

## Program to calculate Activity Coefficient $\gamma_{\text{mix}}$ 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.

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

$\gamma^C$  (Combinatorial Contribution)  
 $\gamma^R$  (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  $i$  (volume fraction),  $\theta_i$  (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  $\Gamma_k$  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:-

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

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

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

where  $\theta_m$  is area fraction of group  $m$ .

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

The group-interaction parameter  $\psi_{mn}$  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  $\theta_{mi}$  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) *  $\frac{Qk(j)}{qi(i)}$ 
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) =  $\frac{Thk(i)}{SumA}$ 
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
    Li(i) = qi(i)/SumA
    Ji(i) = 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
γc = 1 - Ji(i) + ln(Ji(i)) - 5 * qi(i) * (1 - Ji(i)/Li(i)) + ln(Ji(i)/Li(i))
    Next i

```

```

For i = 1 To N
  SumD = 0
  For j = 1 To N
    SumD = SumD + (Thk(j) *  $\frac{Bik(i,j)}{Sk(j)}$  - ek(j,i) *  $\ln\left(\frac{Bik(i,j)}{Sk(j)}\right)$ )
  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**

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# Snapshot

subgroup	k	Rk	Qk	v1	v2	am,k	1	2	33
CH3	1	0.9011	0.848	2	2	1	0	0	255.7
CH2	2	0.6744	0.54	1	5	2	0	0	255.7
CH2NH	33	1.207	0.936	1	0	33	65.33	65.33	0

  

$\gamma_1$	$\gamma_2$
1.13304	1.04702

Example(1)

subgroup	k	Rk	Qk	v1	v2	am,k	1	2	5	33
CH3	1	0.9011	0.848	1	0	1	0	0	986.5	61.13
CH2	2	0.6744	0.54	1	0	2	0	0	986.5	61.13
OH	5	1	1.2	1	0	5	156.4	156.4	0	89.6
ARCH	33	0.5313	0.4	0	6	33	-11.12	-11.12	636.1	0

  

$\gamma_1$	$\gamma_2$
2.91	1.10386

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