

Program to calculate Activity Coefficient γ_{mix} by UNIFAC (UNIQUAC Functional-group Activity Coefficients) Equation

Introduction:-

UNIFAC is a semi-empirical system for the prediction of non-electrolyte activity in non-ideal mixtures. UNIFAC uses the functional groups present on the molecules that make up the liquid mixture to calculate activity coefficients. By using 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. This information can be used to obtain information on liquid equilibria, which is useful in many thermodynamic calculations, such as chemical reactor design, and distillation calculations.

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

γ^C (Combinatorial Contribution)
 γ^R (Residual Contribution)

The combinatorial part, which is dependent on the surface area and volume of each molecule, is calculated from.

$$\ln(\gamma_i^C) = \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{Z}{2} q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{x_i} \sum_j x_j l_j$$

in which x_i represents the mole fraction of component i and the summations are over all components, including component i . The terms φ_i (volume fraction), θ_i (surface area fraction), and l_i are defined by

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad , \quad \varphi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad , \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

Z =lattice coordination number set equal to 10.

The molecular volume, r_i , and the molecular surface area, q_i , are calculated as

$$r_i = \sum_k v_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k v_k^{(i)} Q_k$$

where $v_k^{(i)}$ is the number of k groups present in component i . Values of R and Q for some selected groups and subgroups Table.

The residual part of the activity coefficient describes the intermolecular forces and is calculated from.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

where Γ_k is the contribution of functional group k to the residual activity coefficient, and $\Gamma_k^{(i)}$ is the contribution of group k in the pure fluid i at the same temperature and pressure as the mixture. The term $\Gamma_k^{(i)}$ is needed in the main equation to satisfy the condition that $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$.

The contribution of functional group k in the mixture:-

$$\ln \Gamma_k = Q_k \left[1 + \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right]$$

θ_m is the area fraction of group m , and the summations are over all different groups. θ_m is calculated in a manner similar to that for θ_i .

$$\theta_m = \frac{Q_m X_m}{\sum_j Q_j X_j} \quad X_m = \frac{\sum_j v_j^{(i)} x_j}{\sum_j \sum_n v_n^{(i)} x_j}$$

where θ_m is area fraction of group m .

X_m is the mole fraction of group m in the mixture.

The group-interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \text{Exp} \left(-\frac{U_{mn} - U_{nn}}{RT} \right) \quad \psi_{mn} = \text{Exp} \left(-\frac{a_{mn}}{T} \right)$$

where U_{mn} is a measure of the energy of interaction between groups m and n . The group interaction parameters a_{mn} must be evaluated from experimental phase equilibrium data. Note that a_{mn} has units of Kelvin and $a_{mn} \neq a_{nm}$. Parameters a_{mn} and a_{nm} are obtained from a database using a wide range of experimental results.

The contribution of functional group k in pure component:-

$$\ln \Gamma_{ki} = Q_k \left[1 + \ln \left(\sum_m \theta_{mi} \psi_{mk} \right) - \sum_m \frac{\theta_{mi} \psi_{km}}{\sum_n \theta_{ni} \psi_{nm}} \right]$$

$$\theta_{mi} = \frac{Q_m X_{mi}}{\sum_j Q_j X_{ji}} \quad X_{mi} = \frac{v_{mi}}{\sum_i v_{mi}}$$

where θ_{mi} is area fraction of group m in component i .

X_{mi} is the mole fraction of group m in component i .

Algorithm of UNIFAC Activity Coefficient:-

```

For i = 1 To N
  ri(i) = 0: qi(i) = 0
  For j = 1 To M
    ri(i) = ri(i) + vk(j,i) * Rk(j)
    qi(i) = qi(i) + vk(j,i) * Qk(j)
  Next j
Next i

```

Where

N = Number of component

M = Number of groups

```

SumA = 0: SumC = 0
For i = 1 To N
  For j = 1 To M
    ek(j,i) = vk(j,i) * Qk(j) / qi(i)
  Next j
  SumA = SumA + x(i) * qi(i)
  SumC = SumC + x(i) * ri(i)
Next i

```

Overall Surface area fraction for each subgroup:-

```

For i = 1 To M
  Thk(i) = 0
  For j = 1 To N
    Thk(i) = Thk(i) + x(j) * qi(j) * ek(i,j)
  Next j
  Thk(i) = Thk(i) / SumA
Next i

```

```

    For i = 1 To M
    For j = 1 To M
tmk(i,j) = Exp  $\left(-\frac{a_{ij}(i,j)}{T}\right)$ 
    Next j
    Next i

```

```

    For k = 1 To M
    For i = 1 To N
    SumB = 0
    Li(i) =  $\frac{qi(i)}{SumA}$ 
    Ji(i) =  $\frac{ri(i)}{SumC}$ 
    For j = 1 To M
SumB = SumB + ek(j,i) * tmk(j,k)
    Next j
    Bik(i,k) = SumB
    Next i
    Next k

```

```

    For i = 1 To M
    Sk(i) = 0
    For j = 1 To M
Sk(i) = Sk(i) + Thk(j) * tmk(j,i)
    Next j
    Next i

```

```

    For i = 1 To N
 $\gamma^C = 1 - Ji(i) + \ln(Ji(i)) - 5 * qi(i) * \left(1 - \frac{Ji(i)}{Li(i)}\right) + \ln\left(\frac{Ji(i)}{Li(i)}\right)$ 
    Next i

```

```

For i = 1 To N
  SumD = 0
  For j = 1 To N
    SumD = SumD +  $\left( Thk(j) * \frac{Bik(i,j)}{Sk(j)} - ek(j,i) * \ln\left(\frac{Bik(i,j)}{Sk(j)}\right) \right)$ 
  Next j
   $\gamma^R = qi(i) * (1 - SumD)$ 
   $\gamma_i = Exp(\gamma^R + \gamma^C)$ 
Next i

```

The example(1) From:-

Introduction to Chemical Engineering Thermodynamic, smith six edition

Appendix H

Snapshot

Microsoft Excel - UNIFAC GAMMA BOOK - Copy

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1															
2		Temp													
3		308.15													
4					subgroup	k	Rk	Qk	v1	v2		am,k	1	2	33
5			Xi		CH3	1	0.9011	0.848	2	2		1	0	0	255.7
6		diethylamine	0.4		CH2	2	0.6744	0.54	1	5		2	0	0	255.7
7		n-heptane	0.6		CH2NH	33	1.207	0.936	1	0		33	65.33	65.33	0
8															
9															
10															
11					γ_1	γ_2									
12					1.13304	1.04702									
13															
14															
15															
16															
17															
18															

Example(1)

Microsoft Excel - UNIFAC GAMMA BOOK - Copy

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1																
2		Temp														
3		345														
4					subgroup	k	Rk	Qk	v1	v2		am,k	1	2	5	33
5			Xi		CH3	1	0.9011	0.848	1	0		1	0	0	986.5	61.13
6		Ethanol	0.2		CH2	2	0.6744	0.54	1	0		2	0	0	986.5	61.13
7		Benzene	0.8		OH	5	1	1.2	1	0		5	156.4	156.4	0	89.6
8					ARCH	33	0.5313	0.4	0	6		33	-11.12	-11.12	636.1	0
9																
10																
11					γ_1	γ_2										
12					2.91	1.10386										
13																
14																
15																
16																
17																
18																

Example(2)

Option Explicit

```
Function UNIFAC_GAMMA(T As Double, X As Range, Rk As Range, Qk As Range, Vk As Range, aij As Range)
```

```
Dim i, j, k, N, M As Integer
Dim ri() As Double, qi() As Double, ek() As Double, Thk() As Double, tmk() As Double, Bik() As Double
Dim SUMA As Double, SUMB As Double, Sk() As Double, SUMC As Double, Ji() As Double, Li() As Double
Dim GC() As Double, GR() As Double, SUMD As Double, GAMMA() As Double
N = X.Count: M = Rk.Count
ReDim ri(N) As Double, qi(N) As Double, ek(M, N) As Double, Thk(M) As Double, tmk(M, M) As Double, GAMMA(1 To N) As Double
ReDim Bik(N, M) As Double, Sk(M) As Double, Ji(N) As Double, Li(N) As Double, GC(N) As Double, GR(N) As Double

For i = 1 To N
    ri(i) = 0: qi(i) = 0
    For j = 1 To M
        ri(i) = ri(i) + Vk(j, i) * Rk(j): qi(i) = qi(i) + Vk(j, i) * Qk(j)
    Next j
Next i

SUMA = 0: SUMC = 0
For i = 1 To N
    For j = 1 To M: ek(j, i) = 0
    ek(j, i) = Vk(j, i) * Qk(j) / qi(i)
Next j
SUMA = SUMA + X(i) * qi(i)
SUMC = SUMC + X(i) * ri(i)
Next i

'-----Overall Surface area fraction for each subgroup-----
'-----
For i = 1 To M
    Thk(i) = 0
    For j = 1 To N
        Thk(i) = Thk(i) + X(j) * qi(j) * ek(i, j)
    Next j
    Thk(i) = Thk(i) / SUMA
Next i

For i = 1 To M
    For j = 1 To M
        tmk(i, j) = Exp(-aij(i, j) / T)
```

```

Next j
Next i

For k = 1 To M
For i = 1 To N
SUMB = 0
For j = 1 To M
SUMB = SUMB + ek(j, i) * tmk(j, k)
Next j
Bik(i, k) = SUMB
Next i
Next k

For i = 1 To M
Sk(i) = 0
For j = 1 To M
Sk(i) = Sk(i) + Thk(j) * tmk(j, i)
Next j
Next i

For i = 1 To N
Ji(i) = ri(i) / SUMC
Li(i) = qi(i) / SUMA
Next i

For i = 1 To N
GC(i) = 1 - Ji(i) + Application.Ln(Ji(i)) - 5 * qi(i) * (1 - Ji(i))
/ Li(i) + Application.Ln(Ji(i) / Li(i))
Next i

For i = 1 To N
SUMD = 0
For j = 1 To M
SUMD = SUMD + (Thk(j) * Bik(i, j) / Sk(j) - ek(j, i) *
Application.Ln(Bik(i, j) / Sk(j)))
Next j
GR(i) = qi(i) * (1 - SUMD)
GAMMA(i) = Exp(GR(i) + GC(i))
Next i

UNIFAC_GAMMA = GAMMA
End Function

```

I wish you all the best