ioMosaic®

Minimizing risk. Maximizing potential.®

Reactivity Screening Made Easy

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ANAB ACCREDITED ISO/IEC 17021 MANAGEMENT SYSTEMS CERTIFICATION BODY

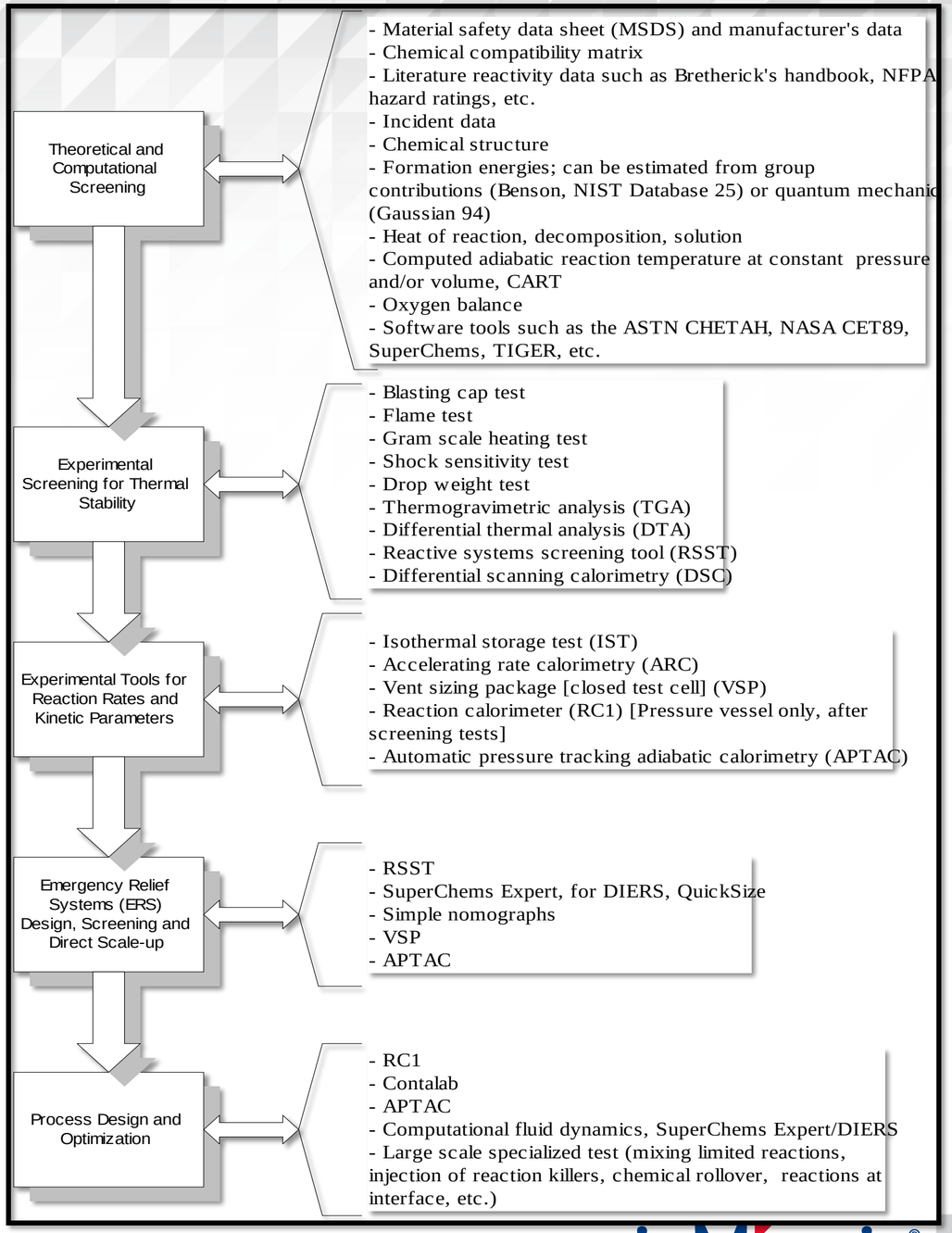
TÜV NORD TUV USA Inc. ISO 9001:2015

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

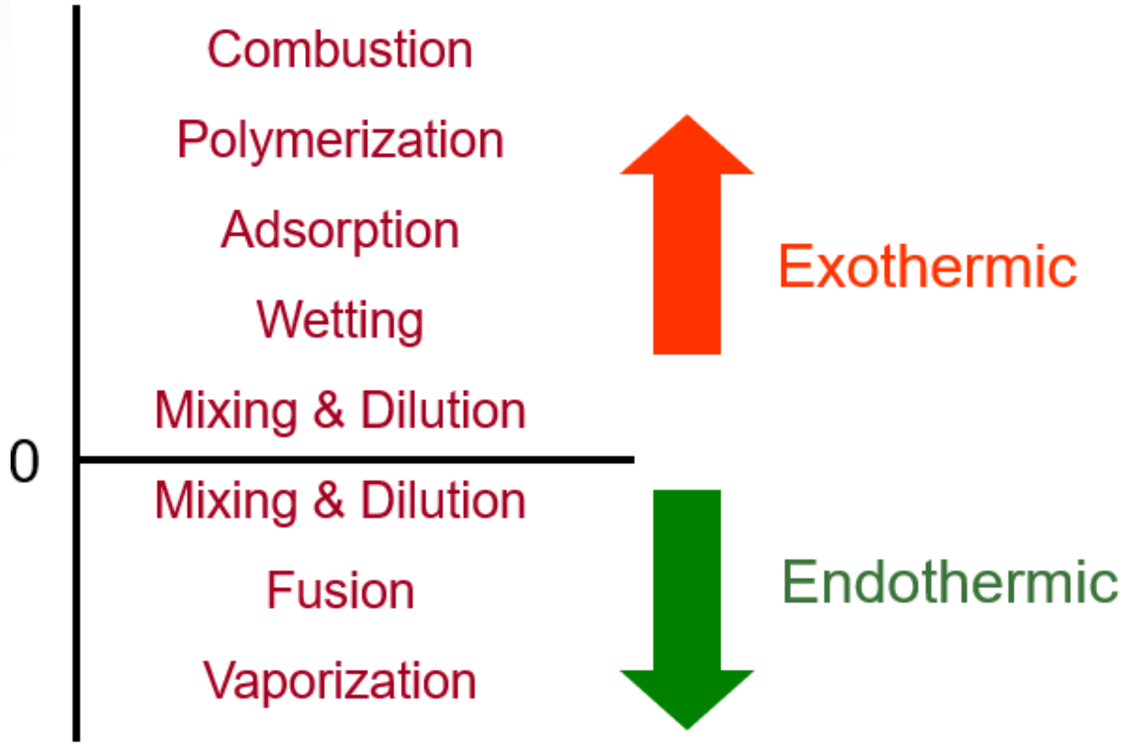
We have developed a systematic chemical hazards evaluation work process

- Screening methods are not intended to replace experimental methods
- Screening methods can aid, refine, and focus experimental work
- Screening methods play an important role in cost-effective reactivity management programs



Proper assessment of hazard potential of chemical reactions requires quantitative data on energy release rates

- Heat release rates (dT/dt)
- Mechanical energy release rates (dP/dt)
- Onset temperature of undesired reaction (To)
- Overall adiabatic heat of reactions (desired/undesired)
- Shock sensitivity data
- Chemical interaction data
- Scale up data



Since 1995, we have focused our research on developing simple and reliable chemical reaction hazard prediction methods

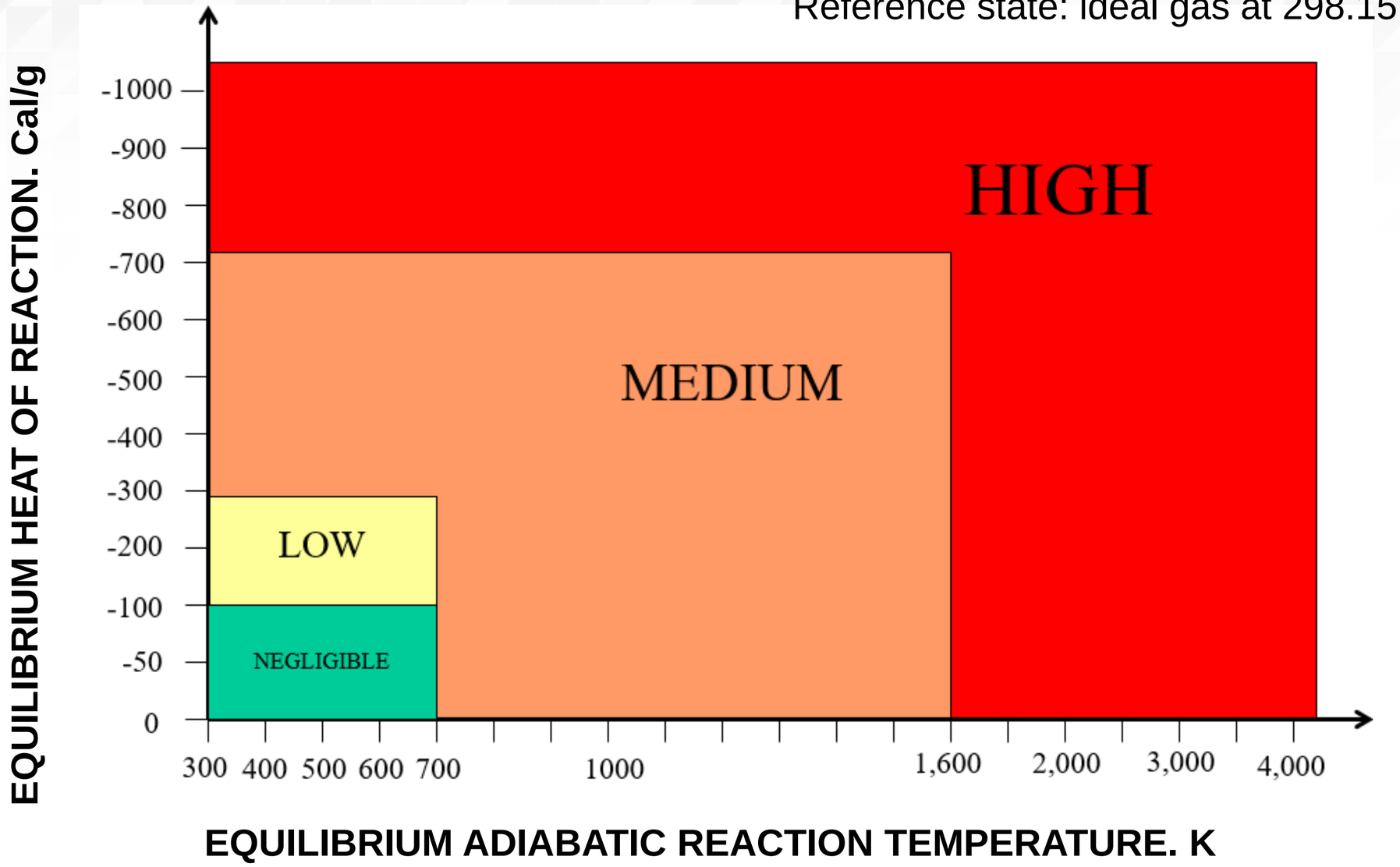
- Reliable hazard prediction is valuable
- Simple screening methods focus on hazard potential
- We developed a combined index of equilibrium heat of reaction (H_{rxn}) and computed equilibrium adiabatic reaction temperature (CART) ~$H_{rxn}/C_{p,avg}$
- Our conclusions are supported by both fundamental and experimental measurements
- Our index can be applied using theoretical estimates and limited experimental data to condensed phase reactions, gas phase reactions, and dusts

We have issued the following guidance on the use of our index for reactivity screening

- **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

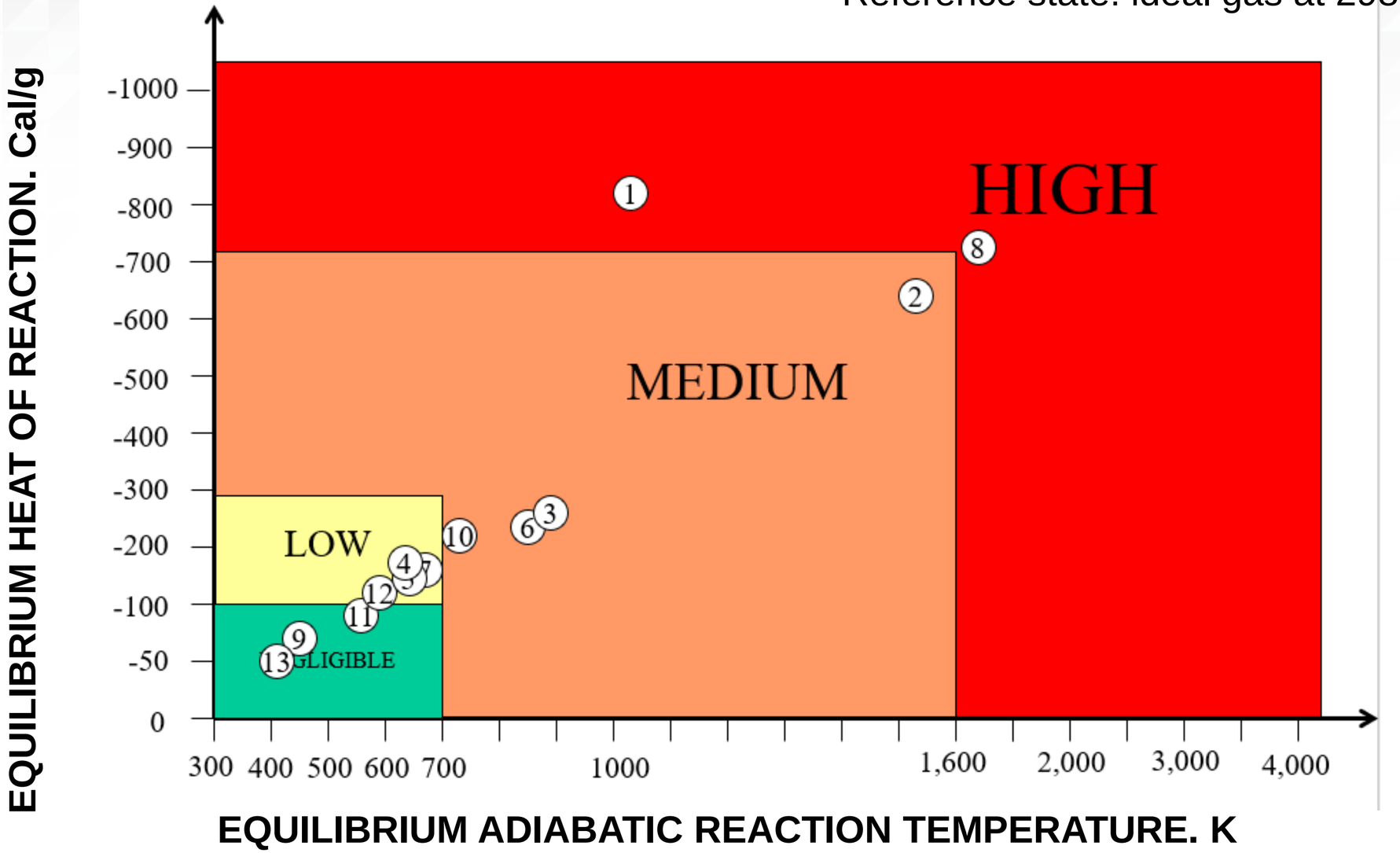
The Melhem Reactivity Hazard Index

Reference state: ideal gas at 298.15 K and 1 bar



The Melhem Reactivity Hazard Index / Crowl's Data

Reference state: ideal gas at 298.15 K and 1 bar



Melhem Index Rankings For 13 Systems Studied by D. Crowl

- All estimates of heats of reactions and CART values were estimated using the chemical equilibrium module of SuperChems™ Version 5.3
- Heats of reactions are estimated at 1 bar and 298.15 K assuming gas phase reactions and the possibility of forming solids as products such as carbon, where appropriate
- Heats of reaction and hazard indices are estimated for the actual mixture used and account for the thermal dilution effects offered by the solvent. The hazard index ratings will increase if the solvent is removed

Melhem Index Rankings For 13 Systems Studied by D. Crowl

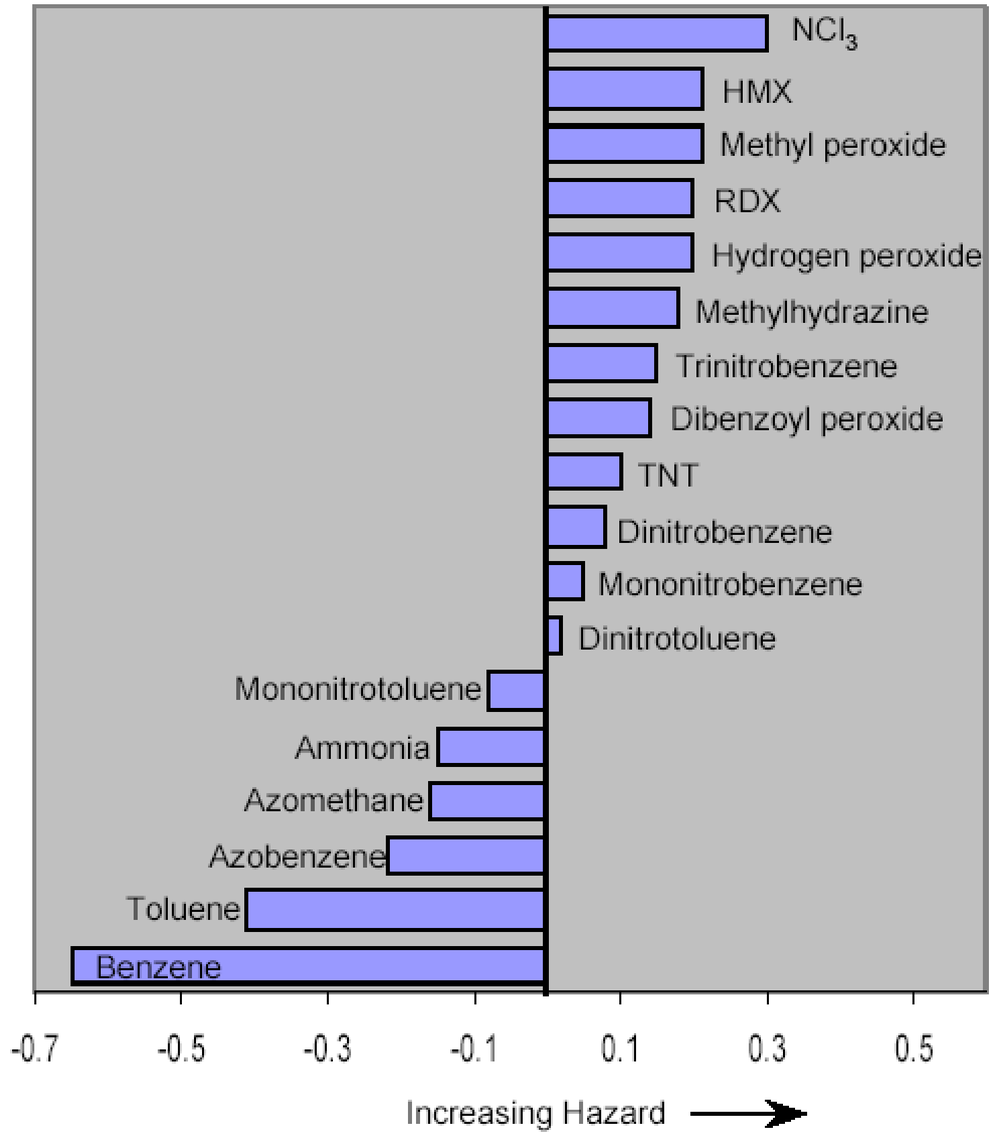
System	Composition	Heat of Reaction (cal/g)	CART (K)	Melhem Index	Comments
1	90 % Propylene oxide / 10 % water	-828	1,170	HIGH	Decomposes to carbon, methane, and water.
2	90 % Ethylene oxide / water	-648.2	1,520	HIGH	Decomposes to CO and Methane
3	50 % Epichlorohydrin / water	-289	876	INTERMEDIATE	Based on Crowl's experimental measurement
4	Hydroxyethylacrylate	-172	645	LOW	Liquid reference state
5	Styrene	-160	650	LOW	Liquid reference state
6	Acrylic acid	-258	858	INTERMEDIATE	Liquid reference state
7	Methacrylic acid	-184	689	LOW	Liquid reference state

Melhem Index Rankings For 13 Systems Studied by D. Crowl

System	Composition	Heat of Reaction (cal/g)	CART (K)	Melhem Index	Comments
8	100 % Ethylene oxide	-720	1,630	HIGH	Decomposition to CO and Methane; Literature value = -730 cal/g
9	20 % di-t-Butyl peroxide / toluene	-60.5	464	NEGLIGIBLE	Weight fraction
10	24.5 % cumene hydroperoxide / cumene	-202	734	INTERMEDIATE	Weight fraction
11	2:1 methanol / acetic acid	-98	566	NEGLIGIBLE	2:1 molar
12	14.2 % cumene hydroperoxide / cumene	-119.2	580	LOW	Weight fraction
13	20 % t-butyl peroxypivilate in ISOPAR-C	-58.5	415	NEGLIGIBLE	Based on Crowl's experimental measurement

Our findings are supported by quantum mechanical estimates

- The energy difference between frontier orbitals that involve the weakest bond in a molecule are compared to the energy that is released when that bond breaks
- The correlation has been found to apply to a wide range of energetic molecules and free radical initiators
- The method works better than estimations based solely on heats of reaction or elemental composition
- It can be applied to molecules whose thermo chemistry is not available (or not measurable)



Source: Arthur D. Little Inc.

Our findings are supported by experimental measurements: Blasting Cap Test Data

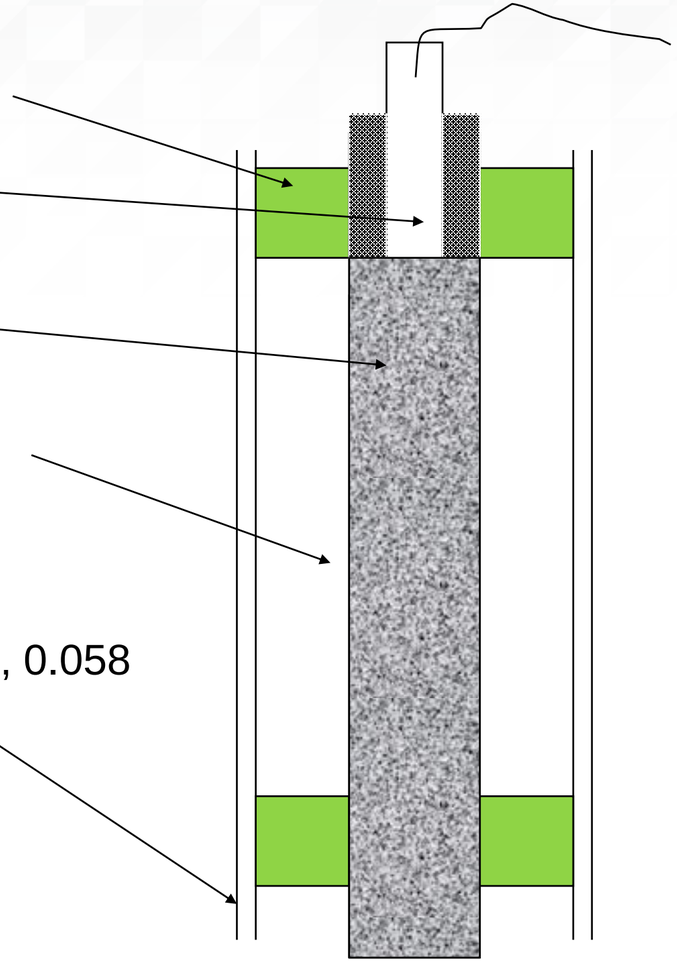
Foam Plastic Spacers

No. 6 Blasting Cap

Test Charge

18x150 mm Test Tube

Aluminum Witness Tube.
Alloy 6061, T6. 1.65 inch O.D., 0.058 inch wall

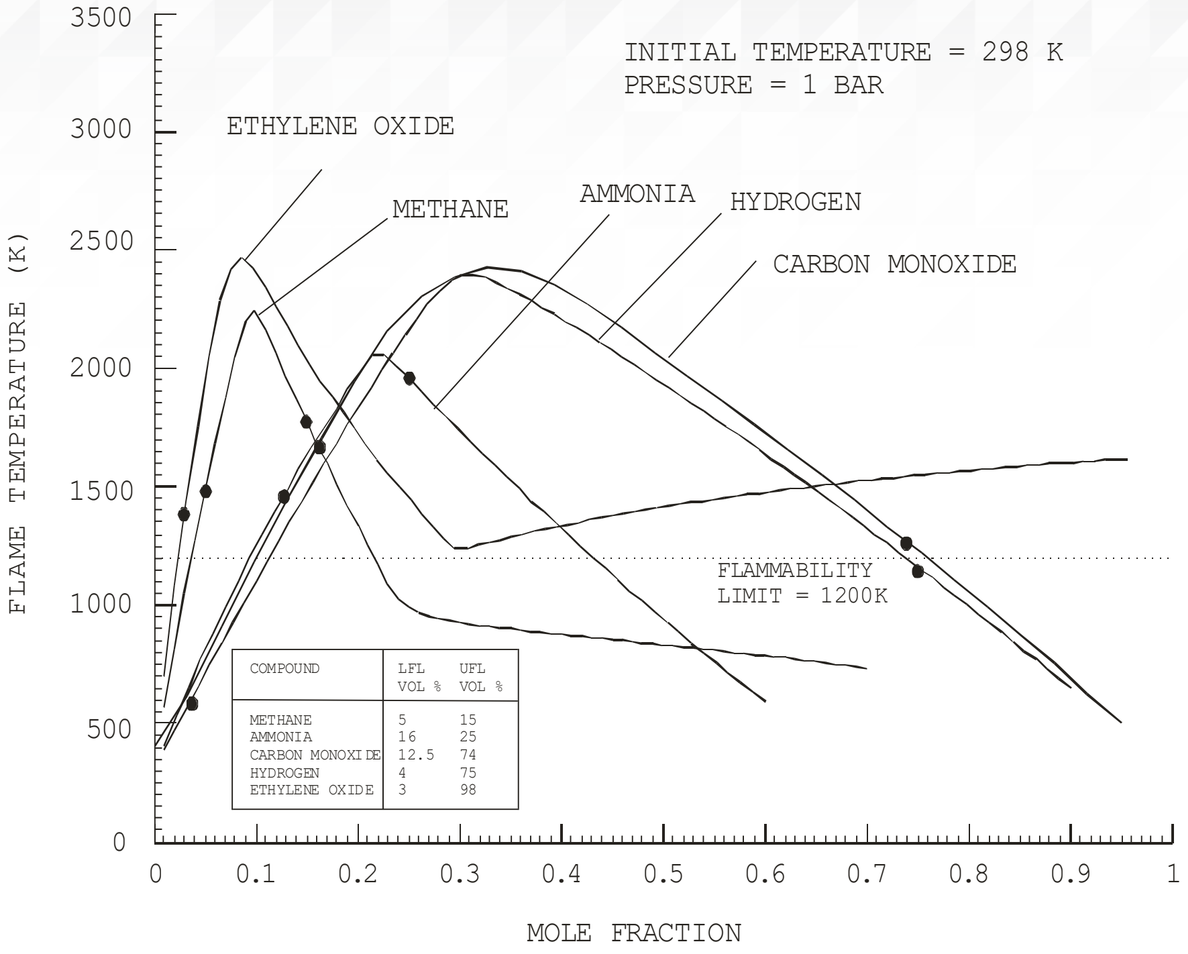


Source: ??

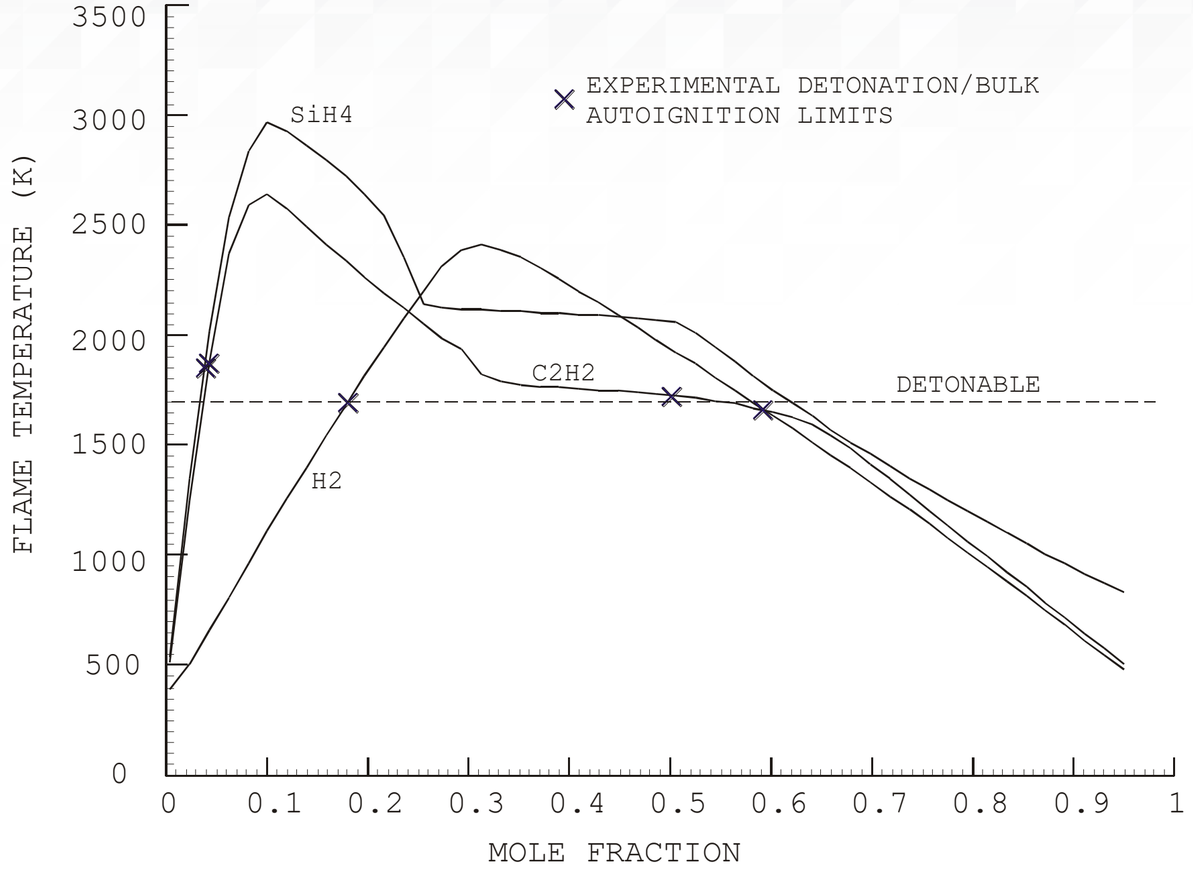
Our findings are supported by experimental measurements

Run #	Composition	D. max. cm	delta D	Volume ml	delta V ml	D g/cc	Condition of Witness tube	delta H(r) kJ/g Gas phase	CART K reactants
1A	Water	4.48	0.25	206	2	1.00			
1	Water	4.52	0.29	210	4	1.00	Small bulge at cap level	0	298
2	Dodecane	4.50	0.27	210	5	0.73	Ditto	-1.67	663
3	Dodencane	4.46	0.23	209	4	0.73	Ditto	-1.67	663
4	Toluene	4.52	0.29	211	6	0.87	Ditto	-2.16	859
5	Toluene	4.33	0.10	209	4	0.87	Ditto	-2.16	859
6	Mononitrotoluene	4.53	0.30	208	3	1.16	Ditto	-4.21	1573
7	Mononitrotoluene	4.47	0.24	208	3	1.16	Ditto	-4.21	1573
8	TNM-Toluene 50/50 wt.	4.62	0.39	209	4	1.14	Ditto	-4.44	1701
9	Sodium chloride	4.31	0.08	205	0	1.28	Ditto	0	298
12	Anthracene	4.68	0.45	210	5	0.72	Ditto	-2.59	983
20	Cumene hydroperoxide 80%	4.52	0.29	209	4	1.02	Ditto	-3.13	956
21	Cumene hydroperoxide 80%	4.57	0.34	209	4	1.02	Ditto	-3.13	956
22	Di t-butyl peroxide	4.52	0.29	210	5	0.79	Ditto	-2.72	847
23	Di t-butyl peroxide	4.50	0.27	208	3	0.79	Ditto	-2.72	847
24	Benzoyl peroxide	4.30	0.07	206	1	0.71	Ditto	-3.47	1016
25	Benzoyl peroxide	4.50	0.27	206	1	0.64	Ditto	-3.47	1016
26	H2O2 40%+EtOH, balanced	4.55	0.32	209	4	1.12	Ditto	-3.39	1874
27	H202 40%+EtOH, balanced	4.49	0.26	210	5	1.12	Ditto	-3.39	1874
10	Ammonium nitrate	4.61	0.38	210	5	0.94	Bulged and split	-2.37	1723
11	Ammonium nitrate	5.00	0.77	215	10	1.00	Ditto	-2.37	1723
14	Dinitrotoluene	4.68	0.45	214	9	1.01	Ditto	-5.76	1511
15	Dinitrotoluene	4.89	0.66	214	9	1.01	Ditto	-5.76	1511
28	H2O2 50%+EtOH, balanced	4.70	0.47	212	7	1.14	Ditto	-4.14	2140
29	H2O2 50%+EtOH, balanced	4.53	0.3	210	5	1.14	Bulge at cap level	-4.14	2140
30	AN + 2.5% dodecane	-----	-----	-----		0.66	Top of tube peeled open	-3.54	2168
31	AN + 2.5% dodecane	-----	-----	-----		0.66	Top of tube peeled open	-3.54	2168
33	Urea nitrate, S.M.	-----	-----	-----		0.75	Half of tube peeled open	-3.74	2468
34	Urea nitrate, S.M.	-----	-----	217	12	0.79	Two splits	-3.74	2468
19	TNM-Toluene, balanced	-----	-----	-----		1.22	Tube shattered	-7.64	3082

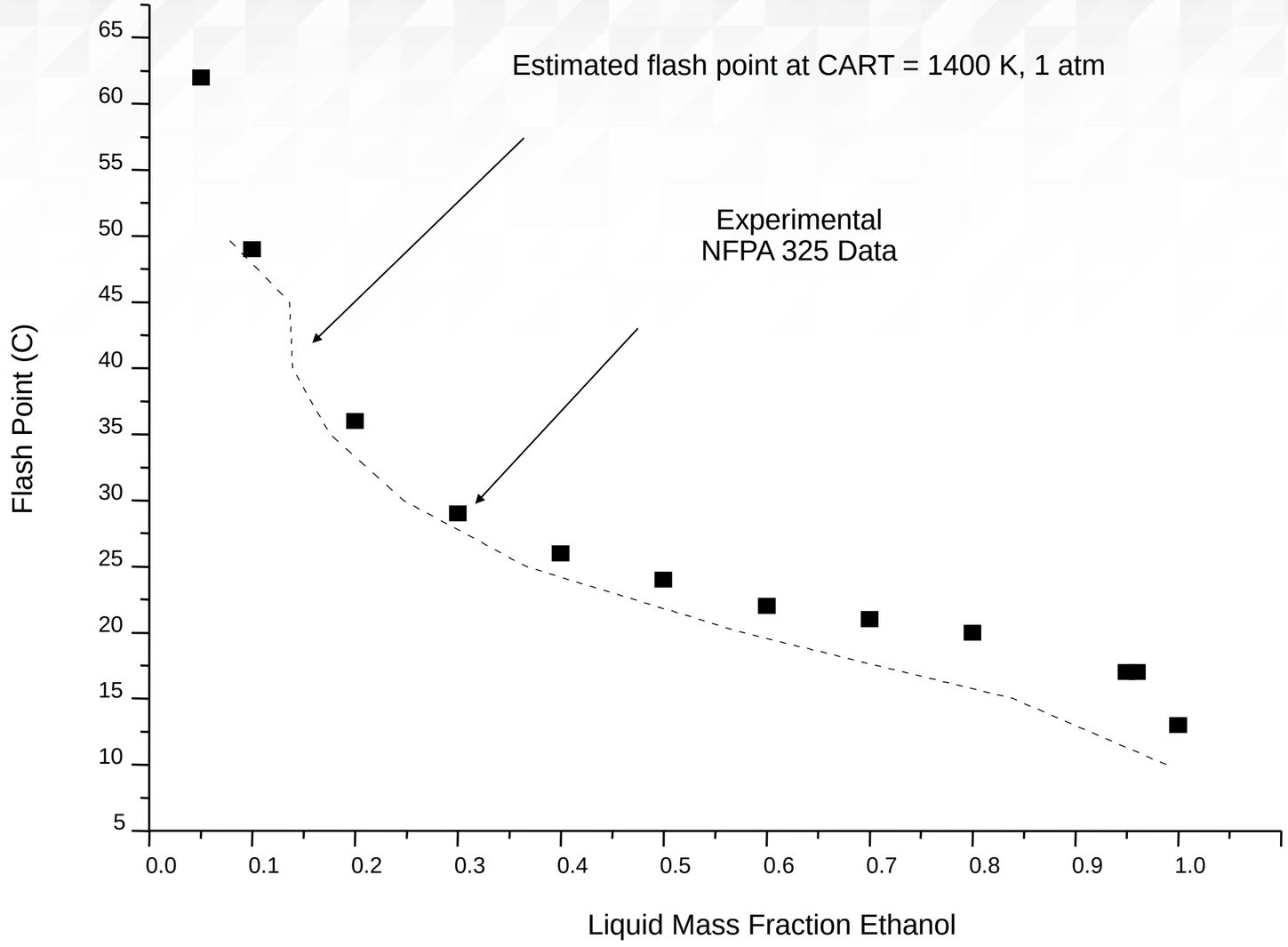
Our index applies to gas flammability and detonation limits



COMPOUND	LFL VOL %	UFL VOL %
METHANE	5	15
AMMONIA	16	25
CARBON MONOXIDE	12.5	74
HYDROGEN	4	75
ETHYLENE OXIDE	3	98

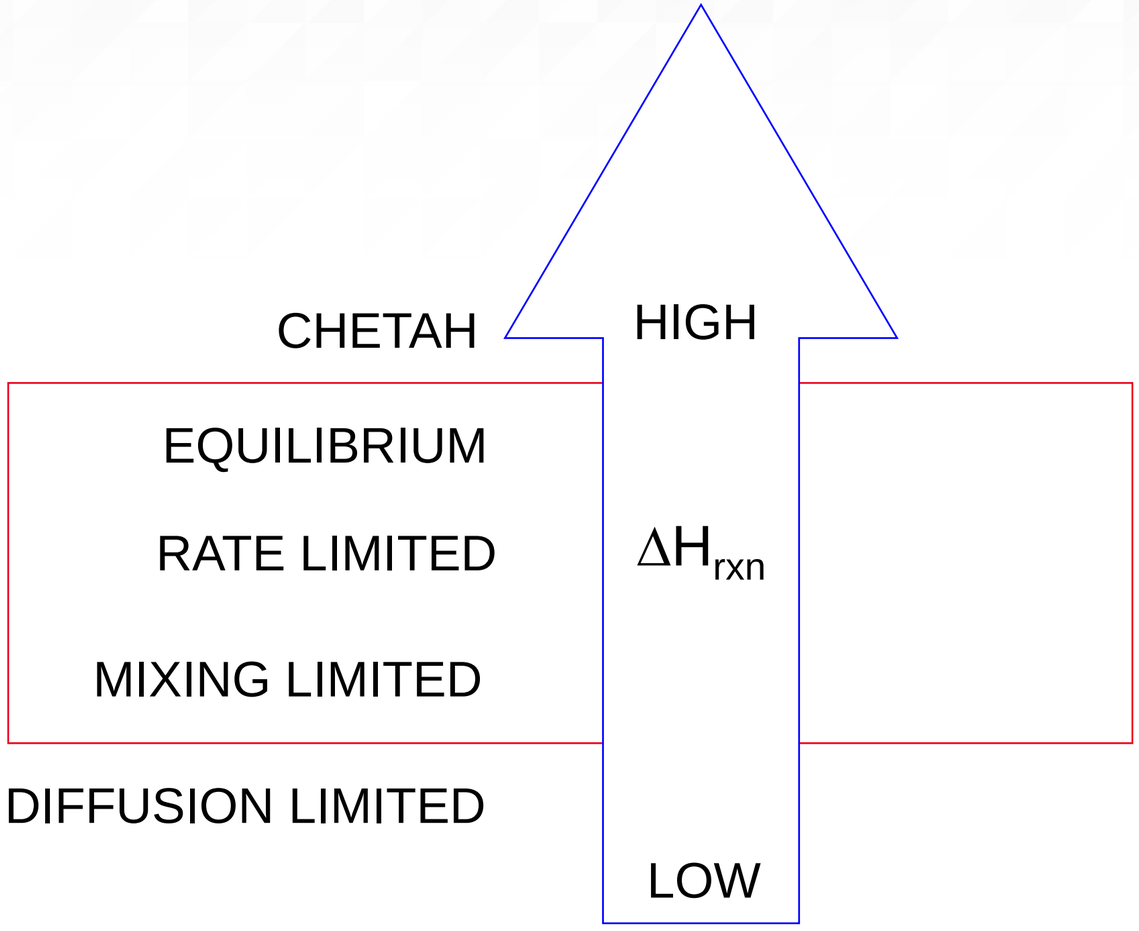


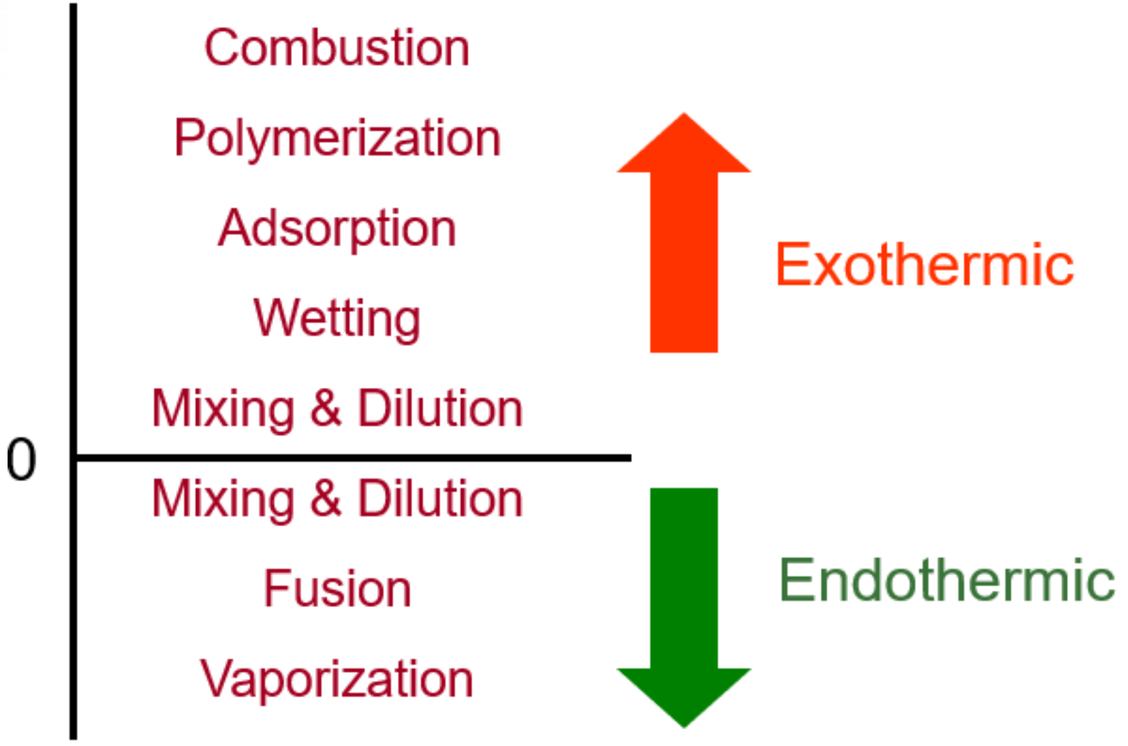
Our index applies to mixture flash points



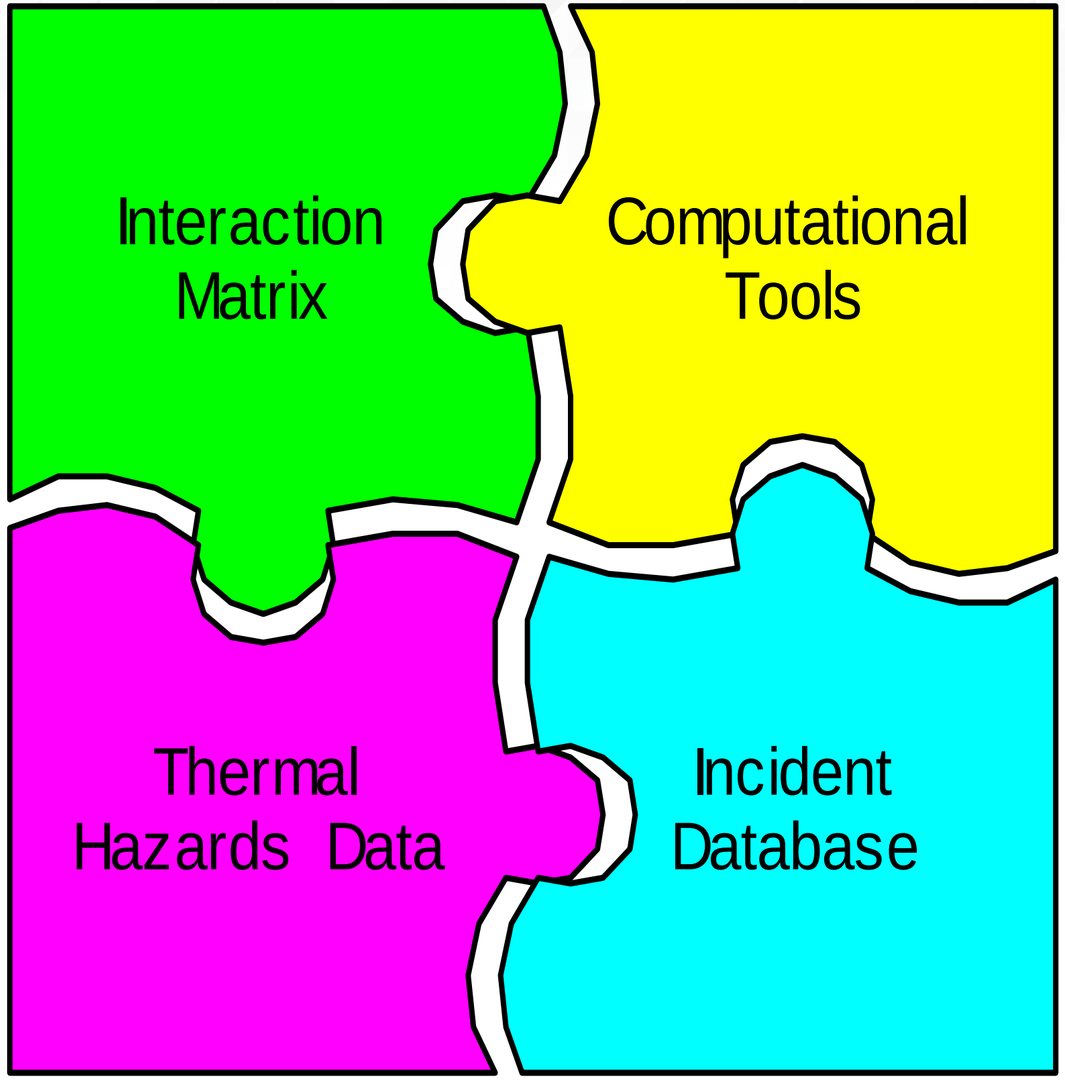
Source: Sharkey et al., DIERS Users Group, October 2002

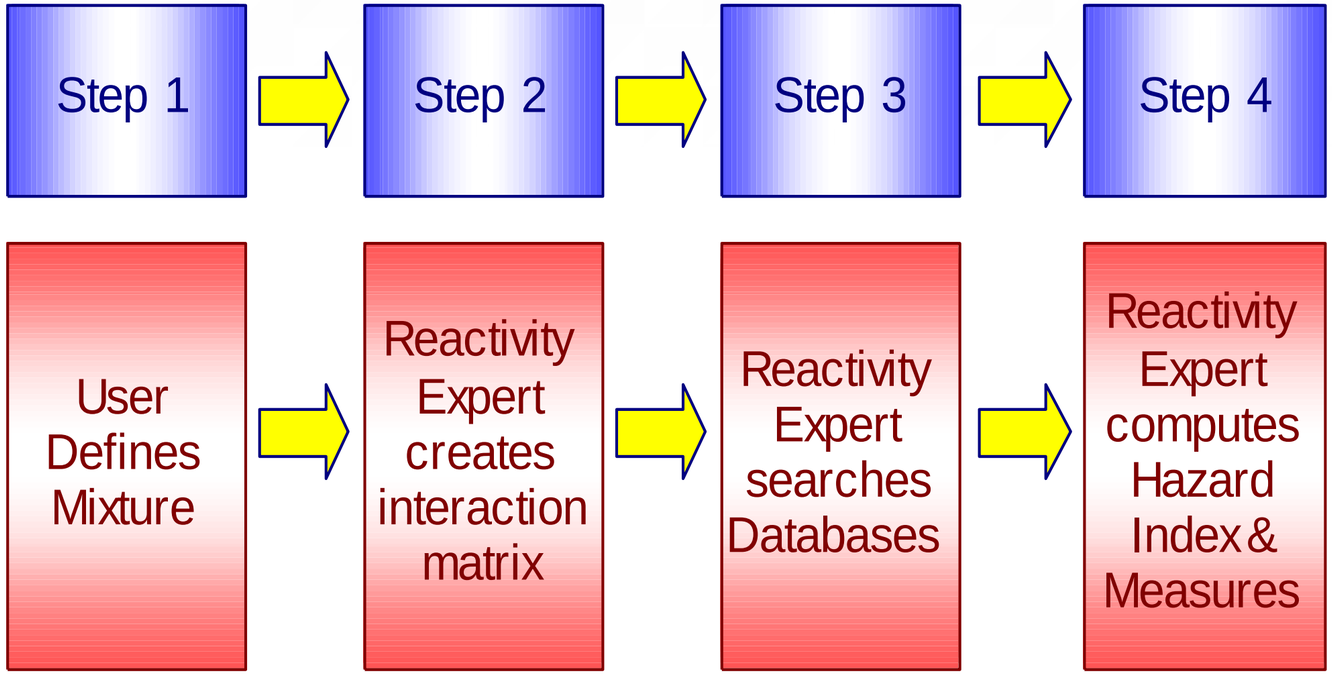
Heats of reaction and computed adiabatic temperature can easily be estimated from a variety of tools





ioMosaic suite of tools include SuperChems Reactivity Expert





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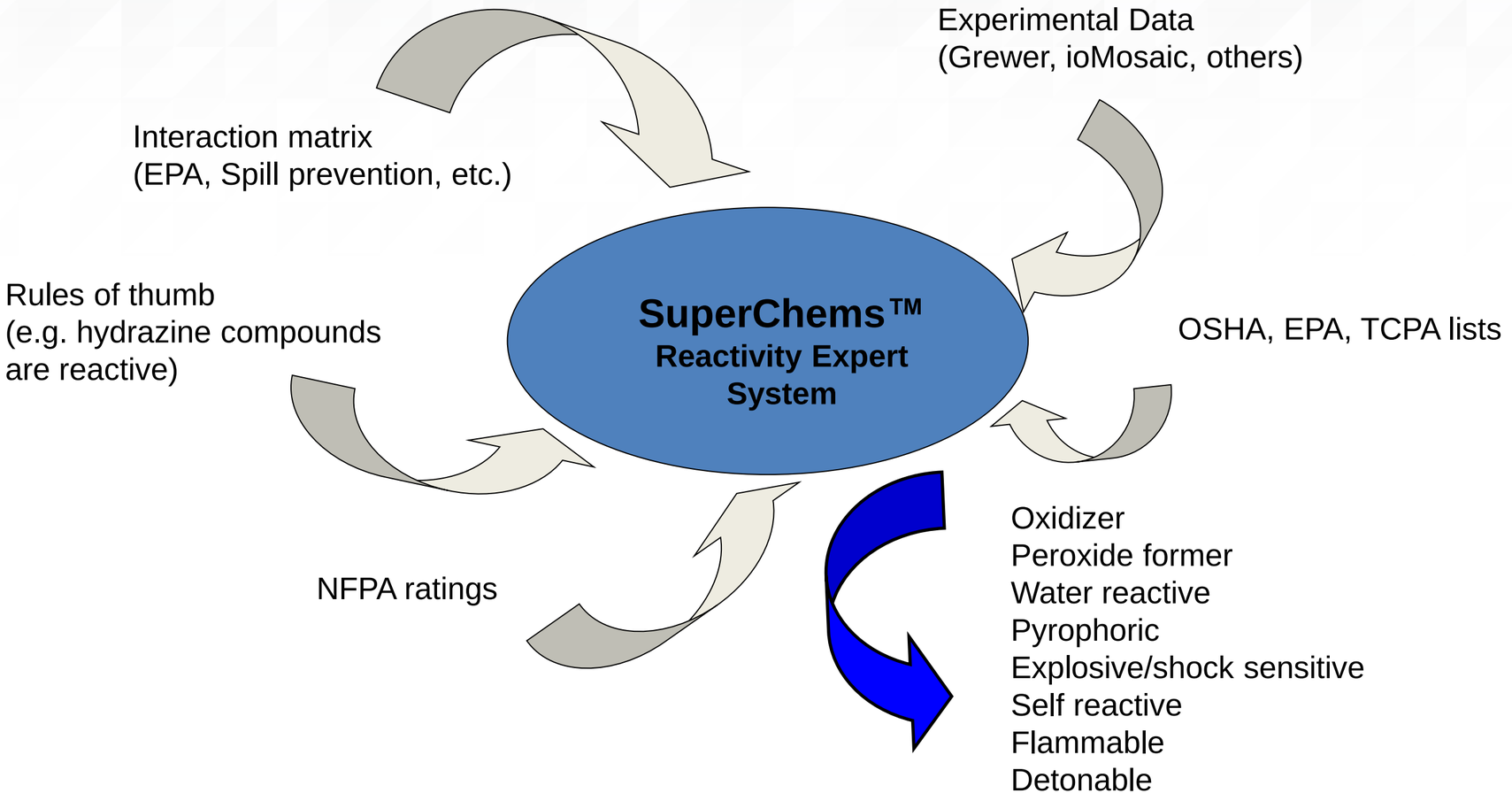
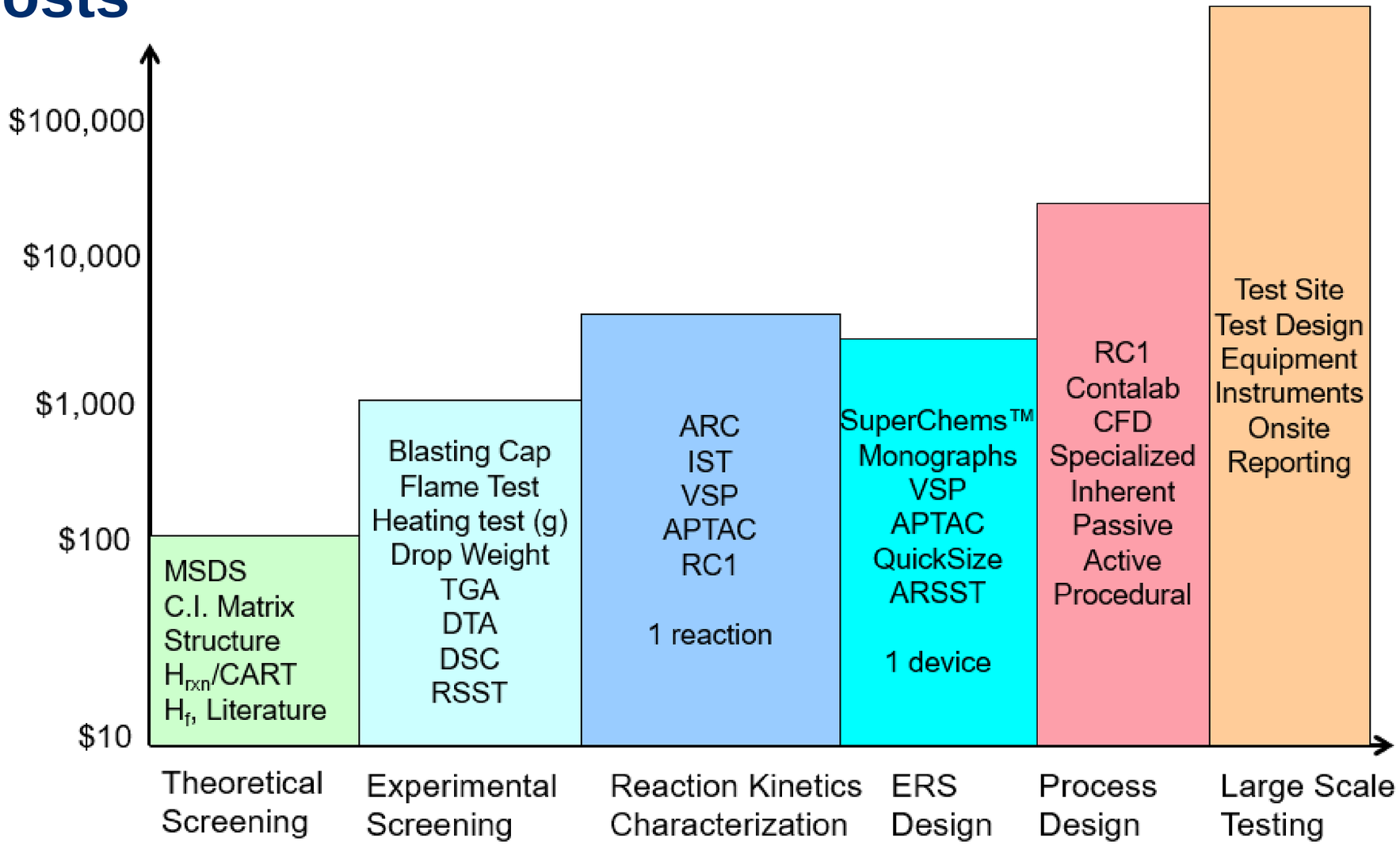


Source: ioMosaic

The SuperChems Reactivity Expert is comprehensive

- EPA Chemical Compatibility Chart
- U.S. Coast Guard Interaction matrix for cargo incompatibility
- Spill Prevention Guidance Document - Chemical / material of construction compatibility
- Proprietary ioMosaic Heuristics
- Exceptions based on known hazard ratings or testing data
- Group Contribution Methods for the Estimation of Heats of Decomposition and Polymerization
- ioMosaic Equilibrium Estimates, CART, and Melhem Index
- Reactive chemicals lists
  - OSHA, EPA, and NJ TCPA
  - SEVESO
  - Peroxide formers
  - Grewer's book on reactive chemicals; 200 chemicals - Heat of decomposition - Onset temperatures
  - ioMosaic; 500+ chemicals - Heats of Reaction and Kinetic information
- Fire Protection Guide to Hazardous Materials, 13th edition, 2002
  - NFPA 49: Hazardous Chemicals Data
    - Fire and hazard data on 325 chemicals
    - Includes NFPA 704 diamond ratings
    - Also includes NFPA 30/OSHA flammable and combustible liquids classification
  - NFPA 491: Guide to Hazardous Chemical Reactions
    - 3600 mixtures of two or more chemicals that may cause fire, explosion or detonation
- Sample ioMosaic Heuristics
  - TCPA functional groups
    - Functional groups prone to explosion or polymerization
  - Pyrophorics
    - Based on list from Bretherick's handbook
  - Water reactive
    - Based on list from Bretherick's handbook

Typical reactivity hazards characterization order of magnitude costs



Key References

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3. G. A. Melhem, H.G. Fisher and D.A. Shaw "An Advanced Method for the Estimation of Reaction Kinetics, Scale-up and Pressure Relief Design", Process Safety Progress, Vol 14, No. 1, 1995.

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9. J. Sharkey, G. Gruber and D. Muzzio, “Prediction of the flammability range for chemical systems using Aspen”, Paper presented at the AIChE DIERS User’s Group Meeting, October 2, 2002.

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.

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