

Solution Thermodynamics III

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Term project

- Title:
- Name and affiliation
- Executive Abstract
- Introduction
- Models and methods
- Results and discusses
- Summary
- References

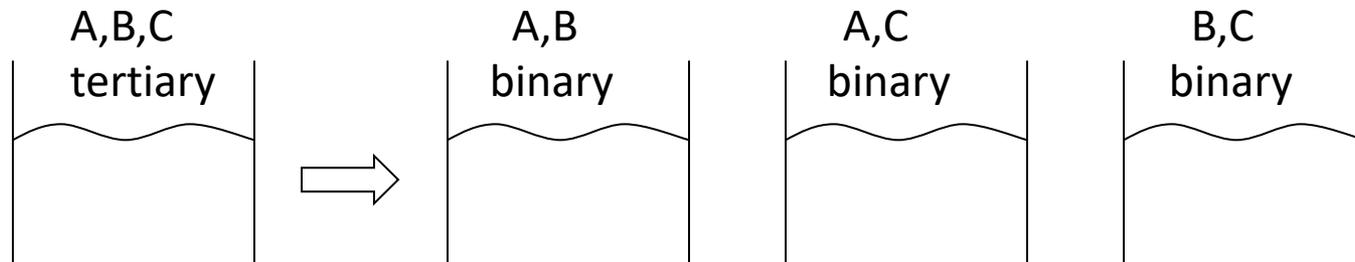
Local Composition Models

• Unfortunately, the earlier 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**, Ω_{ij} , relative to the overall compositions.

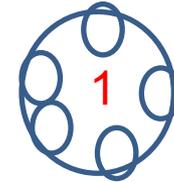
$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \Omega_{21} \quad \frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \Omega_{12}$$

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

Local Composition Models

The local mole balance (**outside 1's**):

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



Writing the local mole fractions x_{21} and x_{11} in terms of the overall mole fractions, x_1 and x_2 ,

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

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

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.

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

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

$$(U - U^{ig})^{(1)} = \frac{N_A}{2} N_{c1} (x_{11}\epsilon_{11} + x_{21}\epsilon_{21})$$

$$(U - U^{ig})^{(2)} = \frac{N_A}{2} N_{c2} (x_{12}\epsilon_{12} + x_{22}\epsilon_{22})$$

where N_{cj} is the coordination number (total number of atoms in the neighborhood of the j th species), **z** in regular solution. U^{ig} , reference.

then

$$U - U^{ig} = \frac{N_A}{2} [x_1 N_{c1} (x_{11}\epsilon_{11} + x_{21}\epsilon_{21}) + x_2 N_{c2} (x_{12}\epsilon_{12} + x_{22}\epsilon_{22})]$$

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

Local Composition Models

Recall,

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

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

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

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

same as regular solution

For ideal solution, *is*

$$(U - U^{ig})^{is} = x_1(U - U^{ig})_{pure1} + x_2(U - U^{ig})_{pure2} = \frac{N_A}{2}[x_1Nc_1\varepsilon_{11} + x_2Nc_2\varepsilon_{22}]$$

Local Composition Models

Recall,

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

Subtracting we have,

$$U^E = U - U^{is} = \frac{N_A}{2} [x_1 N c_1 ((x_{11} \epsilon_{11} + x_{21} \epsilon_{21}) - \epsilon_{11}) + x_2 N c_2 ((x_{12} \epsilon_{12} + x_{22} \epsilon_{22}) - \epsilon_{22})]$$

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

Arriving at $U^E = \frac{N_A}{2} [x_1 x_{21} N c_1 (\epsilon_{21} - \epsilon_{11}) + x_2 x_{12} N c_2 (\epsilon_{12} - \epsilon_{22})]$

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

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

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,

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

where $A^E/(RT)|_{\infty}$ is the infinite temperature limit at the given liquid density independent of temperature but possibly dependent on composition or density.

using H will be $G = H - TS$

Wilson made a bold assumption regarding the temperature dependence of Ω_{ij} .

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

Substitute back and integrate,

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

A convenient simplifying assumption before proceeding further is that $G^E = A^E$. This corresponds to neglecting the excess volume of mixing, ΔV^E relative to the other contributions and is really quite acceptable for liquids.

Separate G^E/RT into an energetic part known as the *residual contribution*, that vanishes at infinite temperature or when $\epsilon_{12} - \epsilon_{22} = 0$ and $\epsilon_{21} - \epsilon_{11} = 0$, 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, **residual** contribution

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

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,

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

Simplified version, when $\Phi_i = x_i$:

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

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:

$$\frac{G^E}{RT} = x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$$
$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left[\frac{-a_{12}}{RT}\right] \quad \Lambda_{21} = \frac{V_1}{V_2} \exp\left[\frac{-a_{21}}{RT}\right]$$

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

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

- 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:

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

- 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:

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

local composition
for non-random

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

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

some Wilson

- α_{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

$$\ln \gamma_1 = x_2^2 [\tau_{21} + \tau_{12}] = Ax_2^2$$

$$\ln \gamma_2 = x_1^2 [\tau_{12} + \tau_{21}] = Ax_1^2$$

- 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).

non-unique results from simple data fitting

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

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

more **Wilson**

- 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.

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

- **Combinatorial contribution** **size and sites**

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

$$\ln \frac{\Phi_i}{x_i}$$

- 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 γ^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.

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

- Residual contribution**

interaction

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

with sites correction

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

Δu_{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**

sub means
local
composition

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 $l_i = (r_i - q_i)z/2 - (r_i - 1)$ $\ln \gamma_i (\text{residual}) = \sum_K v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$

Same as
UNIQUAC
Model

$v_k^{(i)}$ 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*.

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

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

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

X_m = mole fraction of group *m* in mixture

Z=10

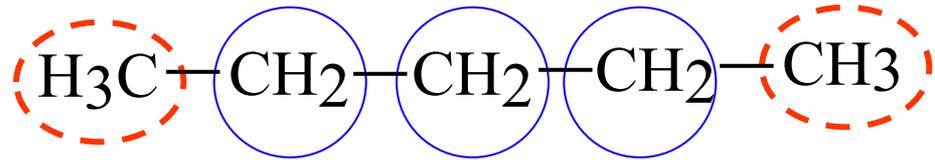
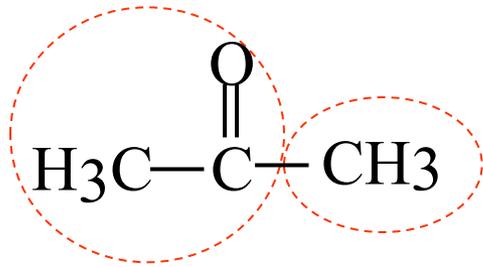
$$l_2 = \left(\frac{z}{2} \right) (r_2 - q_2) - (r_2 - 1)$$

For component 2, γ_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 τ_{21} and τ_{12} depend on that choice. In this work we have consistently used $z = 10$.

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

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



Molecules (<i>i</i>)	Group identification			$\nu_j^{(i)}$	R_j	Q_j
	name	Main No.	Sec. No			
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

“Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures”
 AIChE Journal (Vol. 21, No. 6, pp 1086-1099)

Table III. CNH₂O: All Subgroup Parameters

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 (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 ₂ O"	H ₂ O	17	0.9200	1.400	Water:	1H ₂ O
9 "CH ₂ CO"	CH ₃ CO	19	1.6724	1.488	Acetone:	1CH ₃ CO, 1CH ₃
	CH ₂ CO	20	1.4457	1.180	3-Pentanone:	2CH ₃ , 1CH ₂ CO, 1CH ₂
13 "CH ₂ O"	CH ₃ O	25	1.1450	1.088	Dimethyl ether:	1CH ₃ , 1CH ₃ O
	CH ₂ O	26	0.9183	0.780	Diethyl ether:	2CH ₃ , 1CH ₂ , 1CH ₂ O
	CH-O	27	0.6908	0.468	Diisopropyl ether:	4CH ₃ , 1CH, 1CH-O
15 "CNH"	CH ₃ NH	32	1.4337	1.244	Dimethylamine:	1CH ₃ , 1CH ₃ NH
	CH ₂ NH	33	1.2070	0.936	Diethylamine:	2CH ₃ , 1CH ₂ , 1CH ₂ NH
	CHNH	34	0.9795	0.624	Diisopropylamine:	4CH ₃ , 1CH, 1CHNH
19 "CCN"	CH ₃ CN	41	1.8701	1.724	Acetonitrile:	1CH ₃ CN
	CH ₂ CN	42	1.6434	1.416	Propionitrile:	1CH ₃ , 1CH ₂ CN

†H. K. Hanson, B. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, IEC Research, vol. 30,

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

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

calculation of combinatorial contribution

mole fraction of acetone: $x_A = 0.047$

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

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 **volume fraction** for acetone: $\phi_A = \frac{0.047 \times 2.5735}{3.7666} = 0.0321$

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

Residual error



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

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: $\theta_A = \frac{0.047 \times 2.336}{3.2699} = 0.0336$

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

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

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

Molecule (i)	r_i	q_i	ϕ_i	θ_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

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

for acetone

$$\begin{aligned} \ln \gamma_A &= \ln \frac{0.0321}{0.047} + \frac{10}{2} \times 2.336 \times \ln \frac{0.0336}{0.0321} - 0.386 \\ &\quad - \frac{0.0321}{0.047} [0.047 \times (-0.386) + 0.953 \times (-0.2784)] = -0.0403 \end{aligned}$$

for pentane

$$\begin{aligned} \ln \gamma_P &= \ln \frac{0.9679}{0.953} + \frac{10}{2} \times 3.316 \times \ln \frac{0.9664}{0.9679} - 0.2784 \\ &\quad - \frac{0.9679}{0.953} [0.047 \times (-0.386) + 0.953 \times (-0.2784)] = -0.0007 \end{aligned}$$

-0.0007110

residual contribution

$$\ln \gamma_i(\text{residual}) = \sum_K \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad \text{Pure - Mixture}$$

$\nu_k^{(i)}$ 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 .

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

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

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

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

Ψ

$m n$

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 ₂ O	300.00	362.30	377.60	-229.10	0.00	-195.40	540.50	168.00	112.60
CH ₂ CO	26.76	140.10	365.80	164.50	472.50	0.00	-103.60	-174.20	481.70
CH ₂ O	83.36	52.13	65.69	237.70	-314.70	191.10	0.00	251.50	-18.50
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

† L. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, *IEC Research*, vol. 30, pp. 2352-2355, 199

from table H.2

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

$$a_{1,9} = a_{\text{CH}_3, \text{CH}_3\text{CO}} = 476.4 \Rightarrow \Psi_{1,9} = \exp\left[\frac{-476.4}{307}\right] = 0.2119$$

$$a_{9,1} = a_{\text{CH}_3\text{CO}, \text{CH}_3} = 26.760 \Rightarrow \Psi_{9,1} = \exp\left[\frac{-26.76}{307}\right] = 0.9165$$

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

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

groups forming molecule -- pure

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

Q_i from table H.1

we are dealing a **pure substance!**

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_3O . Let CH_3 be labeled by 1 and CH_3O be labeled by 19.

$$X_1^{(A)} = \frac{v_1^{(A)}}{v_1^{(A)} + v_{19}^{(A)}} = \frac{1}{1+1} = 0.5, \quad X_9^{(A)} = 0.5$$

CH₃ in acetone

$$\Theta_1^{(A)} = \frac{0.5 \times 0.848}{0.5 \times 1.488 + 0.5 \times 0.848} = 0.363, \quad \Theta_9^{(A)} = 0.637$$

Q_i surface area

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

$$\ln \Gamma_1^{(A)} = 0.848 \left[1 - \ln \left(\Theta_1^{(A)} \Psi_{1,1} + \Theta_9^{(A)} \Psi_{9,1} \right) \right. \\ \left. + 0.848 \left[- \left(\frac{\Theta_1^{(A)} \Psi_{1,1} \cdot 0.363 \times 1}{0.363 \times 1 + 0.637 \times 0.9165} + \frac{0.637 \times 0.2119}{0.363 \times 0.2119 + 0.637 \times 1} \right) \right] \right] = 0.409$$

$$\ln \Gamma_{19}^{(A)} = 1.488 \left[1 - \ln \left(\Theta_1^{(A)} \Psi_{1,9} + \Theta_9^{(A)} \Psi_{9,9} \right) \right. \\ \left. + 1.488 \left[- \left(\frac{0.363 \times 0.9165 \cdot \Theta_1^{(A)} \Psi_{9,1}}{0.363 \times 1 + 0.637 \times 0.9165} + \frac{0.637 \times 0.2119}{0.363 \times 0.2119 + 0.637} \right) \right] \right] = 0.139$$

for pure pentane, there are two kinds of subgroups, CH₃ and CH₂ and both subgroups belong to one main group. Let CH₂ be labeled by 2

$$X_1^{(P)} = \frac{v_1^{(P)}}{v_1^{(P)} + v_2^{(P)}} = \frac{2}{5} = 0.4, \quad X_2^{(P)} = 0.6$$

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 $x_A = 0.047$

$$\ln \gamma_i(\text{residual}) = \sum_K v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad \text{groups forming mixture}$$

$\ln \Gamma_k$ now we are dealing a mixture!

for CH₃(labeled 1)

for CH₂(labeled 2)

for CH₃CO
(labeled 9)

$$X_1 = \frac{0.047 \times 1 + 0.953 \times 2}{0.047 \times 2 + 0.953 \times 5} = 0.4019, \quad X_2 = \frac{0.953 \times 3}{0.047 \times 2 + 0.953 \times 5} = 0.5884, \quad X_9 = 0.0097$$

$$0.4019 \times 0.848$$

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

surface area

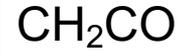
CH₃

CH₂

CH₂CO



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



$$\Theta_9 = \frac{0.0097 \times 1.488}{0.4019 \times 0.848 + 0.5884 \times 0.540 + 0.0097 \times 1.488} = 0.0214$$

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

$\Theta_1 \Psi_{1,1}$

$\Theta_2 \Psi_{2,1}$

$\Theta_9 \Psi_{9,1}$

$\Psi_{21} = 1$

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

$\Theta_9 \Psi_{1,9}$

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

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

$\Theta_1 \Psi_{1,2}$

$\Theta_2 \Psi_{2,2}$

$\Theta_9 \Psi_{9,2}$

$\Theta_1 \Psi_{1,9} + \Theta_2 \Psi_{2,9}$

$\Theta_9 \Psi_{9,9}$

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

$\Theta_9 \Psi_{2,9}$

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

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

$$\ln \Gamma_9 = 1.488 \left[1 - \ln \left((0.5064 + 0.4721) 0.2119 + 0.0214 \right) \right] - 1.488 \left[\frac{(0.5064 + 0.4721) 0.9165}{(0.5064 + 0.4721) 0.9165 + 0.0214} + \frac{0.0214}{(0.5064 + 0.4721) 0.2119 + 0.0214} \right]$$

$$= \mathbf{2.091}$$

The residual contributions to the activity coefficients follow

$$\ln \gamma_i(\text{residual}) = \sum_K v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

$$\ln \gamma_A^R = 1 \times (\overset{\text{mix - pure}}{1.45 \times 10^{-3}} - 0.409) + 1 \times (\overset{\text{mix - pure}}{2.09} - 0.139) = \mathbf{1.54}$$

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

Finally summing up the combinatorial and residual contributions

$$\ln \gamma_A = -0.0403 + 1.54 = \mathbf{1.5}$$

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

or $\gamma_A = \mathbf{4.48}$ $\gamma_P = \mathbf{1.01}$

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