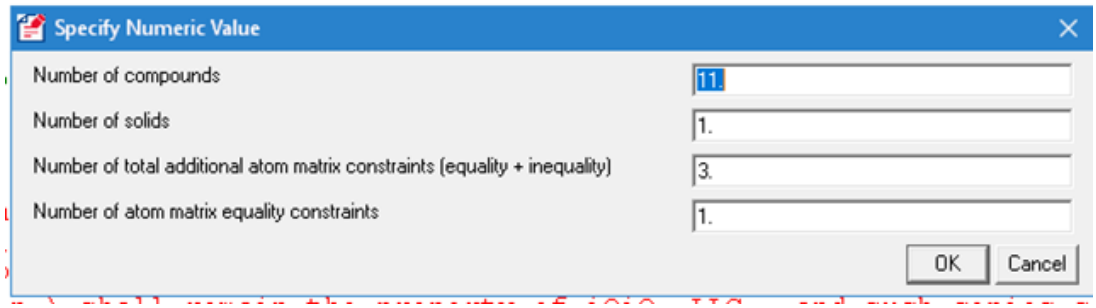
Coming Soon: Capability to Constrain Multiphase Equilibrium Calculations

2021-08-23 - Corporate Communications - Comments (0) - News

The next release of Process Safety Office® SuperChems™ will provide the capability to constrain multiphase chemical and physical equilibrium calculations. This is an important upgrade for all SuperChems™ models using Gibbs free energy minimization including streams, and the Gibbs free energy model. The release will also help users better develop global kinetics (rates and stoichiometries) from calorimetry data where constraints are measured.

Can Specify User-Defined Constraints

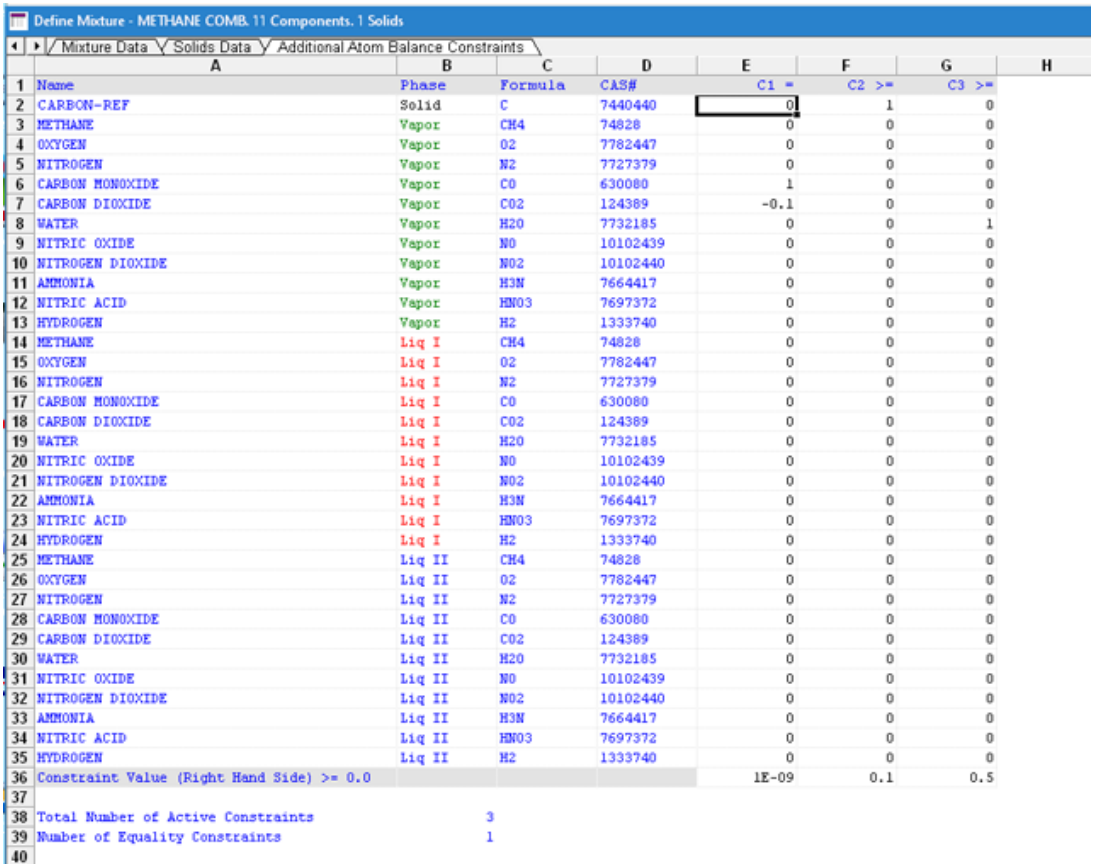
When users create a new mixture or when users edit the number of compounds in a mixture, they can specify user-defined constraints, including both equality and inequality constraints.



Can Constrain Based On Actual Measurements

Equilibrium states are usually difficult to achieve in liquid and heterogeneous reactions. In the next release, users can constrain the equilibrium calculations based on actual measurements, such as the final ratio of non-condensable gas, to force the equilibrium calculation to match reaction data for rate-limited reactions. Users can also use constraints when calculating VLLE to restrict a specific chemical species to one or more phases.

A user specifies the constraints by directly editing the mixture after setting the number of constraints. The figure below shows a mixture that is used to model the combustion of methane. Note that it has three user-defined constraints: one equality constraint and two inequality constraints.



Define Mixture - METHANE COMB. 11 Components. 1 Solids

Mixture Data | Solids Data | Additional Atom Balance Constraints

	A	B	C	D	E	F	G	H
1	Name	Phase	Formula	CAS#	C1 =	C2 >=	C3 >=	
2	CARBON-REF	Solid	C	7440440	0	1	0	
3	METHANE	Vapor	CH4	74828	0	0	0	
4	OXYGEN	Vapor	O2	7782447	0	0	0	
5	NITROGEN	Vapor	N2	7727379	0	0	0	
6	CARBON MONOXIDE	Vapor	CO	630080	1	0	0	
7	CARBON DIOXIDE	Vapor	CO2	124389	-0.1	0	0	
8	WATER	Vapor	H2O	7732185	0	0	1	
9	NITRIC OXIDE	Vapor	NO	10102439	0	0	0	
10	NITROGEN DIOXIDE	Vapor	NO2	10102440	0	0	0	
11	AMMONIA	Vapor	H3N	7664417	0	0	0	
12	NITRIC ACID	Vapor	HNO3	7697372	0	0	0	
13	HYDROGEN	Vapor	H2	1333740	0	0	0	
14	METHANE	Liq I	CH4	74828	0	0	0	
15	OXYGEN	Liq I	O2	7782447	0	0	0	
16	NITROGEN	Liq I	N2	7727379	0	0	0	
17	CARBON MONOXIDE	Liq I	CO	630080	0	0	0	
18	CARBON DIOXIDE	Liq I	CO2	124389	0	0	0	
19	WATER	Liq I	H2O	7732185	0	0	0	
20	NITRIC OXIDE	Liq I	NO	10102439	0	0	0	
21	NITROGEN DIOXIDE	Liq I	NO2	10102440	0	0	0	
22	AMMONIA	Liq I	H3N	7664417	0	0	0	
23	NITRIC ACID	Liq I	HNO3	7697372	0	0	0	
24	HYDROGEN	Liq I	H2	1333740	0	0	0	
25	METHANE	Liq II	CH4	74828	0	0	0	
26	OXYGEN	Liq II	O2	7782447	0	0	0	
27	NITROGEN	Liq II	N2	7727379	0	0	0	
28	CARBON MONOXIDE	Liq II	CO	630080	0	0	0	
29	CARBON DIOXIDE	Liq II	CO2	124389	0	0	0	
30	WATER	Liq II	H2O	7732185	0	0	0	
31	NITRIC OXIDE	Liq II	NO	10102439	0	0	0	
32	NITROGEN DIOXIDE	Liq II	NO2	10102440	0	0	0	
33	AMMONIA	Liq II	H3N	7664417	0	0	0	
34	NITRIC ACID	Liq II	HNO3	7697372	0	0	0	
35	HYDROGEN	Liq II	H2	1333740	0	0	0	
36	Constraint Value (Right Hand Side) >= 0.0				1E-09	0.1	0.5	
37								
38	Total Number of Active Constraints		3					
39	Number of Equality Constraints		1					
40								

The equality constraint constrains the molar ratio of carbon monoxide to carbon dioxide to 10 % or 0.1 for the vapor phase only.

nCO/nCO2 = 0.1 or nCO – 0.1 nCO2 = 0.0

1 and -0.1 are shown for the equality constraint and the right hand side is set to 1.0E-9 to prevent nCO from going to 0.

These types of constraints are preferred to absolute constraints since the total number of moles can change depending on the initial number of moles/flow rate and chemical conversion.

The second constraint is an inequality constraint. It constrains the final number of carbon to 0.1 mole or greater. This is an absolute constraint and regardless of the starting number of moles, it will require that the equilibrium number of moles of carbon cannot be less than 0.1 mole.

nC >= 0.1

The third constraint is also an absolute non-equality constraint which constrains the final number of water moles to 0.5 or greater.

nH2O >= 0.5

The figure below shows that when the Gibbs free energy code is run, starting with two moles of fuel and oxidant, the following solution is returned. Note that the final number of carbon moles is 0.1 and the final number of water moles is 0.666 where both inequality

constraints are satisfied. Also note the ratio of CO/CO2 is 0.1 which satisfies the equality constraint.

This solution is a constrained equilibrium end state yielding a total energy release of -969.43 cal/g.

			Hazard Rating	Heat of reaction	Effective CHNT				
** Energy and Volume Change	** Heilken Index		HIGH	-969.43 cal/g	2498.63 K				
Overall enthalpy change. MJ	-2.2106E+02								
Overall enthalpy change of vessel metal. MJ	0								
Overall entropy change. MJ/C	-2.7709E-04								
Overall volume change. m3	0.091								
Overall enthalpy change. MJ/kg	-4.0561E+00								
Overall volume change. m3/kg	0.002								
Overall entropy change. MJ/C/kg	-5.0656E-06								
MI/Mi [vapor and liquid phases only]	1.01								
COMPOUND NAME	FORMULA	PHASE	INITIAL MOLES	CHANGE	FINAL MOLES	FUGACITY COEFFICIENT	FUGACITY, bara	PHASE MOLE FRACTION	INCLUDED IN DESTRUCTION EFFICIENCY ?
CARBON-REF	C	Solid	0.0000	0.1000	0.1000	1.0000	1.0000	1.0000	
METHANE	CH4	Vapor	0.3330	-0.3330	0.0000	0.9980	0.0000	0.0000	Yes
OXYGEN	O2	Vapor	0.6670	-0.5554	0.1116	0.9999	0.0562	0.0555	
NITROGEN	N2	Vapor	1.0000	0.0000	1.0000	1.0007	0.5043	0.4974	
CARBON MONOXIDE	CO	Vapor	0.0000	0.0212	0.0212	1.0012	0.0107	0.0105	
CARBON DIOXIDE	CO2	Vapor	0.0000	0.2118	0.2118	0.9946	0.1062	0.1054	
WATER	H2O	Vapor	0.0000	0.6660	0.6660	0.9878	0.3315	0.3312	
NITRIC OXIDE	NO	Vapor	0.0000	0.0000	0.0000	1.0008	0.0000	0.0000	
NITROGEN DIOXIDE	NO2	Vapor	0.0000	0.0000	0.0000	0.9886	0.0000	0.0000	
AMMONIA	H3N	Vapor	0.0000	0.0000	0.0000	0.9923	0.0000	0.0000	
NITRIC ACID	HNO3	Vapor	0.0000	0.0000	0.0000	0.9806	0.0000	0.0000	
HYDROGEN	H2	Vapor	0.0000	0.0000	0.0000	1.0032	0.0000	0.0000	
OTHER, < 0 moles			0.0000	0.0000	0.0000				
TOTALS			2.0000	0.1106	2.1106				
Destruction Efficiency					100.0000 Percent				
C -> CO2 Efficiency					63.6096 Percent				

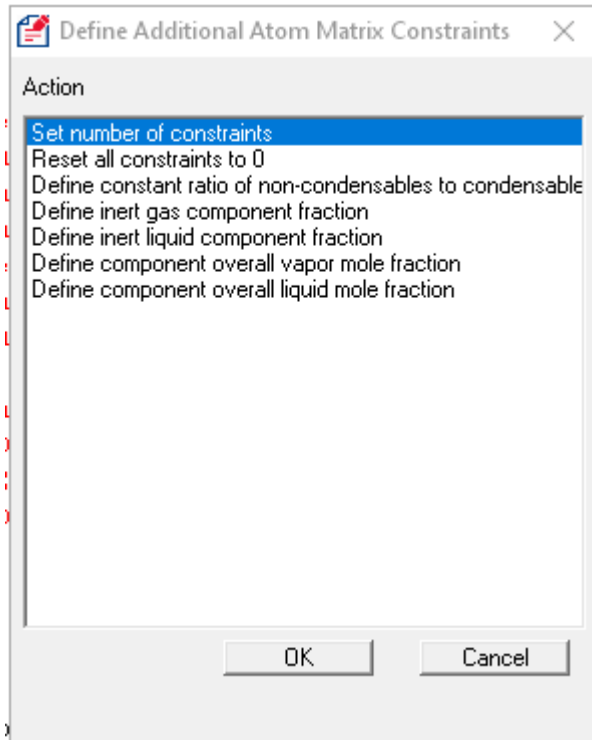
Were the user to run the calculation without the additional constraints, the figure below shows the following equilibrium estimate for the final state.

			Hazard Rating	Heat of reaction	Effective CHNT				
** Energy and Volume Change	** Heilken Index		HIGH	-1167.59 cal/g	2532.69 K				
Overall enthalpy change. MJ	-2.6722E+02								
Overall enthalpy change of vessel metal. MJ	0								
Overall entropy change. MJ/C	-1.8199E-03								
Overall volume change. m3	-0.185								
Overall enthalpy change. MJ/kg	-4.8852E+00								
Overall volume change. m3/kg	-0.003								
Overall entropy change. MJ/C/kg	-3.3271E-05								
MI/Mi [vapor and liquid phases only]	1.00								
COMPOUND NAME	FORMULA	PHASE	INITIAL MOLES	CHANGE	FINAL MOLES	FUGACITY COEFFICIENT	FUGACITY, bara	PHASE MOLE FRACTION	INCLUDED IN DESTRUCTION EFFICIENCY ?
CARBON-REF	C	Solid	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	
METHANE	CH4	Vapor	0.3330	-0.3330	0.0000	0.9981	0.0000	0.0000	Yes
OXYGEN	O2	Vapor	0.6670	-0.6660	0.0010	1.0001	0.0005	0.0005	
NITROGEN	N2	Vapor	1.0000	0.0000	1.0000	1.0009	0.5071	0.5000	
CARBON MONOXIDE	CO	Vapor	0.0000	0.0000	0.0000	1.0014	0.0000	0.0000	
CARBON DIOXIDE	CO2	Vapor	0.0000	0.3330	0.3330	0.9945	0.1670	0.1665	
WATER	H2O	Vapor	0.0000	0.6660	0.6660	0.9875	0.3332	0.3330	
NITRIC OXIDE	NO	Vapor	0.0000	0.0000	0.0000	1.0010	0.0000	0.0000	
NITROGEN DIOXIDE	NO2	Vapor	0.0000	0.0000	0.0000	0.9884	0.0000	0.0000	
AMMONIA	H3N	Vapor	0.0000	0.0000	0.0000	0.9921	0.0000	0.0000	
NITRIC ACID	HNO3	Vapor	0.0000	0.0000	0.0000	0.9800	0.0000	0.0000	
HYDROGEN	H2	Vapor	0.0000	0.0000	0.0000	1.0035	0.0000	0.0000	
OTHER, < 0 moles			0.0000	0.0000	0.0000				
TOTALS			2.0000	0.0000	2.0000				
Destruction Efficiency					100.0000 Percent				
C -> CO2 Efficiency					100.0000 Percent				

Note the total energy release is -1167.59 cal/g and the stoichiometry is different, as the number of C moles and CO moles is zero.

e Specify atom matrix con...

SuperChems™ provides a simple additional utility that can populate the constraints from some typical situations.



These new features in SuperChems™ should prove very useful when dealing with multiphase reactions or VLLE systems. Please note that absolute constraints should be avoided unless the user is clearly aware of the starting number of moles and how that compares to the absolute constraint value(s). It is preferred to create constraints that are relative to either the total number of moles in one or more phases, or a specific component, etc.

Questions?

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