

Technology Updates > News > Coming Soon: Capability to Constrain Multiphase Equilibrium Calculations

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.

	🚰 Specify Numeric Value	×
ſ	Number of compounds	11.
	Number of solids	1.
	Number of total additional atom matrix constraints (equality + inequality)	3.
L	Number of atom matrix equality constraints	1.
)		OK Cancel

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.

A	В	C	D	E	F	G
Name	Phase	Formula	CAS#	C1 =	C2 >=	C3 >=
CARBON-REF	Solid	c	7440440	0	1	0
METHANE	Vapor	CH4	74828	0	0	0
OXYGEN	Vapor	02	7782447	0	0	0
NITROGEN	Vapor	N2	7727379	0	0	0
CARBON MONOXIDE	Vapor	CO	630080	1	0	0
CARBON DIOXIDE	Vapor	C02	124389	-0.1	0	0
WATER	Vapor	H20	7732185	0	0	1
NITRIC OXIDE	Vapor	NO	10102439	0	0	0
NITROGEN DIOXIDE	Vapor	N02	10102440	0	0	0
AMMONIA	Vapor	H3N	7664417	0	0	0
NITRIC ACID	Vapor	HN03	7697372	0	0	0
HYDROGEN	Vapor	H2	1333740	0	0	0
METHANE	Liq I	CH4	74828	0	0	0
OXYGEN	Liq I	02	7782447	0	0	0
NITROGEN	Liq I	N2	7727379	0	0	0
CARBON MONOXIDE	Lig I	CO	630080	0	0	0
CARBON DIOXIDE	Liq I	C02	124389	0	0	0
WATER	Lig I	H20	7732185	0	0	0
NITRIC OXIDE	Liq I	NO	10102439	0	0	0
NITROGEN DIOXIDE	Liq I	N02	10102440	0	0	0
AMMONIA	Liq I	H3N	7664417	0	0	0
NITRIC ACID	Liq I	HN03	7697372	0	0	0
HYDROGEN	Liq I	H2	1333740	0	0	0
METHANE	Lig II	CH4	74828	0	0	0
OXYGEN	Liq II	02	7782447	0	0	0
NITROGEN	Liq II	N2	7727379	0	0	0
CARBON MONOXIDE	Lig II	CO	630080	0	0	0
CARBON DIOXIDE	Liq II	C02	124389	0	0	0
WATER	Liq II	H20	7732185	0	0	0
NITRIC OXIDE	Liq II	NO	10102439	0	0	0
NITROGEN DIOXIDE	Liq II	N02	10102440	0	0	0
AMMONIA	Lig II	H3N	7664417	0	0	0
NITRIC ACID	Lig II	HN03	7697372	0	0	0
HYDROGEN	Liq II	H2	1333740	0	0	0
Constraint Value (Right Hand Side) >= 0.0				1E-09	0.1	0.5
Total Number of Active Constraints		3				

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.

Point Detard Batting Hold of reactions Effective CMB7 Image: Control of the Cont	149	ranks makes on mores, agains	4+14								
0 ** Restry and Volues Change ** Restreme Index 10024 -969, 4) eal/g 2498, 53 K <th>29</th> <th></th> <th></th> <th>Hazard Rating</th> <th>Heat of reaction</th> <th>Effective CRRT</th> <th></th> <th></th> <th></th> <th></th> <th></th>	29			Hazard Rating	Heat of reaction	Effective CRRT					
11 -1.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2.21085+02 -2	30	** Energy and Volume Change	** Belhen Index	HDGH	-969.43 cml/g	2498.63 K					
12 Oversall exclusing changes, B7 -2.1086403 30 Oversall exclusing changes, B7 -2.70025-04 41 Oversall exclusing changes, B7/C -2.70025-04 55 Oversall exclusing changes, B7/C -0.0512 70 Oversall exclusing changes, B7/C -0.0552 71 Oversall exclusing changes, B7/C -0.0552 70 Oversall exclusing changes, B7/C Fillet B0125 70 Oversall exclusing changes exclusing chan	31										
3) Overall exclusing change of vessel setal. 89 0 4) Overall exclusing change. 8/c -2.7092-04 5) Overall vestel exclusion change. 8/c 0.692 6]	32	Overall enthalpy change, BJ	-2.2186E+02								
14 Oversall excernge changes. B1/C -2.7002E-04 <th>33</th> <th>Overall enthalpy change of vessel metal. HJ</th> <th>0</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	33	Overall enthalpy change of vessel metal. HJ	0								
35 Overall volume change. a) 0.921 36 -4.05512-00 -4.05512-00 37 Overall volume change. B/Ag 0.602 39 Overall volume change. B/Ag 0.602 30 RC/R1 (voreall exchange. B/Ag 0.602 41 Composition of the states on th	34	Overall entropy change. BJ/C	-2.7709E-04								
36 37 Overall excharge charge. NJ/kg -4.05512e00 38 Overall excharge charge. NJ/kg -5.0552 -6.0552 39 Overall excharge charge. NJ/kg -5.0552 -6.0552 39 Overall excharge charge. NJ/kg -5.0552 -6.0552 30 Processil excharge charge. NJ/kg -5.0552 -6.0552 30 Processil excharge charge. NJ/kg -5.0552 -6.0555 30 Processil excharge charge. NJ/kg -5.0555 -6.0555 30 Processil excharge charge. NJ/kg -5.0555 -6.0555	35	Overall volume change, m3	0.091								
37 Overall excharge thatage. BA/bg -4.055125-00 38 Overall exclave thatage. BA/bg 0,002 39 -5.05525-64 -5.05525-64 40 BC/B: (vegee contained that and the second the second that and the second the second the second the second the second the second the sec	36										
B Operatil vesitier change, h3/ng 0,002 9) Overali vesitier change, h3/ng -5,055E-66 -5,055E-66 9) R/R21 (vesice and liquid phases only) 1,00 - 1	37	Overall enthalpy change, BJ/kg	-4.0561E+00								
39 Operating stategy states on 110016 bases on 120 -5.0558-66 All States on 110016 bases on 120 FULL States on 110016 bases on 120 FULL States on 120 FULL St	38	Overall volume change, m3/kg	0,002								
00 EXC20: (respect and liquid phases only) 1.0. 1	39	Overall entropy change. BJ/C/kg	-5.0656E-06								
Image: state	40	Nf/Ni (vapor and liquid phases only)	1.01								
Control Number Prise Part La Billes Charge PDIACT TY Control PDIACT TY DiacT TY Control PDIACT TY DiacT	41										
Image: style		COMPOUND NAME	FORMULA	PRASE	INITIAL HOLES	CHANGE	FINAL MOLES	FUGACITY	FUGACITY. baca	PHASE BOLE	INCLUDED IN
All EFFECTATION EFFECTATION 44 (Absel-HEF) 0,0000 0,1000 0,1000 1,0000 1,0000 45	42							CONFERENCE		PRACTION	DESTRUCTION
43	1.00										ENALCIENCA 5
144 (Listed-leff) C 5x1x8 0.0000 0.1000 0.1000 1.0000 1.0000 45	43										
45 46 INTERNARC CE4 Yapet 0,3330 -0.3330 0,0000 0,0000 0,0000 Yes 47 CONTREN 02 Yapet 0,6470 -0.5554 0,1114 0,9999 0,0542 0,0555	144	CAREON-REP	¢	30116	0.0000	0.1000	0.1000	1.0000	1.0000	1.0000	
46 TRTMAR CR4 V mpcc 0.3330 -0.0330 0.0000 0.9998 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.00000 0.00000 0.00000 </th <th>45</th> <th>1</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	45	1									
47 0070EN 02 Vapor 0.6670 -0.5554 0.1116 0.9999 0.0562 0.0555	46	RETHANK	C84	Vapor	0,3330	-0,3330	0.0000	0.9980	0.0000	0.0000	Tes
	47	CORFGEN	02	Vapoc	0.6670	-0.5554	0.1116	0.9999	0.0562	0.0555	
48 NITROEN N2 Vage: 1.0000 0.0000 1.0007 0.5043 0.4974	48	NITROGEN	82	Vapoc	1.0000	0.0000	1.0000	1.0007	0.5043	0.4974	
49 CASEON MINOCIDE CO Vapor 0.0000 0.0212 0.012 0.012 0.0107 0.0105	49	CARBON MONCOLDE	C0	Vapoc	0.0000	0.0212	0.0212	1.0012	0.0107	0.0105	
50 CAPBON DEDUIDE C02 Vapor 0.0000 0.2118 0.2118 0.9946 0.1062 0.1054	50	CARBON DESCIDE	002	Vapoc	0.0000	0.2118	0.2118	0.9946	0.1062	0.1054	
51 WATER H20 Vapoc 0.0000 0.6660 0.6660 0.9078 0.3315 0.3312	51	WATER	820	Vapoc	0.0000	0.6660	0.6660	0.9878	0.3315	0.3312	
52 NITRIC OXIDE NO Vapoε 0.0000 0.0000 1.0008 0.0000 0.0000	52	NITRIC COLDE	80	Vapor	0.0000	0.0000	0.0000	1.0008	0.0000	0.0000	
53 NITROGEN DIGUIDE NO2 Vapor 0.0000 0.0000 0.0000 0.9866 0.0000 0.0000	53	NITROGEN DIGCIDE	802	Vapoc	0.0000	0.0000	0.0000	0.9886	0.0000	0.0000	
54 ATERINITA H38 Vapoc 0.0000 0.0000 0.0000 0.9923 0.0000 0.0000	54	AMMONIA	838	Vapoc	0.0000	0.0000	0.0000	0.9923	0.0000	0.0000	
55 NITRIC ACID ΝΝ03 Υχροε 0.0000 0.0000 0.0000 0.0000 0.0000	55	NITRIC ACID	8003	Vapoc	0.0000	0.0000	0.0000	0.9806	0.0000	0.0000	
56 INTERCER N2 Vaper 0.0000 0.0000 1.0032 0.0000 0.0000	56	NUDROGEN	82	Vapoc	0.0000	0.0000	0.0000	1.0032	0.0000	0.0000	
57	57										
58 (THER. < 0 holes 0.0000 0.0000	58	OTNER. < 0 moles			0.0000	0.0000	0.0000				
59	59										
60 TUTALS 2.0000 0.1106 2.1106	60	TOTALS			2,0000	0.1106	2.1106				
61	61										
C Destruction Efficiency 100.0000 Percent	62	Destruction Efficiency				100.0000	Percent				
63 C → CO2 Efficiency 63.6096 Percent	63	C -> CO2 Efficiency				63,6096	Percent				
64	64										

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

	19	-		Mazard Rating	Neat of reaction	Effective CMT					
B	10 ·	* Energy and Volume Change	** Briben Index	NEGH	-1167.59 cal/g	2532.69 K					
	11										
E	12	Overall enthalpy change, BJ	-2.67228+02								
в	13	Overall enthalpy change of vessel actal, 32	0								
B	14	Overall entropy change. \$2/C	-1.01998-03								
B	15	Overall volume change, all	-0,185								
B	16										
B	17	Overall enthalpy change, BJ/kg	-4,8852E+00								
в	18	Overall volume change, m3/kg	-0,003								
В	19	Dvezall entropy change. B1/C/kg	-3.32718-05								
Į.	10	EC/W1 [vapor and liquid phases only]	1,00								
	11										
E		CORFOUND MARK	FORMULA	PEATE	INITIAL BOLES	CEARCE	FINAL MOLES	POSACITY	FUGACITY, bara	PRASE BOLE	ENCLUDED IN
1	×							CORPTICIENT		19ACTION	DESTRUCTION
5	11										Contract 7
Æ	× 1	1100/00-007		84114	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	
1				20110							
Т	10	WITH LAW	(264	Vania	0.1110	-0.3330	0.0000	0.9981	0.0000	0.0000	Tes
E	6	NOV CALL AND A DECIMAL AND A D	62	Vanis	0.6670	-0.6660	0.0010	1,0001	0.0004	0.0005	
E		NTTR/VEW	87	Vanor	1.0000	0.000	1.0000	1,0003	0.5021	0.5000	
÷	61	CARDON NUMBER	-	Tanks	0.0000	0.0000	0.0000	1,0014	0.0000	0.0000	
6	6	CASHON BARYTAN	000	Vanor	0.0000	0.0000	0.3330	0.9945	0.1678	0.1665	
К	ũ.	TATES	820	Tanks	0.0000	0.6660	0.6660	0.9875	0.3332	0.3330	
	0	STRIC CODE	20	Yanos	0,0000	0,0000	0.0000	1,0010	0,0000	0.0000	
1B	6	NITROOMN DIGGIDE	802	Vapor	0,0000	0,0000	0,0000	0,9884	0,0000	0,0000	
I.	ù I	ANNOLTA	202	Tables	0.0000	0.0000	0.0000	0,9921	0,0000	0.0000	
	8	SITRIC ACID	1903	Vapor	0,0000	0,0000	0,0000	0,9800	0,0000	0,0000	
1	6	RTDBCGER	82	Vapor	0,0000	0,0000	0,0000	1,0035	0,0000	0.0000	
	17										
	58	OTHER, < 0 moles			0.0000	0.0000	0.0000				
ľ	10										
l	10	TOTALS			2.0000	0.0000	2.0000				
1	11										
1	12	Destruction Efficiency				100.0000	Percent				
1	13	C -> CO2 Efficiency				100,0000	Percent				
10.5											

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.



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?

To ask questions or get help from our highly trained technical support experts, please contact us at 1.844.ioMosaic or submit a ticket to our online support center. We'll be glad to assist.

ioMosaic is committed to leveraging the latest technology to maximize tool performance. Check back often to see the latest information about ioMosaic software and technology solutions.