S2. Documentation for NRTL-PA

Documentation Version 1.1
Corresponds to nrtlpa.dll version 2.6.5rel
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1. Overview

This document is a user manual for the implementation of the user Wertheim Gamma model in Aspen Plus as NRTL-PA. Users should be familiar with the basic vocabulary and layout utilized with the Aspen environment. Please refer to the Aspen help documentation for introductory information. The tutorial contained in the following pages will illustrate the steps required to set up and implement a custom user model. This document also describes how to configure the model and demonstrates the model using a binary mixture of methanol and cyclohexane.

The user model provides several options for combinatorial contributions, and the radial distribution function (rdf). The choice of rdf is coupled with the activity coefficient (γ) model, and the covolume parameters will affect the association term for CPA. Several levels of debugging are provided so that the user can print information to the history file to confirm that parameters are entered as intended.

Contributions due to the residual, combinatorial, combinatorial correction, and Wertheim models can be printed to .csv files for the activity coefficient and heat of mixing. Temperature-dependent molar volumes used in calculations can also be printed.

The user model provides options for preserving the built-in NRTL model. To avoid confusion, the user model NRTL parameters are entered in separate custom forms so that the traditional NRTL input form is still available. However, since UNIFAC groups are used for inputting the sites, then the UNIFAC model should never be used.

2. Setup

2.1. Start Aspen Case

For ease in configuration, start with a template for chemical processes with metric units or American engineering units. The examples here will use metric units. The template will default to NRTL which will be changed later.

2.2. Install *.dll* and *dlopt.txt*

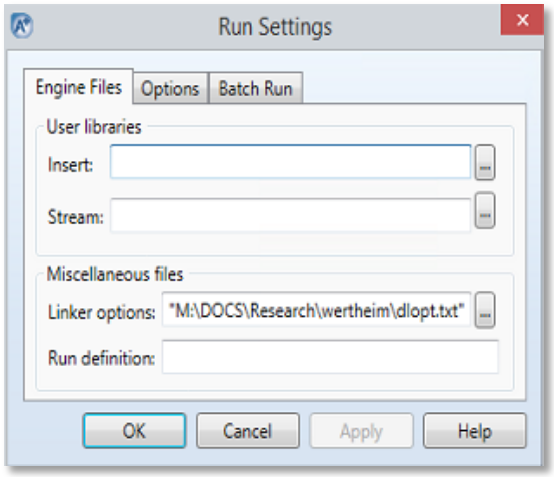
The user model is provided via a file *nrtlpa.dll*. One additional file *dlopt.txt* is a text file that is created by the user. The *dlopt.txt* file is read by Aspen to locate any user .dll files. Each line of the *dlopt.txt* lists the path to a user *.dll* file.

Select a folder to locate *nrtlpa.dll* and *dlopt.txt*. For ease of use, the two files can be placed in the same folder as the Aspen run file, though placement in some other folder is also possible but requires more careful configuration.

Edit the file *dlopt.txt* to provide the path to *nrtlpa.dll*. If the *dlopt.txt* and *nrtlpa.dll* are in a different folder than the run case, include the full path to the .dll. An example would be a single line: M:\DOCS\Research\wertheim\nrtlpa.dll. If the *dlopt.txt* and *nrtlpa.dll* are in the same folder as the run file, the line can be simply: nrtlpa.dll.

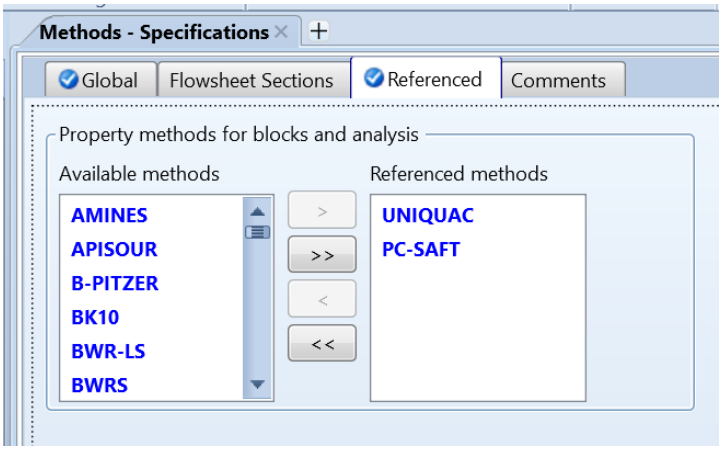
2.3. Provide path the dlopt.txt

The user must configure each run case to inform Aspen where to find the *dlopt.txt* file that contains the path to all user *.dll* files. Within Aspen, find the Customize ribbon at the top of the screen. From here select **Options** and browse to locate *dlopt.txt*. Click **Apply** and then press **OK**.



2.4. Covolume and PC-SAFT Referencing

The van der Waals covolumes are referenced within the code. These parameters are available within Aspen from the UNIQUAC model, but the model must be referenced to load the parameters into memory. These parameters will be used exclusively for the combinatorial correction term. If the VdW covolume (cm^3/mol) is also desired for the g(σ) term, the user must enter the values for COVOL (shown later) as Aspen parameter GMUQR*15.17. To enable the subroutine to locate the UNIQUAC parameters, access **Methods > Specifications.** Under the **Global** tab locate the Method filter dropdown menu select **ALL**. Then navigate to the **Referenced** tab and add UNIQUAC. If you will be using the PC-SAFT association term, also add PC-SAFT.



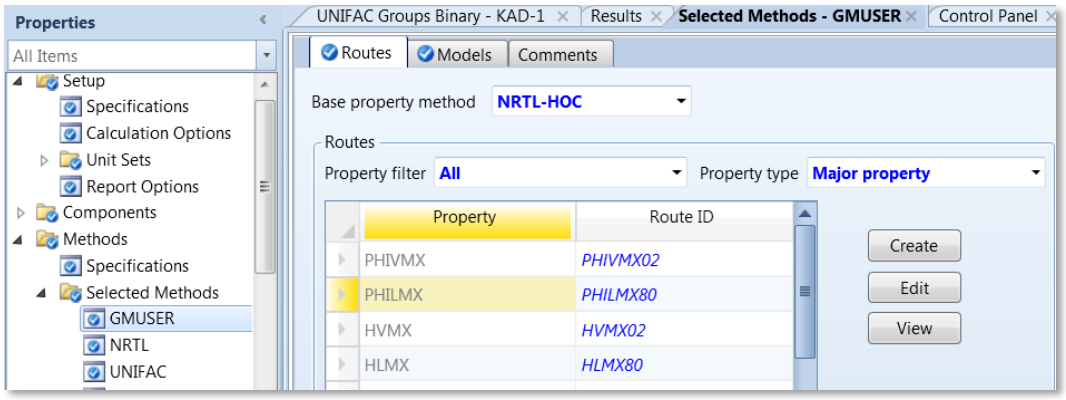
2.5. Create the User Method

2.5.1. Configure for Hayden-O'Connell vapor phase model

Browse to Methods. On the Global tab, set the Method Filter to 'All' and in the Base Method dropdown, select NRTL-HOC.

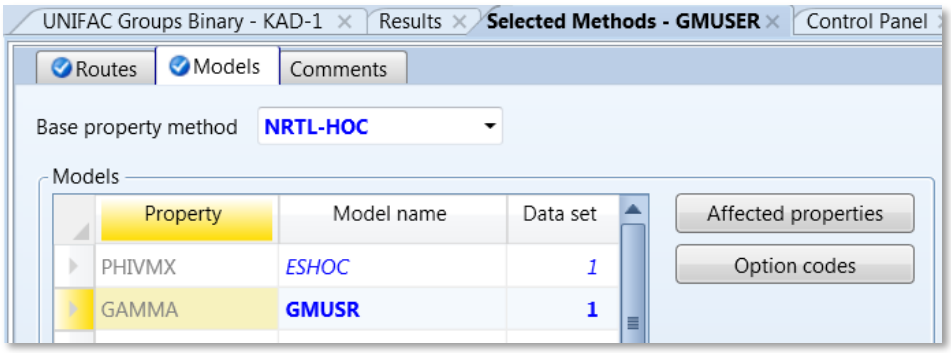
2.5.2. Create GMUSER

Under **Methods** > **Selected Methods** > **Create** <New> **Method**, create **GMUSER** (or name of your choice) based on NRTL-HOC



2.5.3. Specify GAMMA user model is to be used

On the **Models** tab, set GAMMA to **GMUSR**



2.6. Subroutine Options

This section provides an overview of the subroutine options for models and debugging output. While options can be configured now, the settings should always be checked before a run because Aspen sometimes automatically resets them. Modifying the subroutine options should be performed as the last step before a run, but the options are provided here as an overview.

Parameters are configured by selecting the line for GAMMA in the **Models** tab shown in section 2.5.3. Then click the button **Option Codes.** Option codes will defined as kop(i) where (i) indicates the column vector (i.e. kop(2) == 3 sets the second option code to a value of three).

Debug printing is added to the history file. To find debug information quickly search the history file for 'GMU ver'. Examples of output can be seen later in this document.

*NOTE: Selection of kop(1) == 3 will create output files gammas.csv, hxs.csv and vol.csv which will be appended **each time** the gammas are calculated. Because of this, it is advised to delete the generated files between runs when using kop(1) == 3. In addition, kop(3) should be used judiciously. For more information concerning debugging please reference to section 5.*

Debug Options (kop(1))

- kop(1) == 0: no debug printing
- kop(1) == 1: debug printing of gamma contributions and .dll version
- kop(1) == 2: includes printing of X, rho, deltas, in addition to the content above
- kop(1) == 3: includes printing of delta matrix indexes and gamma output to gammas.csv as well partial molar enthalpies to hxs.csv, in addition to the content above

Radial Distribution function (kop(2))

- kop(2) == 0: VdW
- kop(2) == 1: ESD
- kop(2) == 2: CPA (ESD with packing factor divided by four)
- kop(2) == 3: PC-SAFT

Pure Component Liquid Volume (kop(3))

- kop(3) == 0: standard liquid volume
- kop(3) == 1: temperature-dependent volume

Combinatorial Correction (kop(5)) * Ignored when kop(6) == 2

- kop(5) == 0: VdW with standard covolumes (calculated by UNIQUACR*15.17)
- kop(5) == 1: None
- kop(5) == 2: Staverman-Guggenheim
- kop(5) == 3: VdW with COVOL value

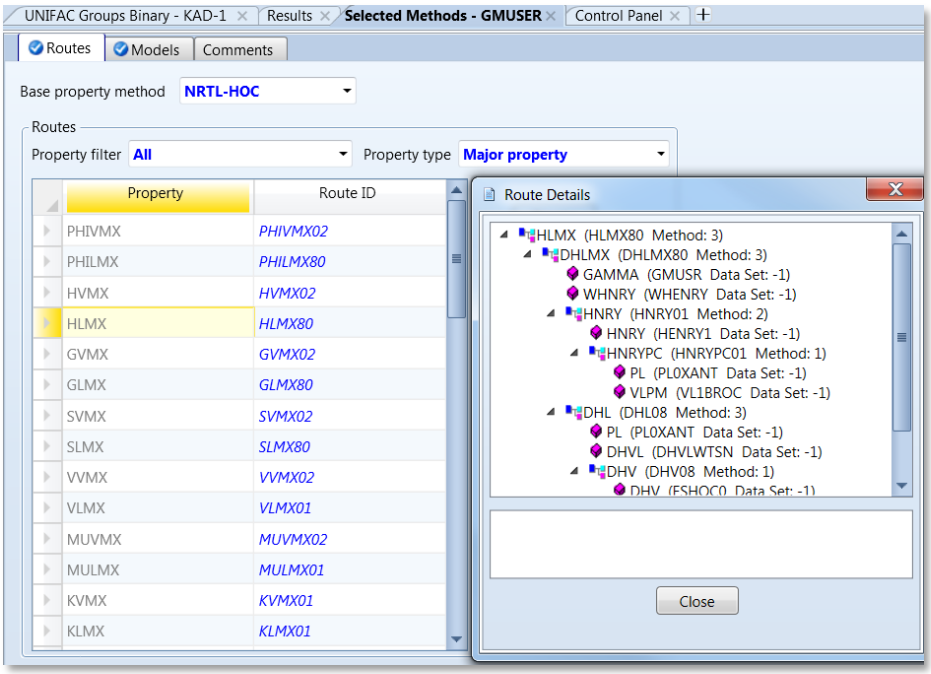
Combinatorial Term (kop(6))

- kop(6) == 0: Flory
- kop(6) == 1: Flory with modified volume ($V^{2/3}$)
- kop(6) == 2: None

2.7. Verify that GMUSR is in the route

Ensure that the route for **PHILMX** and **HLMIX** will use **GMUSR** by selecting the row for each property in the method route tab and clicking **View.**

NOTE: PHILMX and HLMX will still be listed as PHILMX80 and HLMX80 respectively, however the route has been changed to GMUSR (see HLMX example below).



2.8. Create User Parameters

2.8.1. Molar Volume

When temperature-dependent molar volumes are specified in the option settings using kop(3) = 1, then the code uses molar volumes as calculated by Aspen's pre-selected equation and parameters. As with other properties, you may choose to override this selection by entering your own parameter values by specifying user values for DNLDIP. The existing code does not extrapolate the molar volumes beyond the temperature limits specified in the parameters, but clamps the values at the temperature limits. Thus, above the upper temperature limit, the molar volume is calculated at the temperature limit and used in subsequent calculations. The lower limit is handled similarly. The temperature limits are entered in DNLDIP(6) and DNLDIP(7). To specify the equation to use for the constants, set THRSWT (2) to the equation number. See Aspen documentation for the equations.

Locate the **Customize** folder on the left-hand side and enter the four variables as follows; please note that these variable names MUST be used.

2.8.2. Covolume

COVOL, molecular CPA covolume (cm^3/mol) or the VdW covolume (cm^3/mol). The parameter usage is controlled by **GMUSR** option codes kop(2) and kop(5). Pure component, one element.

For VdW, $g(\sigma) = 1/(1-\eta_p)$. For ESD, $g(\sigma) = 1/(1-1.9\eta_p)$, for CPA $g(\sigma) = 1/(1-1.9\eta_p/4)$. The correct covolume is important.

The covolume parameters are not used for $g(\sigma)$ for the SAFT method, but can still be used for combinatorial correction.

2.8.3. Residual Model Parameters

These are binary interaction parameters with the specified number of elements.

GMNRTL: specify three elements; The elements correspond to NRTL parameters $\tau_{ij} = a_{ij} + b_{ij}/T(K)$; third parameter is α_{ij}

NOTE: The parameters are required ONLY for the residual model that will be used as determined by the GMUSR option codes. Currently only the NRTL model is available.

The later examples will provide benchmark parameter values.

2.8.4. Wertheim Parameters

2.8.4.1. CPA

KAD is the CPA bonding volume, in cm^3/mol. UNIFAC group interaction, one element.

EPS is the CPA enthalpy of bonding, eps/k in Kelvin. UNIFAC group interaction, one element.

$$\Delta_{ij} = g(\sigma)K_{ij}^{AD}(\exp\left(\frac{\epsilon_{ij}^{AD}}{kT}\right) - 1)$$

2.8.4.2. SAFT

KADPCS is the SAFT bonding volume parameter (dimensionless). UNIFAC group interaction, one element.

EPSPCS is the SAFT enthalpy of bonding, ϵ_{ij}^{AD}/k in Kelvin. UNIFAC interaction, one element.

$$\Delta_{ij} = g_{ij}(d)d_{ij}^3\kappa_{ij}^{AD}(\exp\left(\frac{\epsilon_{ij}^{AD}}{kT}\right) - 1)$$

The diameter is temperature-dependent

$$d_{ij}(T) = \sigma_{ij}\left(1 - 0.12\exp\left(-\frac{3\epsilon_{ij}}{kT}\right)\right)$$

where ϵ is the physical energy and σ_{ij} is the cross diameter using the combining rules

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad \text{and} \quad \epsilon_{ij} = \sqrt{\epsilon_i\epsilon_j}$$

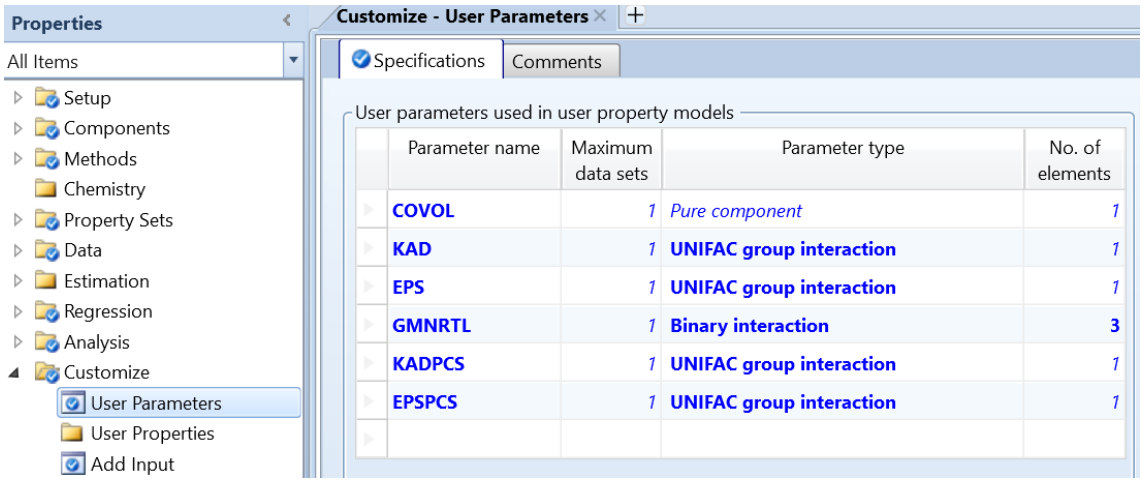
The radial distribution function is

$$g_{ij}^{hs} = \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_i + d_j}\right)\frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2\frac{2\zeta_2^2}{(1-\zeta_3)^3}$$

where

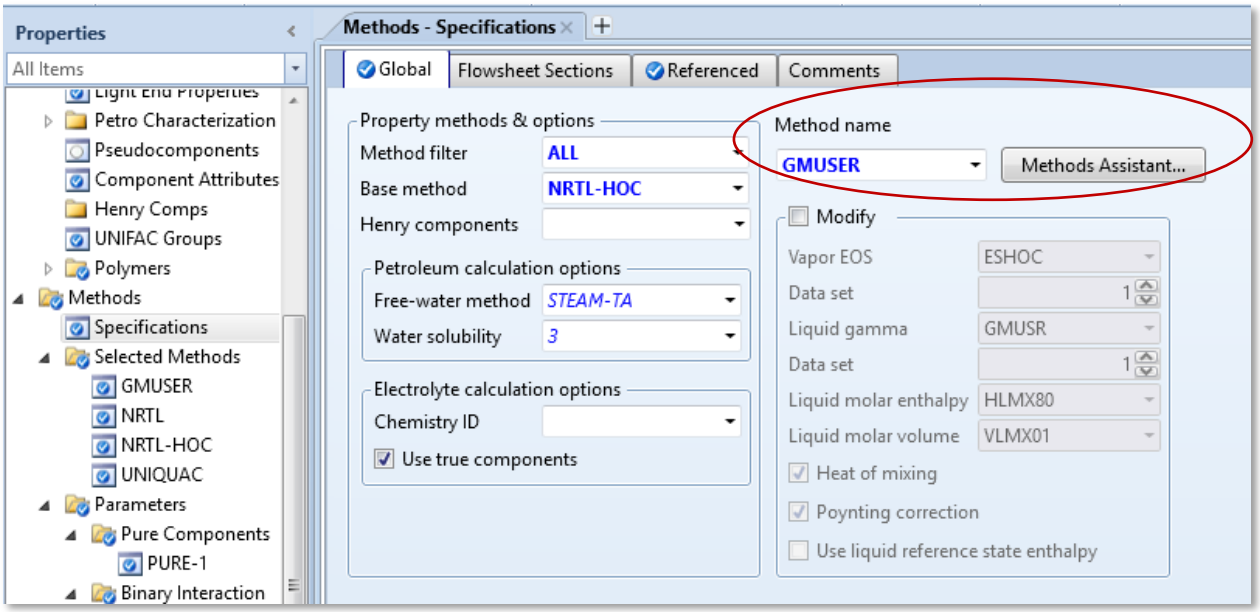
$$\zeta_n = \frac{\pi}{6}\rho \sum_i x_i m_i d_i^n \;\; n \in \{2,3\}$$

The following screenshot provides an example display when CPA and PC-SAFT are both available as association models and GMNRTL is used (NRTL residual model).



2.9. Activate

Navigate to **Specifications** under the **Methods** folder. Set Aspen to use the **GMUSER** (or the name you created) method that has just been created.



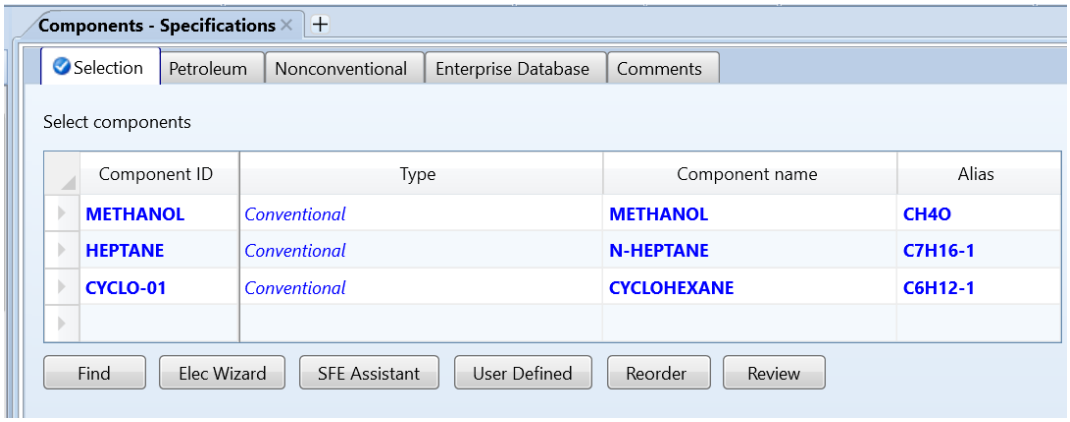
3. Example: Methanol + Cyclohexane (File Setup)

Now that the model has been created, the following steps will introduce the user to its application. An example binary system of methanol + cyclohexane will be used for illustrative purposes. This case is based on database PURE35 and NRTL-HOC is the base method. HOCETA for MeOH = 1.63.

Included with the distribution is an example file MEOH-HEP-CYC_SAFT.bkp for this case. When opening this example in a new version of Aspen, specify to *keep databanks* when performing benchmarking against results summarized herein.

3.1. Set Up Components and Association Sites

Note that n-heptane is not used in this example and can be omitted.



3.1.1. Define Association Sites

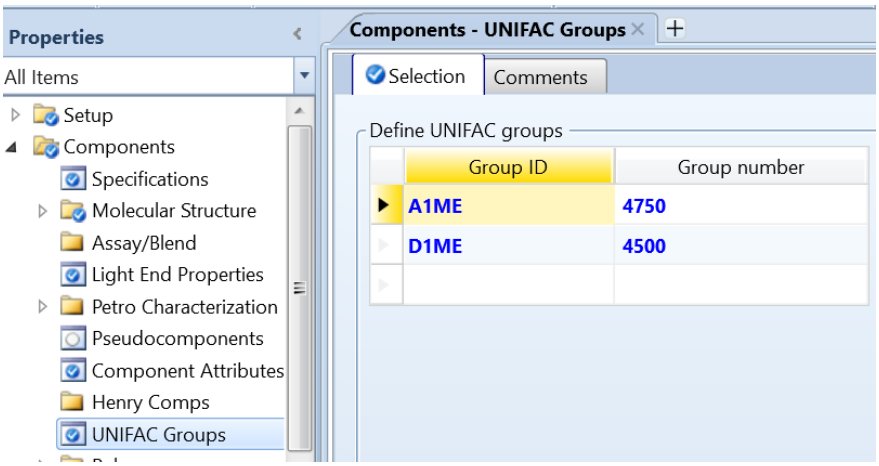
Wertheim sites are entered utilizing the Aspen framework for UNIFAC groups for Aspen 11. The user sites are stored in memory enabling the user UNIFAC groups to be utilized for the Wertheim sites. This is a customization to enter Wertheim sites into the Aspen framework. Files used in this way cannot be used for any UNIFAC calculations because the standard UNIFAC model will misinterpret the parameters.

Select **Components** > **UNIFAC Groups** in the browser menu. Define user Group ID and Group number. Group ID is a text string (8 char max) that provides easy recognition of the site. Here written to match the Group number for clarity. You may wish to name acceptors with an A, donors with a D and bivalent with a B. The Group ID is a user-specified text field.

The Group Number conventions are hard-coded into the calculations as follows:

- 4500-4749 are donors;
- 4750-4949 are acceptors;
- 4950-5000 are bivalent (carboxylic acids).

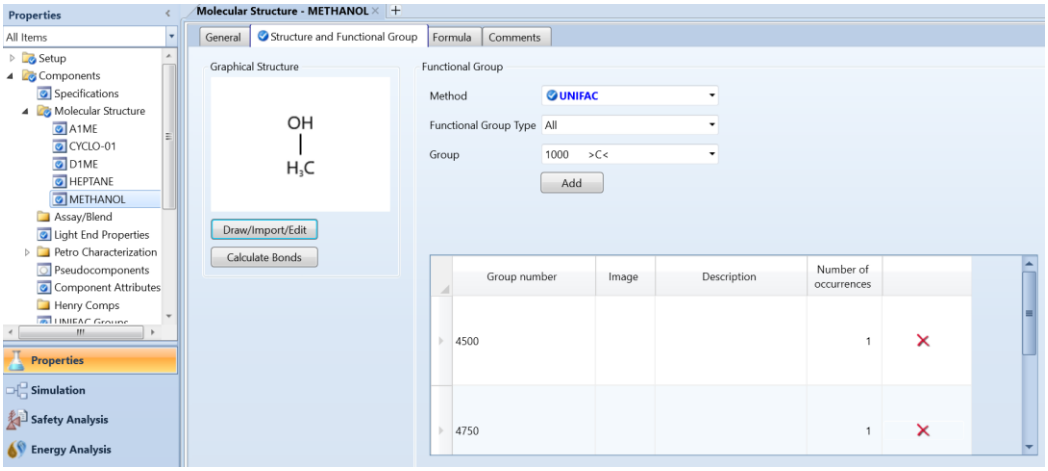
NOTE: These conventions MUST be followed because the Group Number is used within the code to decide bonding (e.g. acceptor with donor, but not donor with donor, etc.) Bivalent will bond to each other in 1:1 stoichiometry blocking further bonding for the sites, but they also will serve can serve as a donor and acceptor with other sites when those bonding parameter values are nonzero.



3.1.2. Designate Site Hosts

Assign sites to molecules using **Components** > **Molecular Structure** > **Functional Group**. Select **UNIFAC** as the functional group method. Do not assign any sites besides the sites to be used for Wertheim calculations.

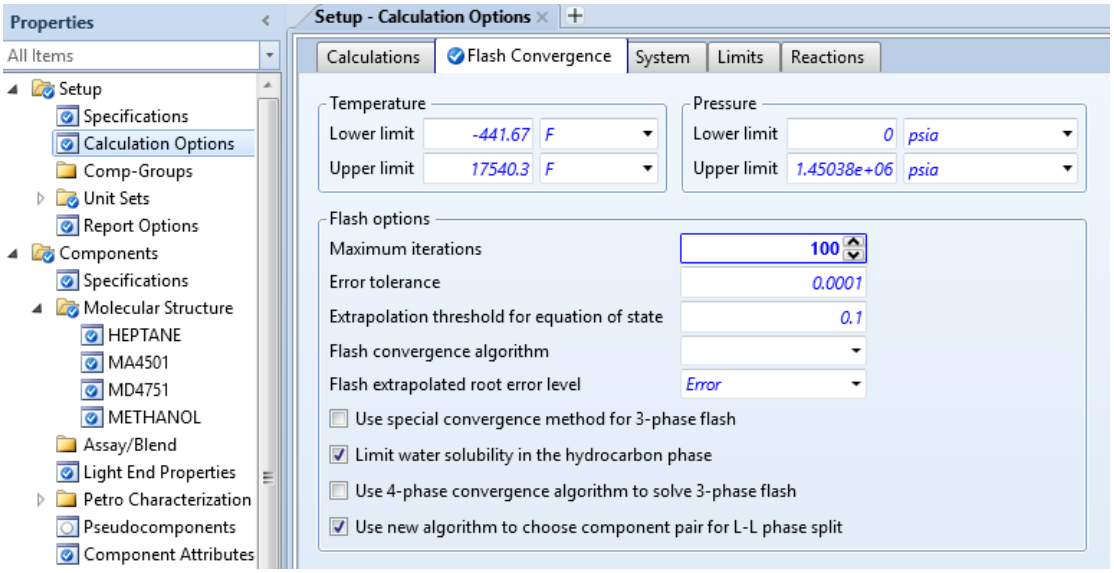
Methanol has one acceptor and one donor, numbered 4500 and 4750.



*NOTE: Nothing is specified for molecules without Wertheim parameters. For instance, the built in UNIFAC group assignments for cyclohexane will be ignored in the Wertheim calculations. In addition, Wertheim sites will appear in the **Molecular Structure** folder of the data browser but require no additional input.*

3.2. LLE systems and flash calculations

For systems with an LLE, it is important to perform flash calculations in the regression simulation. To do this navigate to **Setup > Calculation Options > Flash Convergence** and set the Max Iterations to 100.



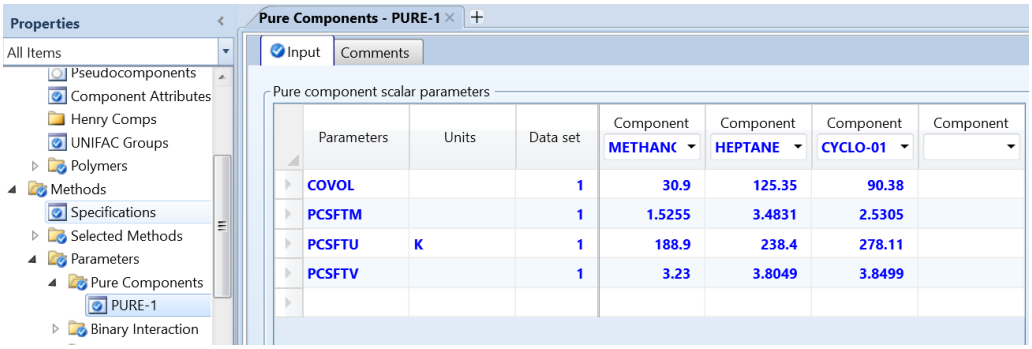
3.3. Enter parameter values

Now enter the parameter values for CPA COVOL in cm^3/mol. To set the value, create an entry form using Methods>Parameters >Pure Component>Scalar (the default form name is OK). Then, in the Parameter dropdown menu, select the COVOL variable that you created earlier. (The value shown for heptane covolume is not needed for this example.) The user model does not use these values for PC-SAFT, but Aspen will set them to 1E35 when missing. A placeholder value can be entered if you are running PC-SAFT.

3.3.1. Association parameters

For SAFT association parameters, the following pure component parameters must be entered;

- PCSFTM – m, number of segments
- PCSFTU – ϵ/k (in K), this is the physical energy parameter, not the association parameter.
- PCSFTV – σ reference segment diameter (in Angstroms)



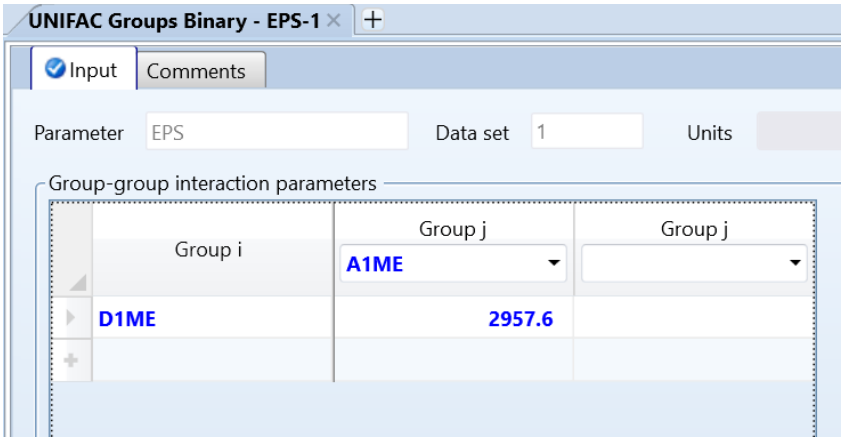
For Wertheim Parameters:

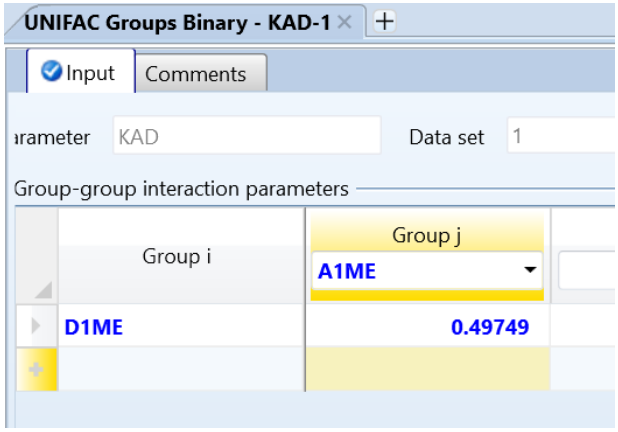
Under **Methods** > **Parameters** > **UNIFAC Groups Binary**, locate **EPS-1** and **KAD-1 for CPA or EPSPCS-1 and KADPCS-1 for PC-SAFT**. Since Wertheim parameters are symmetrical the subroutine will fill the matrix according to the element provided.

The parameter EPS or EPSPCS is ϵ_{ij}^{AD}/k in units of K

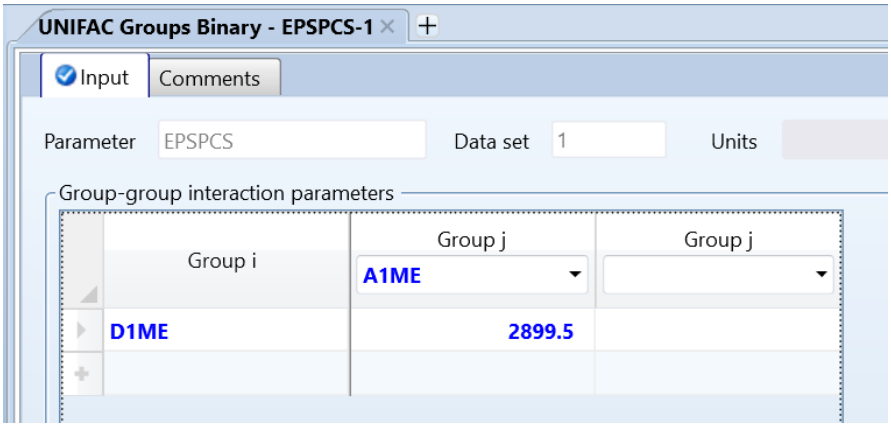
The parameter KAD is K_{ij}^{AD} in units of cm^3/mol, and KADPCS is κ_{ij}^{AD}, dimensionless.

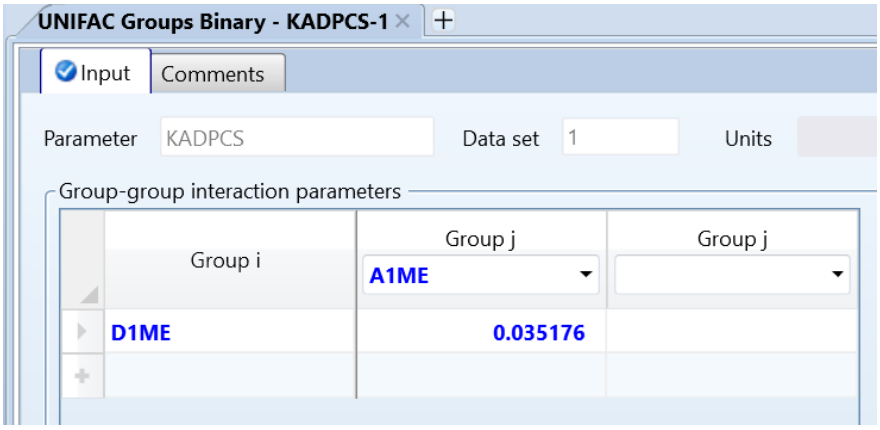
NOTE: You do NOT need to provide both IJ and JI because if the values are different one of them will be overwritten. To minimize confusion, place the acceptors in the columns across the top and the donors along the rows, or vice-versa. The only exception to this will be bivalent molecules which much be in the column and the row.





And for the PC-SAFT association parameters:





3.3.2. Set HOCETA

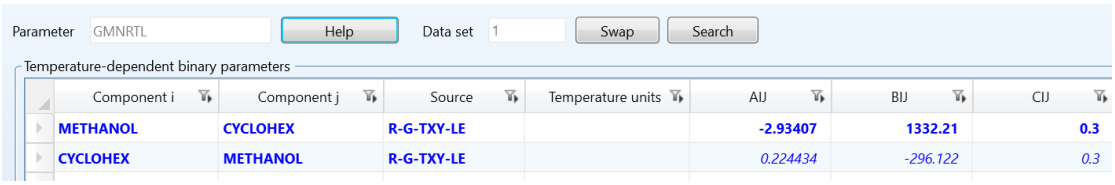
Set the Hayden-O'Connell (η) = 1.63 for methanol using **Methods** > **Parameters** > **Binary Interaction** > **HOCETA**

3.3.3. Residual Model Parameters

This example will use NRTL, so we will use the user parameters GMNRTL. When entered manually, the parameter source will be "USER".

Under **Methods** > **Parameters** > **Binary Interaction** locate **GMNRTL.** To regenerate the solutions given for the example system in Section **Error! Reference source not found.** (NRTL-PA with CPA parameters), set the parameters as shown in the following figure. The screen shot includes parameters not needed for the example, and unneeded parameters are masked with translucent blocks.

Set as follows for the example fit using the PC-SAFT association parameters (Section 4.2):



4. Example: Methanol + Cyclohexane (Running the file)

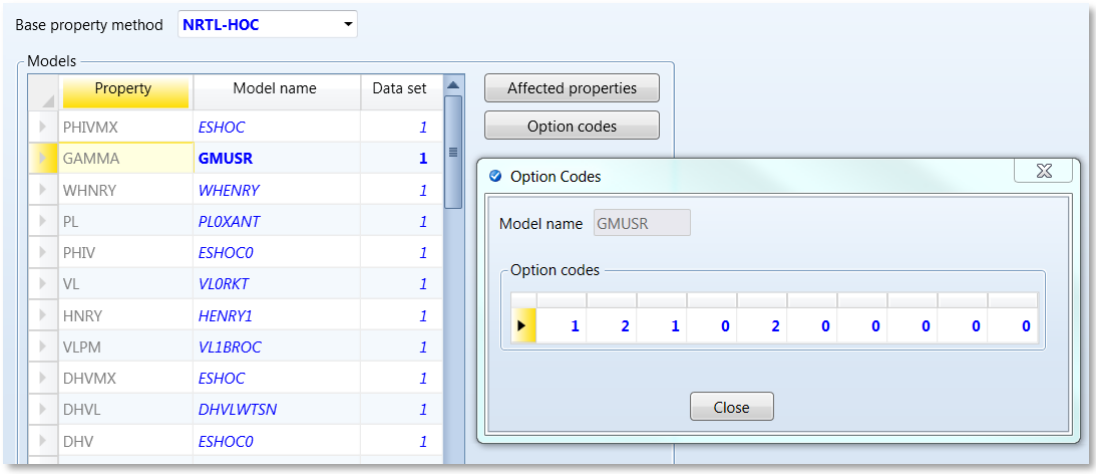
4.1. CPA

This example will use the CPA method with temperature-dependent pure-component volumes, the Flory combinatorial with the Staverman-Guggenheim correction.

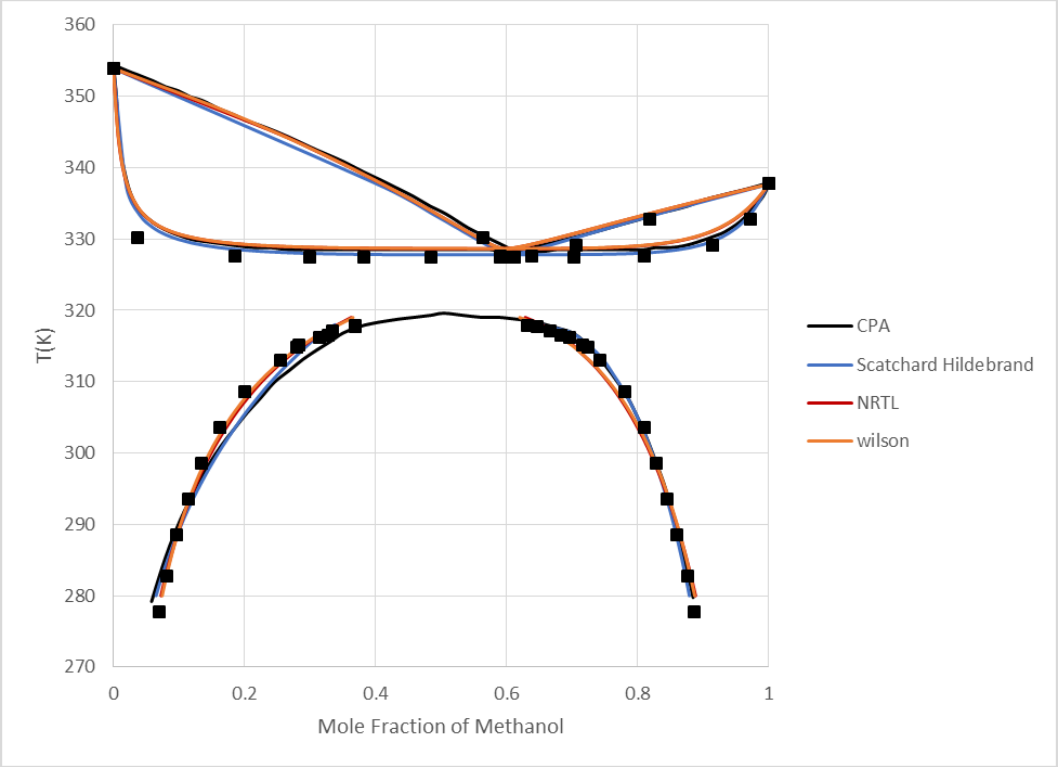
Set the following option codes for this example

- kop(1) = 1; debug printing is set to level 1
- kop(2) = 2; rdf is set to CPA
- kop(3) = 1; temperature-dependent density.
- kop(5) = 2; combinatorial correction is set to Staverman-Guggenheim
- kop(6) = 0; Flory combinatorial term

Set the flags as follows for CPA benchmarking. Note that the kop(1) = 1 is optional but will provide minimal debugging to the history file.



Results of using a variety of residual models are shown below and compared with CPA. The Scatchard-Hildebrand (SH), and Wilson methods are discussed by Bala[1] but not included in the public NRTL-PA distribution. Tabulated calculations follow the figure.



NOTE: NRTL and Wilson yield almost identical results and are therefore overlapped in this figure

Experimental Data plotted in the figure- VLE: Budantseva, L. S.; Lesteva, T. M.; Nemtsov, M. S. Zh. Fiz. Khim., 1975, 49, 260-1 Liquid-vapor equilibriums in methanol-C6 hydrocarbons of different classes. LLE: Katayama, H. Fluid Phase Equilib., 1999, 164, 83-95 Liquid-liquid equilibria of two ternary systems: methanol-cyclohexane including 1,3-dioxolane or 1,4-dioxane in the range of 277.79-308.64 K.

With these values, you can now run a binary analysis of methanol + cyclohexane and generate the following VLE and LLE data points with the model:

Experimental VLE Data				**Experimental LLE Data**			
Temp (K)	Pressure (Pa)	X Methanol	Y Methanol	Temp (K)	Pressure (Pa)	X1	X2
353.82885	101320	0	0	277.79	101300	0.886	0.0705
334.33413	101320	0.05	0.492	282.8	101300	0.876	0.0816
329.3352	101320	0.1	0.566	288.54	101300	0.861	0.0964
327.53573	101320	0.2	0.598	293.61	101300	0.845	0.114
327.3358	101320	0.3	0.603	298.63	101300	0.828	0.134
327.3358	101320	0.4	0.603	303.63	101300	0.81	0.162
327.3358	101320	0.5	0.603	308.64	101300	0.781	0.2
327.3358	101320	0.6	0.603	313	101300	0.743	0.256
327.3358	101320	0.7	0.603	314.75	101300	0.724	0.28
327.53573	101320	0.8	0.605	315.14	101300	0.717	0.284
328.63541	101320	0.9	0.67	316.15	101300	0.696	0.314
330.83483	101320	0.95	0.764	316.48	101300	0.683	0.328

337.83343	101320	1	1	317.05	101300	0.667	0.335
				317.65	101300	0.647	0.369
				317.94	101300	0.632	0.37

The stable phase at 298.15 K will split into two liquid phases. The table below is a Gibbs Energy of Mixing Analysis calculated with the flash suppressed to provide validation of user calculations.

MOLEFRAC METHANOL	LIQUID DGMIX	LIQUID GAMMA METHANOL	LIQUID GAMMA CYCLO-01	LIQUID HXS
	kJ/kmol			kJ/kmol
0	0		1	0
0.02	-41.6106	32.9999	1.01162	229.825
0.04	-57.0513	19.336	1.02794	354.393
0.06	-67.1492	13.8108	1.04609	451.761
0.08	-74.499	10.7768	1.06568	534.609
0.1	-80.1293	8.84619	1.08661	608.011
0.12	-84.5793	7.50448	1.10888	674.6
0.14	-88.1763	6.51541	1.1325	735.934
0.16	-91.1396	5.75475	1.15755	793.018
0.18	-93.6262	5.15079	1.18412	846.534
0.2	-95.7546	4.65913	1.21229	896.961
0.22	-97.6178	4.2508	1.24219	944.641
0.24	-99.2914	3.90604	1.27396	989.819
0.26	-100.839	3.61094	1.30775	1032.67
0.28	-102.313	3.35539	1.34373	1073.32
0.3	-103.763	3.13188	1.38209	1111.83
0.32	-105.228	2.9347	1.42305	1148.27
0.34	-106.746	2.75944	1.46687	1182.63
0.36	-108.351	2.60264	1.5138	1214.9
0.38	-110.074	2.46153	1.56418	1245.06
0.4	-111.942	2.33389	1.61834	1273.04
0.42	-113.982	2.21791	1.67668	1298.77
0.44	-116.216	2.1121	1.73967	1322.16
0.46	-118.666	2.01521	1.8078	1343.1
0.48	-121.351	1.92622	1.88168	1361.45
0.5	-124.288	1.84425	1.96196	1377.07
0.52	-127.49	1.76856	2.04943	1389.8
0.54	-130.97	1.69852	2.14498	1399.46
0.56	-134.734	1.6336	2.24964	1405.84
0.58	-138.786	1.57332	2.3646	1408.74
0.6	-143.126	1.51729	2.49127	1407.89
0.62	-147.746	1.46517	2.63128	1403.06
0.64	-152.634	1.41666	2.78657	1393.95

0.66	-157.767	1.3715	2.95941	1380.27
0.68	-163.112	1.32946	3.15253	1361.67
0.7	-168.623	1.29036	3.36916	1337.81
0.72	-174.237	1.25403	3.6132	1308.29
0.74	-179.872	1.22033	3.88938	1272.72
0.76	-185.415	1.18916	4.20343	1230.63
0.78	-190.721	1.16041	4.5624	1181.55
0.8	-195.595	1.13402	4.97498	1124.96
0.82	-199.78	1.10993	5.45198	1060.32
0.84	-202.932	1.08812	6.00697	987.005
0.86	-204.58	1.06857	6.65712	904.388
0.88	-204.071	1.05131	7.42436	811.771
0.9	-200.468	1.03636	8.33701	708.409
0.92	-192.369	1.0238	9.43202	593.497
0.94	-177.531	1.01372	10.7582	466.17
0.96	-151.96	1.00627	12.3807	325.494
0.98	-106.917	1.00161	14.3881	170.466
1	0	1		0

T-XY at 1.01325 bar.

MOLEFRAC METHANOL	TOTAL TEMP	LIQUID1 GAMMA METHANOL	LIQUID1 GAMMA CYCLO-01	VAPOR MOLEFRAC METHANOL	VAPOR PHIMX METHANOL	VAPOR PHIMX CYCLO-01	LIQUID HXS
	C						kJ/kmol
0	80.78173	31.5451	1	0		0.962373	0
0.02	64.79257	20.19029	1.007354	0.399531	0.977662	0.964326	361.3668
0.04	60.91491	13.93458	1.020723	0.477669	0.970422	0.967155	570.564
0.06	59.13668	10.64938	1.036494	0.511936	0.967105	0.968807	732.05
0.08	58.09947	8.632651	1.053942	0.531803	0.965148	0.969902	868.1386
0.1	57.41826	7.265193	1.07283	0.544985	0.963844	0.970689	987.5474
0.12	56.93877	6.274535	1.093077	0.554455	0.96291	0.971286	1094.703
0.14	56.58615	5.52238	1.114671	0.56161	0.96221	0.971755	1192.193
0.16	56.31941	4.931009	1.137636	0.567209	0.961669	0.972134	1281.672
0.18	56.10618	4.453518	1.162033	0.571828	0.961228	0.972454	1364.12
0.2	55.95137	4.059184	1.187916	0.575343	0.960898	0.972702	1440.678
0.22	55.82101	3.72822	1.215392	0.57841	0.960614	0.972922	1511.494
0.24	55.71852	3.446211	1.244556	0.580961	0.960384	0.973107	1577.167
0.26	55.63448	3.203029	1.275531	0.583112	0.960191	0.973265	1637.915
0.28	55.57109	2.991061	1.308445	0.58491	0.960037	0.973399	1694.078
0.3	55.51782	2.804727	1.34346	0.586477	0.959904	0.973516	1745.65
0.32	55.47588	2.639614	1.380742	0.587781	0.959796	0.973614	1792.806
0.34	55.44252	2.492316	1.420485	0.588909	0.959705	0.9737	1835.587
0.36	55.4157	2.360129	1.462904	0.589884	0.959628	0.973774	1874.004
0.38	55.39471	2.240869	1.508239	0.590713	0.959565	0.973837	1908.067
0.4	55.37803	2.132773	1.556762	0.591436	0.959511	0.973893	1937.738
0.42	55.36461	2.034388	1.608777	0.59209	0.959463	0.973944	1962.962
0.44	55.35452	1.944505	1.664626	0.592629	0.959425	0.973985	1983.691
0.46	55.34625	1.862125	1.724696	0.593137	0.959391	0.974025	1999.82
0.48	55.33953	1.787431	1.788472	0.593616	0.959359	0.974062	
0.5	55.33411	1.716612	1.859308	0.594075	0.95933	0.974098	2017.881

0.52	55.32963	1.652152	1.934911	0.594547	0.959301	0.974135	2019.575
0.54	55.32596	1.592497	2.016876	0.595049	0.95927	0.974174	2016.195
0.56	55.32311	1.537197	2.10594	0.59561	0.959238	0.974219	2007.593
0.58	55.32125	1.485864	2.202947	0.596258	0.959202	0.97427	1993.605
0.6	55.32071	1.438161	2.30887	0.597029	0.959161	0.974331	1974.06
0.62	55.32204	1.393798	2.424832	0.597962	0.959113	0.974405	1948.771
0.64	55.32609	1.352522	2.552133	0.599107	0.959057	0.974497	1917.543
0.66	55.33402	1.314112	2.692287	0.600521	0.95899	0.97461	1880.168
0.68	55.34742	1.278378	2.847057	0.602277	0.958911	0.974751	1836.424
0.7	55.36839	1.245158	3.018508	0.604459	0.958817	0.974927	1786.076
0.72	55.39972	1.214309	3.209064	0.607179	0.958706	0.975148	1728.876
0.74	55.44509	1.185715	3.421576	0.610573	0.958575	0.975424	1664.556
0.76	55.50927	1.159275	3.659407	0.614811	0.95842	0.975771	1592.831
0.78	55.59853	1.134911	3.926532	0.620117	0.95824	0.976208	1513.394
0.8	55.72109	1.11256	4.227647	0.626776	0.958029	0.97676	1425.912
0.82	55.88779	1.09218	4.568297	0.635167	0.957785	0.97746	1330.023
0.84	56.11294	1.073746	4.955001	0.645793	0.957505	0.978354	1225.326
0.86	56.41562	1.057251	5.39537	0.659336	0.95719	0.979503	1111.376
0.88	56.82134	1.042709	5.898167	0.676734	0.956842	0.980995	987.6712
0.9	57.36466	1.030155	6.473233	0.699316	0.956474	0.982955	853.6387
0.92	58.0924	1.019645	7.131171	0.728974	0.956118	0.985568	708.6121
0.94	59.06864	1.01126	7.882509	0.768485	0.95584	0.989112	551.8038
0.96	60.3811	1.005103	8.736	0.82201	0.955781	0.994026	382.2642
0.98	62.14953	1.001301	9.695511	0.895903	0.956227	1.001016	198.8225
1	64.53476	1	10.75497	1	0.957769		0

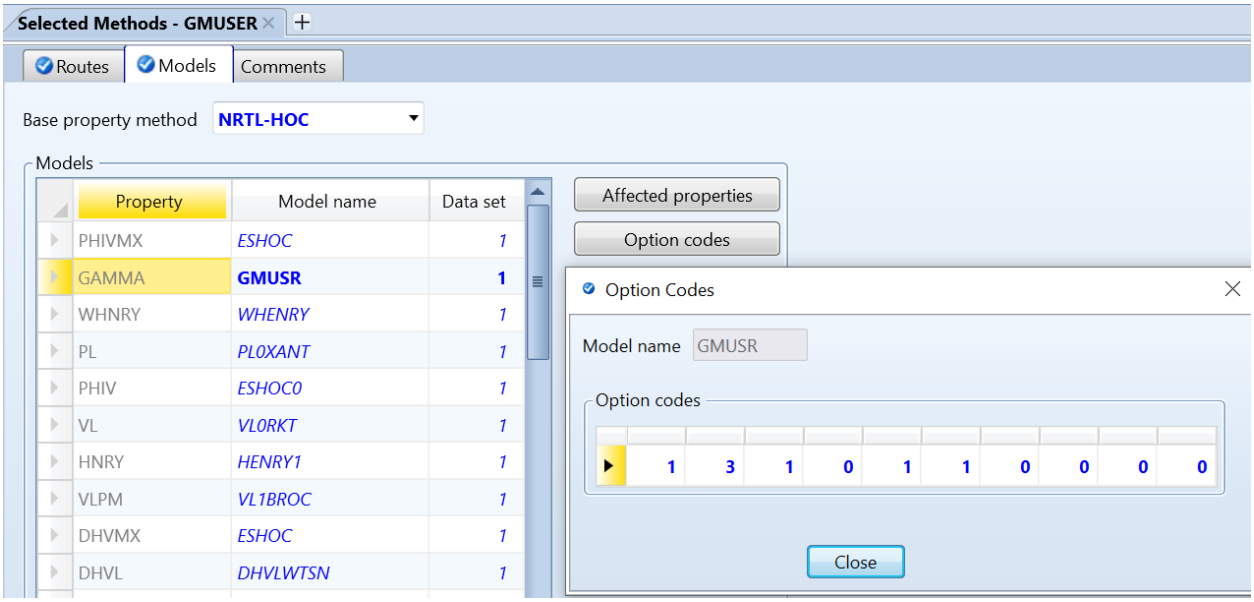
An LLE Flash results in the following coexisting mole fractions

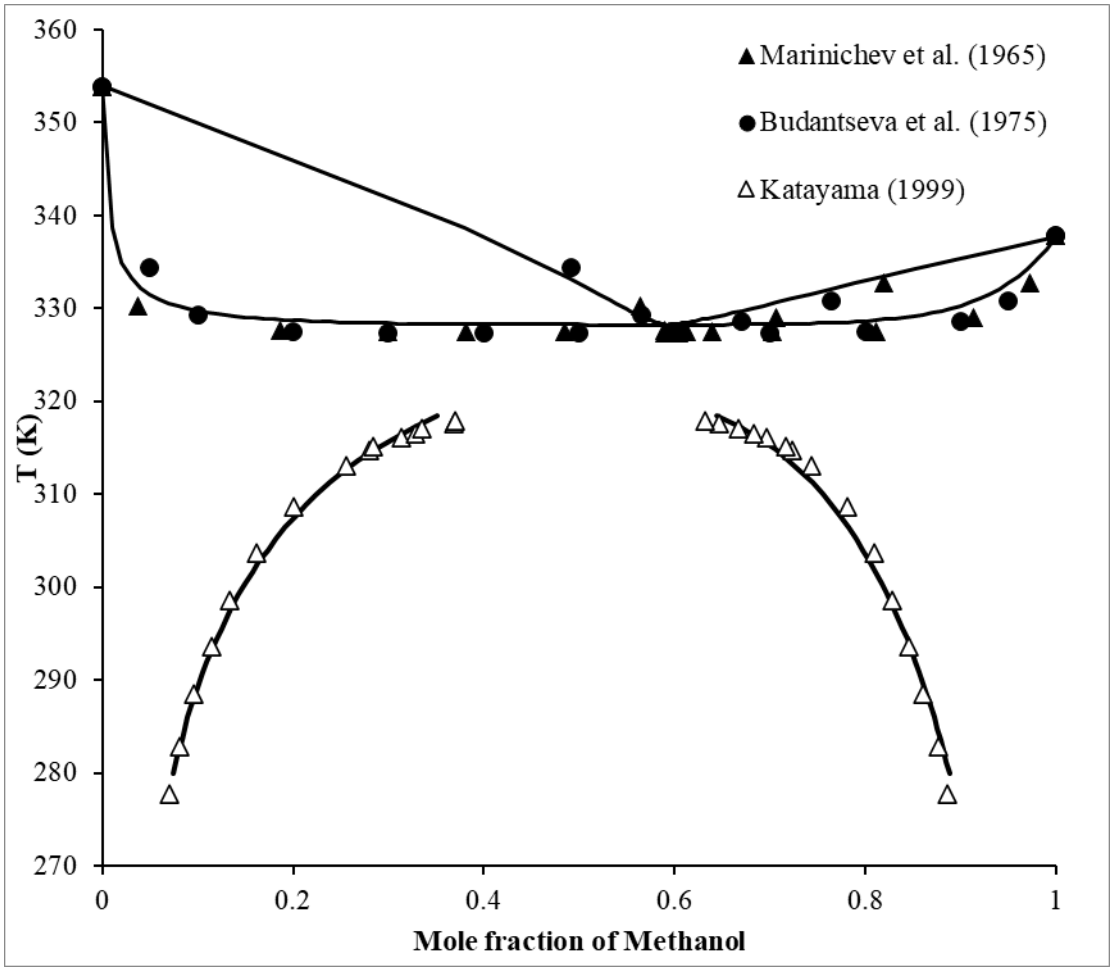
TEMP K	LIQUID1 GAMMA METHANOL	LIQUID1 GAMMA CYCLO-01	LIQUID2 GAMMA METHANOL	LIQUID2 GAMMA CYCLO-01	LIQUID1 MOLEFRAC METHANOL	LIQUID2 MOLEFRAC METHANOL
318	2.54836	1.44969	1.34096	2.75894	0.345161	0.655912
317	2.73811	1.40248	1.3106	2.9042	0.321881	0.672508
316	2.8839	1.3732	1.28187	3.06371	0.306317	0.689065
315	3.07582	1.33969	1.26095	3.20132	0.28773	0.701898
314	3.24253	1.3155	1.2416	3.34535	0.2735	0.714274
313	3.41088	1.29437	1.22395	3.49404	0.260531	0.72604
312	3.58891	1.27483	1.20939	3.63417	0.248084	0.736202
311	3.76626	1.25786	1.19577	3.77992	0.236861	0.746033
310	3.9502	1.24233	1.18393	3.92213	0.226256	0.754906
309	4.14037	1.22812	1.17349	4.06195	0.216257	0.763014
308	4.33557	1.21518	1.16401	4.20201	0.206889	0.770603
307	4.53021	1.20374	1.15465	4.35188	0.198362	0.778269
306	4.73485	1.19292	1.1466	4.49554	0.190119	0.785095
305	4.94413	1.18301	1.13906	4.6421	0.182385	0.791649
304	5.1612	1.17375	1.13224	4.78751	0.175006	0.797747
303	5.38292	1.16524	1.12579	4.93648	0.168076	0.803649
302	5.61274	1.15725	1.11995	5.08408	0.161454	0.809144
301	5.84869	1.14984	1.11444	5.23442	0.155187	0.81444
300	6.09242	1.14289	1.10934	5.38515	0.149211	0.819453
299	6.34343	1.13638	1.10457	5.53764	0.143525	0.824254
298	6.60201	1.13029	1.10008	5.69191	0.138112	0.828858
297	6.8684	1.12456	1.09587	5.84804	0.132951	0.833277
296	7.14286	1.11917	1.0919	6.00607	0.128029	0.837523
295	7.42565	1.1141	1.08815	6.16606	0.123329	0.841605
294	7.71702	1.10932	1.08462	6.32808	0.118839	0.845536
293	8.01722	1.1048	1.08128	6.49219	0.114548	0.849322
292	8.32652	1.10053	1.07811	6.65846	0.110443	0.852974
291	8.64516	1.09649	1.07512	6.82694	0.106514	0.856497
290	8.97339	1.09266	1.07227	6.99769	0.102753	0.8599
289	9.31147	1.08903	1.06957	7.1708	0.099151	0.863189
288	9.65966	1.08559	1.067	7.34631	0.095699	0.866369
287	10.0183	1.08232	1.06456	7.52424	0.092388	0.869446
286	10.3874	1.07921	1.06223	7.7048	0.089215	0.872427
285	10.7674	1.07626	1.06001	7.88798	0.086172	0.875315
284	11.1584	1.07344	1.0579	8.07384	0.083252	0.878116
283	11.5607	1.07077	1.05588	8.26246	0.080449	0.880832
282	11.9746	1.06822	1.05395	8.45391	0.077758	0.883468
281	12.4003	1.06578	1.0521	8.64827	0.075175	0.886028
280	12.8379	1.06347	1.05033	8.84562	0.072694	0.888515

4.2. PC-SAFT Association

Set options as follows for PC-SAFT benchmarking. Note that kop(1) = 1 is optional but will provide minimal debugging information to the history file.

- kop(1) = 1; debug printing is set to level 1
- kop(2) = 3; rdf is set to PC-SAFT
- kop(3) = 1; temperature-dependent density.
- kop(5) = 1; no combinatorial correction
- kop(6) = 1; modified Flory combinatorial term using $V^{2/3}$





Experimental Data plotted in the figure:

VLE: Budantseva, L. S.; Lesteva, T. M.; Nemtsov, M. S. Zh. Fiz. Khim., 1975, 49, 260-1 Liquid-vapor equilibriums in methanol-C6 hydrocarbons of different classes

VLE: Marinichev, A. N.; Susarev, M. P. Zh. Prikl. Khim., 1965, 38, 1619

LLE: Katayama, H. Fluid Phase Equilib., 1999, 164, 83-95 Liquid-liquid equilibria of two ternary systems: methanol-cyclohexane including 1,3-dioxolane or 1,4-dioxane in the range of 277.79-308.64 K.

T-xy

MOLEFRAC METHANOL	TOTAL TEMP	LIQUID1 GAMMA METHANOL	LIQUID1 GAMMA CYCLO-01	VAPOR MOLEFRAC METHANOL	VAPOR PHIMX METHANOL	VAPOR PHIMX CYCLO-01
	K					
0	353.9317	60.00196	1	0		0.962373
0.02	334.9717	25.68309	1.010375	0.455282	0.972399	0.96616
0.04	332.1696	15.93922	1.02618	0.508361	0.967233	0.968561
0.06	330.9378	11.64115	1.043887	0.531211	0.964939	0.969811
0.08	330.2221	9.200973	1.063014	0.544598	0.963584	0.970611

0.1	329.7507	7.620118	1.083418	0.553592	0.962676	0.97118
0.12	329.4167	6.509104	1.105069	0.560147	0.96202	0.97161
0.14	329.1637	5.683932	1.127987	0.565255	0.961514	0.971955
0.16	328.9779	5.045554	1.152209	0.569177	0.961131	0.972227
0.18	328.8285	4.536658	1.177809	0.572419	0.960819	0.972455
0.2	328.7122	4.120988	1.204866	0.575104	0.960566	0.972646
0.22	328.6194	3.775335	1.233433	0.577323	0.96036	0.972807
0.24	328.5416	3.482076	1.263755	0.579282	0.960183	0.97295
0.26	328.48	3.23101	1.295824	0.58092	0.960037	0.97307
0.28	328.43	3.013295	1.329826	0.582327	0.959914	0.973175
0.3	328.3896	2.822657	1.36592	0.583539	0.959811	0.973266
0.32	328.3569	2.654321	1.404285	0.584587	0.959724	0.973345
0.34	328.3307	2.504583	1.445118	0.585495	0.959651	0.973413
0.36	328.3096	2.370529	1.488643	0.586283	0.959589	0.973473
0.38	328.2927	2.249832	1.535108	0.586969	0.959536	0.973526
0.4	328.2793	2.140614	1.584794	0.58757	0.959491	0.973572
0.42	328.2686	2.04134	1.638016	0.588102	0.959453	0.973613
0.44	328.2601	1.950746	1.695126	0.588578	0.959419	0.973649
0.46	328.2533	1.867781	1.756527	0.589014	0.959389	0.973683
0.48	328.2478	1.791566	1.822671	0.589427	0.959362	0.973715
0.5	328.2432	1.721359	1.894072	0.589831	0.959336	0.973747
0.52	328.2395	1.656528	1.971316	0.590247	0.95931	0.973779
0.54	328.2365	1.596538	2.055071	0.590695	0.959283	0.973814
0.56	328.2342	1.540928	2.146103	0.591198	0.959254	0.973854
0.58	328.2329	1.489302	2.245289	0.591784	0.959221	0.9739
0.6	328.2327	1.441319	2.353643	0.592486	0.959183	0.973956
0.62	328.2344	1.396683	2.472335	0.593344	0.959139	0.974024
0.64	328.2386	1.355141	2.602723	0.594403	0.959086	0.974108
0.66	328.2466	1.31647	2.746386	0.595722	0.959023	0.974214
0.68	328.26	1.280481	2.905168	0.597371	0.958948	0.974346
0.7	328.2807	1.247011	3.081227	0.599435	0.958858	0.974512
0.72	328.3117	1.21592	3.277099	0.602024	0.958751	0.974721
0.74	328.3566	1.18709	3.495766	0.605277	0.958624	0.974986
0.76	328.4202	1.160426	3.74075	0.609365	0.958473	0.97532
0.78	328.5091	1.13585	4.016205	0.614513	0.958295	0.975742
0.8	328.6316	1.113302	4.327039	0.621015	0.958085	0.97628
0.82	328.7988	1.092742	4.679033	0.629255	0.957841	0.976965
0.84	329.0256	1.074148	5.078965	0.639749	0.957559	0.977845
0.86	329.3319	1.057516	5.534706	0.653197	0.957237	0.978983
0.88	329.744	1.042863	6.055243	0.670566	0.95688	0.980469
0.9	330.2982	1.030224	6.650538	0.693227	0.956499	0.98243
0.92	331.0433	1.019658	7.331065	0.723141	0.956124	0.985058
0.94	332.0461	1.011243	8.106734	0.763189	0.955825	0.988642

0.96	333.3981	1.005082	8.984778	0.817693	0.955746	0.993634
0.98	335.2229	1.001292	9.965999	0.893246	0.956189	1.000767
1	337.6848	1	11.03886	1	0.957769	

LLE:

TEMP	LIQUID1 GAMMA METHANOL	LIQUID1 GAMMA CYCLO-01	LIQUID2 GAMMA METHANOL	LIQUID2 GAMMA CYCLO-01	LIQUID1 MOLEFRAC METHANOL	LIQUID2 MOLEFRAC METHANOL
K						
315.578	2.97085	1.37577	1.27397	3.16654	0.298033	0.695019
315	3.07524	1.35785	1.26151	3.25069	0.28824	0.702692
314	3.24974	1.33157	1.243	3.39015	0.273304	0.714542
313	3.43555	1.30746	1.22592	3.5349	0.259004	0.725909
312	3.60184	1.28896	1.21	3.68624	0.247553	0.736904
311	3.78768	1.2706	1.19694	3.82752	0.235845	0.746334
310	3.97652	1.25424	1.18509	3.96997	0.225058	0.755182
309	4.17116	1.23933	1.17456	4.11068	0.214941	0.763316
308	4.3701	1.22583	1.16494	4.25233	0.205519	0.770974
307	4.57441	1.21348	1.15613	4.39497	0.19668	0.778198
306	4.78422	1.20216	1.14805	4.53824	0.188375	0.785004
305	4.99949	1.19174	1.14057	4.68314	0.180565	0.791478
304	5.22061	1.18212	1.1337	4.82832	0.173201	0.797577
303	5.44811	1.17319	1.12735	4.97451	0.166236	0.803366
302	5.68174	1.16491	1.12144	5.12204	0.159653	0.80888
301	5.92379	1.15713	1.11606	5.26804	0.153364	0.814019
300	6.16808	1.15002	1.11077	5.42132	0.147518	0.819163
299	6.41914	1.14337	1.10584	5.5759	0.141965	0.82407
298	6.68051	1.13704	1.10141	5.72741	0.136609	0.828597
297	6.94764	1.13115	1.09718	5.88213	0.131547	0.832995
296	7.2199	1.12565	1.09312	6.04086	0.126768	0.837292
295	7.49947	1.12049	1.08931	6.20077	0.122215	0.8414
294	7.78726	1.1156	1.08578	6.36088	0.11786	0.8453
293	8.08203	1.111	1.08243	6.52308	0.113715	0.84906
292	8.38379	1.10667	1.07926	6.68741	0.109768	0.852689
291	8.69253	1.10258	1.07625	6.85392	0.106008	0.856192
290	9.0082	1.09873	1.0734	7.02267	0.102425	0.859576
289	9.33076	1.09508	1.07068	7.1937	0.09901	0.862849
288	9.6601	1.09164	1.0681	7.36709	0.095754	0.866014
287	9.99612	1.08839	1.06564	7.54288	0.092648	0.869078
286	10.3386	1.08531	1.0633	7.72115	0.089687	0.872046
285	10.6875	1.0824	1.06107	7.90195	0.086863	0.874922

284	11.0424	1.07965	1.05893	8.08535	0.08417	0.87771
283	11.4032	1.07704	1.0569	8.27142	0.081601	0.880415
282	11.7694	1.07457	1.05495	8.46024	0.079151	0.883041
281	12.1408	1.07223	1.05309	8.65186	0.076816	0.885591
280	12.5168	1.07001	1.05131	8.84637	0.07459	0.888068

Excess Gibbs Energy and Excess Enthalpy at 323.15 K

MOLEFRAC METHANOL	LIQUID DGMIX	LIQUID GAMMA METHANOL	LIQUID GAMMA CYCLO-01	LIQUID HXS
	kJ/kmol			kJ/kmol
0	0		1	0
0.02	-51.7844	29.2044	1.01158	263.783
0.04	-75.0004	17.1619	1.0278	415.229
0.06	-92.2718	12.2905	1.0458	537.054
0.08	-106.416	9.61526	1.06518	642.702
0.1	-118.546	7.91288	1.08583	737.54
0.12	-129.245	6.72986	1.10773	824.343
0.14	-138.864	5.85783	1.1309	904.747
0.16	-147.636	5.18725	1.15539	979.801
0.18	-155.726	4.65487	1.18128	1050.21
0.2	-163.258	4.22152	1.20865	1116.46
0.22	-170.327	3.86165	1.2376	1178.89
0.24	-177.009	3.55784	1.26824	1237.75
0.26	-183.367	3.29782	1.30072	1293.22
0.28	-189.452	3.07268	1.33518	1345.39
0.3	-195.307	2.87578	1.37178	1394.33
0.32	-200.971	2.70209	1.41071	1440.08
0.34	-206.477	2.54772	1.45217	1482.64
0.36	-211.851	2.40962	1.4964	1521.98
0.38	-217.12	2.28534	1.54366	1558.06
0.4	-222.303	2.17294	1.59424	1590.8
0.42	-227.419	2.07081	1.64848	1620.12
0.44	-232.483	1.97763	1.70673	1645.91
0.46	-237.508	1.89232	1.76943	1668.06
0.48	-242.502	1.81396	1.83705	1686.43
0.5	-247.471	1.74179	1.91013	1700.87
0.52	-252.417	1.67514	1.98928	1711.22
0.54	-257.339	1.61348	2.07523	1717.28
0.56	-262.23	1.55632	2.16876	1718.88
0.58	-267.079	1.50325	2.27083	1715.79

0.6	-271.868	1.45393	2.38251	1707.8
0.62	-276.572	1.40805	2.50505	1694.65
0.64	-281.157	1.36535	2.63992	1676.09
0.66	-285.58	1.32561	2.78882	1651.84
0.68	-289.782	1.28862	2.95375	1621.61
0.7	-293.691	1.25423	3.1371	1585.09
0.72	-297.214	1.22229	3.34168	1541.94
0.74	-300.234	1.19267	3.57084	1491.81
0.76	-302.6	1.16528	3.82863	1434.33
0.78	-304.124	1.14004	4.11991	1369.11
0.8	-304.561	1.11689	4.45059	1295.71
0.82	-303.596	1.09578	4.82792	1213.71
0.84	-300.814	1.07668	5.26081	1122.62
0.86	-295.663	1.05959	5.76031	1021.94
0.88	-287.388	1.04452	6.34027	911.153
0.9	-274.921	1.0315	7.01817	789.687
0.92	-256.684	1.02058	7.81624	656.949
0.94	-230.183	1.01184	8.76311	512.304
0.96	-191.018	1.00539	9.89599	355.081
0.98	-129.639	1.00139	11.2638	184.566
1	0	1		0

5. Understanding Debugging Information

Debug information which has been outputted to the history file (.his) is available to permit users to double-check the parameters being used in the calculations. If parameters are missing, Aspen sets the values to 1E35 or zero.

To generate the debug information, set kop(1) > 0 (section 2.6). After running the case, view the history file locate the icon on the Home ribbon and search for 'GMU ver'. The output occurs each time an activity coefficient calculation occurs, so debugging should be used sparingly and disabled after confirming the parameters.

When matrices are outputted, they are generally listed by *column* because that is the default storage convention in FORTRAN.

Below is an example from the methanol + cyclohexane system at 323.15K using the PC-SAFT parameters above with debug level 2. With debug level 1, the table of gamma contributions is printed, but not the complete set of parameters.

```
-------------------------------------------------------------------------------------------------------
-----------------------
 GMU - Print debug info. Start of func call. GMU version 2.6.5rel
 GMUSR Option codes   2  3  1  0  1  1  0  0  0  0
 KCALC, N, T, P =  1   2   323.150   0.101325E+06
  *** Aspen Component Identifiers
      1   METHANOL
```

```
      3   CYCLO-01
 Component id, m, sigma, epsok
   1  1.5255      3.2300      188.90
   3  2.5305      3.8499      278.11
 Component id, volume and covolume
  volume and covolume
   1  41.890      30.900
   3  112.18      90.380
  *** GMNRTL Physical aij
  0.0000     0.22443     -2.9341      0.0000
  *** GMNRTL Physical bij
  0.0000     -296.12      1332.2      0.0000
  *** GMNRTL Physical alpha
  0.0000     0.30000     0.30000      0.0000
  *** GMNRTL Physical tau
  0.0000    -0.69193      1.1885      0.0000
  *** GMNRTL - User Site in Aspen Simulation (subset may be used)
  1  A1ME      4750
  2  D1ME      4500
 Sites Present: site present in call, site in Aspen file, id, name, host, host x
  1    1  4750  A1ME        1     0.50000
  2    2  4500  D1ME        1     0.50000
 Site1, Site2, index1, index2, Keps, eps, kad
  A1ME      A1ME       1   1  0.0000      0.0000      0.0000
  D1ME      A1ME       2   1  277.30      2899.5     0.35176E-01
  A1ME      D1ME       1   2  277.30      2899.5     0.35176E-01
  D1ME      D1ME       2   2  0.0000      0.0000      0.0000
 Site hosts-----------------
    1    1
 Site name
A1ME      D1ME
 Site fractions, in order of sites
     0.09076     0.09076
 del matrix by row
  0.0000      17006.
  17006.      0.0000
 Pure component-------------
 Site name
D1ME      A1ME
 Site fractions, in order of sites
     0.04877     0.04877
 del matrix by row
  0.0000      16755.
  16755.      0.0000
 *** Combinatorial Method: Flory using molar volume^(2/3)
 *** GAMMA RESULTS
 KCALC, N, T, P =  1   2   323.150   0.101325E+06
 I     NAME         X        lnGAMMAres    lnGAMMAcomb  lnGAMMAcombcorr      lnGAMMAw      lnGAMMA
dlnGAMMA
  1 METHANOL      0.500000      0.077267     -0.064281      0.000000      0.541924      0.554911
0.000000
  3 CYCLO-01      0.500000      0.030408     -0.041654      0.000000      0.658415      0.647169
0.000000
 End of function call
*****************************************************************************************
**********************
```

When using kop(1) = 3, all of the user parameters and many of the intermediate calculations are printed to the history file. Additionally, the files *gammas.csv, hxs.csv* and *vol.csv* are created. The output provides contributions to the activity coefficients, the enthalpy of mixing and molar volumes. This option appends calculations *every time* that the gamma routine is called, so the file can grow very large if the case involves a lot of gamma calculations. The program runs slowly when kop(1) = 3. We recommend using this level of debugging only for isothermal property

calculations such as binary excess Gibbs energy. Then turn down/off the debugging information for normal runs.

5.1. Reading gammas.csv

The columns in *gammas.csv* are as follows: T(K), P(Pa), Aspen component index for the order entered in components list, component name, ln(gamma_res), ln(gamma_comb), ln(gamma_comb_correction), ln(gamma_wertheim), ln(gamma), d(ln(gamma))/dT where T is in K.

The columns for components are repeated for each component in the function call. Aspen will sometimes change the order of components in the function call, which results in a change in order of the component columns. To see temperature derivatives, perform a calculation such an excess enthalpy calculation and view the *hxs.csv* file.

5.2. Reading *hxs.csv*

The columns in *hxs.csv* give the contributions to the partial molar excess enthalpy and are as follows: T(K), P(Pa), Aspen component index for the order entered in components list, component name, -RTd(ln(gamma_res))/dT, -RTd(ln(gamma_comb))/dT, -RTd(ln(gamma_comb_correction))/dT, -RTd(ln(gamma_wertheim))/dT, -RTd(ln(gamma))/dT, d(ln(gamma))/dT where R is in J/mol-K, and T is in K for all rows.

The columns for components are repeated for each component in the function call. Aspen will sometimes change the order of components in the function call, which results in a change in order of the component columns.

5.3. Reading vol.csv

The columns in *vol.csv* are as follows:

T(K), ideal solution mixture molar volume (cm^3/mol), then for each component: id, name, component molar volume (cm^3/mol)

6. Appendix A – Model details

The **NRTL** residual model uses:

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$\tau_{ij} = a_{ij} + b_{ij}/T$; $\alpha_{ij} = \alpha_{ji} = c_{ij}$. GMNRTL parameters are a_{ij}, b_{ij}, c_{ij}

7. Appendix B – Conversion of CPA values

7.1. Pure Compound Parameters for the CPA Equations of State

This appendix summarizes CPA parameters from literature and conversion to units used with the user model.

For components that self-associate:

$$KAD = \beta_{CPA}^{AD} * b_{CPA}\left(\frac{cm3}{mol}\right)$$
$$EPS = \varepsilon^{AD}/k(K)$$

For cross-association, the user enters the desired values of the cross interactions directly, so any custom value can be used. For cross-interactions of similar compounds, such as two alcohols, Elliott's combining rules (ECR) can be used:

$$\Delta^{A_iD_j} = \sqrt{\Delta^{A_iD_i}\Delta^{A_jD_j}}$$

We suggest a modification relative to CPA. The original combining rule includes the radial distribution function of the pure components *i* and *j* and calculates their geometric means. However, this removes the compositional dependence of the association strength term. Therefore, we suggest the rule as follows:

$$\Delta^{A_iD_j} = g(\sigma)\sqrt{\frac{\Delta^{A_iD_i}}{g(\sigma_i)}\frac{\Delta^{A_jD_j}}{g(\sigma_j)}}$$

To accomplish this, we suggest the following parameters for cross-association when the associating sites are the same type (e.g. hydroxyls), and assume that $\exp\left(\frac{\varepsilon^{AD}}{RT}\right) - 1 \cong \exp\left(\frac{\varepsilon^{AD}}{RT}\right)$:

$$KAD = KA_iD_j = \sqrt{KA_iD_i * KA_jD_j}$$
$$EPS = EPS_{ij} = \frac{\varepsilon^{A_iD_i} + \varepsilon^{A_jD_j}}{2k}$$

8. References

[1] A.M. Bala Ahmed, Fundamental Studies and Engineering Modeling of Hydrogen Bonding, Ph.D. Thesis, Michigan State University, 2018.

[2] G.M. Kontogeorgis, G.K. Folas, Chapter 9, Appendix A, in: Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories, John Wiley & Sons, 2009. https://www.wiley.com/go/kontogeorgis.

[3] I.G. Economou, G.D. Ikonomou, P. Vimalchand, M.D. Donohue, Thermodynamics of Lewis acid-base mixtures, AIChE Journal. 36 (1990) 1851–1864. https://doi.org/10.1002/aic.690361209.