ioMosaic®

Minimizing risk. Maximizing potential.®

DIERS Fall Meeting, Houston, October 2025

Chemical Reactivity Assessment Using Quantum Mechanical Methods

melhem@iomosaic.com

QMS_7.3_7.4.F06 Rev.11

ANAB ACCREDITED ISO/IEC 17021 MANAGEMENT SYSTEMS CERTIFICATION BODY

TÜV NORD TÜV USA Inc. ISO 9001:2015

Meet your presenter

- Over 35 years of Engineering and Process Safety Experience
- Pressure Relief and Flare Systems
- PRV Stability and Fluid Dynamics
- Chemical Reaction Systems
- Fire, Explosion, and Dispersion Dynamics
- Quantitative and Transportation Risk Analysis
- LNG, LPG, and Hydrogen Safety
- Process Safety Management
- Litigation Support and Public Testimony

Georges A. Melhem, Ph.D., *FAIChE*
President and CEO
melhem@ioMosaic.com

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Why are we interested in chemical reactivity screening and assessment?

Why do we need chemical reactivity screening?

It may not be practical to obtain an actual or sufficient chemical sample to test during early development

It may not be practical or cost effective to test large numbers of chemicals and/or chemical mixtures and/or contaminants

Screening can help to prioritize testing and to risk rank chemicals and chemical mixtures

Multiphase chemical equilibrium calculations can provide insight into maximum potential hazards and risks

Chemical interaction matrices can provide guidance about mixing and storage potential hazards and materials incompatibilities

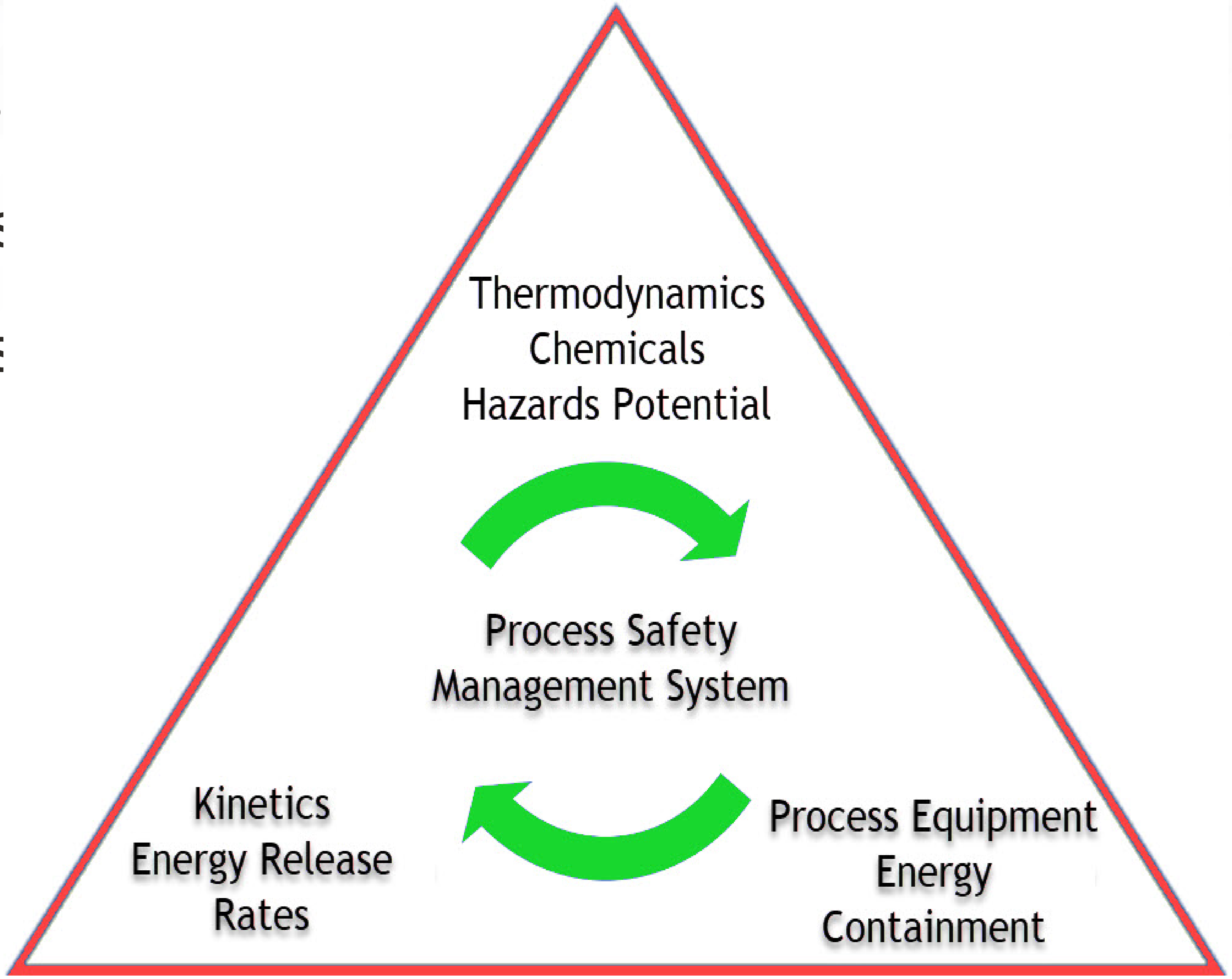
Is your facility vulnerable?

- Failure to identify and quantify runaway reactions hazards
- Undersized pressure relief systems for unintended chemical reactions
- Improper equipment selection and design
- Cooling systems that are susceptible to single point failure
- Process knowledge management
- Management of organizational change and succession planning
- Deficient process safety information (PSI) and SDS information
- Improper scaleup considerations by bench scale chemists

"We cannot manage chemical reaction hazards if we cannot first identify them"

Companies, toll manufacturers, and certified contract, development, and manufacturing organizations (CDMO) often use the same equipment for different chemistries or recipes

- Hazard potential of different chemicals and chemis
- Chemical reaction rates for both desired and undes
- Suitability of the process equipment to handle the s conditions and chemicals
- Robust process safety management system
- Adequate reactive chemicals technology transfer package



Source: ioMosaic Corporation

Thermochemistry can be used to determine chemical hazards potential, but, thermochemistry requires formation energies and heat capacities data

A reaction that is thermodynamically possible but lacks a rapid mechanism is said to be "*kinetically limited*"

$$\text{Reactants} \underset{k_r}{\overset{k_f}{\leftrightarrow}} \text{Products}$$

Many factors can drive a chemical reaction in either direction

$$K_{eq} = k_f / k_r$$

Quantity of Interest	Question	Methods
Degree of conversion	How complete is the reaction?	Thermochemistry Theoretical
Speed of conversion	How fast is the reaction?	Kinetics Measurements
Identity of components	What is the composition?	Equilibrium Constraints Measurements

Chemical reactions with higher thermodynamic potential are highly likely to have faster reaction rates

Given a sufficiently long duration and/or favorable process conditions, a chemical reaction can reach an equilibrium state

- Rate of product creation = Rate of product destruction
- The use of a catalyst can speed the approach to equilibrium but does not change the equilibrium

$$K_P = \frac{k_f}{k_r} = \frac{A_f \exp\left(-\frac{E_f}{R_g T}\right)}{A_r \exp\left(-\frac{E_r}{R_g T}\right)}$$

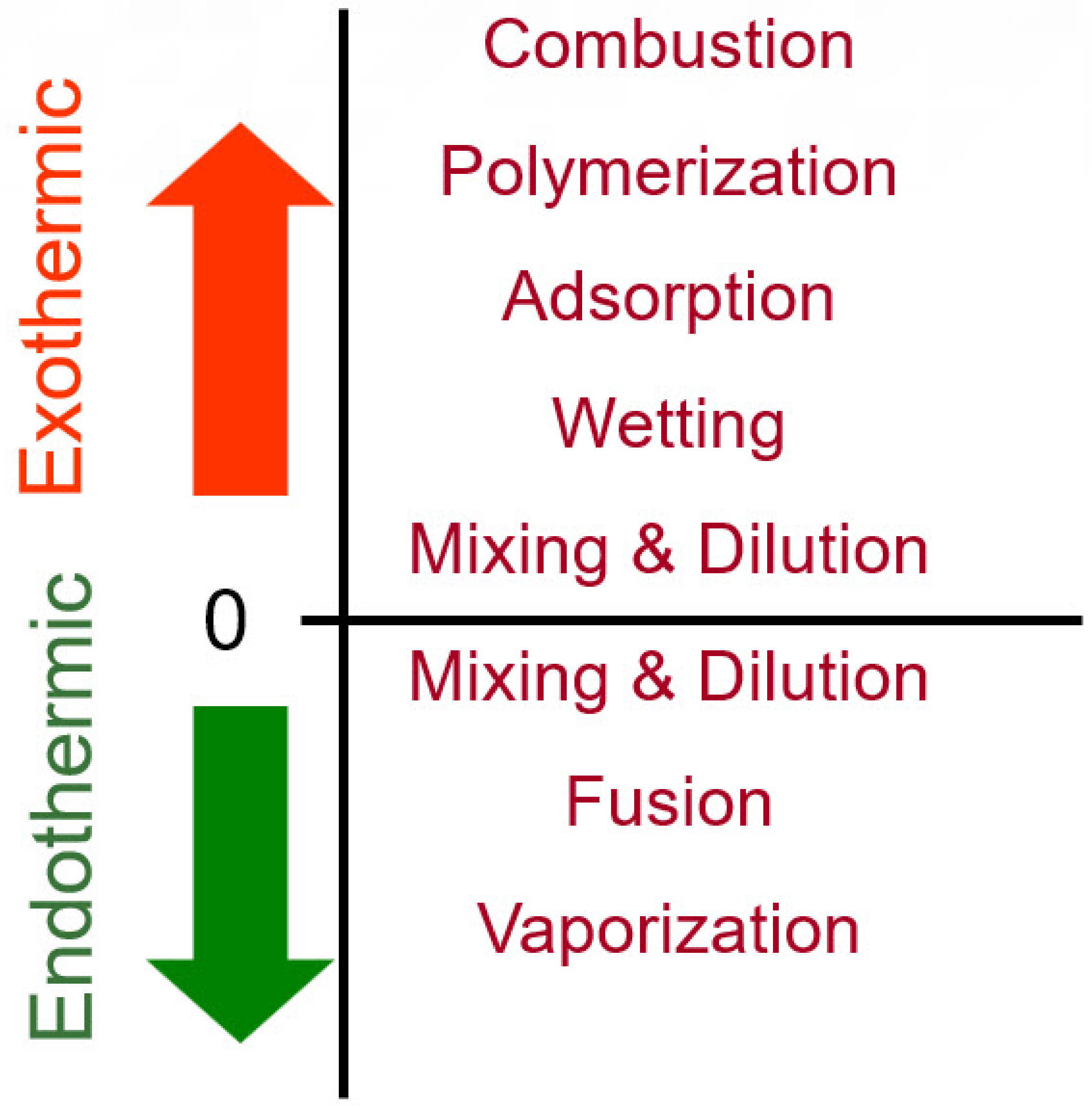
$$k = A \exp\left(-\frac{E}{R_g T}\right)$$

$$\ln K_p = \ln\left(\frac{A_f}{A_r}\right) + \frac{E_r - E_f}{R_g T}$$

$$\Delta S_{rxn} = R_g \ln\left(\frac{A_f}{A_r}\right)$$

$$\ln K_P = \frac{\Delta S_{rxn}}{R_g} - \frac{\Delta H_{rxn}}{R_g T}$$

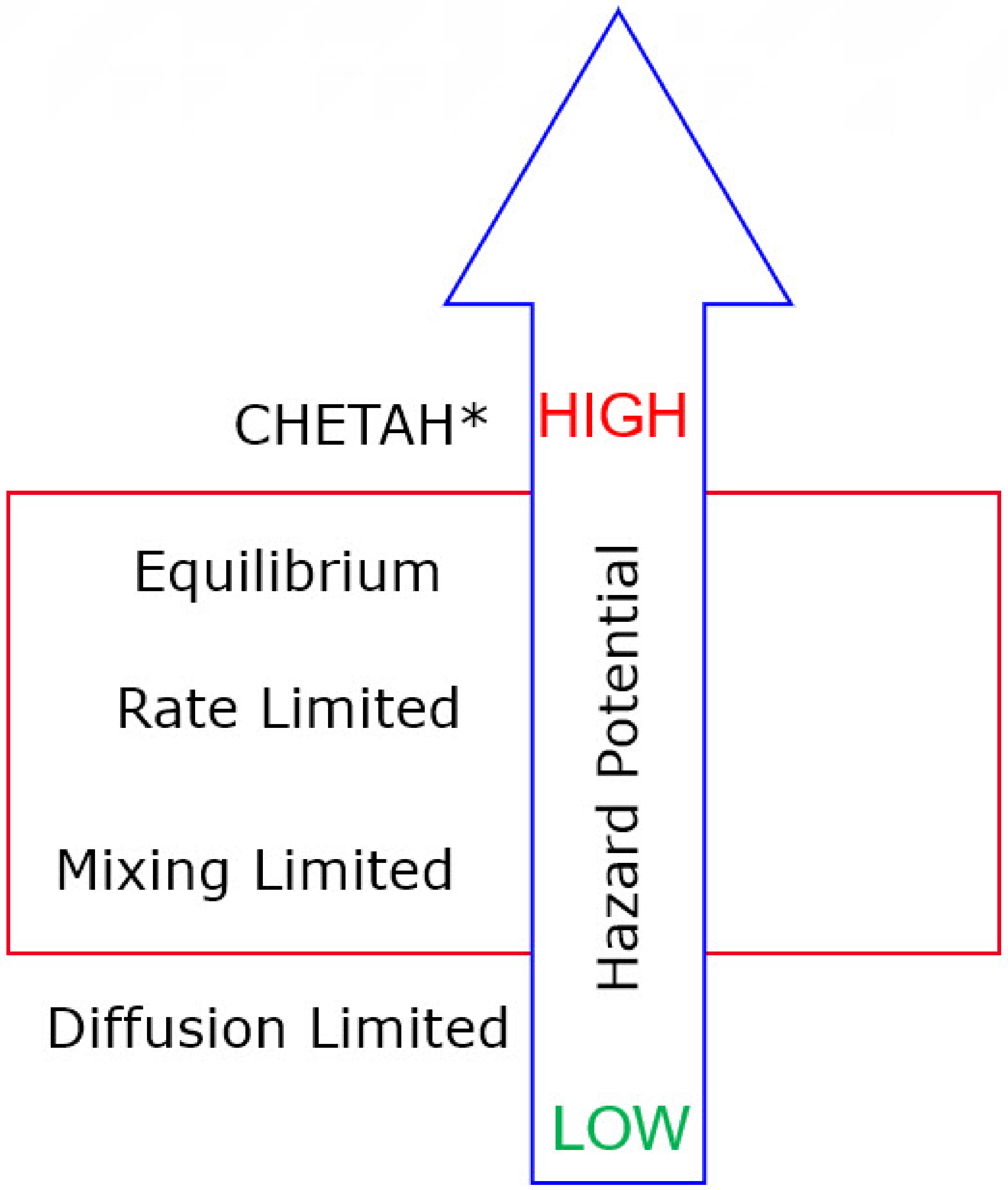
$$\Delta H_{rxn} = E_f - E_r$$



Source: ioMosaic Corporation

Kinetic rates and the equilibrium constant depend strongly on temperature

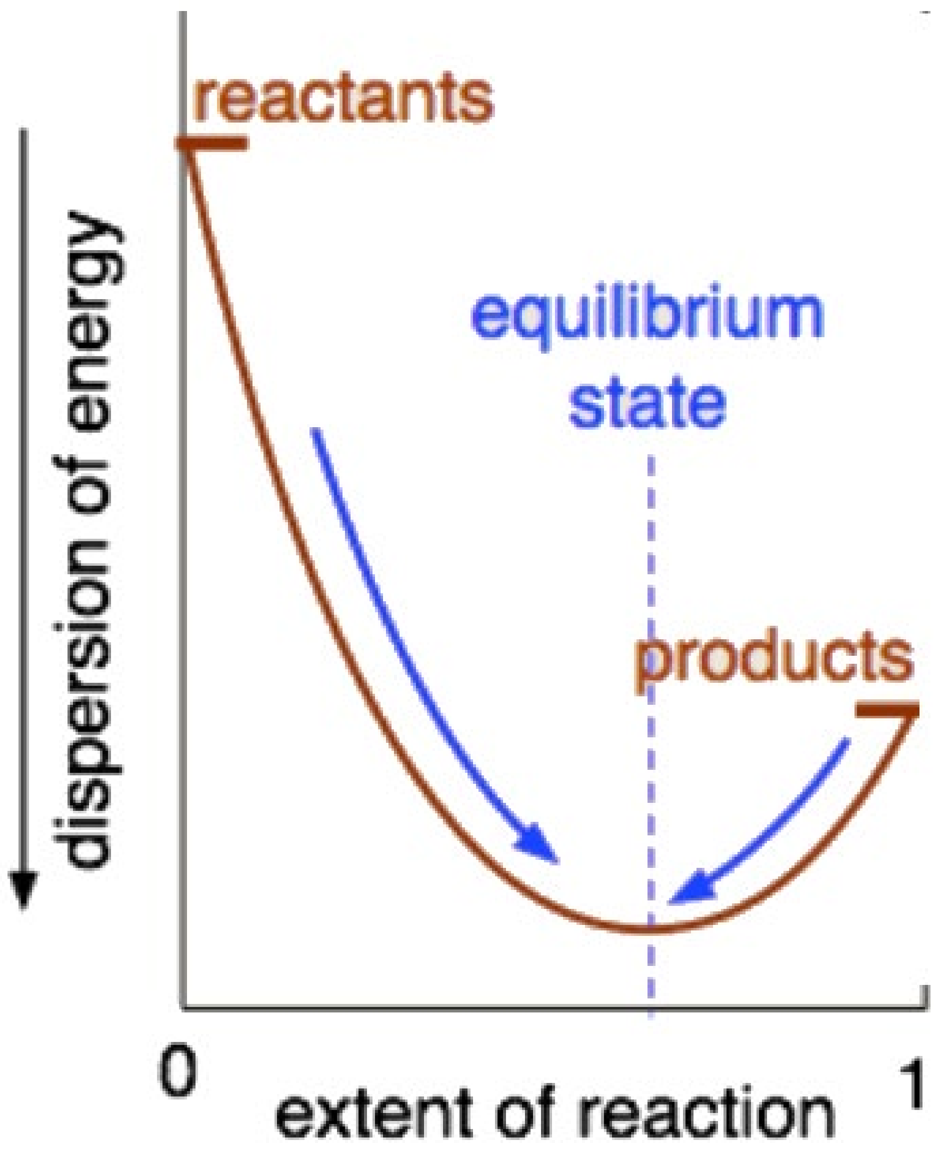
- Screen and rank potential reaction hazards using the computed equilibrium adiabatic reaction temperature (**CART**) obtained from direct minimization of the Gibbs free energy
- Estimate potential hazards of chemical reactions using the gas phase state
- **CART** values must be calculated using a chemical equilibrium software such as Process Safety Office® SuperChems® or the NASA computer code (include in CHETAH v11)



Source: ioMosaic Corporation

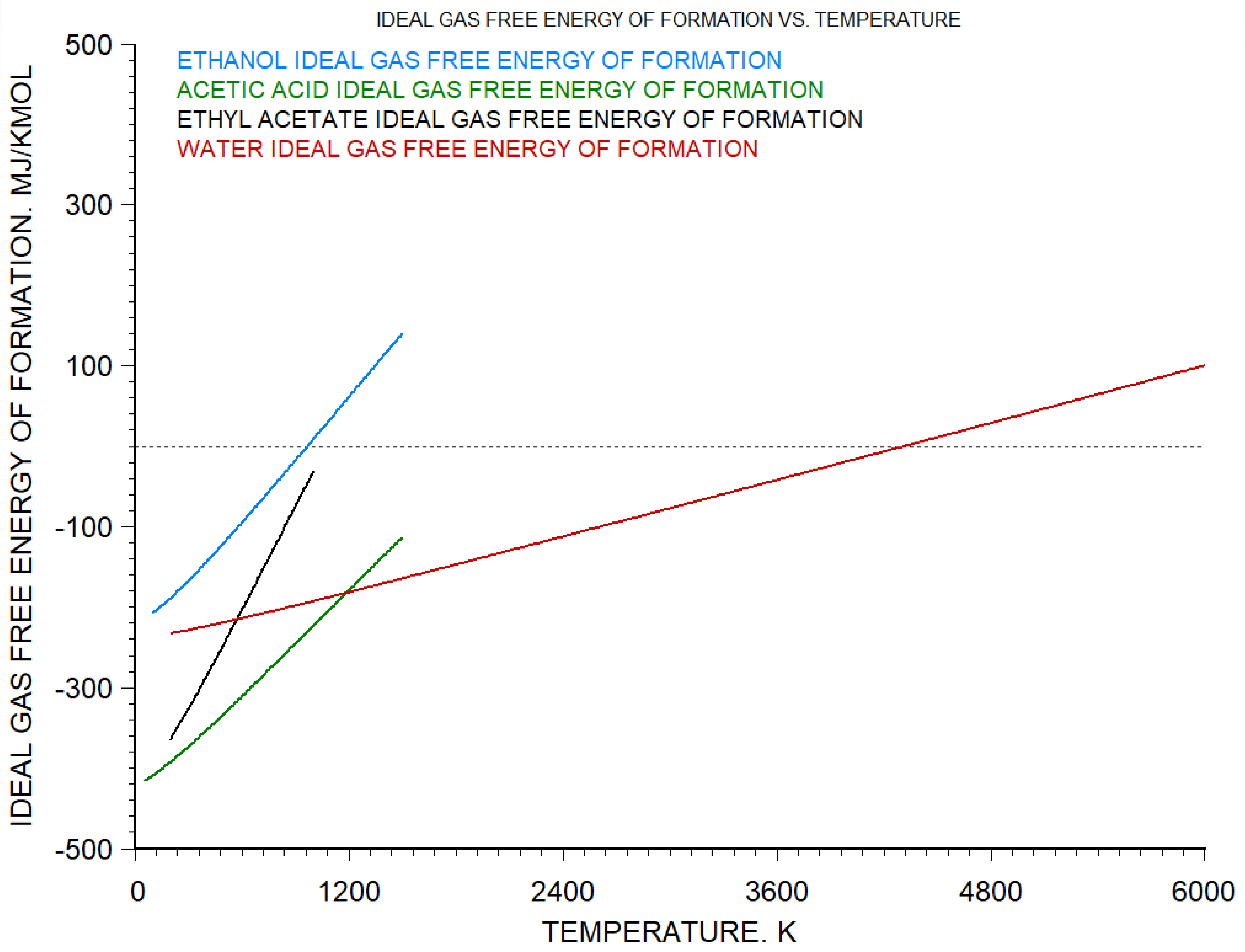
Direct minimization of the Gibbs free energy is the most effective method for calculating chemical equilibrium

- Can be used for multiphase systems (Solids, Liquids, Vapor)
- Can be constrained using limited measurements to aid in the development of reaction stoichiometry
- Can be used to screen the hazard potential of chemical reactions
- Requires an atom matrix
- Requires a large selection of potential reaction products
- Requires thermodynamic properties
- Difficult to solve for multiphase systems
- Equilibrium states are often flat and require accurate numerics



Source: ioMosaic Corporation

A thermodynamically consistent Gibbs free energy of each component must be provided at the system temperature



$$G_i^o(T) = -RT \ln K_i = \sum_{j=1}^{M} \nu_j G_{j,F}(T)$$

Source: Process Safety Office® SuperChems®

Although chemical equilibrium calculations can be multiphase, ideal gas phase estimates are sufficient for screening

```
SQP: 102, Fnew         -89.73501248, Fold         -89.73501248
SQP: 103, Fnew         -89.73501248, Fold         -89.73501248
NLP Exit Fmin = -89.735, 103 iterations, code = 1

Overall material balance:
```

Component Name		Initial kmol	Change kmol	Final kmol	Mole Fraction	Fugacity	Fugacity Coefficient
ETHANOL	(V)	4.90000E-01	-4.41522E-01	4.84783E-02	0.04848	4.7553E-02	9.8091E-01
ACETIC ACID	(V)	1.00000E-02	3.84783E-02	4.84783E-02	0.04848	4.6988E-02	9.6927E-01
ETHYL ACETATE	(V)	0.00000E+00	4.51522E-01	4.51522E-01	0.45152	4.3795E-01	9.6993E-01
WATER	(V)	0.00000E+00	4.51522E-01	4.51522E-01	0.45152	4.4690E-01	9.8977E-01
Totals:		5.00000E-01	5.00000E-01	1.00000E+00			
ETHANOL	(L1)	9.00000E-03	-9.00000E-03	-1.00000E-11	-0.00013	-2.4955E-04	1.9524E+00
ACETIC ACID	(L1)	4.41000E-01	-4.41000E-01	9.21074E-09	0.11773	3.3801E-02	2.8711E-01
ETHYL ACETATE	(L1)	0.00000E+00	6.52347E-10	6.52347E-10	0.00834	4.0644E-02	4.8744E+00
WATER	(L1)	0.00000E+00	6.83833E-08	6.83833E-08	0.87406	5.8901E-01	6.7388E-01
Totals:		4.50000E-01	-4.50000E-01	7.82364E-08			
ETHANOL	(L2)	1.00000E-03	-1.00000E-03	-1.00000E-11	-0.00012	-2.4082E-04	1.9887E+00
ACETIC ACID	(L2)	4.90000E-02	-4.90000E-02	9.51012E-09	0.11516	3.3322E-02	2.8935E-01
ETHYL ACETATE	(L2)	0.00000E+00	5.17021E-10	5.17021E-10	0.00626	3.1669E-02	5.0583E+00
WATER	(L2)	0.00000E+00	7.25631E-08	7.25631E-08	0.87870	5.8681E-01	6.6781E-01
Totals:		5.00000E-02	-4.99999E-02	8.25802E-08			
Overall Totals:		1.00000E+00	2.22045E-16	1.00000E+00			

```
Mass Balance = -3.47294788E-10, -3.47295E-09 percent.
Gibbs VLE Block Success = 1
```


Source: Process Safety Office® SuperChems®

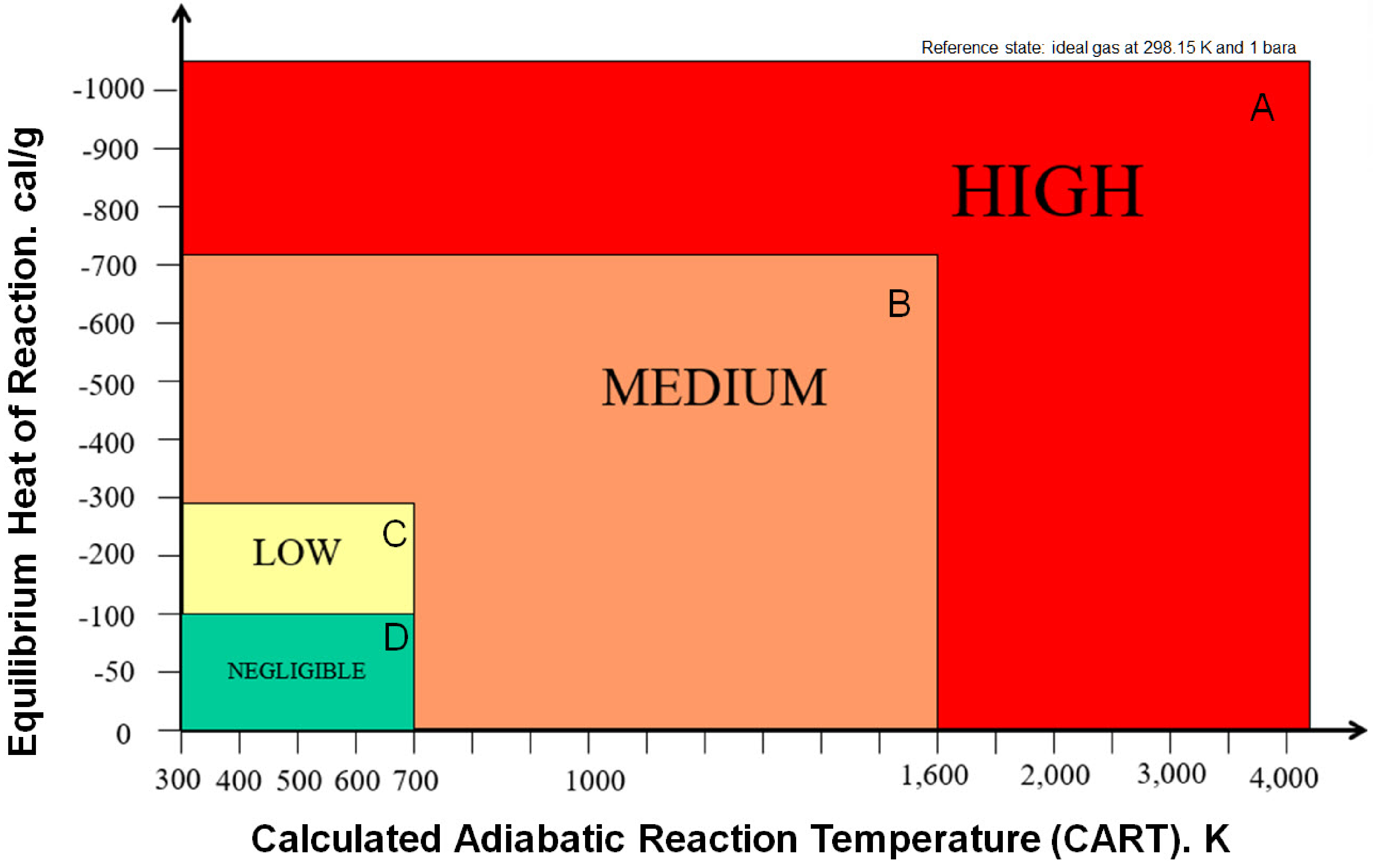
Since 1995 we have been conducting experimental and theoretical work to develop reliable chemical reaction hazard prediction methods

- **NEGLIGIBLE OR NO HAZARD group**:
  - Heat of reaction no more negative than -100 cal/g
- **LOW reactivity hazard group:**
  - Heat of reaction between -100 cal/g and -287 cal/g, and CART no more than 700 K
- **INTERMEDIATE hazard group:**
  - Heat of reaction between -287 cal/g and -717 cal/g, or CART greater than 700 K and less than 1,600 K
- **HIGH reactivity hazard group:**
  - Heat of reaction more negative than -717 cal/g, or CART higher than 1,600 K

The Melhem index is based on the heat of reaction and the computed equilibrium adiabatic reaction temperature (CART)

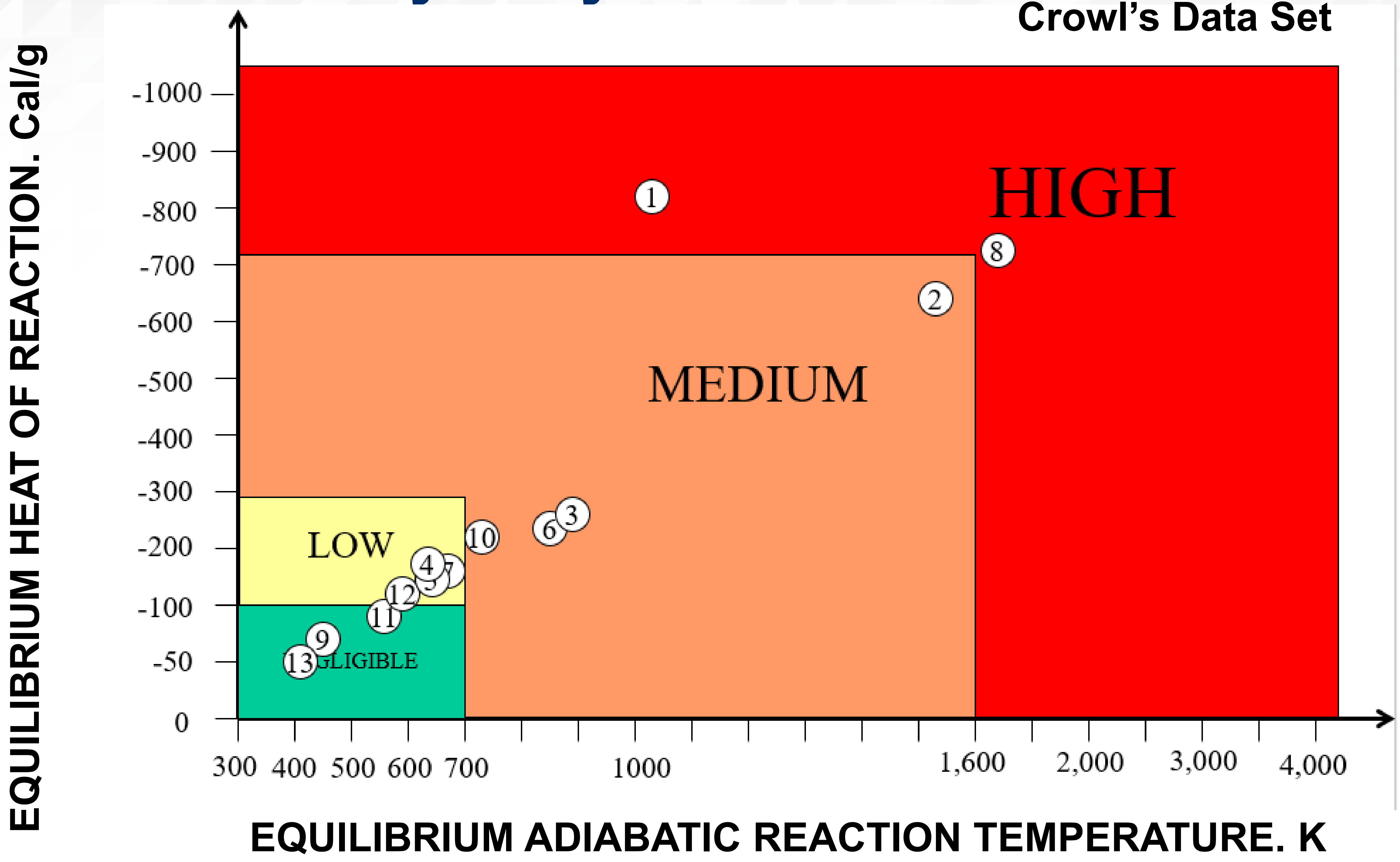
- Set starting number of moles
- Select potential reaction products based on chemical structure (auto select)
- Calculate equilibrium heat of reaction at 25 C and 1 bara and CART at 1 bara
- Scale the value of CART to **eCART**
- Rank chemicals within hazard index groups A, B, C, and D according to their **eCART** values

$$\text{eCART} = \text{CART} \times \left(\frac{Np}{Nr}\right)^{1/3}$$



Source: ioMosaic Corporation

The Melhem Reactivity Hazard Index has been demonstrated to work on a variety of systems



Reference state: ideal gas at 298.15 K and 1 bar

Source: ioMosaic Corporation

The development of a chemical interaction matrix can provide insight into which mixture of chemicals may have a higher reactivity potential before detailed chemical equilibrium calculations

Reactivity Expert >> VA-MATRIX Mixture Summary - C:\IOIQ\PSO8.4\SuperChems\BANKS\hzdbanks_v8.5.dat

Chemical Hazard Report | Chemical Interaction Matrix | Chemical Interaction Listing | Glossary

Chemical Incompatibility Matrix For Mixture VA-MATRIX

		VINYL ACETATE	OXYGEN	WATER	IRON	n-HEXANE
		A	B	C	D	E
VINYL ACETATE	A	400	200, 300, 402, 403, 105	300, 204, 402	300, 204, 400, 200, 403, 105	300, 200, 403
OXYGEN	B			204, 300	300, 200, 403, 105	200, 300
WATER	C				300, 204, 402	204, 300
IRON	D				302, 902	300, 200, 403
n-HEXANE	E					

105	May form explosive peroxides
200	May cause fire
204	Flammable gas generation
300	Heat generation by chemical reaction
302	Water reactive
400	May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction, causes pressurization
402	Contact with substances liberate toxic gas; causes pressurization
403	Innocuous and non-flammable gas generation; causes pressurization
900	Materials are compatible
902	Thermodynamically unstable

Source: Process Safety Office® SuperChems®

How to screen and rank multiple recipes?

- First develop a chemical interaction matrix to determine the mixture reactivity potential of each recipe or mixture
- The chemical interaction matrix should include expected contaminants such as water, rust, heat transfer fluids, chlorides, etc.
- Include any cleaning solvent/solution that may be used in between products and consider materials of construction issues
- Calculate the Melhem index for mixtures and for all individual components
- The mixture(s) or chemical(s) that yield the highest value of the Melhem Index can then be subjected to further reactivity screening testing

Formation energies are needed for chemical reactivity screening and assessment

In general, formation energies in the ideal gas phase are sufficient to evaluate hazard potential

$$
\begin{aligned}
\Delta H_{f,l} &= \Delta H_{f,g} - \Delta H_{\text{vaporization}} \\
\Delta H_{f,s} &= \Delta H_{f,g} - \Delta H_{\text{vaporization}} - \Delta H_{\text{fusion}} = \Delta H_{f,l} - \Delta H_{\text{fusion}} \\
&= \Delta H_{f,g} - \Delta H_{\text{sublimation}}
\end{aligned}
$$

Phase change (fusion, vaporization, sublimation) energies are typically small compared to the formation energy absolute values

Formation energy data must be thermodynamically consistent before use in simulation software such as SuperChems®

$$\Delta G_{f_{298.15K}} = \Delta H_{f_{298.15K}} - 298.15 \left[S_{o_{298.15K}} - \sum_i n_i s_{o_{i_{298.15K}}} \right]$$

$$S_{o_{298.15K}} = \frac{\Delta H_{f_{298.15K}} - \Delta G_{f_{298.15K}}}{298.15} + \sum_i n_i s_{o_{i_{298.15K}}} \quad \text{or}$$

$$\Delta H_{f_{298.15K}} = \Delta G_{f_{298.15K}} + 298.15 \left[S_{o_{298.15K}} - \sum_i n_i s_{o_{i_{298.15K}}} \right]$$

We can estimate heat of formation energies using one or more of these methods

- Group contribution methods or Quantum chemical calculations
- Heat of combustion measurements
- Heat of decomposition or reaction using adiabatic calorimetry measurements
- Heat of decomposition or reaction using differential scanning calorimetry measurements

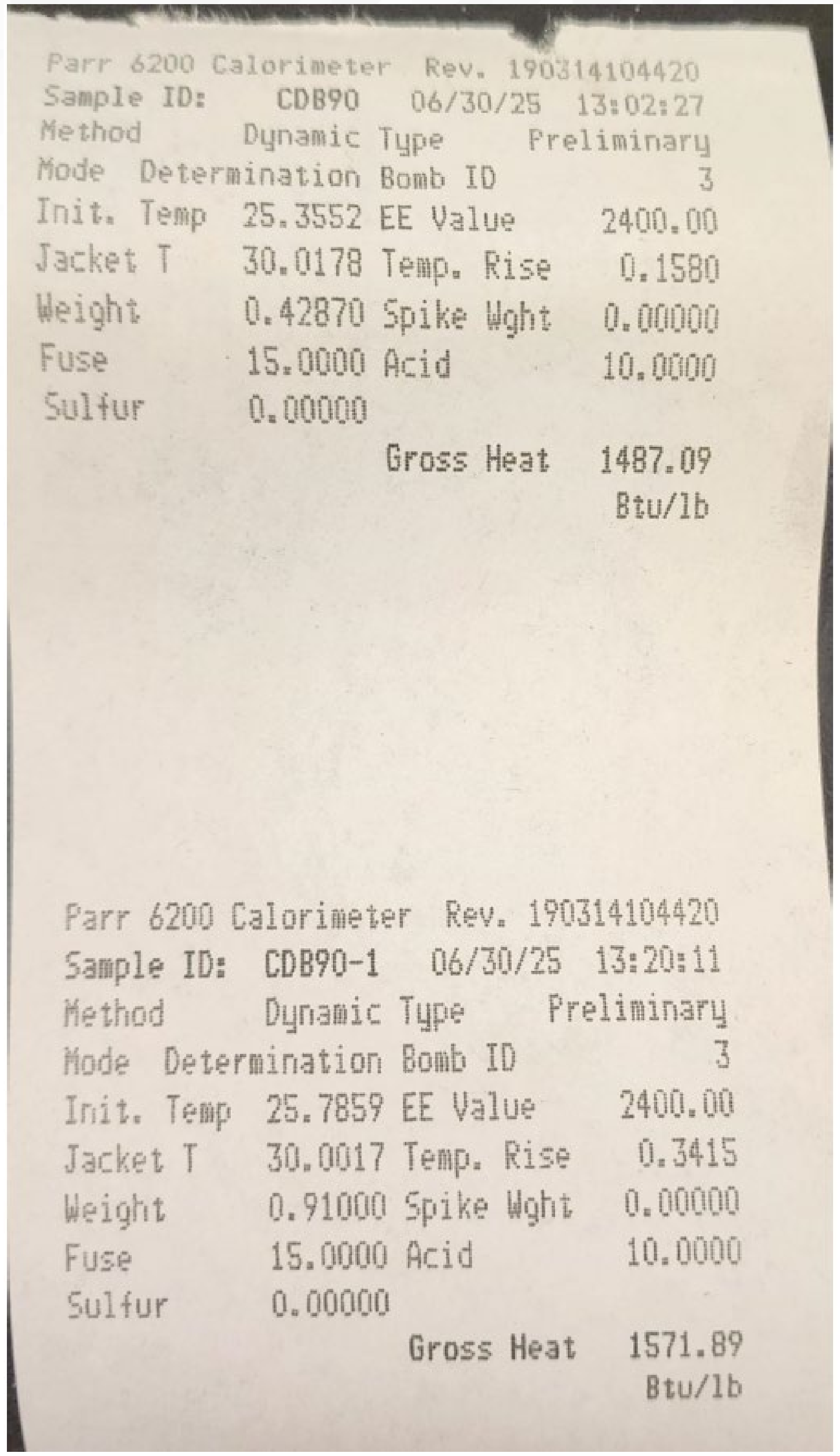
Chemical	Measured Heat of Combustion (MJ/kg) [BTU/lb]	CAS #
Benzoic Acid	26.53 [11419.8]	65-85-0
Nicotinic Acid	22.09 [9506.43]	59-67-6
Lycopodium	30.64 [13183.1]	8023-70-9

The heat of formation can be calculated from a measured heat of combustion using an instrument such as the Parr 6200 calorimeter

Source: ioMosaic Corporation

Using the measured heat of combustion, we can iterate to find the formation energies

- Calculate S_o and heat capacity data using quantum chemical software
- Guess the value of ΔH_f
- Calculate value of ΔG_f using S_o
- Run the SuperChems® Gibbs Equilibrium code until calculated heat of combustion matches the measured heat of combustion


Parr 6200 Calorimeter Rev. 190314104420
Sample ID: CDB90 06/30/25 13:02:27
Method Dynamic Type Preliminary
Mode Determination Bomb ID 3
Init. Temp 25.3552 EE Value 2400.00
Jacket T 30.0178 Temp. Rise 0.1580
Weight 0.42870 Spike Wght 0.00000
Fuse 15.0000 Acid 10.0000
Sulfur 0.00000
Gross Heat 1487.09
Btu/lb

Parr 6200 Calorimeter Rev. 190314104420
Sample ID: CDB90-1 06/30/25 13:20:11
Method Dynamic Type Preliminary
Mode Determination Bomb ID 3
Init. Temp 25.7859 EE Value 2400.00
Jacket T 30.0017 Temp. Rise 0.3415
Weight 0.91000 Spike Wght 0.00000
Fuse 15.0000 Acid 10.0000
Sulfur 0.00000
Gross Heat 1571.89
Btu/lb

Combustion reactions are fast and tend to reach an equilibrium end state

Source: ioKinetic

Typically, formation energies are estimated using group contribution methods

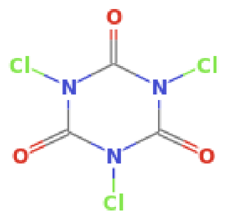
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
U.S. DEPARTMENT OF COMMERCE

NIST Chemistry WebBook, SRD 69

Search ▾ | NIST Data ▾ | About ▾

Symclosene

- **Formula:** $C_3Cl_3N_3O_3$
- **Molecular weight:** 232.409
- **IUPAC Standard InChI:** InChI=1S/C3Cl3N3O3/c4-7-1(10)8(5)3(12)9(6)2(7)11 InChI v 1.06
- **IUPAC Standard InChIKey:** YRIZYWQGELRKNT-UHFFFAOYSA-N
- **CAS Registry Number:** 87-90-1
- **Chemical structure:**



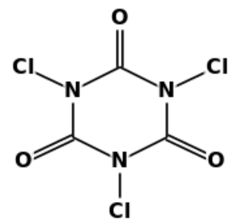
This structure is also available as a 2d Mol file or as a computed 3d SD file
View 3d structure (requires JavaScript / HTML 5)
- **Other names:** Trichloroisocyanuric acid; Trichlorocyanuric acid; 1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-trichlo trichloisokyanurova; N,N',N''-Trichloroisocyanuric acid; Symclosen; Trichlorinated isocyanuric acid; Trichloro-s-tria Trichloro-2,4,6-trioxohexahydro-s-triazine; 1,3,5-Trichloroisocyanuric acid; CBD 90; NA 2468; NSC-405124; UN 2468; Queschlor; Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-trichloro-; Trichloroiminocyanuric acid; Neochlor 90
- **Permanent link** for this species. Use this link for bookmarking this species for future reference.
- **Information on this page:**
  - Notes
- **Other data available:**
  - IR Spectrum
  - Mass spectrum (electron ionization)
- **Options:**
  - Switch to calorie-based units

Properties Database and Estimation Program, NIST:Gaithersburg, MD, 1991.

The software used by this model was developed by: *S.E. Stein*, *R.L. Brown*, and *Y.A. Mirokhin*.

Species Information

- Structure (2d):



- Chemical formula: $C_3Cl_3N_3O_3$
- Matching species in NIST Chemistry WebBook (stereochemistry ignored in matches)
  - Trichlorocyanuric acid

Information from the Structure

Quantity	Value
Total symmetry number	6
Extra symmetry from non-methyl R-HX rotors	1
Methyl groups	0
Assymetric carbon atoms	0
Optical isomer centers	1
Cis / trans groups	0
Cis groups	0
Gauche conformations	0
Ortho groups	0
Pyridine groups	0

Groups

Center	Attachments	Modified	Quantity	Increments								
				$\Delta_f H°_{gas,est}$ (kJ/mol)	$S°_{gas,est}$ (J/mol*K)	$Cp_{gas,est}$ (J/mol*K)						
						300. K	400. K	500. K	600. K	800. K	1000. K	1500. K
C=O	N N		3	Group not found.								
N	C=O C=O Cl		3	Group not found.								

Note: The "modified" column indicates if the group was modified to match a group for which data is available. This is done when data is not available for a specified gr is labeled as "yes", then a similar group has been used in place of the required group. For example, if the group C | $C_{a\text{-ring}}$ $C_{a\text{-ring}}$ H H is required but not available, the grc

Note: The group increments in this model are at best accurate to 0.5 kJ/mol (0.1 kcal/mol) for $\Delta_f H°_{gas}$, and 0.05 J/mol*K (0.01 cal/mol*K) for $S°_{gas}$ and Cp_{gas}.

Calculations Failed

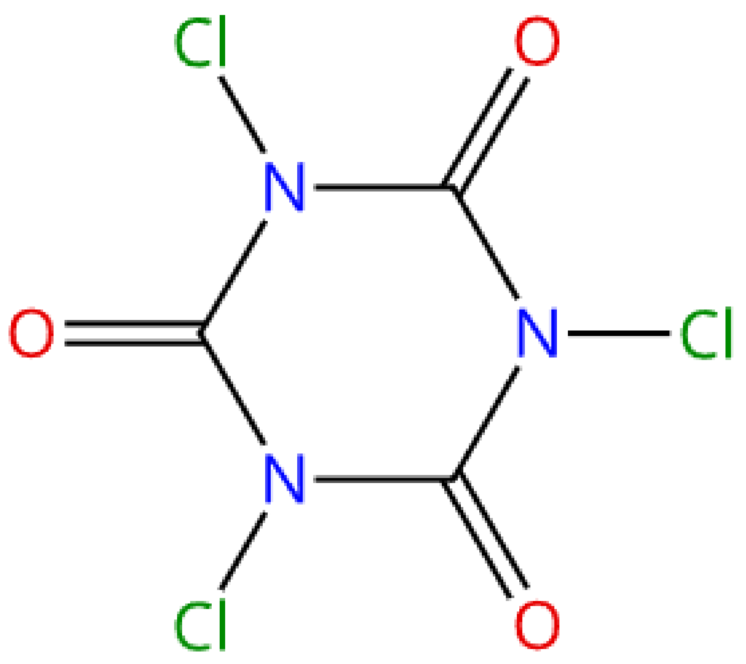
Unable to calculate estimates, the structure contains unrecognized groups.

Source: NIST Webbook

Let's consider trichloroisocyanuric acid (TCCA) as a test molecule

CAS Registry Number®

87-90-1



CAS Name

Trichloroisocyanuric acid

Molecular Formula

$C_3Cl_3N_3O_3$

Molecular Mass

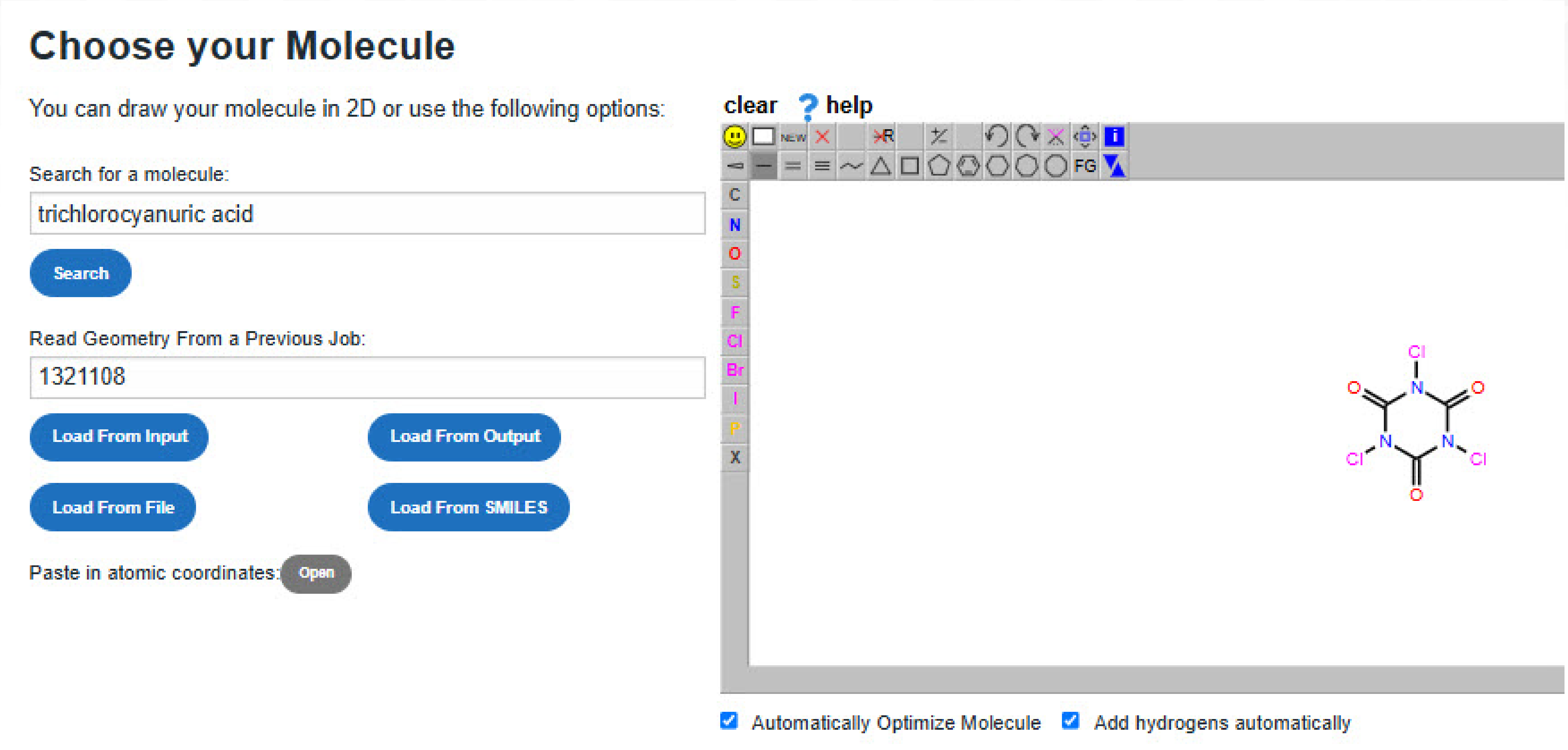
232.41

- Quantum chemical estimates for formation energies and absolute entropy were calculated using GAMESS
  - S_o = 430.435 kJ/gmol/K or 0.10288 kcal/gmol/K
  - ΔH_f = -1.831 x 10^{+8} J/kmol/K or -43.77 kcal/gmol or
- ΔG_f = Calculate using S_o and ΔH_f and SuperChems® reference elements:

$$\Delta G_{f_{298.15K}} = \Delta H_{f_{298.15K}} - 298.15 \left[S_{o_{298.15K}} - \sum_i n_i s_{o_{i_{298.15K}}} \right]$$

Source: ioMosaic Corporation

GAMESS provides an intuitive and easy to use interface



GAMESS provides an option for directly calculating formation energies (a very useful option)

Set Parameters for Quantum Mechanical Calculation

Reset Settings to Default

Select your package:	(●) GAMESS ( ) Psi4
Name for input file:	trichlorocyanuric acid
Comment:	
Charge:	0
Multiplicity:	1
Type:	( ) Single-Point Energy (●) Geometry Optimization ( ) Saddle Point Search
Add-Ons:	( ) IR ( ) Thermodynamics ( ) UV-Vis ( ) NMR ( ) Raman (●) ΔH_f (g3mp2) ( ) NBO (def2-tzpp) ( ) None

▲ g3mp2 ignores your basis set choice and automatically uses 6-31G(d), MP2, CCSD(T), and G3Large. You must use HF only, not DFT

Basis Set:	( ) AM1 ( ) PM3 ( ) PM6 ( ) STO-3G ( ) 3-21G (●) 6-31G* ( ) 6-311G** ( ) 6-311+G** ( ) aug-cc-pVDZ ( ) SPK-DZP
Molecular Orbital Method:	(●) RHF ( ) ROHF ( ) UHF
DFT Functional:	(●) None ( ) B3LYP ( ) PBE0 ( ) M06 ( ) wB97X-D
PCM Solvent:	(●) None ( ) Water ( ) Methanol ( ) Ethanol ( ) Acetone ( ) THF

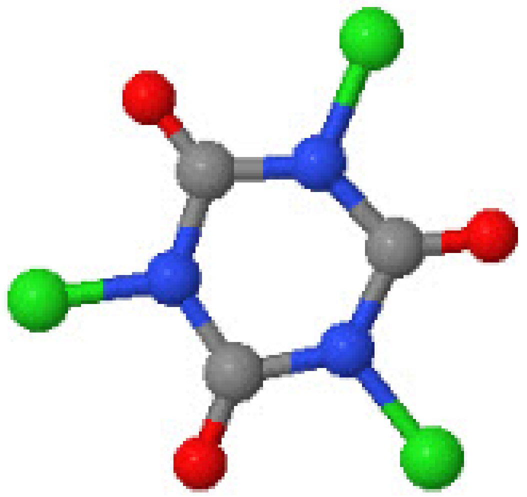
GAMESS provides heat of formation estimates but large molecules require long computation times and large computer memory

Summary | Real Time Output | Input File | Output File

Job 1321855 (Jetstream2) Success

```
trichlorocyanuric_acid g3mp2 6-31G*  neutral singlet

SUMMARY OF G3(MP2) CALCULATIONS (ENERGIES in au)
E(G3(MP2)) @ OK = -1882.803516   E(G3(MP2)) @298K = -1882.793354
HEAT OF FORMATION   (0K):      -41.13 KCAL/MOL
HEAT OF FORMATION (298K):      -43.77 KCAL/MOL
 EXECUTION OF GAMESS TERMINATED NORMALLY Sat Oct 18 15:41:04 2025
```



Energy Units: a.u.

Electronic Energy = -1882.4458 a.u.

Let's confirm the GAMESS predicted formation energies values using a heat of combustion test and SuperChems® Expert

	A	B
1	** Initial Conditions	
2		
3	Initial system temperature. C	25
4	Initial system pressure. psia	400
5		
6	** Final Conditions	
7		
8	Final system temperature. C	25
9	Final system pressure. psia	400
10		
11	☑ Consider a vapor phase ?	
12	☐ Consider a liquid phase I ?	
13	☐ Consider a liquid phase II ?	
14	☐ Generate automatic guess using linear programming ?	
15	☐ User specified guess	
16		
17	☐ Restrict estimate to VLE, LLE, and VLLE. No solids.	
18		
19	☑ Vary Final Temperature at User Defined Final Pressure	
20	☐ Vary Final Pressure at User Defined Final Temperature	
21	☐ Perform Constant Volume Estimate	
22	☑ Show stoichiometry of independent chemical reactions	

Gibbs Free Energy Minimization / Working Scenario = TCCA-THERMO, Expert []

	A	B	C	D
24	Vapor and Liquid Components	Formula	Initial Vapor. kmol	Initial Liquid I. kmol
25	TRICHLOROISOCYANURIC ACID	C3Cl3N3O3	0.5	
26	WATER	H2O	1E-06	
27	CYANURIC ACID	C3H3N3O3	0	
28	HYPOCHLOROUS ACID	ClHO	0	
29	NITROGEN TRICHLORIDE	Cl3N	0	
30	CARBON DIOXIDE	CO2	0	
31	NITROGEN	N2	0	
32	CHLORINE	Cl2	0	
33	HYDROGEN CHLORIDE	ClH	0	
34	HYDROGEN CYANIDE	CHN	0	
35	CYANIC ACID	CHNO	0	
36	NITROSYL CHLORIDE	ClNO	0	
37	PHOSGENE	CCl2O	0	
38	CYANOGEN CHLORIDE	CClN	0	
39	OXYGEN	O2	0.75	
40	CARBON MONOXIDE	CO	0	
41	CYANOGEN	C2N2	0	
42	ETHANE	C2H6	0	
43	METHANE	CH4	0	
44	NITRIC OXIDE	NO	0	
45	NITROGEN DIOXIDE	NO2	0	
46	NITROUS OXIDE	N2O	0	
47	AMMONIA	H3N	0	
48	METHYL CHLORIDE	CH3Cl	0	
49	Dichloromethylene	CCl2	0	
50	NITRYL CHLORIDE	ClNO2	0	
51	2-BUTYNEDINITRILE	C4N2	0	
52	NITROGEN TRIOXIDE	N2O3	0	
53	CHLORINE DIOXIDE	ClO2	0	
54	CARBONYL CHLORIDE	CClO	0	
55	NITROGEN TRIOXIDE (NO3)	NO3	0	
56	CHLORINE MONOXIDE	ClO	0	
57	Chloromethylidyne	CCl	0	
58	CNN RADICAL	CN2	0	
59	NCN RADICAL	CN2	0	
60	CNC RADICAL	C2N	0	
61	CCO RADICAL	C2O	0	
62	MONOCHLORAMINE	ClH2N	0	
63	DICHLORAMINE	Cl2HN	0	
64				
65	Solids Components	Formula	Initial. kmol	Guess Final. kmol
66	CARBON-REF	C	0	
67				

The types of calculations are only possible if the SuperChems® databanks contain thermochemical data for all potential reaction products

SuperChems® calculates all possible chemical reactions using the atom matrix and user defined constraints (when used)

```
Return Code = 1, Normal return

Scaled Gibbs free energy _____________________________        -185.48678

  +0.333 C3H3N3O3 +0.167 C2H6 <--->  + H2O +0.167 N2 +0.333 C4N2
  +0.667 C3H3N3O3 <--->  + CO2 +0.917 N2 +0.333 C2H6 +0.0833 C4N2
  +0.333 C3H3N3O3 +0.333 Cl3N <--->  + ClHO +0.417 N2 +0.25 C4N2
  +0.667 Cl3N <--->  +0.333 N2 + Cl2
  +0.333 Cl3N +0.167 C2H6 <--->  +0.0833 N2 + ClH +0.0833 C4N2
  +0.333 N2 +0.167 C2H6 +0.167 C4N2 <--->  + CHN
  +0.333 C3H3N3O3 +2.78E-17 C4N2 <--->  + CHNO
  +0.333 C3H3N3O3 +0.333 Cl3N +5.55E-17 N2 <--->  + ClNO +0.167 C2H6 +0.167 C4N2
  +0.333 C3H3N3O3 +0.667 Cl3N +0.0833 C4N2 <--->  +0.917 N2 + CCl2O +0.167 C2H6
  +0.333 Cl3N +0.0833 N2 +0.25 C4N2 <--->  + CClN
  +0.667 C3H3N3O3 <--->  +0.667 N2 + O2 +0.333 C2H6 +0.333 C4N2
  +0.333 C3H3N3O3 +0.0833 C4N2 <--->  +0.583 N2 + CO +0.167 C2H6
  +0.5  N2 +0.5  C4N2 <--->  + C2N2
  +0.25 C4N2 <--->  + C +0.25 N2
  +0.0833 N2 +0.667 C2H6 <--->  + CH4 +0.0833 C4N2
  +0.333 C3H3N3O3 +0.167 N2 <--->  +0.167 C2H6 + NO +0.167 C4N2
  +0.667 C3H3N3O3 <--->  +0.167 N2 +0.333 C2H6 + NO2 +0.333 C4N2
  +0.333 C3H3N3O3 +0.667 N2 <--->  +0.167 C2H6 + N2O +0.167 C4N2
  +0.75 N2 +0.5  C2H6 <--->  + H3N +0.25 C4N2
  +0.333 Cl3N +0.5  C2H6 <--->  +0.167 N2 + CH3Cl
  +0.667 Cl3N +0.25 C4N2 <--->  +0.583 N2 + CCl2
  +0.667 C3H3N3O3 +0.333 Cl3N <--->  +0.333 N2 +0.333 C2H6 + ClNO2 +0.333 C4N2
  + C3H3N3O3 + Cl3N +0.25 C4N2 <--->  + C3Cl3N3O3 +0.75 N2 +0.5  C2H6
  + C3H3N3O3 <--->  +0.5  C2H6 +0.5  C4N2 + N2O3
  +0.667 C3H3N3O3 +0.333 Cl3N <--->  +0.833 N2 +0.333 C2H6 +0.333 C4N2 + ClO2
  +0.333 C3H3N3O3 +0.333 Cl3N +0.0833 C4N2 <--->  +0.75 N2 +0.167 C2H6 + CClO
  + C3H3N3O3 <--->  +0.5  N2 +0.5  C2H6 +0.5  C4N2 + NO3
  +0.333 C3H3N3O3 +0.333 Cl3N <--->  +0.5  N2 +0.167 C2H6 +0.167 C4N2 + ClO
  +0.333 Cl3N +0.25 C4N2 <--->  +0.417 N2 + CCl
  +0.75 N2 +0.25 C4N2 <--->  + CN2
  +0.75 N2 +0.25 C4N2 <--->  + CN2
  +0.5  C4N2 <--->  + C2N
  +0.333 C3H3N3O3 +0.333 C4N2 <--->  +0.833 N2 +0.167 C2H6 + C2O
  +0.333 Cl3N +0.5  N2 +0.333 C2H6 <--->  +0.167 C4N2 + ClH2N
  +0.667 Cl3N +0.25 N2 +0.167 C2H6 <--->  +0.0833 C4N2 + Cl2HN

MODEL CPU = 68.736 seconds or 1.1456 minutes
```


Source: Process Safety Office® SuperChems®

The final estimates can include a multitude of thermodynamic options and hazard screening

Results Summary | Vary Final Temperature

	A	B	C	D	E	F	G
3	** Thermodynamic Options						
4							
5	Liquid Density	Equation of state					
6	PVT/VLE	Ideal gas phase					
7							
8	** Initial State						
9							
10	Initial temperature. C	25.00					
11	Initial pressure. psia	400.00					
12	Initial enthalpy. kJ	-9.1567E+04					
13	Initial entropy. kJ/C	-2.9261E+02					
14	Initial volume. m3	1.124					
15	Initial density. kg/m3	124.79					
16	Initial mass. kg	140.20					
17	Initial number of moles. kgmol	1.25					
18							
19	** Final State						
20							
21	Final temperature. C	25.00					
22	Final pressure. psia	400.00					
23	Final enthalpy. kJ	-5.9028E+05					
24	Final entropy. kJ/C	-7.7969E+01					
25	Final volume. m3	2.697					
26	Final density. kg/m3	51.99					
27	Final mass. kg	140.20					
28	Final number of moles. kgmol	3.00					
29							
30	** Energy and Volume Change						
31							
32	Overall enthalpy change. kJ	-4.9871E+05		** Melhem Index			
33	Overall enthalpy change of vessel metal. kJ	0		Hazard Rating	Heat of reaction	CART	Effective CART
34	Overall entropy change. kJ/C	2.1464E+02		High	-850.16 cal/g	3061.78 K	4099.31 K
35	Overall volume change. m3	1.573					
36					-95.36 kcal/gmol; 1.25 gmol basis		
37	Overall enthalpy change. kJ/kg	-3.5571E+03					
38	Overall volume change. m3/kg	0.011					
39	Overall entropy change. kJ/C/kg	1.5309E+00					
40	Nf/Ni [vapor and liquid phases only]	2.40					
41							
42	Chemical Name	Formula	Phase	Initial Moles	Change	Final Moles	Fugacity Coefficient
43							
44	TRICHLOROISOCYANURIC ACID	C3Cl3N3O3	Vapor	0.5000	-0.5000	0.0000	1.0000
45	CARBON DIOXIDE	CO2	Vapor	0.0000	1.5000	1.5000	1.0000
46	NITROGEN	N2	Vapor	0.0000	0.7500	0.7500	1.0000
47	CHLORINE	Cl2	Vapor	0.0000	0.7500	0.7500	1.0000
48	OXYGEN	O2	Vapor	0.7500	-0.7500	0.0000	1.0000
49							
50	Other. < 1E-05 moles			0.0000	0.0000	0.0000	
51							
52	Totals			1.2500	1.7500	3.0000	
53							
54	Destruction Efficiency				0.0000	Percent	
55	C -> CO2 Efficiency				99.9998	Percent	
56							

Measured heat of combustion = -1571 BTU/lb or -872 cal/g of TCCA

Calculated heat of combustion using formation energies predicted by GAMESS = -850.16/0.82 = -1036 cal/g of TCCA

Not bad for first pass!

15.8 % difference

Source: Process Safety Office® SuperChems® Expert

These methods were also applied to calculate the formation energies of sucrose (table sugar)

- The NIST WebBook reports a heat of combustion value of -5,638.0 kJ/gmol and an absolute entropy of 392.40 J/gmol/K for **solid** sucrose
- ioKinetic measured a heat of combustion of solid sucrose at -5,616 kJ/gmol
- GAMESS was used to calculate an **ideal gas** absolute entropy of 673.67 J/gmol/K at standard conditions
- Using the measured heat of combustion value and the estimated absolute entropy value we calculated using SuperChems® Expert an ideal gas heat of formation of −1,790 kJ/gmol and an ideal gas free energy of formation of −1,200 kJ/gmol

Calculated combustion equilibrium data at standard conditions using SuperChems® Expert yielding -5,594 kJ/gmol of sucrose or -668 cal/g of mixture

		Hazard Rating	Heat of reaction	CART	Effective CART
** Energy and Volume Change	** Melhem Index	HIGH	-668.03 cal/g	2276.89 K	2399.85 K
Chemical Name	Formula	Phase	Initial Moles	Change	Final Moles
SUCROSE	C12H22O11	Vapor	0.0833	-0.0833	0.0000
OXYGEN	O2	Vapor	1.0000	-0.9996	0.0004
NITROGEN	N2	Vapor	3.7900	0.0000	3.7900
WATER	H2O	Vapor	0.0000	0.9163	0.9163
CARBON DIOXIDE	CO2	Vapor	0.0000	0.9996	0.9996
OTHER. < 0.0001 moles			0.0000	0.0000	0.0000
TOTALS			4.8733	0.8330	5.7063

Source: Process Safety Office® SuperChems® Expert

Closing remarks and comments

Proper chemical reactivity management requires a coherent and forever green process safety management system

- OSHA's Process Safety Management Standard (performance based)
- Process safety information (PSI) and asset/mechanical integrity (AI/MI) data are typically deficient in chemical processing facilities
- Process Safety Management System Automation

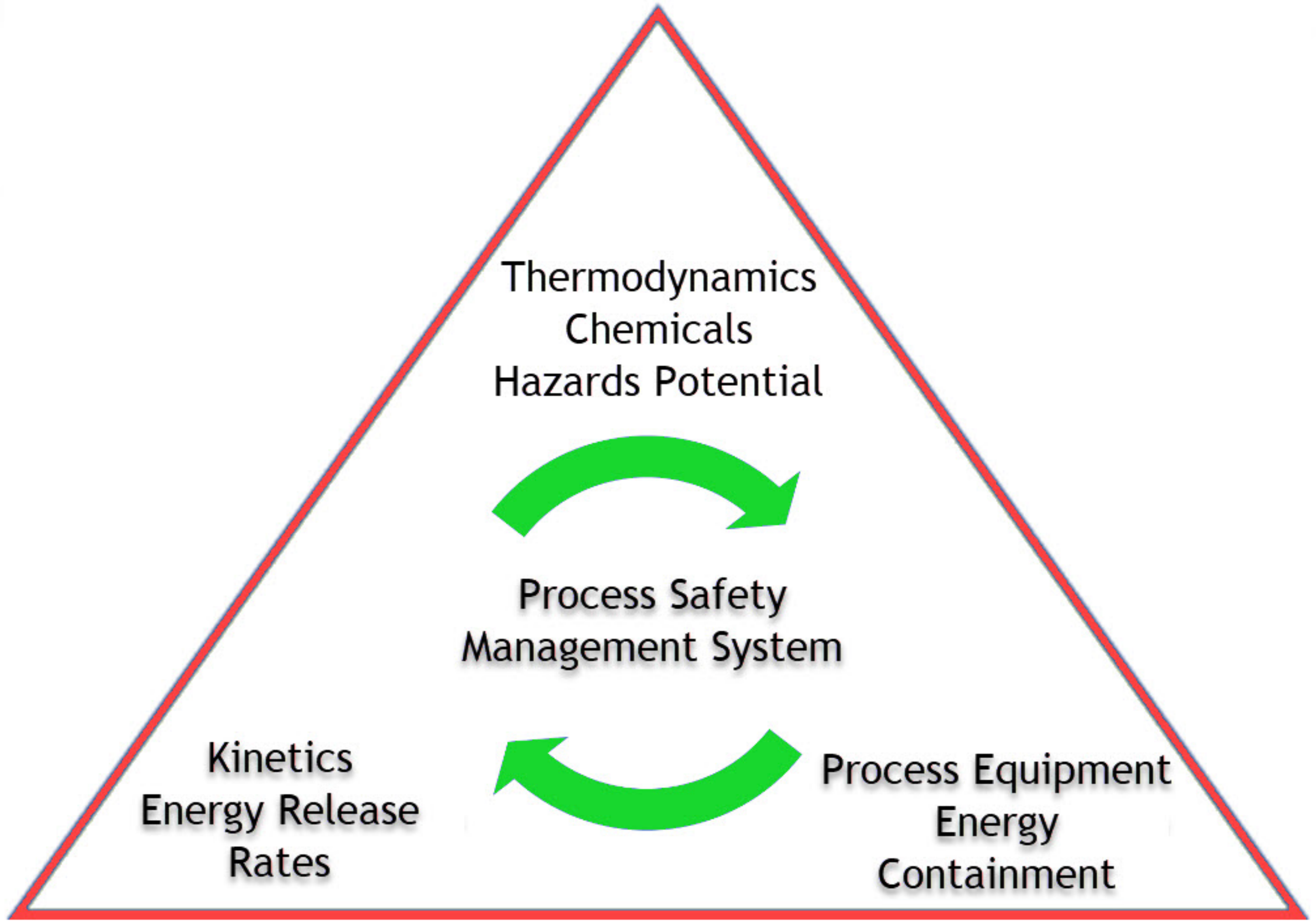
Source: ioMosaic Corporation

A chemical reactivity technology transfer package should be prepared and transmitted to the manufacturing site or CDMO

- The package should have sufficient information about the properties of the chemicals, as well as energy release rates for both intended/desired chemistries and unintended chemistries
- Recommended safe operating limits should be included
- Properties should include relevant thermodynamic, flammability, toxicity, environmental, and transport properties
- A well-developed technology transfer package contains most if not all the required chemical reactivity process safety information for PSM regulated facilities
- Thermal stability indicators can be included

Companies, toll manufacturers, and certified contract, development, and manufacturing organizations (CDMO) often use the same equipment for different chemistries or recipes

- Hazard potential of different chemicals and chemistries
- Chemical reaction rates for both desired and undesired reactions
- Suitability of the process equipment to handle the scaleup with different process conditions and chemicals
- Robust process safety management system
- Adequate reactive chemicals technology transfer package



Source: ioMosaic Corporation

Recommended reading

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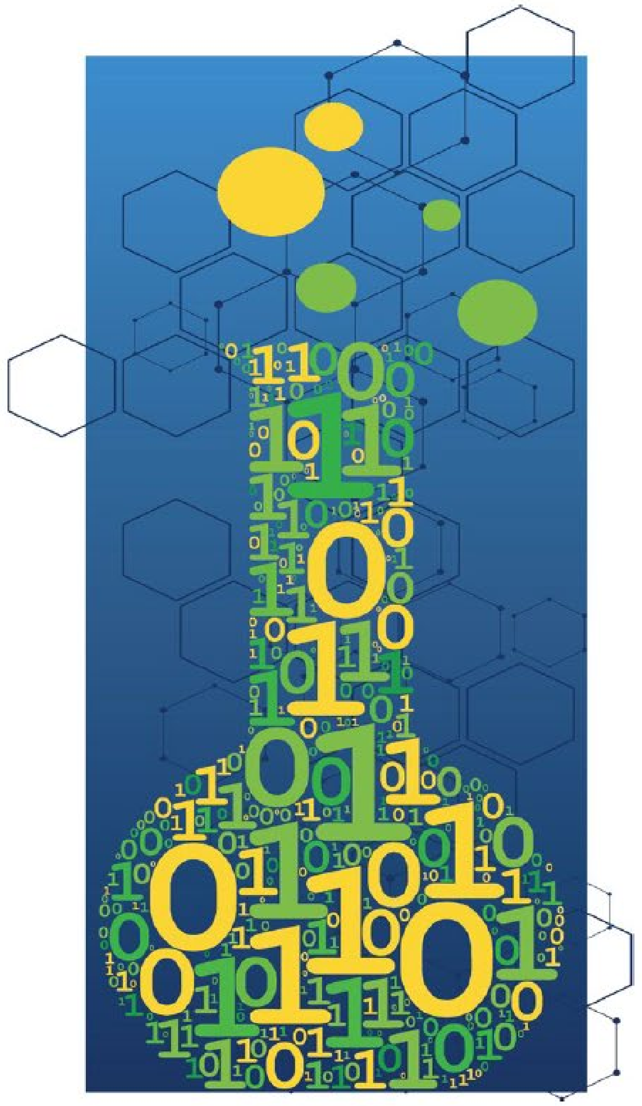
Source: ioMosaic Corporation White Paper

Recommended reading

ioMosaic®
Minimizing risk. Maximizing potential.®

Thermochemistry and Chemical Hazard Potential

Sucrose and Sucrose Reactions

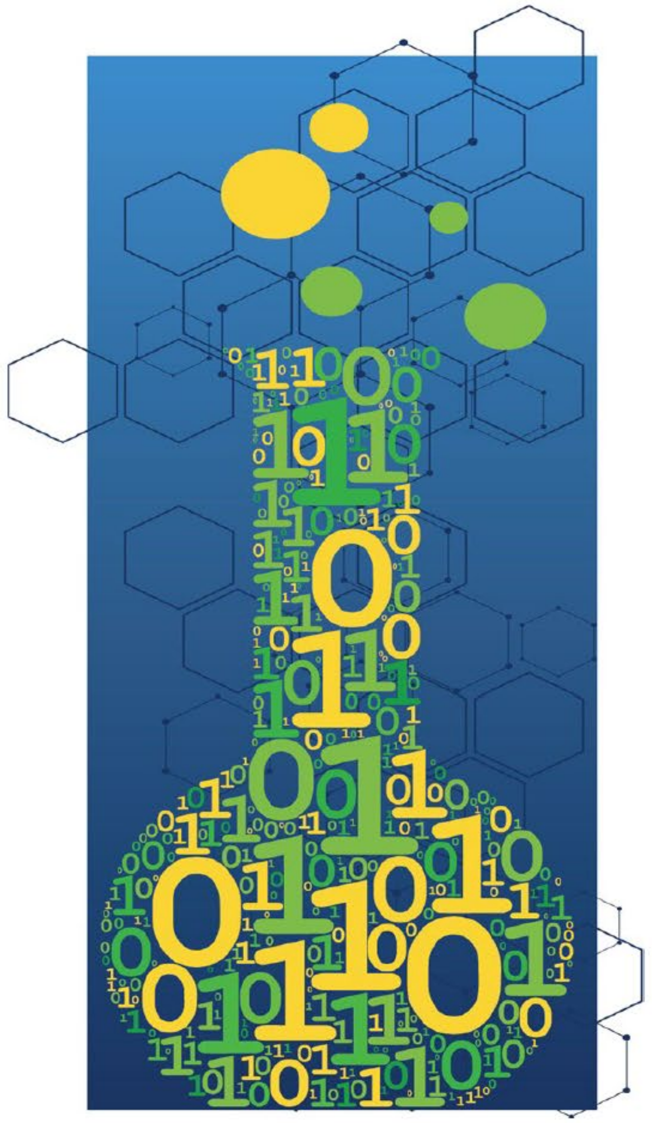


An ioMosaic® Publication

G. A. Melhem, Ph.D., FAIChE

ioMosaic®
Minimizing risk. Maximizing potential.®

Overlooked Inherent Hazards of Commonly Used Pool Treatment Chemicals



An ioMosaic® Publication

G. A. Melhem, Ph.D., FAIChE, E. Shaaban, Ph.D., and A. Iskandar, Ph.D.

Source: ioMosaic Corporation White Paper

For more information, please contact

G. A. Melhem, Ph.D., FAIChE
melhem@iomosaic.com
603-475-3646

1.844.ioMosaic
sales@ioMosaic.com
www.ioMosaic.com

About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training, and software development.

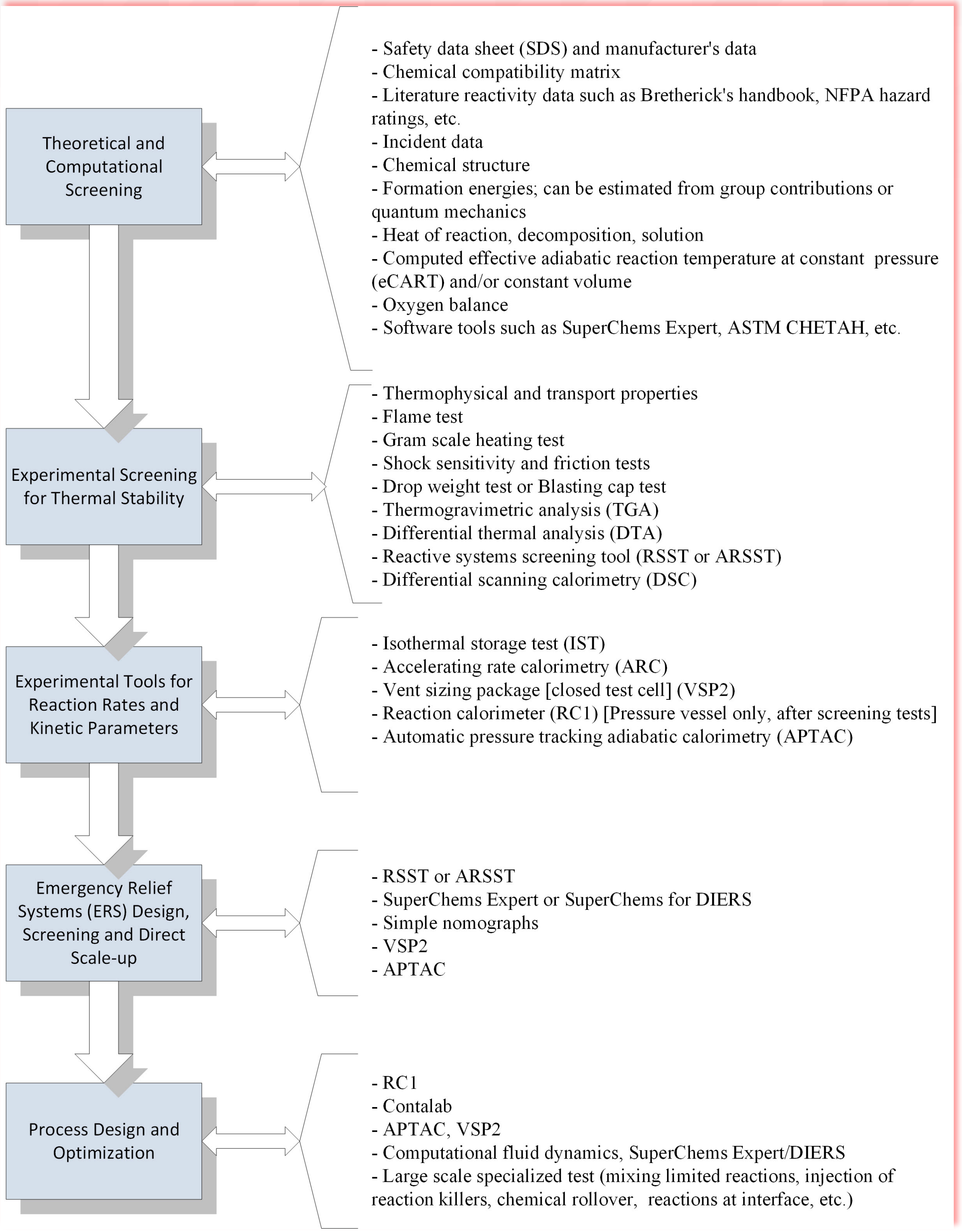
ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

For more information on ioMosaic, please visit: **www.ioMosaic.com**

Alternate slides for Q&A

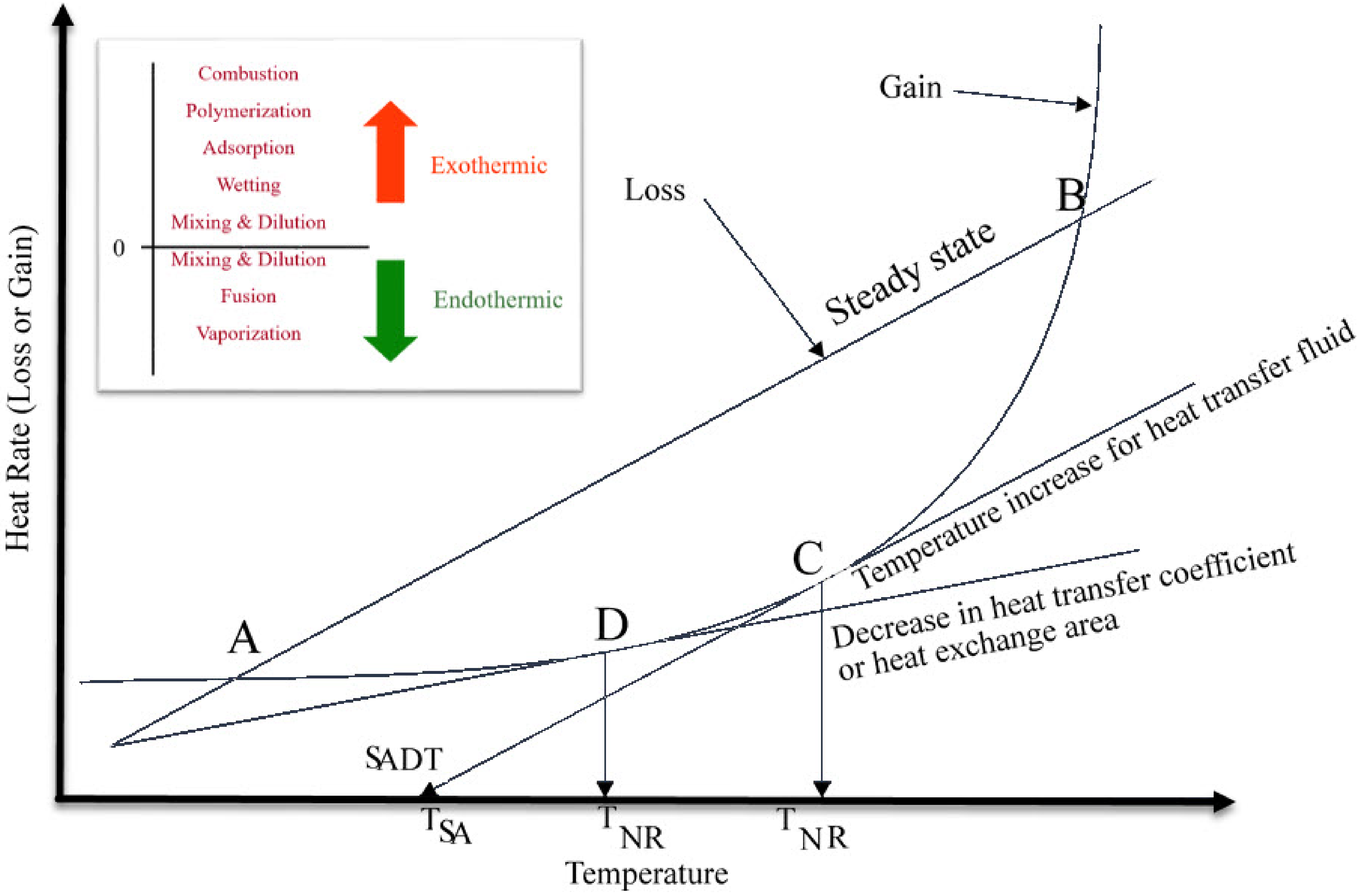
Theoretical screening methods are not intended to replace testing. They are intended to focus testing



- Heat release rates (dT/dt) and Pressure rise rates (dP/dt)
- Detected onset temperature
- Overall adiabatic heat of reaction and overall adiabatic temperature rise
- Shock sensitivity and Friction sensitivity
- Time to maximum rate temperature for 8 hours, 24 hours, and 48 hours
- Thermal diffusivity and thermal effusivity
- Final ratio of non-condensible components after reaction completion
- Chemical identity of reaction products and/or intermediates

The first layer of protection/containment during a runaway chemical reaction is provided by the processing equipment

- Operational error
- Hot spots
- Reactant accumulation
- Phase separation
- Heating or fire exposure
- Extended residence time / thermal cycling
- Chemical rollover
- Inhibitor depletion
- Preferential depletion of reactants
- Agitator failure
- Other scenarios



Source: ioMosaic Corporation

Temperature control is critical for reactive chemicals safety

- The heating and cooling capacities of the equipment used must be verified prior to use of the equipment
- The achievable rate of cooling or heating depends on many factors including but not limited to:
  - Rate of reaction,
  - Geometry of the vessel,
  - Degree of mixing within the vessel,
  - Viscosity of the reacting mixture,
  - Vessel wall thickness and the presence of insulation,
  - Thermal diffusivity and thermal effusivity of the reacting mixture, etc.

Materials of construction should be confirmed to be compatible with the intended chemical service

- The selected material of construction cannot chemically interact with the contents and should be corrosion resistant
- Changes in pH during the batch reaction steps should be considered when selecting materials of construction
- Instrumentation, valves, fittings, and piping components have to be confirmed to be compatible for the chemical service
- Materials of construction thickness, pressure, and temperature ratings have to be checked and confirmed suitable

What about pressure relief safe discharge location?

- Pressure relief systems may be the last line of defense, but it should not be the only line of defense
- Regulatory drivers influencing safe discharge requirements
- Atmospheric discharge sources (PRVs, flares, vent stacks, etc.)
- Flammable and / or toxic dispersion; thermal radiation / toxicity impacts
- Immediate vs. delayed ignition considerations
- Release duration and transient nature of release
- Meteorological data and site topography requirements
- Single vs. multiphase and condensing discharges