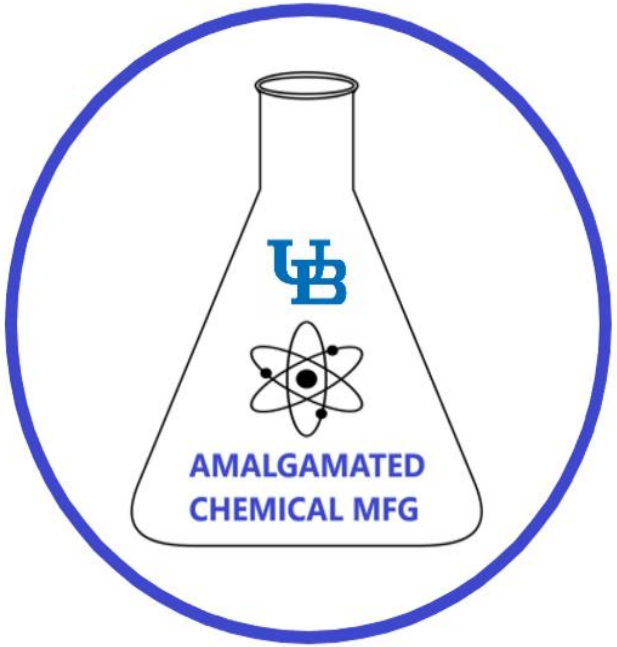
CE407 SEPARATIONS

Lecture 10

Instructor: David Courtemanche

University at Buffalo
Department of Chemical and Biological Engineering
School of Engineering and Applied Sciences

Amalgamated Chemical Manufacturing



References

1. Poling, Prausnitz, and O'Connell (2001)

2. Smith, van Ness, Abbott, and Swihart (2018)

- Appendix G:

https://wwwcourses.sens.buffalo.edu/ce408/ce408_design_project/ce408_design_notes_thermodynamic_properties/Smith_etal_2018_Appendix_G.pdf

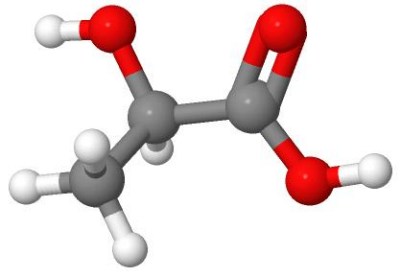
UNIFAC METHOD FOR ESTIMATING ACTIVITY COEFFICIENTS

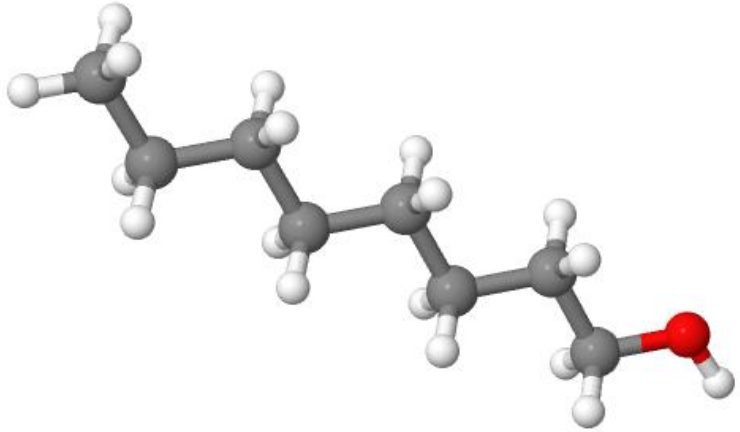
1. Why is this important?

2. Breakdown of molecules into UNIFAC (sub)groups

3. UNIFAC parameters

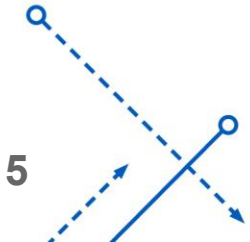
4. Formulas for activity coefficients





Why Is This Important?

- For non-ideal mixtures our methods using Raoult's Law break down
- Data may be difficult to find for a mixture of interest
  - If actual experimental data is available, it is preferred!
  - Going to ternary or higher mixtures makes it even harder to find data!



Start by Breaking Down Molecule Structures into UNIFAC Groups and Subgroups

- Poling, Prausnitz, and O'Connell(2001) Tables
- Fragments of molecular structures

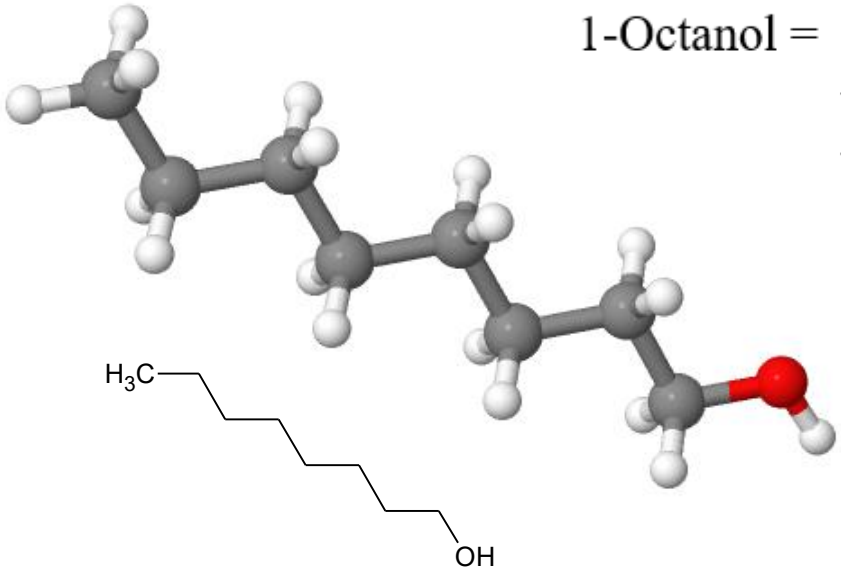
TABLE 8-23 UNIFAC Group Specifications and Sample Group Assignments (Hansen, et al., 1991)

Group numbers					
Main	Secondary	Name	Volume R	Surface Area Q	Sample Assignments = (Number of Occurrences) × (Secondary Group Number)
1	1	CH_3	0.9011	0.848	Hexane = (2)(1) + (4)(2)
	2	CH_2	0.6744	0.540	2-Methylpropane = (3)(1) + (1)(3)
	3	CH	0.4469	0.228	Neopentane = (4)(1) + (1)(4)
	4	C	0.2195	0.000	2,2,4-Trimethylpentane = (5)(1) + (1)(2) + (1)(3) + (1)(4)
2	5	CH_2=CH	1.3454	1.176	3-Methyl-1-hexene = (2)(1) + (2)(2) + (1)(3) + (1)(5)
	6	CH=CH	1.1167	0.867	Hexene-2 = (2)(1) + (2)(2) + (1)(6)
	7	CH_2=C	1.1173	0.988	2-Methyl-1-butene = (2)(1) + (1)(2) + (1)(7)
	8	CH=C	0.8886	0.676	2-Methyl-2-butene = (3)(1) + (1)(8)
	70	C=C	0.6605	0.485	2,3-Dimethylbutene = (4)(1) + (1)(70)
3	9	ACH	0.5313	0.400	Benzene = (6)(9)
	10	AC	0.3652	0.120	Styrene = (1)(5) + (5)(9) + (1)(10)
4	11	$ACCH_3$	1.2663	0.968	Toluene = (5)(9) + (1)(11)
	12	$ACCH_2$	1.0396	0.660	Ethylbenzene = (1)(1) + (5)(9) + (1)(12)
	13	ACCH	0.8121	0.348	Cumene = (2)(1) + (5)(9) + (1)(13)
5	14	OH	1.0000	1.200	Ethanol = (1)(1) + (1)(2) + (1)(14)
6	15	CH_3OH	1.4311	1.432	Methanol = (1)(15)

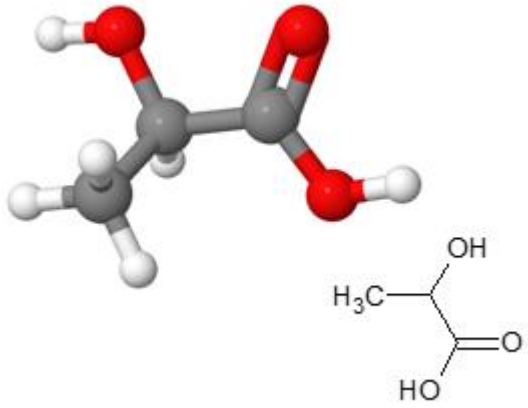
Start by Breaking Down Molecule Structures into UNIFAC Groups and Subgroups

- A very few small molecules (H_2O, CH_3OH, HCOOH) are subgroups themselves; use if available; do not expect in general

20	42	COOH	1.3013	1.224	Acetic Acid = (1)(1) + (1)(42)
	43	HCOOH	1.5280	1.532	Formic Acid = (1)(43)



1-Octanol = 1 CH_3 (1)
+ 7 CH_2 (2)
+ 1 OH (14)

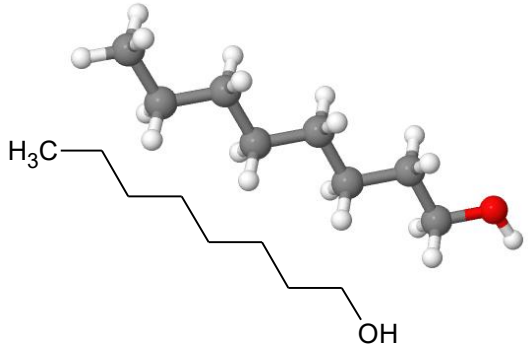


Stereoisomers are not on the radar of UNIFAC;

L-lactic acid = 1 CH_3 (1)
+ 1 CH (3)
+ 1 OH (14)
+ 1 COOH (42)

Main Groups and Subgroups

- Main Groups are categories of building blocks, subgroups refer to specific building block
  - Both numbers are important
  - CH single bonded units are Main Group 1
  - CH_3, CH_2, CH, and C are subgroups and have their own subgroup numbers
- When detailing a molecule, it is important to note both numbers and the quantities



1-Octanol = 1 CH_3 (1) (1)
+ 7 CH_2 (2) (1)
+ 1 OH (14) (5)

The black numbers are the Subgroup, the red numbers are the Main Group for each building block

Master Table of Correspondence

- Only need to do this for the subgroups comprising the molecules of interest
- If considering interactions between 1-Octanol and Lactic Acid

	sub	main
CH_3	(1)	(1)
CH_2	(2)	(1)
CH	(3)	(1)
OH	(14)	(5)
COOH	(42)	(20)

- This could be an array in Matlab or a two columns in Excel, recommend one variable (possible k1) for main group numbers and another (k2) for subgroup

```
index( 1) =  1;
index( 2) =  1;
index( 3) =  1;
index(14) =  5;
index(42) = 20;
```

Specifying the Molecules

$\nu_k^{(i)}$ is the number of subgroups of type k in a molecule of species i.

1-Octanol =		
	1 CH_3	(1)
	+ 7 CH_2	(2)
	+ 1 OH	(14)

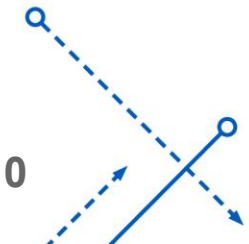
L-lactic acid =		
	1 CH_3	(1)
	+ 1 CH	(3)
	+ 1 OH	(14)
	+ 1 COOH	(42)

1-Octanol (1)

$$\nu_1^{(1)} = 1$$
$$\nu_2^{(1)} = 7$$
$$\nu_{14}^{(1)} = 1$$

L-lactic acid (2)

$$\nu_1^{(2)} = 1$$
$$\nu_3^{(2)} = 1$$
$$\nu_{14}^{(2)} = 1$$
$$\nu_{42}^{(2)} = 1$$

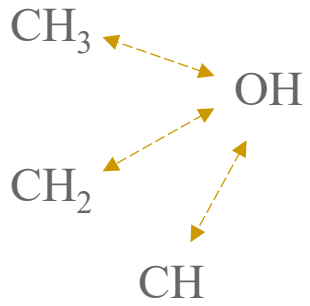


UNIFAC Parameters

- Volume and Surface Parameters
- Called R_k and S_k
  - Somewhat dimensionless, but R has dimensions of volume and S has dimensions of area
  - Following earlier suggestion of calling subgroup number k2 could be called
    - R_{k2} and S_{k2}
- Values depend on the subgroup (refer to tables on slides 5 and 6)

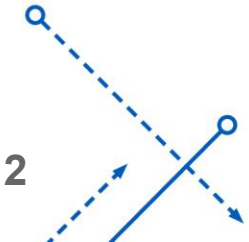
$$
\begin{aligned}
R_1 &= 0.9011, \quad Q_1 = 0.848 \\
R_2 &= 0.6744, \quad Q_2 = 0.540 \\
R_3 &= 0.4469, \quad Q_3 = 0.228 \\
R_{14} &= 1.0000, \quad Q_{14} = 1.200 \\
R_{42} &= 1.3013, \quad Q_{42} = 1.224
\end{aligned}
$$

UNIFAC Parameters



- Interaction Parameters
- Values depend on the main groups
- Called a_{mn} or a_{km}
  - Interaction between building block m and building block n
    - Or k and m
  - Have units of K
  - Following earlier suggestion of calling main group number k1 could be called
    - $a_{m1,n1}$ or $a_{m1,k1}$

$a_{1,1}$ (numbered by main groups) = 0.0
$a_{1,5}$ (numbered by main groups) = 986.5
$a_{1,20}$ (numbered by main groups) = 663.5
$a_{5,1}$ (numbered by main groups) = 156.4
$a_{5,5}$ (numbered by main groups) = 0.0
$a_{5,20}$ (numbered by main groups) = 199.0
$a_{20,1}$ (numbered by main groups) = 315.3
$a_{20,5}$ (numbered by main groups) = −151.0
$a_{20,20}$ (numbered by main groups) = 0.0



Where do these numbers come from?

The second table (based on main group numbers; spread over more pages; need to hunt)

TABLE 8-24 UNIFAC Group-Group Interaction Parameters, a_{mn}, in Kelvins

Main group	n = 1	2	3	4	5	6	7	8	9
m = 1	0.0	86.02	61.13	76.50	986.5	697.2	1318	1333	476.4
2	−35.36	0.0	38.81	74.15	524.1	787.6	270.6	526.1	182.6
3	−11.12	3.446	0.0	167.0	636.1	637.4	903.8	1329	25.77
4	−69.70	−113.6	−146.8	0.0	803.2	603.3	5695	884.9	−52.10
5	156.4	457.0	89.60	25.82	0.0	−137.1	353.5	−259.7	84.00
6	16.51	−12.52	−50.00	−44.50	249.1	0.0	−181.0	−101.7	23.39
7	300.0	496.1	362.3	377.6	−229.1	289.6	0.0	324.5	−195.4
8	275.8	217.5	24.34	244.2	−451.6	−265.2	−601.8	0.0	−356.1
9	26.76	42.92	140.1	365.8	164.5	108.7	472.5	−133.1	0.0
10	505.7	56.30	23.39	106.0	529.0	−340.2	480.8	−155.6	128.0
11	114.8	132.1	85.84	−170.0	245.4	249.6	200.8	−36.72	372.2
12	329.3	110.4	18.12	428.0	139.4	227.8	NA	NA	385.4
13	83.36	26.51	52.13	65.69	237.7	238.4	−314.7	−178.5	191.1
14	−30.48	1.163	−44.85	296.4	−242.8	−481.7	−330.4	NA	NA
15	65.33	−28.70	−22.31	223.0	−150.0	−370.3	−448.2	NA	394.6
16	−83.98	−25.38	−223.9	109.9	28.60	−406.8	−598.8	NA	225.3
17	1139	2000	247.5	762.8	−17.40	−118.1	−341.6	−253.1	−450.3
18	−101.6	−47.63	31.87	49.80	−132.3	−378.2	−332.9	−341.6	29.10
19	24.82	−40.62	−22.97	−138.4	185.4	162.6	242.8	NA	−287.5
20	315.3	1264	62.32	89.86	−151.0	339.8	−66.17	−11.00	−297.8
21	91.46	40.25	4.680	122.9	562.2	529.0	698.2	NA	286.3
22	34.01	−23.50	121.3	140.8	527.6	669.9	708.7	NA	82.86
23	36.70	51.06	288.5	69.90	742.1	649.1	826.8	NA	552.1
24	−78.45	160.9	−4.700	134.7	856.3	709.6	1201	10000	372.0
25	106.8	70.32	−97.27	402.5	325.7	612.8	−274.5	622.3	518.4
26	−32.69	−1.996	10.38	−97.05	261.6	252.6	417.9	NA	−142.6
27	5541	NA	1824	−127.8	561.6	NA	360.7	NA	−101.5
28	−52.65	16.62	21.50	40.68	609.8	914.2	1081	1421	303.7
29	−7.481	NA	28.41	19.56	461.6	448.6	NA	NA	160.6
30	−25.31	82.64	157.3	128.8	521.6	NA	23.48	NA	317.5

TABLE 8-24 UNIFAC Group-Group Interaction Parameters, a_{mn}, in Kelvins (*Continued*)

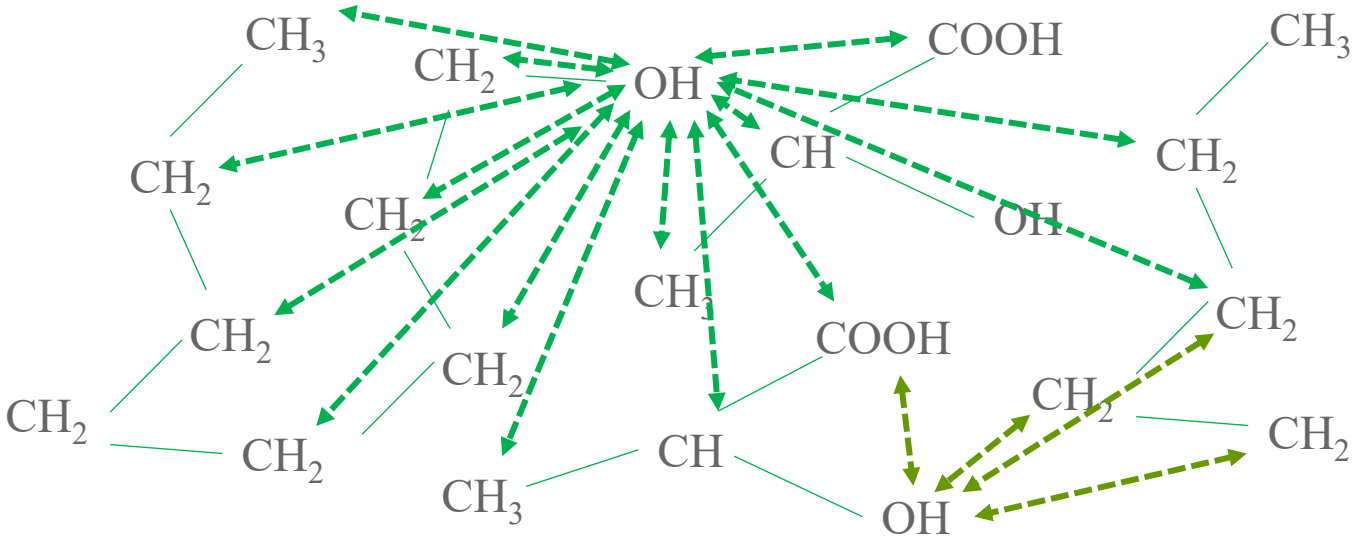
Main group	n = 19	20	21	22	23	24	25	26	27
m = 1	597.0	663.5	35.93	53.76	24.90	104.3	11.44	661.5	543.0
2	336.9	318.9	−36.87	58.55	−13.99	−109.7	100.1	357.5	NA
3	212.5	537.4	−18.81	−144.4	−231.9	3.000	187.0	168.0	194.9
4	6096	872.3	−114.1	−111.0	−80.25	−141.3	−211.0	3629	4448
5	6.712	199.0	75.62	65.28	−98.12	143.1	123.5	256.5	157.1
6	53.28	−202.0	−38.32	−102.5	−139.4	−44.76	−28.25	75.14	NA
7	112.6	−14.09	325.4	370.4	353.7	497.5	133.9	220.6	399.5
8	NA	408.9	NA	NA	NA	1827	6915	NA	NA
9	481.7	669.4	−191.7	−130.3	−354.6	−39.20	−119.8	137.5	548.5
10	NA	497.5	751.9	67.52	−483.7	NA	NA	NA	NA
11	494.6	660.2	−34.74	108.9	−209.7	54.57	442.4	−81.13	NA
12	−47.25	−268.1	NA	NA	−126.2	179.7	24.28	NA	NA
13	−18.51	664.6	301.1	137.8	−154.3	47.67	134.8	95.18	NA
14	358.9	NA	−82.92	NA	NA	−99.81	30.05	NA	NA
15	147.1	NA	NA	NA	NA	71.23	−18.93	NA	NA
16	NA	NA	NA	−73.85	−352.9	−262.0	−181.9	NA	NA
17	−281.6	−396.0	287.0	−111.0	NA	882.0	617.5	NA	−139.3
18	−169.7	−153.7	NA	−351.6	−114.7	−205.3	NA	NA	2845
19	0.0	NA	4.933	−152.7	−15.62	−54.86	−4.624	−0.5150	NA
20	NA	0.0	13.41	−44.70	39.63	183.4	−79.08	NA	NA
21	54.32	519.1	0.0	108.3	249.6	62.42	153.0	32.73	86.20
22	258.6	543.3	−84.53	0.0	0.0	56.33	223.1	108.9	NA
23	74.04	504.2	−157.1	0.0	0.0	−30.10	192.1	NA	NA
24	492.0	631	11.80	17.97	51.90	0.0	−75.97	490.9	534.7
25	363.5	993.4	−129.7	−8.309	−0.2266	248.4	0.0	132.7	2213
26	0.2830	NA	113.0	−9.639	NA	−34.68	132.9	0.0	533.2
27	NA	NA	1971	NA	NA	514.6	−123.1	−85.12	0.0
28	335.7	NA	−73.09	NA	−26.06	−60.71	NA	277.8	NA
29	161.0	NA	−27.94	NA	NA	NA	NA	NA	NA
30	NA	570.6	NA	NA	48.48	−133.2	NA	NA	NA

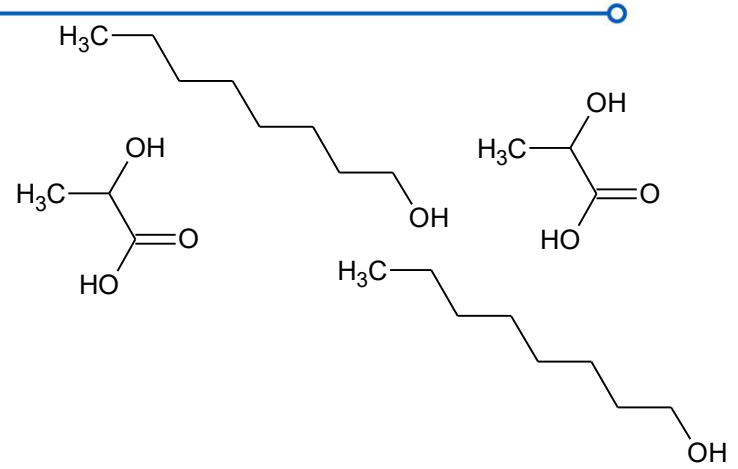
Note that a_{mn} is generally **not** equal to a_{nm}

$a_{mm} = 0$

4. Formulas for activity coefficients

Mixture of chemical species as a soup of groups





Some subgroups happen to be covalently bonded to other subgroups

Every subgroup interacts with every other subgroup in the soup

Comments on formulas for activity coefficients

Smith et al.'s formulas are mathematically equivalent to, and easier to use than, Poling et al.'s formulas

It is perfectly fine to use Smith et al.'s formulas with the more extensive tables given by Poling et al.

One should consistently use **either** Smith et al.'s tables **or** Prausnitz et al.'s tables (i.e., not mix and match between the two tables), because the group numbers do not match up perfectly between them

Summations over i and j run over all molecular species, whereas summations over k and m run over all subgroups in the soup

Formulas

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \text{(G.7)}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \qquad \text{(G.13)}$$

$$\ln \gamma_i^R = q_i\left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right] \qquad \text{(G.14)}$$

$$J_i = \frac{r_i}{\sum_j r_j x_j} \qquad \text{(G.10)}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \qquad \text{(G.11)}$$

i refers to the species number (chemical 1, 2, 3, etc)
j and k are dummy variables

Formulas

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right)$$

$$\ln \gamma_i^R = q_i\left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right]$$

$$J_i = \frac{r_i}{\sum_j r_j x_j}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j}$$

$$r_i = \sum_k v_k^{(i)} R_k$$

$$q_i = \sum_k v_k^{(i)} Q_k$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i}$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j}$$

$$s_k = \sum_m \theta_m \tau_{mk}$$

$$\tau_{mk} = \exp\frac{-a_{mk}}{T}$$

Do **not** use earlier formulas for the UNIQUAC equation ((G.1)–(G.9) and (G.12)) in applying The UNIFAC method

Each equation seems to add a new variable to the mix!
We will do an example in a few more slides…

Do **not** waste the reader's time by writing all these formulas in reports!

Coding the formulas in Matlab

You are **not** solving nonlinear equations

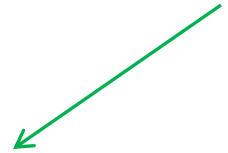
You are **not** solving differential equations

You **are** using `for` loops

You **are** reading and coding formulas carefully

$$r_i = \sum_k v_k^{(i)} R_k$$

$$q_i = \sum_k v_k^{(i)} Q_k$$



```
%r, q
for i = 1 : unifac_imax
    r(i) = 0;
    q(i) = 0;
    for k = 1 : unifac_kmax
        r(i) = r(i) + unifac_nu(k,i) * unifac_R(k);
        q(i) = q(i) + unifac_nu(k,i) * unifac_Q(k);
    end
end
```

Sample Problem

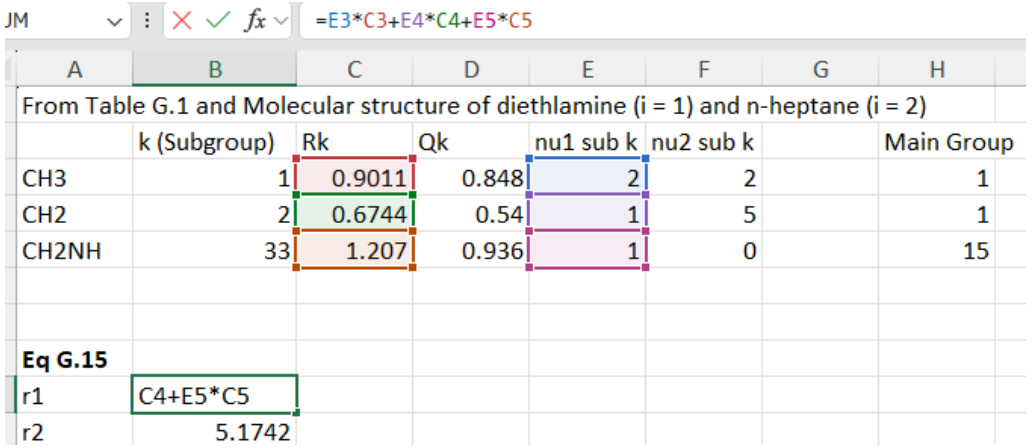
Consider a binary mixture comprising 40 mole % diethylamine (component 1), 60 mole % n-heptane (component 2) at 35 °C. Calculate the activity coefficients of both components using the UNIFAC method.

Sample Problem

- Determine the Subgroups present in each component
  - 1 = diethylamine $CH_3 - CH_2NH - CH_2 - CH_3$ (1)
  - 2 = n-heptane $CH_3 - (CH_2)_5 - CH_3$ (2)

From Table G.1 and Molecular structure of diethlamine (i = 1) and n-heptane (i = 2)							
	k (Subgroup)	Rk	Qk	nu1 sub k	nu2 sub k		Main Group
CH3	1	0.9011	0.848	2	2		1
CH2	2	0.6744	0.54	1	5		1
CH2NH	33	1.207	0.936	1	0		15

$$r_i = \sum_k v_k^{(i)} R_k \qquad \text{(G.15)}$$



- $r_1 = 2 * 0.9011 + 1 * 0.6744 + 1 * 1.207 = 3.6836$
- $r_2 = 2 * 0.9011 + 5 * 0.6744 + 0 * 1.207 = 5.1742$

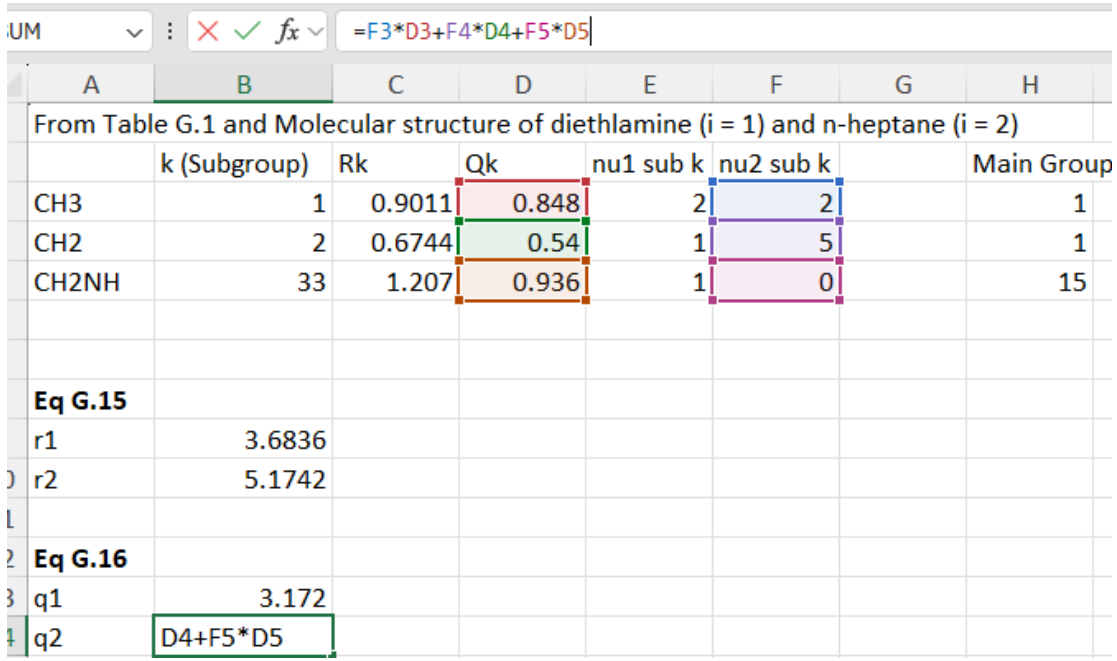
Sample Problem

- Determine the Subgroups present in each component
  - 1 = diethylamine $CH_3 - CH_2NH - CH_2 - CH_3$ (1)
  - 2 = n-heptane $CH_3 - (CH_2)_5 - CH_3$ (2)

From Table G.1 and Molecular structure of diethlamine (i = 1) and n-heptane (i = 2)							
	k (Subgroup)	Rk	Qk	nu1 sub k	nu2 sub k		Main Group
CH3	1	0.9011	0.848	2	2		1
CH2	2	0.6744	0.54	1	5		1
CH2NH	33	1.207	0.936	1	0		15

$$q_i = \sum_k v_k^{(i)} Q_k \qquad \text{(G.16)}$$

- $q_1 = 2 * 0.848 + 1 * 0.54 + 1 * 0.936 = 3.172$
- $q_2 = 2 * 0.848 + 5 * 0.54 + 0 * 0.936 = 4.936$



Sample Problem

- Now we can calculate the epsilon values

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \qquad \text{(G.17)}$$

- $e_{1,1} = \frac{v_1^1 Q_1}{q_1} = \frac{2*0.848}{3.172} = 0.5347$
- $e_{2,1} = \frac{v_2^1 Q_2}{q_1} = \frac{1*0.54}{3.172} = 0.1702$
- $e_{33,1} = \frac{v_{33}^1 Q_{33}}{q_1} = \frac{1*0.936}{3.172} = 0.2951$

SUM =F5*D5/B14

	A	B	C	D	E	F	G	H
1	From Table G.1 and Molecular structure of diethlamine (i = 1) and n-heptane (i = 2)							
2		k (Subgroup)	Rk	Qk	nu1 sub k	nu2 sub k		Main Group
3	CH3	1	0.9011	0.848	2	2		1
4	CH2	2	0.6744	0.54	1	5		1
5	CH2NH	33	1.207	0.936	1	0		15
6								
7								
8	**Eq G.15**							
9	r1	3.6836						
10	r2	5.1742						
11								
12	**Eq G.16**							
13	q1	3.172						
14	q2	4.396						
15								
16	**Eq G.17**		e_{ki}					
17	k	i = 1	i = 2					
18	1	0.5347	0.3858					
19	2	0.1702	0.6142					
20	33	0.2951	B14					

Sample Problem

From Table G2: Note these values depend on the main group, not sub groups				
k=1 : main group 1		k= 2: main group 1		K = 33: main group 15
a_{mk}				
m	k=	1 (1)	2 (1)	33 (15)
1 (1)		0	0	255.7
2 (1)		0	0	255.7
33 (15)		65.33	65.33	0

$$\tau_{mk} = \exp\frac{-a_{mk}}{T} \qquad (G.21)$$

- For T = 35C = 308.15 K
- $\tau_{1,1} = exp\frac{-a_{1,1}}{T} = exp\frac{-0}{308.15} = 1$
- $\tau_{1,33} = exp\frac{-a_{1,33}}{T} = exp\frac{-255.7}{308.15} = 0.4361$
- $\tau_{33,1} = exp\frac{-a_{33,1}}{T} = exp\frac{-65.33}{308.15} = 0.80896$

SUM | =EXP(-E26/C30)

	A	B	C	D	E
24	a_{mk}				
25	m	k=	1 (1)	2 (1)	33 (15)
26	1 (1)		0	0	255.7
27	2 (1)		0	0	255.7
28	33 (15)		65.33	65.33	0
29					
30	**Eq G.21**	T =	308.15	Kelvin	
31			Tau_{mk}		
32	m	k=	1	2	33
33	1		1	1	E26/C30)
34	2		1	1	0.43614
35	33		0.80896	0.80896	1

Sample Problem

$$\beta_{ik} = \sum_m e_{mi}\tau_{mk} \qquad (G.18)$$

- i is the chemical species, k is subgroup, m is dummy variable

- $\beta_{1,1} = e_{1,1} * \tau_{1,1} + e_{2,1} * \tau_{2,1} + e_{33,1} * \tau_{33,1}$
  $= 0.5347 * 1 + 0.1702 * 1 + 0.2951 * 0.80896 = 0.94363$
- $\beta_{1,2} = e_{1,1} * \tau_{1,2} + e_{2,1} * \tau_{2,2} + e_{33,1} * \tau_{33,2}$
  $= 0.5437 * 1 + 0.1702 * 1 + 0.2951 * 0.80896 = 0.94363$
- $\beta_{1,33} = e_{1,1} * \tau_{1,33} + e_{2,1} * \tau_{2,33} + e_{33,1} * \tau_{33,33}$
  $= 0.5437 * 0.43614 + 0.1702 * 0.43614 + 0.2951 * 1 = 0.60253$

- $\beta_{2,1} = e_{1,2} * \tau_{1,1} + e_{2,2} * \tau_{2,1} + e_{33,2} * \tau_{33,1}$
  $= 0.3858 * 1 + 0.6142 * 1 + 0 * 0.80896 = 1$
- $\beta_{2,2} = e_{1,2} * \tau_{1,2} + e_{2,2} * \tau_{2,2} + e_{33,2} * \tau_{33,2}$
  $= 0.3858 * 1 + 0.6142 * 1 + 0 * 0.80896 = 1$
- $\beta_{2,33} = e_{1,2} * \tau_{1,33} + e_{2,2} * \tau_{2,33} + e_{33,2} * \tau_{33,33}$
  $= 0.3858 * 0.43164 + 0.6142 * 0.43164 + 0 * 1 = 0.43164$

SUM | =B18*C33+B19*C34+B20*C35

	A	B	C	D	E	F	G
15							
16	**Eq G.17**		e_{ki}				
17	k	i = 1	i = 2				
18	1	0.5347	0.3858				
19	2	0.1702	0.6142				
20	33	0.2951	0				
21							
22	From Table G2: Note these values depend on the main group, not sub groups						
23	k=1 : main group 1		k= 2: main group 1		K = 33: main group 15		
24	a_{mk}						
25	m	k=	1 (1)	2 (1)	33 (15)		
26	1 (1)		0	0	255.7		
27	2 (1)		0	0	255.7		
28	33 (15)		65.33	65.33	0		
29							
30	**Eq G.21**	T =	308.15	Kelvin			
31			Tau_{mk}				
32	m	k=	1	2	33		
33	1		1	1	0.43614		
34	2		1	1	0.43614		
35	33		0.80896	0.80896	1		
36							
37							
38	**Eq G.18**						
39			$Beta_{ik}$				
40	i	k=1	k=2	k=33			
41	1	*C35	0.94363	0.60253			
42	2	1	1	0.43614			

Sample Problem

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \qquad (G.19)$$

- We have already calculated q_i and e_{ki}, the j is the same as i, just keeping the two summations separate. Mole fractions are x_i
  - $x_1 = 0.4$, $x_2 = 0.6$
- $\theta_1 = \frac{x_1 * q_1 * e_{1,1} + x_2 * q_2 * e_{1,2}}{x_1 * q_1 + x_2 * q_2} = \frac{0.4 * 3.172 * 0.5347 + 0.6 * 4.396 * 0.3858}{0.4 * 3.172 + 0.6 * 4.396} = 0.43416$

SUM | =(D44*B13*B18+D45*B14*C18)/(D44*B13+D45*B14)

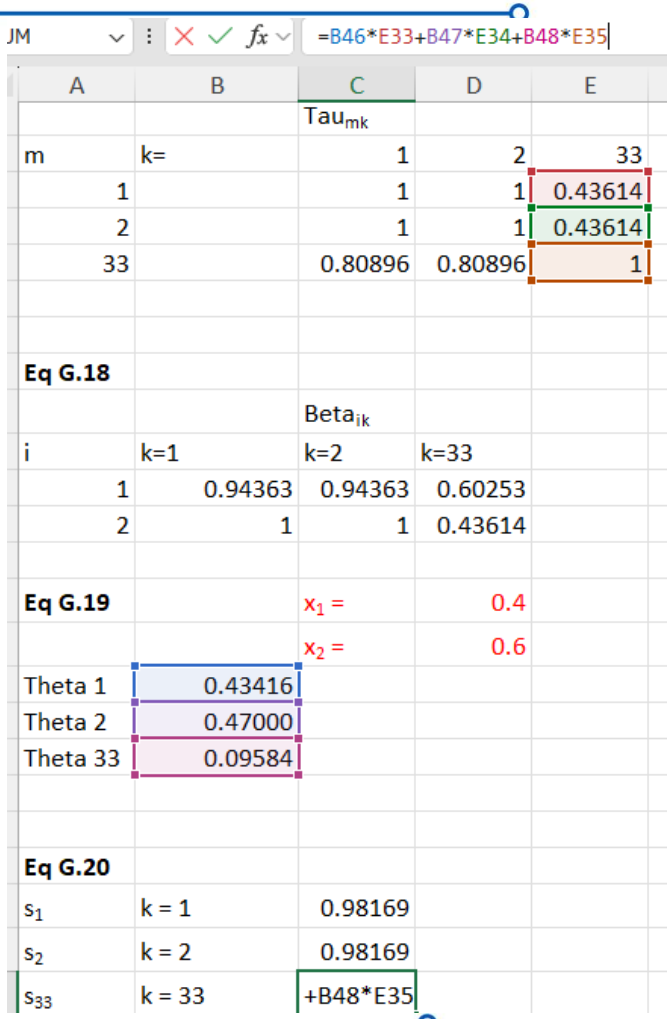
	A	B	C	D	E	F	G
12	**Eq G.16**						
13	q1	3.172					
14	q2	4.396					
15							
16	**Eq G.17**		e_{ki}				
17	k	i = 1	i = 2				
18	1	0.5347	0.3858				
19	2	0.1702	0.6142				
20	33	0.2951	0				

Eq G.19		x_1 =	0.4
		x_2 =	0.6
Theta 1	B14)		
Theta 2	0.469997952		
Theta 33	0.09584272		

Sample Problem

$$s_k = \sum_m \theta_m \tau_{mk} \qquad \text{(G.20)}$$

- $s_1 = \theta_1 * \tau_{1,1} + \theta_2 * \tau_{2,1} + \theta_{33} * \tau_{33,1}$
  $= 0.43416 * 1 + 0.4700 * 1 + 0.09584 * 0.80896 = 0.98169$
- $s_2 = \theta_1 * \tau_{1,2} + \theta_2 * \tau_{2,2} + \theta_{33} * \tau_{33,2}$
  $= 0.43416 * 1 + 0.4700 * 1 + 0.09584 * 0.80896 = 0.98169$
- $s_{33} = \theta_1 * \tau_{1,33} + \theta_2 * \tau_{2,33} + \theta_{33} * \tau_{33,33}$
  $= 0.43416 * 0.43416 + 0.4700 * 0.43416 + 0.09584 * 1 = 0.49018$



Sample Problem

$$J_i = \frac{r_i}{\sum_j r_j x_j} \qquad \text{(G.10)}$$

Eq G.15	
r1	3.6836000
r2	5.1742000

- $J_1 = \frac{r_1}{r_1 * x_1 + r_2 * x_2} = \frac{3.6836}{3.6836 * 0.4 + 5.1742 * 0.6} = 0.804638$

- $J_2 = \frac{r_2}{r_1 * x_1 + r_2 * x_2} = \frac{5.1742}{3.6836 * 0.4 + 5.1742 * 0.6} = 1.130241$

Sample Problem

$$L_i = \frac{q_i}{\sum_j q_j x_j} \qquad \text{(G.11)}$$

Eq G.16	
q1	3.172
q2	4.396

- $L_1 = \frac{q_1}{q_1 * x_1 + q_2 * x_2} = \frac{3.172}{3.172 * 0.4 + 4.396 * 0.6} = 0.812001$

- $L_2 = \frac{q_2}{q_1 * x_1 + q_2 * x_2} = \frac{4.396}{3.172 * 0.4 + 4.396 * 0.6} = 1.125333$

Sample Problem

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \qquad \text{(G.13)}$$

- $\ln \gamma_1^C = 1 - J_1 + \ln J_1 - 5 * q_1\left(1 - \frac{J_1}{L_1} + \ln \frac{J_1}{L_1}\right)$

$$= 1 - 0.80464 + ln\,0.80464 - 5 * 3.172 * \left(1 - \frac{0.80464}{0.812001} + ln\frac{0.80464}{0.812001}\right)$$
$$= -0.021345$$

- $ln\,\gamma_2^C = 1 - J_2 + ln\,J_2 - 5 * q_2\left(1 - \frac{J_2}{L_2} + ln\frac{J_2}{L_2}\right)$

$$= 1 - 1.13024 + ln\,1.13024 - 5 * 3.172 * \left(1 - \frac{1.13024}{1.125333} + ln\frac{1.13024}{1.125333}\right)$$
$$= -0.007602$$

Sample Problem

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k} \right) \right] \qquad \text{(G.14)}$$

- $\ln \gamma_1^R = q_1 * \left[1 - \left(\theta_1 * \frac{\beta_{1,1}}{s_1} - e_{1,1} * \ln \frac{\beta_{1,1}}{s_1} + \theta_2 * \frac{\beta_{1,2}}{s_2} - e_{2,1} * ln \frac{\beta_{1,2}}{s_2} + \theta_{33} * \frac{\beta_{1,33}}{s_{33}} - e_{33,1} * ln \frac{\beta_{1,33}}{s_{33}}\right)\right]$
  $= 0.146248$
- $ln \gamma_2^R = q_2 * \left[1 - \left(\theta_1 * \frac{\beta_{2,1}}{s_1} - e_{1,2} * \ln \frac{\beta_{2,1}}{s_1} + \theta_2 * \frac{\beta_{2,2}}{s_2} - e_{2,2} * ln \frac{\beta_{2,2}}{s_2} + \theta_{33} * \frac{\beta_{2,33}}{s_{33}} - e_{33,2} * ln \frac{\beta_{2,33}}{s_{33}}\right)\right]$
  $= 0.053553$
- There are just too many numbers to type in here, they are all in the previous slides

Sample Problem

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \text{(G.7)}$$

- $\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = -0.021354 + 0.146248 = 0.124904$
- $\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R = -0.007602 + 0.053553$

γ_1=1.133
γ_2=1.047

Sample Problem, let's go further…

- We can look up Antoine coefficients for both compounds
- We can calculate P_{sat} for each compound
- We can calculate K_i for each compound

$$k_i = {P_{sat,i}}/{P}$$

- Bubble Point Calculation:

$$\textbf{Bubble Point Sum} = \sum_{i=1}^{n} x_i * \gamma_i * k_i$$

- Solve for temperature where Bubble Point Sum = 1
- Run through a series of x values for the light component to obtain y value for that temperature
- Plot y versus x for VLE diagram
- Plot T versus x and T versus y for T_{xy} diagram

Sample Problem