}_i}$

**where superscripts *I* and *II* denotes phases of different composition**

- **Recall** $\boxed{\bar{G}_i^{IG}(T, P, \underline{x}) = \underline{G}_i^{pure}(T, P) + RT \ln x_i}$ **then,**

$$\bar{G}_i(T, P, \underline{x}^{II}) - \bar{G}_i(T, p, \underline{x}^{I}) = \bar{G}_i^{IG}(T, p, \underline{x}^{I}) + RT \ln \phi_i^{I}(T, p, \underline{x}^{I})$$

$$- \bar{G}_i^{IG}(T, p, \underline{x}^{II}) - RT \ln \phi_i^{II}(T, p, \underline{x}^{II})$$

$$= \underline{G}_i^{pure}(T, p) + RT \ln x_i^{I} + RT \ln \phi_i^{I}(T, p, \underline{x}^{I})$$

$$- \underline{G}_i^{pure}(T, p) - RT \ln x_i^{II} - RT \ln \phi_i^{II}(T, p, \underline{x}^{II})$$

$$= RT \ln x_i^{I} \phi_i^{I} - RT \ln x_i^{II} \phi_i^{II}$$

$$\boxed{\phi_i = \hat{f}_i / p x_i} \quad \Rightarrow \quad = RT \ln \left( \hat{f}_i^{I} / P \right) - RT \ln \left( \hat{f}_i^{II} / P \right) = RT \ln \hat{f}_i^{I} - RT \ln \hat{f}_i^{II}$$

**at equilibrium** $\Delta \bar{G}_i = \bar{G}_i(T, P, \underline{x}^{II}) - \bar{G}_i(T, P, \underline{x}^{I}) = 0 \quad \Rightarrow \quad \boxed{\hat{f}_i^{I} = \hat{f}_i^{II}}$

# Fugacity and fugacity coefficient for a species in a mixture from an equation of state

- **Recall** $$\hat{\phi}_i = \frac{\hat{f}_i}{x_i P} = \exp\left\{ \frac{1}{RT} \int_0^p \left( \overline{V}_i - \overline{V}_i^{IG} \right) dp \right\}$$
- **Therefore,** $$\ln \hat{\phi}_i = \ln\left( \frac{\hat{f}_i}{x_i p} \right) = \frac{1}{RT} \int_0^p \left( \overline{V}_i - \overline{V}_i^{IG} \right) dp$$
- **normally volumetric equation of state are pressure explicit. The integral is easier if the integration is based on volume.**

$$\left( \frac{\partial V}{\partial N_i} \right)_{T,P,N_{j \neq i}} \left( \frac{\partial P}{\partial V} \right)_{T,N_j} \left( \frac{\partial N_i}{\partial P} \right)_{T,V,N_j} = -1 \quad \Rightarrow \quad \left( \frac{\partial V}{\partial N_i} \right)_{T,P,N_{j \neq i}} \left( \frac{\partial P}{\partial V} \right)_{T,N_j} = -\left( \frac{\partial P}{\partial N_i} \right)_{T,V,N_j}$$

$$\Rightarrow \quad \left( \frac{\partial V}{\partial N_i} \right)_{T,P,N_{j \neq i}} dP = \overline{V}_i dP = -\left( \frac{\partial P}{\partial N_i} \right)_{T,V,N_j} dV = -N \left( \frac{\partial P}{\partial N_i} \right)_{T,V,N_j} d\underline{V}$$

$$\ln \hat{\phi}_i = \ln\left(\frac{\hat{f}_i}{x_i P}\right) = \frac{1}{RT}\int_0^p \left(\bar{V}_i - \bar{V}_i^{IG}\right) dP = \frac{1}{RT}\int_0^p \bar{V}_i \, dP - \frac{1}{RT}\int_0^p \bar{V}_i^{IG} \, dP$$

$$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} dP = \bar{V}_i \, dP = -\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} dV = -N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} d\underline{V}$$

$$\frac{1}{RT}\int_0^p \bar{V}_i \, dP = \frac{-1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} N\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{j\neq i}} d\underline{V}$$

$$dP = \frac{1}{\underline{V}} d\left(P\underline{V}\right) - \frac{P}{\underline{V}} d\underline{V} = \frac{1}{\underline{V}} d\left(ZRT\right) - \frac{P}{\underline{V}} d\underline{V} = \frac{RT}{\underline{V}} dZ - \frac{P}{\underline{V}} d\underline{V} = \frac{P}{Z} dZ - \frac{P}{\underline{V}} d\underline{V}$$

$$\frac{1}{RT}\int_0^p \bar{V}_i^{IG} \, dP = -\frac{1}{RT}\left\{\int_1^Z \frac{\bar{V}_i^{IG}}{Z} p\,dZ - \int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} \frac{\bar{V}_i^{IG}}{\underline{V}} p\,d\underline{V}\right\}$$

$$\ln \hat{\phi}_i = \frac{-1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} N\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{j\neq i}} d\underline{V} - \frac{p\bar{V}_i^{pure}}{RT}\int_1^Z \frac{1}{Z} dZ + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} \frac{p\bar{V}_i^{pure}}{\underline{V}} d\underline{V}$$

$$\boxed{\overline{V}_i^{IG} = \overline{V}_i^{pure} = \frac{RT}{P}}$$

$$\ln\hat{\phi}_i = \frac{-1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} N\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{j\neq i}} d\underline{V} - \overset{=1}{\boxed{\frac{p\overline{V}_i^{pure}}{RT}}}\int_1^Z \frac{1}{Z}\,dZ + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p} \boxed{\begin{array}{c}\dfrac{p\overline{V}_i^{pure}}{\underline{V}}\\ =RT\end{array}}\, d\underline{V}$$

$$\Rightarrow\ \boxed{\ln\hat{\phi}_i = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p}\left\{\frac{RT}{\underline{V}} - N\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right\} d\underline{V} - \ln Z}$$

**fugacity coefficient for pure substance :**

$$\boxed{\ln\phi = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/p}\left(\frac{RT}{\underline{V}} - P\right) d\underline{V} - \ln Z + (Z-1)}$$

# Excess Gibbs Free Energy and Gibbs-Duhem Equation

**If** $\underline{G}^{ex}(T,P,\underline{x}) = ax_1x_2$ **then** $\overline{G}_1^{ex} = ax_2^2 = RT\ln\gamma_1$ **,** $\overline{G}_2^{ex} = ax_1^2 = RT\ln\gamma_2$

$$\sum_{i=1}^{C} x_i d\overline{G}_i^{ex}\Big|_{T,P} = x_1 d\overline{G}_1^{ex} + x_2 d\overline{G}_2^{ex} = x_1 d\left(ax_2^2\right) + x_2 d\left(ax_1^2\right)$$

$$= 2ax_1x_2\left(dx_2 + dx_1\right) = 2ax_1x_2 d\left(x_1 + x_2\right) = 0$$

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = x_1\frac{a}{RT}\left[\frac{\partial(1-x_1)^2}{\partial x_1}\right]_{T,P} + x_2\frac{a}{RT}\left[\frac{\partial(1-x_2)^2}{\partial x_1}\right]_{T,P}$$

$$= -\frac{2ax_1}{RT}(1-x_1) + x_2\frac{a}{RT}\left[\frac{\partial x_1^2}{\partial x_1}\right] = -\frac{2ax_1x_2}{RT} + \frac{2ax_1x_2}{RT} = 0$$

**All activity coefficients derived from an excess Gibbs free energy expression that satisfies boundary conditions of being zero at $x_1=0$ and 1 will satisfy the Gibbs-Duhem equation.**

at $x_1 = 0$ and $x_1 = 1$ $\quad \underline{G}^{ex} = 0$ then the activity coefficients satisfy $0 = \sum_{i=1}^{C} x_i d\ln\gamma_i\Big|_{T,P}$

# Activity Coefficient Model

$$\ln \gamma_i = \overline{G}^{ex}_i / RT \qquad \underline{G}^{ex} / RT = \sum_i x_i \ln \gamma_i$$

- **Random mixing assumption (Wohl's expansion):**

$$\frac{\underline{G}^{ex}}{RT \sum_i q_i x_i} = \sum_i \sum_j a_{ij} z_i z_j + \sum_i \sum_j \sum_k a_{ijk} z_i z_j z_k + \ldots..$$

  - **Redlich-Kister model**
  - **Margules model**
  - **van Laar model**

# Margules’ Equations

- **While the simplest Redlich/Kister-type correlation is the Symmetric Equation, but a more accurate equation is the Margules correlation:**

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

- **let,**

$$\ln\gamma_1^\infty = \lim_{x_1\to 0}\frac{G^E}{RTx_1x_2} \qquad \left.\frac{G^E}{RTx_1x_2}\right|_{x_1\to 0} = A_{12}$$

- **so that**

$$A_{12} = \ln\gamma_1^\infty$$

$$A_{21} = \ln\gamma_2^\infty$$

# Margules' Equations

- **If you have Margules parameters, the activity coefficients can be derived from the excess Gibbs energy expression:**

$$\frac{G^E}{RTx_1 x_2} = A_{21} x_1 + A_{12} x_2$$

- **to yield:**

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1]$$

$$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$$

- **These empirical equations are widely used to describe binary solutions. A knowledge of $A_{12}$ and $A_{21}$ at the given T is all we require to calculate activity coefficients for a given solution composition.**

# Van Laar Correlation

- Another two-parameter excess Gibbs energy model was developed from an expansion of $(RTx_1x_2)/G^E$ instead of $G^E/RTx_1x_2$. The end results are:

$$\frac{G^E}{RTx_1x_2} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}$$

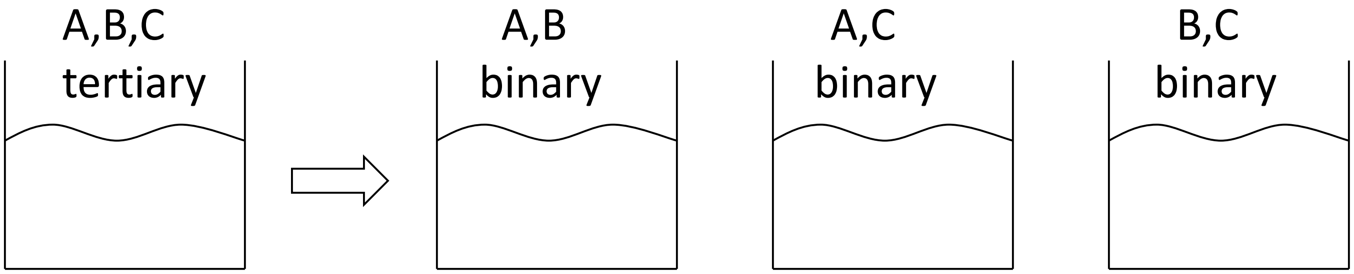
- for the excess Gibbs energy and:

$$\ln\gamma_2 = A'_{21}\left(1+\frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \qquad \ln\gamma_1 = A'_{12}\left(1+\frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}$$

- for the activity coefficients.
- **as** $x_1 \rightarrow 0$, $\ln\gamma_1^\infty \rightarrow A'_{12}$ **as** $x_2 \rightarrow 0$, $\ln\gamma_2^\infty \rightarrow A'_{21}$

# Local Composition Models

- Unfortunately, the previous approach cannot be extended to systems of 3 or more components. For these cases, local composition models are used to represent multi-component systems.
    - Wilson's Theory
    - Non-Random-Two-Liquid Theory (NRTL)
    - Universal Quasichemical Theory (Uniquac)
- While more complex, these models have two advantages:
    - the model parameters are temperature dependent
    - the activity coefficients of species in multi-component liquids can be calculated using information from binary data.



# Local Composition Models

Introductory Chemical Engineering Thermodynamics

J.Richard Elliott, Carl T. Lira

| **Composition around a "1" molecule** | **Composition around a "2" molecule** |
|---|---|
| $x_{21}$ – mole fraction of "2's" around "1" | $x_{12}$ – mole fraction of "1's" around "2" |
| $x_{11}$ – mole fraction of "1's" around "1" | $x_{22}$ – mole fraction of "2's" around "2" |
| local mole balance, $x_{11} + x_{21} = 1$ | local mole balance, $x_{22} + x_{12} = 1$ |

Assume that the local compositions are given by some weighting factor, $\Omega_{ij}$, relative to the overall compositions.

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

Therefore, if $\Omega_{12} = \Omega_{21} = 1$, the solution is random.

# Local Composition Models

The local mole balance:

$$x_{11} + x_{21} = 1$$

Writing the local mole fractions $x_{21}$ and $x_{11}$ in terms of the overall mole fractions, $x_1$ and $x_{2,}$

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

Substitute back to (1),

$$x_{11}\left(1 + \frac{x_2}{x_1}\Omega_{21}\right) = 1$$

Rearrange,

$$x_{11} = \frac{x_1}{x_1 + x_2\Omega_{21}}$$

Substitute back to (2),

$$x_{21} = \frac{x_2\Omega_{21}}{x_1 + x_2\Omega_{21}}$$

# Local Composition Models

Similar for type ”2”

$$x_{22} = \frac{x_2}{x_1\Omega_{12} + x_2}$$

$$x_{12} = \frac{x_1\Omega_{12}}{x_1\Omega_{12} + x_2}$$

Apply this local composition theory to properties using two-fluid theory,

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

The local composition environment of the type 1 molecules determines the first term, local composition environment of the type 2 molecules determines the second term.

# Local Composition Models

Introduce the local interaction energy ($\varepsilon_{ij}$), allowing that the $\varepsilon_{12} = \varepsilon_{21}$

Neglecting the excess volume of mixing relative to the other contributions, which should be quite acceptable for liquids.

$$(U - U^{ig})^{(1)} = \frac{N_A}{2} N c_1 (x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21})$$

$$(U - U^{ig})^{(2)} = \frac{N_A}{2} N c_2 (x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22})$$

then

$$U - U^{ig} = \frac{N_A}{2}\left[x_1 N c_1 (x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) + x_2 N c_2 (x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22})\right]$$

Should using H as we discussed in regular solution. Since excess volume of mixing is neglected, U = H.

# Local Composition Models

Recall,

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

Notice that when $x_1$ approaches unity, $x_2$ goes to zero, and $x_{21}$ goes to zero, and $x_{11}$ goes to one,

$$(U - U^{ig})_{pure1} = (N_A/2)Nc_1\varepsilon_{11}$$

$$(U - U^{ig})_{pure2} = (N_A/2)Nc_2\varepsilon_{22}$$

where $Nc_j$ is the coordination number, the total number of atoms in the neighborhood of the $j$th species). We have,

$$(U - U^{ig})^{is} = x_1(U - U^{ig})_{pure1} + x_2(U - U^{ig})_{pure2} = \frac{N_A}{2}[x_1 Nc_1\varepsilon_{11} + x_2 Nc_2\varepsilon_{22}]$$

# Local Composition Models

Recall,

$$U - U^{ig} = \frac{N_A}{2}\left[x_1 Nc_1(x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) + x_2 Nc_2(x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22})\right]$$

Subtracting we have,

$$U^E = U - U^{is} = \frac{N_A}{2}[x_1 Nc_1((x_{11}\varepsilon_{11} + x_{21}\varepsilon_{21}) - \varepsilon_{11}) + x_2 Nc_2((x_{12}\varepsilon_{12} + x_{22}\varepsilon_{22}) - \varepsilon_{22})]$$

using $(x_{11} - 1)\varepsilon_{11} = -x_{21}\varepsilon_{11} \quad (x_{22} - 1)\varepsilon_{22} = -x_{12}\varepsilon_{22}$

Arriving at $U^E = \frac{N_A}{2}\left[x_1 x_{21} Nc_1(\varepsilon_{21} - \varepsilon_{11}) + x_2 x_{12} Nc_2(\varepsilon_{12} - \varepsilon_{22})\right]$

Replace $x_{21}$, and $x_{12}$,

$$\boxed{U^E = \frac{N_A}{2}\left[\frac{x_1 x_2 \Omega_{21} Nc_1(\varepsilon_{21} - \varepsilon_{11})}{x_1 + x_2\Omega_{21}} + \frac{x_2 x_1 \Omega_{12} Nc_2(\varepsilon_{12} - \varepsilon_{22})}{x_1\Omega_{12} + x_2}\right]}$$

# Wilson’s Equations for Binary Solution Activity

Recall,

$$A = U - TS \;\Rightarrow A/RT = U/RT - S/R$$

then,

$$T\left(\frac{\partial(A/RT)}{\partial T}\right)_V = \frac{T}{RT}\left(\frac{\partial U}{\partial T}\right)_V - \frac{TU}{RT^2} - \frac{T}{R}\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{R} - \frac{U}{RT} - \frac{T}{R}\frac{C_V}{T} = -\frac{U}{RT}$$

We have,

$$\int_{\infty}^{T} d\left(\frac{A^E}{RT}\right) = \frac{A^E}{RT} - \left.\frac{A^E}{RT}\right|_{\infty} = -\int_{\infty}^{T}\frac{U^E}{RT^2}dT$$

where $A_E \Delta (RT)$ □ is the infinite temperature limit at the given liquid density independent of temperature but possibly dependent on composition or density.

# Wilson's Equations for Binary Solution Activity

Wilson made a bold assumption regarding the temperature dependence of $\Omega_{ij}$.

$$\Omega_{ij} = \Lambda_{ji} = \frac{V_i}{V_j}\exp\left(\frac{-N_A N c_j(\varepsilon_{ij} - \varepsilon_{jj})}{2RT}\right) = \frac{V_i}{V_j}\exp\left(\frac{-A_{ji}}{RT}\right)$$

Substitute back and integrate,

$$\frac{A^E}{RT} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) + \cancel{\frac{A^E}{RT}}\bigg|_{\infty}$$

Separate $G^E/RT$ into an energetic part known as the *residual* contribution, that vanishes at infinite temperature or when $\varepsilon_{12} - \varepsilon_{22} = 0$ and $\varepsilon_{21} - \varepsilon_{11} = 0$, and a size/shape part known as the *combinatorial* contribution, that represents the infinite temperature limit at the liquid density.

# Wilson's Equations for Binary Solution Activity

Therefore,

$$(G^E/RT)^{RES} = -x_1\ln(\Phi_1 + \Phi_2\exp(-A_{12}/RT)) - x_2\ln(\Phi_1\exp(-A_{21}/RT) + \Phi_2)$$

For the combinatorial contribution, Wilson used Flory's equation,

$$G^E/(RT)\Big|_\infty = (G^E/RT)^{COMB} = x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2)$$

Combine, the above, Wilson's equation becomes,

$$\frac{G^E}{RT} = -x_1\ln\left(\Phi_1 + \Phi_2\exp\left(\frac{-A_{12}}{RT}\right)\right) - x_2\ln\left(\Phi_1\exp\left(\frac{-A_{21}}{RT}\right) + \Phi_2\right) + x_1\ln\frac{\Phi_1}{x_1} + x_2\ln\frac{\Phi_2}{x_2}$$

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

# Wilson's Equations for Binary Solution Activity

•**A versatile and reasonably accurate model of excess Gibbs Energy was developed by Wilson in 1964. For a binary system, $G^E$ is provided by:**

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

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left[\frac{-a_{12}}{RT}\right] \qquad \Lambda_{21} = \frac{V_1}{V_2}\exp\left[\frac{-a_{21}}{RT}\right]$$

**$V_i$ is the molar volume at T of the pure component *i*.**

**$a_{ij}$ is determined from experimental data.**

**The notation varies greatly between publications. This includes,**

- **$a_{12} = (\lambda_{12} - \lambda_{11})$, $a_{21} = (\lambda_{12} - \lambda_{22})$ that you will encounter in Holmes, M.J. and M.V. Winkle (1970) *Ind. Eng. Chem.* 62, 21-21.**

# Wilson's Equations for Binary Solution Activity

- **Recall**

$$RT \ln \gamma_i = \overline{G}_i^E = \left. \frac{\partial nG^E}{\partial n_i} \right|_{T,P,n_j}$$

- **When applied to Wilson's :**

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

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

# Wilson’s Equations for Multi-Component Mixtures

- The strength of Wilson’s approach resides in its ability to describe multi-component (3+) mixtures using binary data.
  - Experimental data of the mixture of interest (ie. acetone, ethanol, benzene) is not required
  - We only need data (or parameters) for acetone-ethanol, acetone-benzene and ethanol-benzene mixtures
- The excess Gibbs energy for multicomponent mixtures is written:

$$\frac{G^E}{RT} = -\sum_i x_i \ln\left(\sum_j x_j \Lambda_{ij}\right)$$

- and the activity coefficients become:

$$\ln \gamma_i = 1 - \ln \sum_i x_j \Lambda_{ij} - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$

- where $\Lambda_{ij}$ = 1 for i=j.  Summations are over all species.

# Wilson's Equations for 3-Component Mixtures

- For three component systems, activity coefficients can be calculated from the following relationship:

$$\ln \gamma_i = 1 - \ln(x_1\Lambda_{i1} + x_2\Lambda_{i2} + x_3\Lambda_{i3}) - \frac{x_1\Lambda_{1i}}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2\Lambda_{2i}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3\Lambda_{3i}}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3}$$

- Model coefficients are defined as ($\Lambda_{ij} = 1$ for i=j):

$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left[\frac{-a_{ij}}{RT}\right]$$

# Non-Random-Two-Liquid Theory (NRTL)

- **NRTL model (Non-Random Two-Liquid; Renon and Prausnitz, 1968)**
  - **For binary systems:**

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

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

$$where \qquad G_{12} = exp \left[ - \alpha_{12} \left( \frac{g_{12} - g_{22}}{RT} \right) \right]; \quad G_{21} = exp \left[ - \alpha_{12} \left( \frac{g_{21} - g_{11}}{RT} \right) \right]$$

  - **$\alpha_{12}$ ,** the so-called non-randomness parameter
  - **Good for both miscible and partially miscible systems**

# Non-Random-Two-Liquid Theory (NRTL)

- For a liquid, in which the local distribution is random around the center molecule, the parameter $\alpha_{12}$ = 0. In that case the equations reduce to the one-parameter Margules activity model

$$\ln \gamma_1 = x_2^2 [\tau_{21} + \tau_{12}] = A x_2^2$$

$$\ln \gamma_2 = x_1^2 [\tau_{12} + \tau_{21}] = A x_1^2$$

- The NRTL parameters are fitted to activity coefficients that have been derived from experimentally determined phase equilibrium data
- Noteworthy is that for the same liquid mixture there might exist several NRTL parameter sets. It depends from the kind of phase equilibrium (i.e. solid-liquid, liquid-liquid, vapor-liquid).

# Universal Quasichemical Theory

- **UNIQUAC (Abrams and Prausnitz, 1975)**
- **In the UNIQUAC model the activity coefficients of the i$^{th}$ component of a two component mixture are described by a combinatorial and a residual contribution**

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

- **The first is an entropic term quantifying the deviation from ideal solubility as a result of differences in molecule shape. The latter is an enthalpic correction caused by the change in interacting forces between different molecules upon mixing.**

# UNIQUAC

- **Combinatorial contribution**

$$\ln \gamma_i^C = 1 - V_i + \ln V_i + \frac{z}{2} q_i \left( 1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)$$

  - **$V_i$, is the Volume fraction per mixture mole fraction for the i$^{th}$ component**
  - **$F_i$, is the surface area fraction per mixture molar fraction for the i$^{th}$ component**
  - **Z=10**
- **The excess entropy $\gamma^C$ is calculated exclusively from the pure chemical parameters, using the relative Van der Waals volumes $r_i$ and surface areas $q_i$ of the pure chemicals.**

# UNIQUAC

- **Residual contribution**

$$\ln \gamma_i^R = q_i \left( 1 - \ln \frac{\sum_j q_j x_j \tau_{ij}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ij}}{\sum_k q_k x_k \tau_{kj}} \right)$$

$$\tau_{ij} = e^{-\Delta u_{ij} / RT}$$

**$\Delta u_{ij}$ [J/mol] is the binary interaction energy parameter. Theory defines $\Delta u_{ij} = u_{ij} - u_{ii}$, and $\Delta u_{ji} = u_{ji} - u_{jj}$, where $u_{ij}$ is the interaction energy between molecules i and j.**

- **Data is derived from experimental activity coefficients, or from phase diagrams**

# The UNIFAC model

**A. Fredenslund, R.L. Jones, and J.M. Prausnitz, AIChE Journal (Vol.21, No.6 1975)**

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

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

**with** $l_i = (r_i - q_i)z/2 - (r_i - 1)$ $\qquad \ln\gamma_i(\text{residual}) = \sum_K \nu_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right]$

**Same as UNIQUAC Model**

$\nu_k^{(i)}$ **is the number of *k* groups present in species *i***

$\Gamma_k^{(i)}$ **is the residual contribution to the activity coefficient of group *k* in a pure fluid of species *i*.**

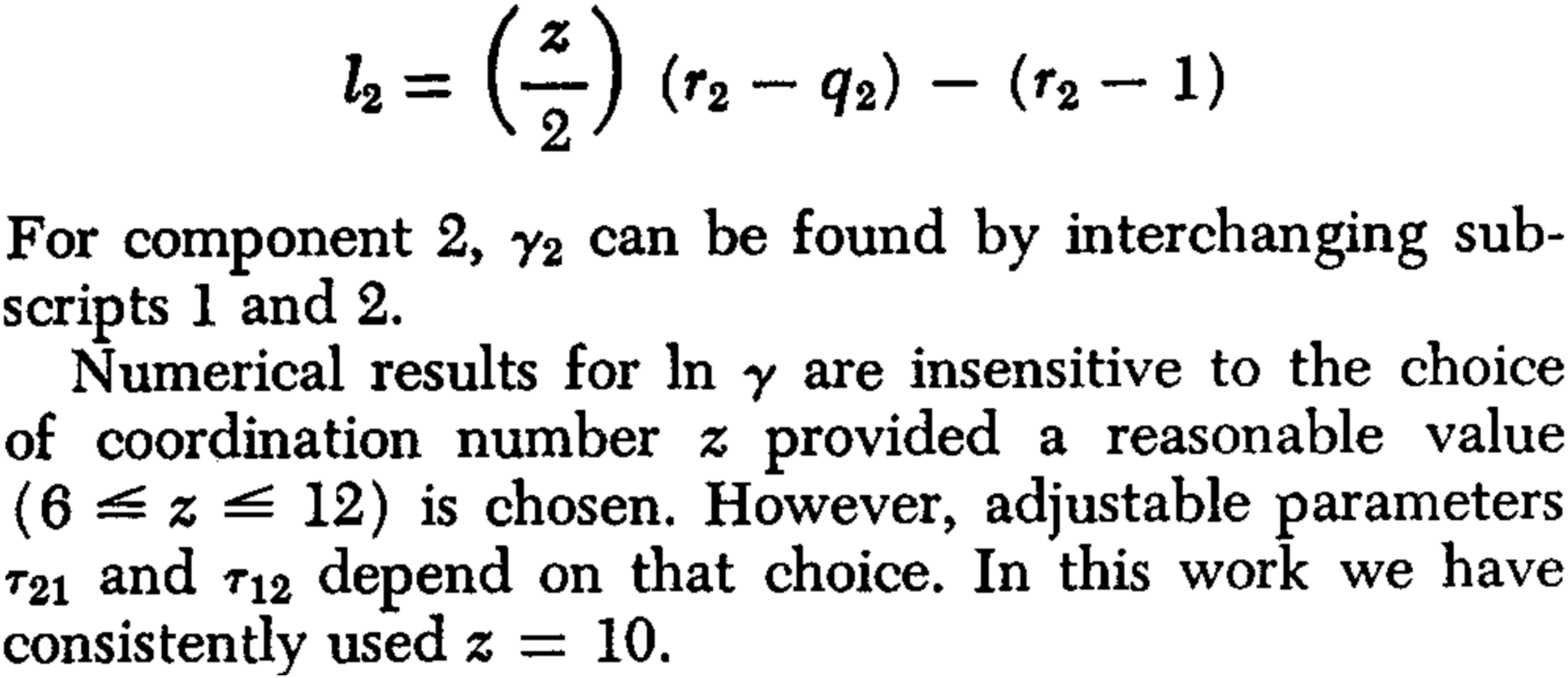
$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m\Psi_{mk}\right) - \sum_m \frac{\Theta_m\Psi_{km}}{\sum_n \Theta_n\Psi_{nm}}\right]$$

$$\Theta_m = \left\{\textbf{surface area fraction of group m}\right\} = \frac{X_m Q_m}{\sum_n X_n Q_n}$$

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

$X_m =$ **mole fraction of group *m* in mixture**

Z=10



$$l_2 = \left(\frac{z}{2}\right)(r_2 - q_2) - (r_2 - 1)$$

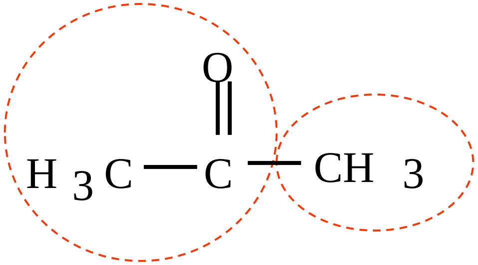
For component 2, $\gamma_2$ can be found by interchanging subscripts 1 and 2.

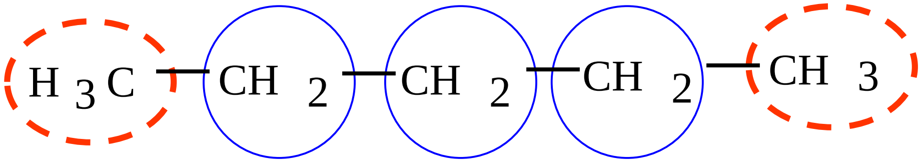
Numerical results for $\ln \gamma$ are insensitive to the choice of coordination number $z$ provided a reasonable value ($6 \leq z \leq 12$) is chosen. However, adjustable parameters $\tau_{21}$ and $\tau_{12}$ depend on that choice. In this work we have consistently used $z = 10$.

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

**D.S. Abrams and J.M. Prausnitz, AIChE J. Vol. 21:116-128, 1975**

# Example: obtain activity coefficients for the acetone/n-pentane system at 307 K and $x_{acetone}$=0.047.





| Molecules *(i)* | Group identification | | | | | |
|---|---|---|---|---|---|---|
| | name | Main No. | Sec. No | $\nu_j^{(i)}$ | $R_j$ | $Q_j$ |
| Acetone (1) | $CH_3$ | 1 | 1 | 1 | 0.9011 | 0.848 |
| | $CH_3CO$ | 9 | 19 | 1 | 1.6724 | 1.488 |
| n-pentane | $CH_3$ | 1 | 1 | 2 | 0.9011 | 0.848 |
| | $CH_2$ | 1 | 2 | 3 | 0.6744 | 0.540 |

| Main group | Subgroup | k | $R_k$ | $Q_k$ | Examples of molecules and their constituent groups | |
|---|---|---|---|---|---|---|
| 1 "$CH_2$" | $CH_3$ | 1 | 0.9011 | 0.848 | n-Butane: | $2CH_3, 2CH_2$ |
| | $CH_2$ | 2 | 0.6744 | 0.540 | Isobutane: | $3CH_3, 1CH$ |
| | CH | 3 | 0.4469 | 0.228 | 2,2-Dimethyl | |
| | C | 4 | 0.2195 | 0.000 | propane: | $4CH_3, 1C$ |
| 3 "ACH<br>(AC = aromatic carbon) | ACH | 10 | 0.5313 | 0.400 | Benzene: | 6ACH |
| 4 "$ACCH_2$" | $ACCH_3$ | 12 | 1.2663 | 0.968 | Toluene: | $5ACH, 1ACCH_3$ |
| | $ACCH_2$ | 13 | 1.0396 | 0.660 | Ethylbenzene: | $1CH_3, 5ACH, 1ACCH_2$ |
| 5 "OH | OH | 15 | 1.0000 | 1.200 | Ethanol: | $1CH_3, 1CH_2, 1OH$ |
| 7 "$H_2O$" | $H_2O$ | 17 | 0.9200 | 1.400 | Water: | $1H_2O$ |
| 9 "$CH_2CO$" | $CH_3CO$ | 19 | 1.6724 | 1.488 | Acetone: | $1CH_3CO, 1CH_3$ |
| | $CH_2CO$ | 20 | 1.4457 | 1.180 | 3-Pentanone: | $2CH_3, 1CH_2CO, 1CH_2$ |
| 13 "$CH_2O$" | $CH_3O$ | 25 | 1.1450 | 1.088 | Dimethyl ether: | $1CH_3, 1CH_3O$ |
| | $CH_2O$ | 26 | 0.9183 | 0.780 | Diethyl ether: | $2CH_3, 1CH_2, 1CH_2O$ |
| | CH–O | 27 | 0.6908 | 0.468 | Diisopropyl ether: | $4CH_3$, 1CH, 1CH–O |
| 15 "CNH" | $CH_3NH$ | 32 | 1.4337 | 1.244 | Dimethylamine: | $1CH_3, 1CH_3NH$ |
| | $CH_2NH$ | 33 | 1.2070 | 0.936 | Diethylamine: | $2CH_3, 1CH_2, 1CH_2NH$ |
| | CHNH | 34 | 0.9795 | 0.624 | Diisopropylamine: | $4CH_3$, 1CH, 1CHNH |
| 19 "CCN" | $CH_3CN$ | 41 | 1.8701 | 1.724 | Acetonitrile: | $1CH_3CN$ |
| | $CH_2CN$ | 42 | 1.6434 | 1.416 | Propionitrile: | $1CH_3, 1CH_2CN$ |

† H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, IEC *Research*, vol. 30

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

$$\ln \gamma_i(\mathit{combinatorial}) = \ln \frac{\phi_i}{x_i} + \frac{z}{2} \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \qquad l_i = (r_i - q_i) z / 2 - (r_i - 1)$$

## calculation of combinatorial contribution

mole fraction of acetone: $x_A = 0.047$

segment volume for acetone: $r_A = 1 \times 0.9011 + 1 \times 1.6724 = 2.5735$

segment volume for pentane: $r_P = 2 \times 0.9011 + 3 \times 0.6744 = 3.8254$

total volume at $x_A = 0.047$: $r_{tot} = 0.047 \times 2.5735 + 0.953 \times 3.8254 = 3.7666$

the segment fraction for acetone: $\phi_A = \dfrac{0.047 \times 2.5735}{3.7666} = 0.0321$

the segment fraction for pentane: $\phi_P = 1 - \phi_A = 0.9679$

Residual error

area for acetone: $q_A = 1 \times 0.848 + 1 \times 1.488 = 2.336$

area for pentane: $q_P = 2 \times 0.848 + 3 \times 0.540 = 3.316$

total area at $x_A$=0.047: $q_{tot} = 0.047 \times 2.336 + 0.953 \times 3.316 = 3.2699$

area fraction for acetone: $\theta_A = \dfrac{0.047 \times 2.336}{3.2699} = 0.0336$

area fraction for pentane: $\theta_P = 1 - \theta_A = 0.9664$

$$l_A = \frac{Z}{2}\left(r_A - q_A\right) - (r_A - 1) = \frac{10}{2}\left(2.5735 - 2.336\right) - (2.5735 - 1) = -0.3860$$

$$l_P = \frac{10}{2}\left(3.8254 - 3.316\right) - \left(3.8254 - 1\right) = -0.2784$$

| Molecule (i) | $r_i$ | $q_i$ | $\phi_i$ | $\theta_i$ | $l_i$ |
|---|---|---|---|---|---|
| acetone | 2.5735 | 2.336 | 0.0321 | 0.0336 | -0.3860 |
| pentane | 3.8254 | 3.316 | 0.9679 | 0.9664 | -0.2784 |

# combinatorial contribution

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

for acetone

$$\ln\gamma_A = \ln\frac{0.0321}{0.047} + \frac{10}{2}\times 2.336 \times \ln\frac{0.0336}{0.0321} - 0.386$$

$$-\frac{0.0321}{0.047}\left[0.047 \times (-0.386) + 0.953 \times (-0.2784)\right] = -0.0403$$

for pentane

$$\ln\gamma_P = \ln\frac{0.9679}{0.953} + \frac{10}{2}\times 3.316 \times \ln\frac{0.9664}{0.9679} - 0.2784$$

$$-\frac{0.9679}{0.953}\left[0.047 \times (-0.386) + 0.953 \times (-0.2784)\right] = -0.0007$$

# residual contribution

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

$\nu_k^{(i)}$ is the number of *k* groups present in species *i*

$\Gamma_k^{(i)}$ is the residual contribution to the activity coefficient of group *k* in a pure fluid of species *i*.

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

$$\Theta_m = \left\{ \text{surface area fraction of group m} \right\} = \frac{X_m Q_m}{\sum_n X_n Q_n}$$

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

$X_m$ = mole fraction of group *m* in mixture

$$\Psi_{\boxed{m\ n}}$$

main group labels

## Table H.2 UNIFAC–VLE Interaction Parameters, $a_{mk}$, in kelvins[†]

| | 1 | 3 | 4 | 5 | 7 | 9 | 13 | 15 | 19 |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2$ | 0.00 | 61.13 | 76.50 | 986.50 | 1,318.00 | 476.40 | 251.50 | 255.70 | 597.00 |
| ACH | −11.12 | 0.00 | 167.00 | 636.10 | 903.80 | 25.77 | 32.14 | 122.80 | 212.50 |
| $ACCH_2$ | −69.70 | −146.80 | 0.00 | 803.20 | 5,695.00 | −52.10 | 213.10 | −49.29 | 6,096.00 |
| OH | 156.40 | 89.60 | 25.82 | 0.00 | 353.50 | 84.00 | 28.06 | 42.70 | 6.71 |
| $H_2O$ | 300.00 | 362.30 | 377.60 | −229.10 | 0.00 | −195.40 | 540.50 | 168.00 | 112.60 |
| $CH_2CO$ | 26.76 | 140.10 | 365.80 | 164.50 | 472.50 | 0.00 | −103.60 | −174.20 | 481.70 |
| $CH_2O$ | 83.36 | 52.13 | 65.69 | 237.70 | −314.70 | 191.10 | 0.00 | 251.50 | −18.51 |
| CNH | 65.33 | −22.31 | 223.00 | −150.00 | −448.20 | 394.60 | −56.08 | 0.00 | 147.10 |
| CCN | 24.82 | −22.97 | −138.40 | 185.40 | 242.80 | −287.50 | 38.81 | −108.50 | 0.00 |

K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, IEC ***Research,*** vol. 30, pp. 2352–2355, 199 from table H.2

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

$$a_{1,9} = a_{\text{CH3, CH3CO}} = 476.4 \Rightarrow \Psi_{1,9} = \exp\left[\frac{-476.4}{307}\right] = 0.2119$$

$$a_{9,1} = a_{\text{CH3CO, CH3}} = 26.760 \Rightarrow \Psi_{9,1} = \exp\left[\frac{-26.76}{307}\right] = 0.9165$$

$$a_{1,1} = a_{9,9} = 0 \Rightarrow \Psi_{1,1} = \Psi_{9,9} = 1$$

Calculation of $\Gamma_k^{(i)}$

we are dealing a pure substance!

$Q_i$ from table H.1

$X_m =$ mole fraction of group *m* in mixture

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

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

for pure acetone, there are only two different kinds of groups: CH$_3$ and CH$_3$O. Let CH$_3$ be labeled by 1 and CH$_3$O be labeled by 19.

$$X_1^{(A)} = \frac{\nu_1^{(A)}}{\nu_1^{(A)} + \nu_{19}^{(A)}} = \frac{1}{1+1} = 0.5, \quad X_{19}^{(A)} = 0.5$$

$$\Theta_1^{(A)} = \frac{0.5 \times 0.848}{0.5 \times 1.488 + 0.5 \times 0.848} = 0.363, \qquad \Theta_{19}^{(A)} = 0.637$$

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

$$\ln \Gamma_1^{(A)} = 0.848 \left[1 - \ln\left(\overset{\boxed{\Theta_1^{(A)}\Psi_{1,1}}}{0.363 \times 1} + \overset{\boxed{\Theta_{19}^{(A)}\Psi_{9,1}}}{0.637 \times 0.9165}\right)\right] \qquad \boxed{\Theta_{19}^{(A)}\Psi_{1,9}}$$

$$+ 0.848 \left[ - \left( \frac{\overset{\boxed{\Theta_1^{(A)}\Psi_{1,1}}}{0.363 \times 1}}{\underset{\boxed{\Theta_1^{(A)}\Psi_{1,1}}}{0.363 \times 1} + \underset{\boxed{\Theta_{19}^{(A)}\Psi_{9,1}}}{0.637 \times 0.9165}} + \frac{0.637 \times 0.2119}{\underset{\boxed{\Theta_1^{(A)}\Psi_{1,9}}}{0.363 \times 0.2119} + \underset{\boxed{\Theta_{19}^{(A)}\Psi_{9,9}}}{0.637 \times 1}} \right) \right] = 0.409$$

$$\ln \Gamma_{19}^{(A)} = 1.488 \left[1 - \ln\left(0.363 \times 0.2119 + 0.637\right)\right]$$

$$+ 1.488 \left[ - \left( \frac{0.363 \times 0.9165}{0.363 \times 1 + 0.637 \times 0.9165} + \frac{0.637 \times 0.2119}{0.363 \times 0.2119 + 0.637} \right) \right] = 0.139$$

for pure pentane, there are two kinds of subgroups, $CH_3$ and $CH_2$ and both subgroups belong to one main group. Let $CH_2$ be labeled by 2

$$X_1^{(P)} = \frac{\nu_1^{(P)}}{\nu_1^{(P)} + \nu_1^{(P)}} = \frac{2}{5} = 0.4, \quad X_2^{(P)} = 0.6$$

Since both subgroups are belong to the same main group

$$\ln \Gamma_1^{(P)} = \ln \Gamma_2^{(P)} = 0$$

Calculation of group residual activity at $x_A = 0.047$

now we are dealing a mixture!

for $CH_3$(labeled 1)

for $CH_2$(labeled 2)

for $CH_3CO$ (labeled 19)

$$X_1 = \frac{0.047 \times 1 + 0.953 \times 2}{0.047 \times 2 + 0.953 \times 5} = 0.4019, \quad X_2 = \frac{0.953 \times 3}{0.047 \times 2 + 0.953 \times 5} = 0.5884, \quad X_{19} = 0.0097$$

$$\Theta_1 = \frac{0.4019 \times 0.848}{0.4019 \times 0.848 + 0.5884 \times 0.540 + 0.0097 \times 1.488} = 0.5064$$

$$\Theta_2 = \frac{0.5884 \times 0.540}{0.4019 \times 0.848 + 0.5884 \times 0.540 + 0.0097 \times 1.488} = 0.4721$$

$$\Theta_{19} = \frac{0.0097 \times 1.488}{0.4019 \times 0.848 + 0.5884 \times 0.540 + 0.0097 \times 1.488} = 0.0214$$

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

$$\ln \Gamma_1 = 0.848 \left[ 1 - \ln \left( 0.5064 + 0.4721 + 0.0214 \times 0.9165 \right) \right]$$

$$- 0.848 \left[ \frac{0.5064 + 0.4721}{0.5064 + 0.4721 + 0.0214 \times 0.9165} + \frac{0.0214 \times 0.2119}{(0.5064 + 0.4721) \times 0.2119 + 0.0214} \right]$$

$$= 1.45 \times 10^{-3}$$

$$\ln \Gamma_2 = 0.540 \left[ 1 - \ln \left( 0.5064 + 0.4721 + 0.0214 \times 0.9165 \right) \right]$$

$$- 0.540 \left[ \frac{0.5064 + 0.4721}{0.5064 + 0.4721 + 0.0214 \times 0.9165} + \frac{0.0214 \times 0.2119}{(0.5064 + 0.4721) \times 0.2119 + 0.0214} \right]$$

$$= 9.26 \times 10^{-4}$$

$$\ln\Gamma_{19} = 1.488\left[1 - \ln\left(0.5064 + 0.4721 + 0.0214\times 0.9165\right)\right]$$

$$-1.488\left[\frac{(0.5064 + 0.4721)\times 0.9165}{0.5064 + 0.4721 + 0.0214\times 0.9165} + \frac{0.0214}{(0.5064 + 0.4721)\times 0.2119 + 0.0214}\right]$$

$$= 2.21$$

The residual contributions to the activity coefficients follow

$$\ln\gamma_A^R = 1\times\left(\overset{M}{1.45\times 10^{-3}} - \overset{p}{0.409}\right) + 1\times\left(\overset{M}{2.21} - \overset{p}{0.139}\right) = 1.66$$

$$\ln\gamma_P^R = 2\times\left(1.45\times 10^{-3} - 0.0\right) + 3\times\left(2.21 - 0.0\right) = 5.68\times 10^{-3}$$

Finally summing up the combinatorial and residual contributions

$$\ln\gamma_A = -0.403 + 1.66 = 1.62$$

$$\ln\gamma_P = -0.0007 + 5.68\times 10^{-3} = 4.98\times 10^{-3}$$

or $\boxed{\gamma_A = 5.07\,,\quad \gamma_P = 1.01}$

experimental data: $\boxed{\gamma_A = 4.41\,,\quad \gamma_P = 1.11}$