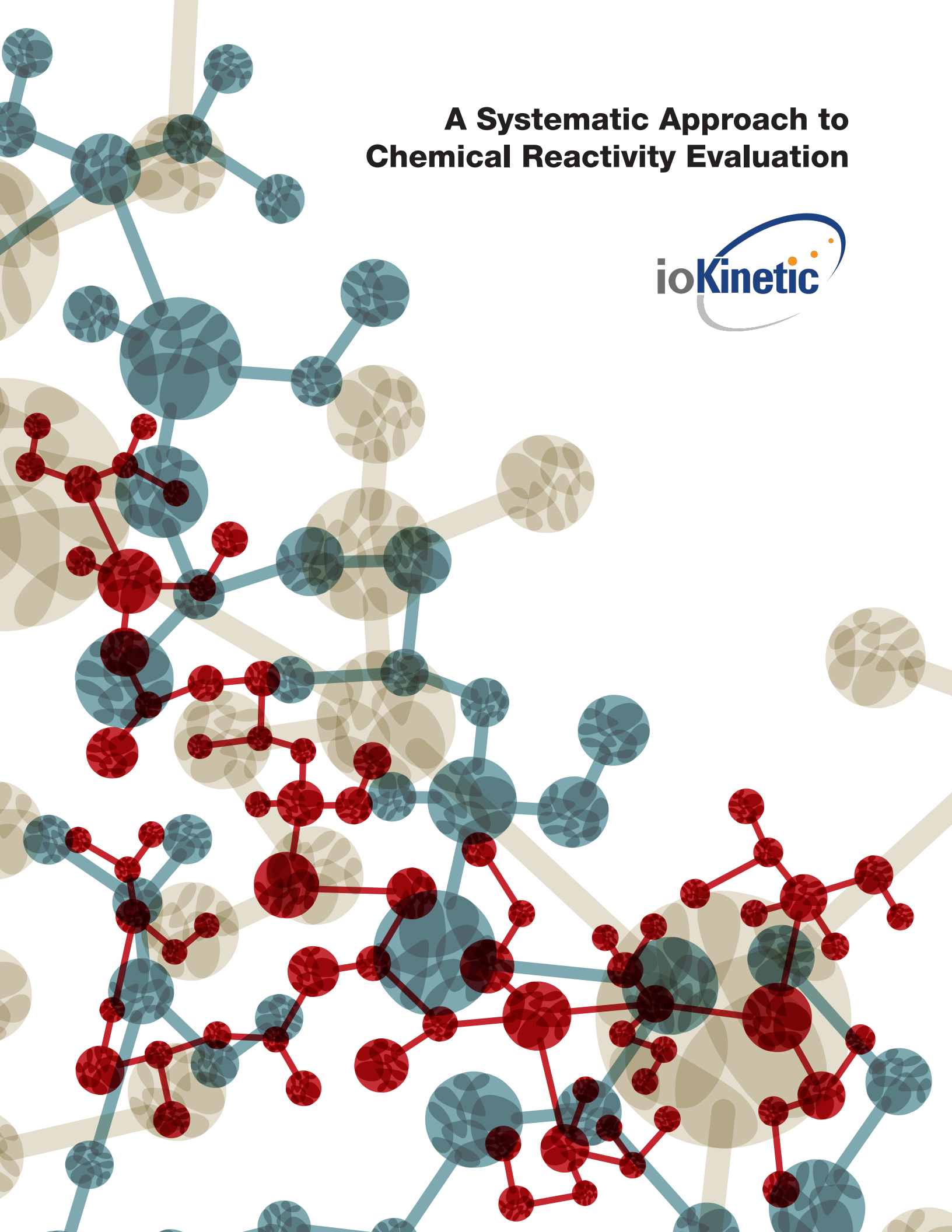
A Systematic Approach to Chemical Reactivity Evaluation

ioKinetic



Introduction

Reactive chemicals are materials capable of giving rise to an uncontrolled chemical reaction (a.k.a., a runaway reaction). Reactions with a significant release of heat, gas and/or toxic materials have the potential to cause harm to people, property or the environment.

Despite OSHA's Process Safety Management Standard (PSM) and EPA's Risk Management Plan (RMP) regulations, accidents with reactive chemicals continue to happen. In their 2002 report, the U.S. Chemical Safety and Hazard Investigation Board (CSB) identified failure of management systems for reactive chemistry as a key root cause of reactive chemical accidents.

Managing reactive chemistry involves a systematic approach. The approach presented here incorporates both screening and experimental steps. As seen in Table 1, it begins with computational assessment, followed by experimental screening and finally, experimental testing.

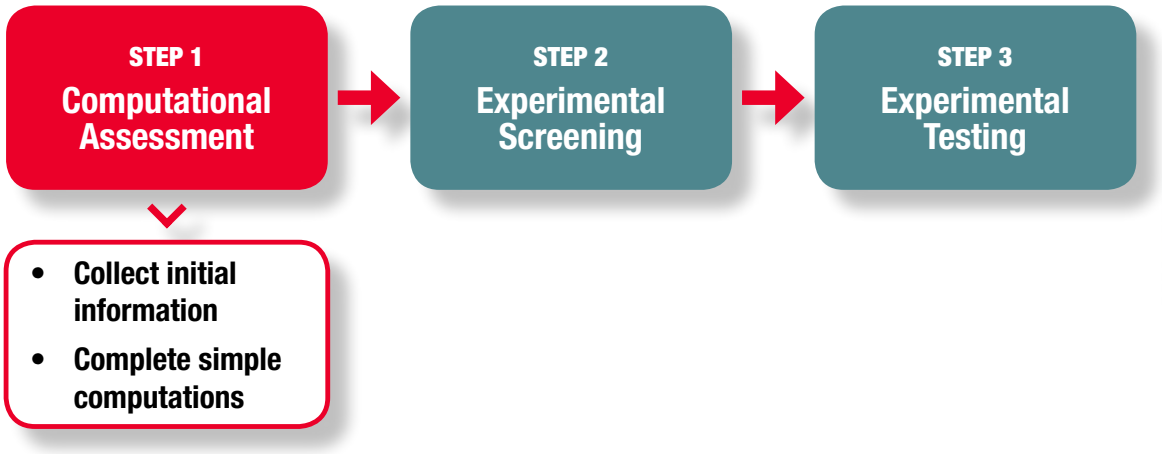
Initial screening efforts involve reviewing existing data sources and completing basic computations, such as calculating heats of formation, heats of decomposition, and calculated adiabatic reaction temperatures.[1, 2] Where screening methods suggest thermal instability, the next step is experimental screening tests. These relatively quick and inexpensive tests can be completed to further evaluate any reactivity concerns. Coupling screening results with process operating information (e.g., temperature and pressure ranges, composition, order of addition) will determine if more comprehensive tests are necessary. Detailed calorimetry experiments are conducted to measure the system's chemical reactivity. These experimental tools are used to more accurately measure reaction onset temperatures, heats of reaction, rates of temperature and pressure rise, etc. Data from these tests can also be used to develop reaction kinetics. This data, combined with process design information, can help to define safe operating limits, size pressure relief devices and ultimately, a safer chemical process.

Table 1:
Management Approach to Reactive Chemicals

Approach	Result	Reference / Test
Computational Assessment	Initial information on chemical reactivity from available sources and computational tools	• Literature review (e.g., MSDSs, Bretherick's Handbook, NFPA, CAMEO) • Chemical structural evaluation (e.g., NIST WebBook) • Chemical compatibility matrix (e.g., NOAA Matrix) • Reactivity evaluation (e.g., estimated heats of formation, reaction, decomposition, solution, CART, oxygen balance)[3]
Experimental Screening	Basic information on the chemical reactivity of material/mixture	• Thermogravimetric Analysis (TG) • Differential Scanning Calorimetry (DSC) • Reactive Systems Screening Tool (RSST) • Basic tests (e.g., flame, gram-scale heating, drop weight)
Experimental Testing	Detailed information on the chemical reactivity of the material/mixture (e.g., reaction onset temperatures, rates of temperature and pressure rise, reaction kinetics)	• Adiabatic calorimetry (ARC©, APTAC™) • Isothermal storage test (ARC©) • Reaction calorimetry (RC1)

References
1. Murphy, M. R., et. al., "Computationally Evaluate Self—Reactivity Hazards," CEP, (February 2003)
2. Melhem, G., "Strategy for Managing Reactivity Hazards," ioMosaic Corporation Whitepaper (2006)
3. Software tools include ASTM's Chetah©, ioMosaic's SuperChems™, NIST Chemistry WebBook, EPA/NOAA's CAMEO

Step 1: Computational Assessments for Chemical Reactivity



In Step 1, we provide details for how to complete the first step: Computational Assessment. This step involves collecting initial information about the chemical characteristics from literature and completing simple computations.

To complete a computational assessment, chemical and physical characteristics of the compounds and mixtures to be handled should be gathered. Table 1 lists the characteristics that can provide insight into the chemical reactivity potential of a chemical or mixture.

If many of the characteristics listed in Table 1 are not readily available, experimental screening can be conducted to develop them.

If some or all of the values are available, they can be compared against known criteria to determine the potential for reactive chemical hazards. Several sources have documented such criteria. Based on preliminary analysis of this nature, it is possible to predict reactive or explosive potential.

For example, Lothrop and Handrick (1949) presented an oxygen balance criteria between -80 and +120 as potentially reactive. The Chemical Reactivity Help Guide V1.0 (January 2012) states that when the heat of reaction is greater than 100 cal/g, further evaluation is needed. Murphy et al. (2005) presented a means of predicting reactive behavior using calculated heats of reaction and calculated adiabatic temperature rise (CART) values compared with known hazards of compounds in the same family. Melhem (2004) concluded that when theoretical heats of reaction of >100 cal/g are found in combination with CART values >700K, a small scale (i.e., milligram) experimental screening test is recommended.

In the same paper, Melhem went a step further in postulating the Melhem Index. Similar to Murphy, this index for

References:
1. CCPS, 2005, Guidelines for Safe Handling of Powders and Bulk Solids, AIChE, New York, NY
2. Lothrop, W.C.; Handrick, G.R. Relationship between performance and constitution of pure organic explosive compounds, Chemcial Reviews, 1949, 44, 419
3. Melhem, G., 2004, "Reactivity Screening Made Easy", Process Safety Progress, Volume 23, No. 2, 2004
4. G. A. Melhem. and E. S. Shanley, "The Oxygen Balance For Thermal Hazards Assessment", Process Safety Progress, Vol.14, No. 1, 1995. Paper also appeared in Plant Safety, pp. 153, AIChE
5. Chemical Reactivity Evaluation Tool Help Guide, V1.0 January 2012, pp 19, AIChE
6. Murphy, M., Singh, S. and Shanley, E., 2003, "Computationally Evaluate Self-Reactivity Hazards," Chemical Engineering Progress, 99 (2): 54-61

chemical reactivity uses the CART value and equilibrium heat of reaction to predict reactive behavior. Application of this index can be seen in Figure 1.

Applicability of any of these criteria will provide a basis for screening for chemical reactivity hazards. For those chemicals/mixtures showing the potential for reactivity hazards, the next step involves experimental screening. Step 2 will present a variety of inexpensive and quick experimental screening methods.

Figure 1:

Application of the Melhem Index

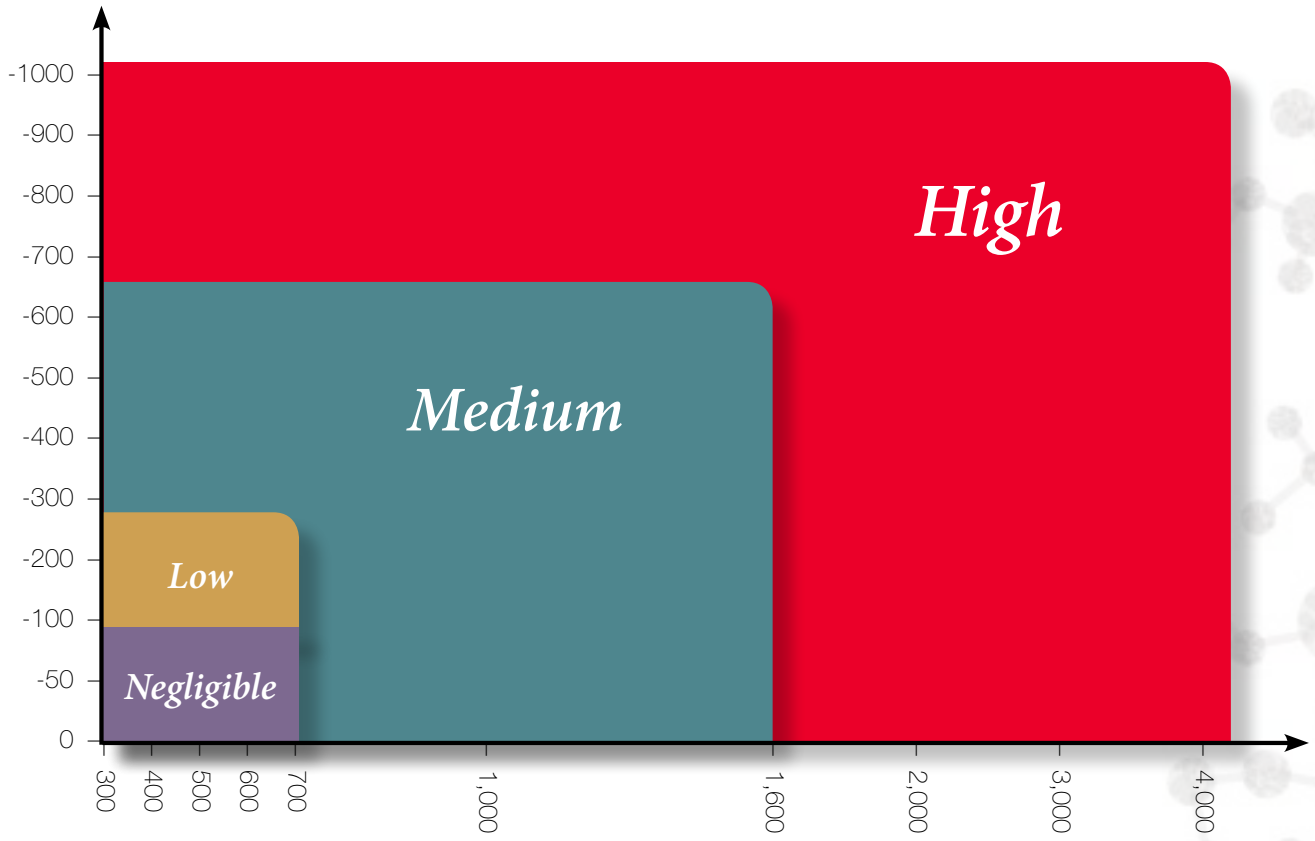
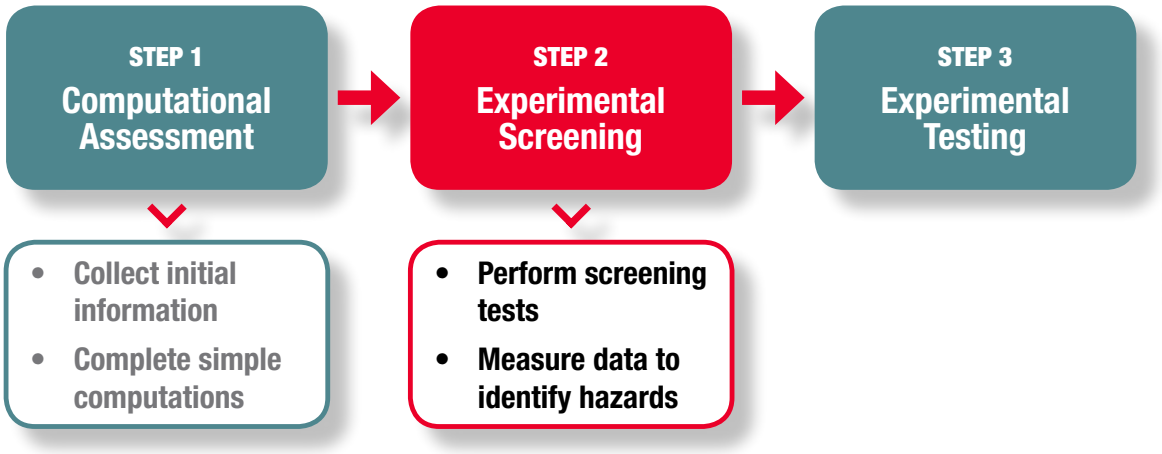


Table 2:
Computational Screening of Chemicals for Chemical Reactivity

Characteristics	Information	Potential Sources
Chemical and Physical Properties	Chemical structure defines the atoms, bonds and functional groups present in a particular compound. These can be compared to chemical structures of known reactive chemicals. Physical properties like physical state, melting/freezing point, boiling/condensation point, density, vapor pressure, flash point, auto-ignition temperature, flammability range, etc. provide additional insight into the potential reactivity of a material.	Safety Data Sheets (SDSs), handbooks, industry and consensus guidelines, chemical reactivity analysis software, codes and standards (e.g., Brethericks's Handbook, Merck Index, NIST WebBook, SuperChems™, OSHA, NFPA)
Chemical Compatibility	Compatibility describes the behavior of two substances after they have come in contact. If substances do not react (change) they are considered compatible.	MSDS, NOAA Matrix (chemical reactivity worksheet) and SuperChems™
Heat of Reaction	Heat of reaction is a thermodynamic unit representing the amount of energy either emitted or produced in a reaction and is typically denoted by the unit kilojoules/mole. Heat of combustion and decomposition are two heats of reaction that provide insight into chemical reactivity potential.	Heat of reaction is estimated from standard formation energies found in standard reference texts (see above) or estimated from group contributions using software programs such as ASTM's CHETAH, SuperChems™, and NIST Database. Formation energies can also be estimated from quantum mechanics.
Heat of Combustion	Heat of combustion is the energy released as heat when a compound undergoes complete combustion under standard conditions.	Heat of combustion is estimated from heats of formation as described above for heat of reaction. In this case, the balanced reaction goes to combustion products. For example: CH_4 (g) + 2 O_2 (g) = CO_2 (g) + 2 H_2O (g) ΔH_c = 802.3 kJ
Heat of Decomposition	Heat of decomposition is the heat of reaction resulting from the decomposition of a compound into a set of simple decomposition products.	Heat of decomposition can be estimated similar to heat of combustion. Functional group energies could also be used for the estimation of decomposition energies. For example: A hydrazine group with –N-N- bond releases 15-21 kcal/mole upon decomposition when heated. Functional group energies could also be found in T. Grewer's book, "Thermal Hazard of Chemical Reactions."
Calculated Adiabatic Reaction Temperature (CART)	CART is the maximum temperature reached if the chemical compounds decompose to their most stable products.	It can be calculated using computer codes that minimize the Gibbs Free Energy of the product at constant pressure or volume using the NASA-Lewis program CEAgui or SuperChems™.
Reaction Kinetics	Chemical kinetics information provides the rate of heat and pressure generated in the system. These values provide insight into the protections that need to be incorporated.	This information may be found using the NIST Chemical Kinetics Database or other literature, where available.
Oxygen Balance	The oxygen balance is the difference between the available oxidizing atoms and the available reducing atoms in a particular chemical compound. It provides a measure of potential instability for materials where structural oxygen contributes to an oxidative decomposition mechanism, e.g., $–NO_3$, $– NO_2$, $– ClO_3$, – OCl compounds. Multiple references, including the CCPS Guidelines for Safe Storage and Handling of Reactive Materials provides cautions regarding the interpretation of oxygen balance for prediction of chemical reactivity.	Oxygen balance is estimated using the formula: $\text{Oxygen Balance} = \frac{-1600\left[2x + \frac{y}{2} - z\right]}{MW}$ Where x, y, z are found from: $C_xH_yO_zN_q$

Step 2: Experimental Screening of Chemicals for Chemical Reactivity



In Step 2, we provide details for how to complete the Experimental Screening. An experimental screening is recommended if either there is no literature available for the chemical reactivity of a sample or if a similar compound or mixture has a computed heat of reaction >100 cal/g, and is expected to be of high hazard (>100 cal/g in combination with CART value >700K) or oxygen balance between -80 and +120.

Experimental screening involves measuring data to identify the existence of chemical reactivity hazards using commonly available screening tools. These tools include

Table 3:

Chemical Reactivity Screening Test Options

Test	Measurement	Phenomenon Observed
Thermogravimetric Analysis	Changes in mass in response to a temperature program	Determines characteristics of materials such as degradation temperatures, moisture content of materials, material composition, level of inorganic and organic compounds in materials, and decomposition points of explosives
Differential Scanning Calorimeter (DSC) Test	Temperatures and heat flows associated with transitions in materials as a function of time and temperature	Provides quantitative and qualitative information about physical and chemical changes that involve endothermic and exothermic processes or changes in heat capacity
Ignitability Test	Tendency of a substance to catch fire from an external ignition source; provides ignitability and burning properties	Ignition/no ignition, ignited and burned, ignited and became bright, ignited and released smoke, ignited and burst into flame, ignited and exploded, and flameless decomposition with release of smoke
Combustibility Test	If a solid substance is ignitable and combustible	Ignition/no ignition, fire extinguished just after ignition, localized burning, no flame propagation or flame propagation
Ignition Point Test	Ignition temperature of a dry solid substance	N/A
Drop-Weight (Or Hammer Sensitivity) Test	Impact sensitivity of high explosives at elevated temperatures	Fire, sparks or smoke and detonation (>10dB (A) noise higher than the standard value); this test is required by the DOT for all materials being shipped

combustibility tests, drop-weight or hammer sensitivity test, differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA).

The example in Figure 2 shows TGA and DSC scans for 100% dicumyl peroxide. In the figure, the TGA scan is blue and the DSC is green. Looking only at the TGA scan, the weight loss curve reveals two degradation reactions: the first major one starting at 74 °C and the second one at 213 °C. Looking at the DSC scan, two (2) major reactions were observed, beginning at 40 °C and 140 °C.

In this example, the DSC was able to detect the change in physical state occurring at 40 °C (melting) due to its measurement of heat flow. Alternatively, TGA was able to detect two reactions within the temperature range of 70 °C to 450 °C due to its ability to measure weight changes very accurately. The second reaction had a small heat flow and runs the risk of being confused with a slow baseline change in the DSC. The difference in information shows the benefit of using both DSC and TGA instruments in experimental screening. The figure below summarizes the chemical and physical characteristics measured by DSC and TGA, which can provide insight into the chemical reactivity potential of a chemical or mixture.

Physical Properties	Technique	Reaction 1	Reaction 2	Reaction 3
Onset T (°C)	TGA	*	144	*
	DSC	40	140	200
Peak T (°C)	TGA	*	160	*
	DSC	42	164	380
End T (°C)	TGA	*	200	*
	DSC	60	199	480

Figure 2:

Comparison of TGA and DSC Test Results for Dicumyl Peroxide

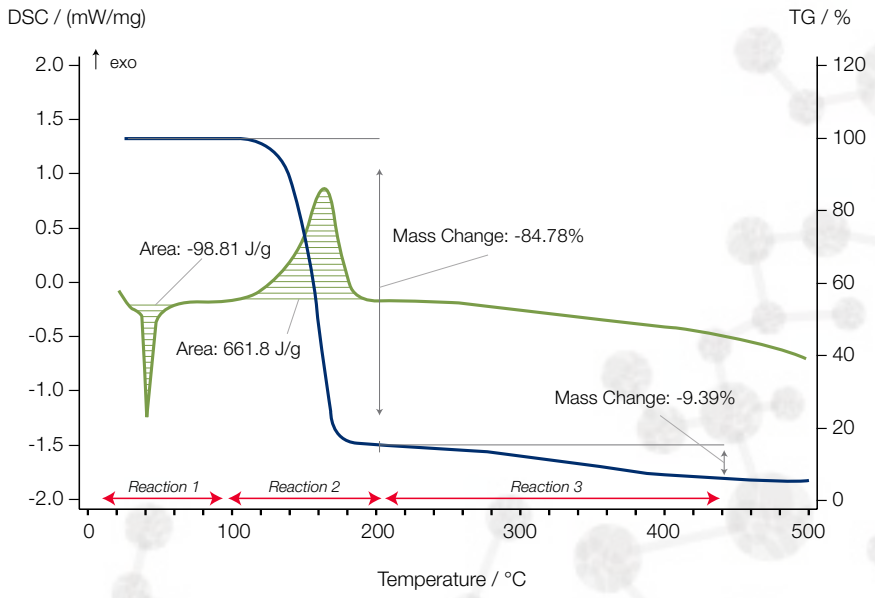
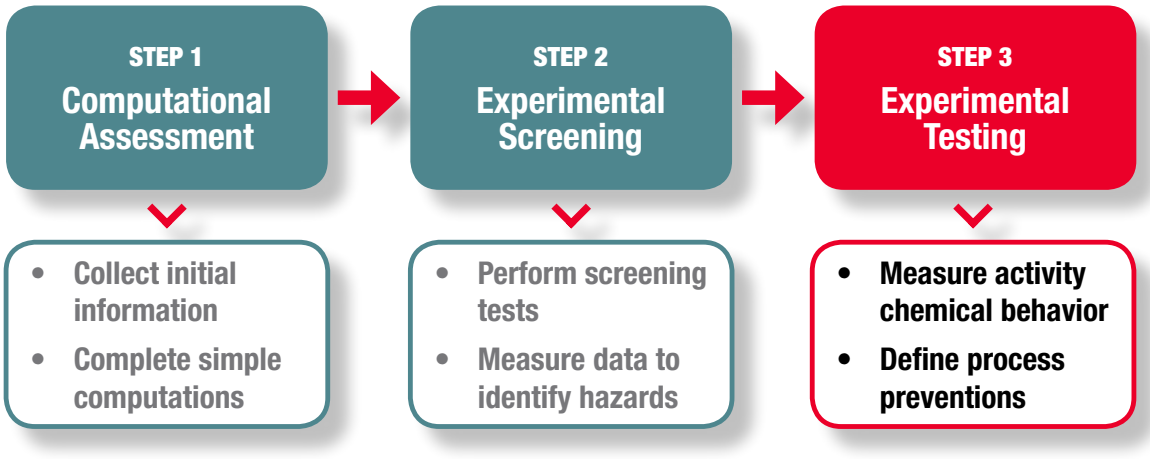


Table 4:

Chemical and Physical Properties Useful During Experimental Screening

Techniques	Experimental Options	Properties Measured
Differential Screening Calorimetry (DSC)	• Typically employ milligram scale samples (e.g., 1-20 mg) • Highly accurate temperature measurement/control but relatively low thermal detection sensitivity due to inertial effects • Experimental options include: open and closed sample containers, system pressurization and noble metal containers (to avoid catalysis/inhibition effects) • Heating options include: scanning, isothermal and isoperibolic • Good for thermal characterization and heat of reaction	• Transitions like melt, glass transition, phase change, and curing • Existence of endotherm/exotherm • Heat of reaction (ΔH_r) • Heat of decomposition (ΔH_d) • Heat of combustion (ΔH_c) • Onset temperature (T_o) • End temperature of reaction (T_f) • Peak reaction temperature (T_p)
Thermogravimetric Analysis	• Typically employ milligram scale samples (e.g., 1-20 mg) • Highly accurate temperature measurement/control, but relatively low thermal detection sensitivity due to inertial effects • Heating options include scanning and isothermal • Good for samples that lose weight when heated	• Onset temperature of reaction (T_o) • Peak reaction temperature (T_p) • End of reaction temperature (T_f)

Step 3: Experimental Testing of Chemicals for Chemical Reactivity



Experimental testing uses commonly available experimental techniques to measure the chemical reactivity of the material/mixture. These techniques can include calorimetry testing in reaction and adiabatic calorimeters. Once experimental screening identifies a reactivity hazard, experimental testing will develop accurate reactivity parameters. These parameters can be used to:

- Optimize processing conditions
- Develop operating and safe limits
- Understand the consequences of deviations
- Design emergency relief systems

Often used for process development and optimization of desired reactions, reaction calorimeters, such as the RC1 from Mettler-Toledo, provide information about critical process parameters like heat release, thermal conversion, specific heat capacity, adiabatic temperature rise and maximum temperature of synthesis reaction (MTSR).

Adiabatic calorimeters include instruments like the Accelerating Rate Calorimeter (ARC®), Automatic Pressure Tracking Adiabatic Calorimeter (APTAC™) or Vent Sizing Package (VSP2™). The ARC uses a heavy walled test vessel and results in a moderate thermal inertia (>1.4) system. Alternatively, the VSP2 and APTAC use a pressure balancing technique that allows for thinner walled test vessels and ultimately, low thermal inertia (>1.05) operation. They use a larger sample size (30 to 100 ml) in comparison to the ARC's 0.5g to 7g. By measuring the temperature and pressure response of a sample heated from room temperature to 400°C, the material characteristics listed in Table 1 can be measured/developed.

Table 5:
Characteristics from caloirmetry testing

Characteristic	ARC	APTAC
Thermal inertia	3.37	1.73
Onset T (°C)	96	100
Maximum heating rate (°C/min)	5.3	439 (lost adiabaticity)
T at max. heating rate (°C)	168	218
Maximum pressure rise rate (psi/min.)	17	1243
End T of exotherm (°C)	187	238
Adiabatic T (°C)	405	>339
Heat of reaction (cal/g mixture)	124	>95
Time to maximum rate (minutes)	175	88
Pressure at the end of exotherm (Psia)	242	201
Amount of no-condensable gas (cc/g-peroxide)	63	Not available

For comparison purposes, Table 5 (previous page) shows the results of calorimetry testing of a di-cumyl peroxide (50%) solution in toluene using ARC and APTAC techniques. Figures 3-5 provide comparable plots of ARC and APTAC data of 50% di-cumyl peroxide. Measured, adjusted and calculated characteristics are reported in the table.

Figure 3:

Temperature and pressure vs. time plot of 50% dicumyl peroxide in toluene

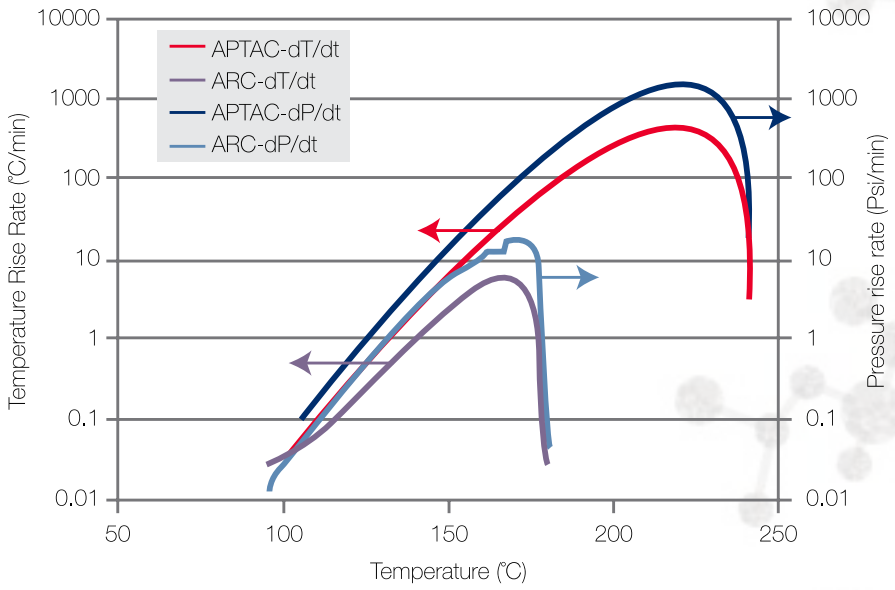


Figure 4:

Temperature and pressure rise rate vs. temperature plot of 50% dicumyl peroxide in toluene

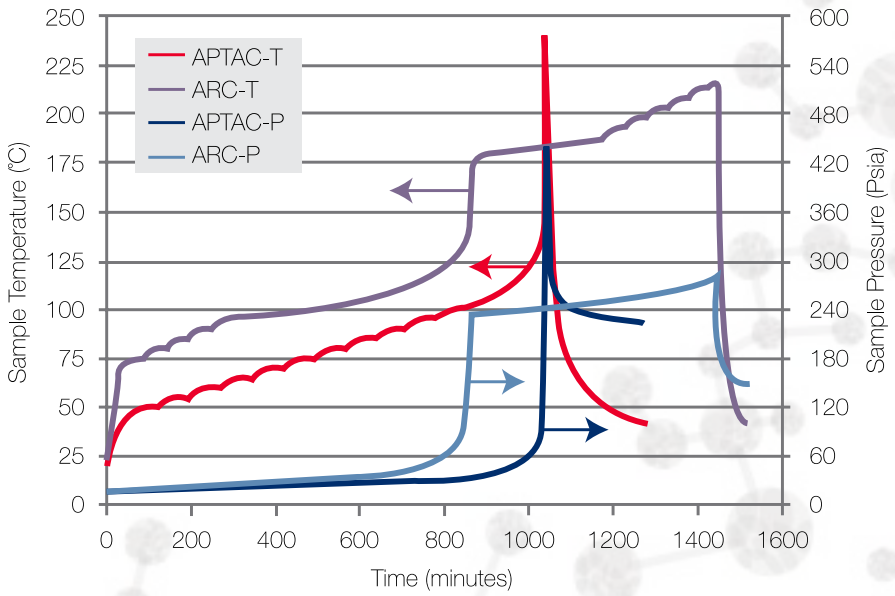
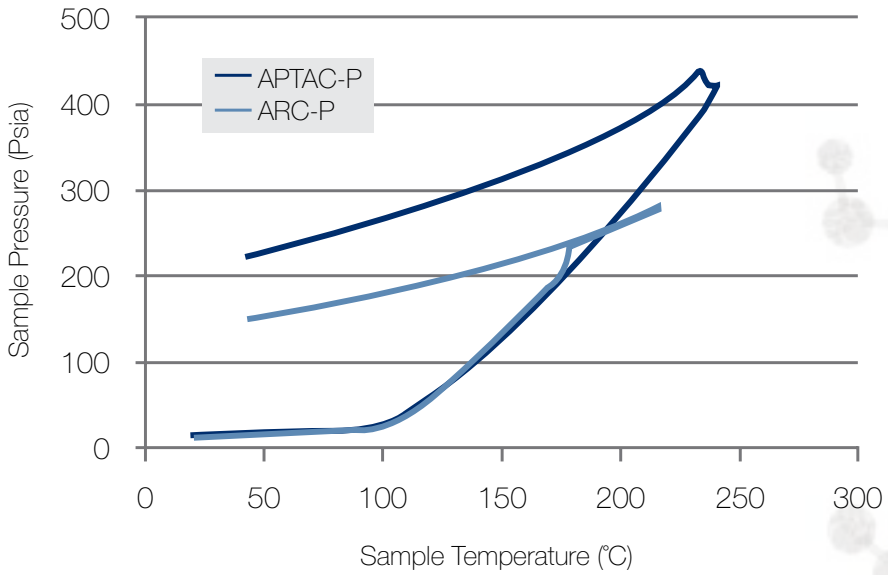


Figure 5:

Pressure vs. temperature plot of 50% dicumyl peroxide in toluene



The data measured and the characteristics developed can be used to understand incompatibilities, define heating/cooling requirements, develop safe operating limits, emergency relief system design, etc. For example, the safe operating temperature and pressure limits can be determined using the onset temperature and pressure measured. The measured temperature and pressure rise rates and total pressure generated can be used as input to emergency relief system design scenario development.

Conclusion

Understanding the chemical reactivity potential of our systems is integral to managing process safety. Implementing a step-wise approach can be a time saving and cost effective approach for conducting the evaluation. First, computational assessment defines whether or not there is any chemical reactivity concern. Second, experimental screening tests provide qualitative information about the potential for chemical reactivity hazards and the magnitude of the hazards. Finally, experimental testing measures the behavior of reactive systems and helps to define the process protections needed to prevent or mitigate reactive hazards.

References

1. Georges A. Melhem, Ph.D., FAIChE (May 2022)
2. Surendra K. Singh, Ph.D., Michelle Murphy (December 10, 2013)