# A SYSTEMATIC APPROACH TO REACTIVE CHEMICALS ANALYSIS

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Reactive chemicals are chemicals that can, under certain conditions, release very large and potentially dangerous amounts of energy. Reactive chemicals can lead to reactions that differ from the routine mainly in the rate at which they progress. A chemical reaction can be considered routine if the reaction rate is relatively slow or can be easily controlled. It is this question of rate of reaction and ability to control that marks certain chemicals as warranting special precautions and the label "reactive chemical." The primary difficulty in identifying reactive chemicals stems from the variety of conditions under which certain chemicals can undergo an uncontrollable hazardous reaction. Some chemicals are simply unstable and can vigorously polymerize, decompose or condense, or become self-reactive. Other chemicals can react violently when exposed to common environmental chemicals or conditions. A major difficulty, which arises when one considers the problem as a whole, is that it is often not appreciated that the reactive chemical hazards is seldom a unique characteristic of the chemical or the process itself but highly dependent on the process conditions and mode of operation. For example, a simple property such as flash point can be used to determine the fire or explosion hazard of a substance. In contrast, the identification of a reactive hazard requires the detailed evaluation of both the properties of the substances used and the operating conditions. The dilemma is that many so-called "benign" reactions can become highly reactive or undergo a runaway reaction under slightly different conditions or the introduction of minute impurities. This paper provides a background of the reactive chemicals problem including a summary of chemical incidents that can be attributed to reactive chemical events. Based on the extent of the problem, a systematic approach to reactive chemicals analysis is suggested. The approach is a tiered framework where one can start with simple screening tools based on thermophysical property and thermodynamic analysis, use of quantum mechanics and transitional state theory, and finally the use of experimental measurements.

Keywords: Process Safety, Reactive Chemicals Analysis, Loss Prevention, Quantum Mechanics, Calorimetric Measurements

## INTRODUCTION

Some chemicals react spontaneously with very common chemicals in the environment such as water or the components of the atmosphere. Many pure metals for example will oxidize on exposure to the atmosphere. Many chemicals are stable except when combined with certain other chemicals.

Some chemicals require very little energy of activation to initiate a spontaneous reaction. If the reaction is exothermic the energy initially produced may accelerate a continued reaction and a release of energy too violent to be controlled. Temperature, shock, static, or light may trigger an uncontrollable reaction. In some combinations one chemical will act as a catalyst reducing the amount of energy normally needed to initiate or sustain a reaction.

Spontaneous decomposition or changes in physical state, even at a slow rate, may create a reactive hazard by creating a less stable chemical. For some chemicals this decomposition is rapid and violent. For others it is so slow as to be imperceptible but results in a byproduct with a much higher reactivity hazard. Peroxides, which can form when certain organic chemicals are exposed to air, will radically increase the hazards of working with those chemicals. The formation of shock sensitive picric acid crystals from an aqueous solution is a serious hazard created by a simple physical state change in the same chemical.

There are some additional hazardous conditions that are not usually attributed to "reactive chemicals" but should be mentioned. Extreme differences in physical state can cause an uncontrollable release of energy. For example, bringing a hot liquid such as an oil into contact with a liquid with a lower boiling point such as water will cause instantaneous vaporization of the lower boiling point liquid and a violent release of energy.

## CHARACTERIZATION OF CHEMICAL REACTIVITY

Many procedures have been suggested in the recent literature for categorizing reactive chemicals. Since the needs for an assessment procedure varies from one industry to another, much effort has been addressed to this subject. A generalized approach to an assessment process stills remains an ultimate goal. A successful approach should be based on an understanding of the stoichiometry, thermodynamics, and kinetics of the reactive system and ideally should require minimum time and inexpensive procedures. In this section we will refer to some of the relevant work during the last few years.

Application of thermal analysis techniques to evaluate reactive chemical hazards has been a major concern for researchers. Zatka (1979) discussed the ability to solve, to some extent, the reactivity questions of substances and reaction mixtures by using commercial differential scanning calorimeter (DSC) and differential thermal analysis (DTA) equipment. In 1985, Kohlbrand presented an experimental procedure to test the runaway potential of reactive chemicals. He suggested using the DSC as a first step and then the accelerated rate calorimeter (ARC) in a more advanced reactivity investigation, especially for pilot plant operations. Gygax (1990) suggested a two-level thermal analysis procedure. The first level was to determine the energy potential and the temperature region of significant thermal activity using microthermal analysis and isoperibolic experiments. The second level was to determine the thermokinetic parameters of the overall reaction using isothermal and adiabatic experiments.

Estimating process safety parameters is another goal of applying thermal analysis testing. Kellet et al. (1997) suggested the use of dynamic DSC and isothermal DSC measurements to evaluate the time to maximum rate under adiabatic conditions ($\Delta TMR_{ad}$) and comparing to values based on simulation. They concluded that this estimation method is useful for preliminary screening procedures for reactive chemical hazard evaluation.

Many other studies were conducted to present the uses of calorimetry in reactivity evaluations or to present modified calorimeters. LeBlond et al. (1996) presented the importance of using reaction calorimetry to obtain high quality kinetics parameters even for complex multi-step reactions. Since adiabatic conditions are maintained during runaway reactions, adiabatic calorimeters are considered the most representative of the behavior of real processes. Sempere et al. (1997) studied the suitability of using various adiabatic equipment in evaluating exothermic reaction hazards such as for decompositions. Heldt and Anderson (1996) discussed the application of modified adiabatic calorimeters to perform chemical reactivity analysis. Townsend and Tou (1980) presented development of accelerated rate calorimeter (ARC) to study reactions taking place under adiabatic conditions to provide time-temperature-pressure data. Fauske (1998) described the use of the reactive system screening tool (RSST) as an early testing step for evaluating reactive chemical hazards.

For each of the suggested techniques there are advantages and disadvantages. Kars and Visser (1996) suggested as a screening tool the shell-modified Sikares calorimeter, which combines some advantages of adiabatic and DSC techniques. Other researchers conducted studies to compare the various techniques. Duh et al. (1996) performed a study to compare the Arrhenius parameters obtained from isothermal, adiabatic, and temperature programmed methods. Leonhardt and Hugo (1997) presented comparisons of thermokinetic data obtained by isothermal, isoperiolic, adiabatic, and temperature programmed measurements. Pastré et al. (2000) conducted a comparison between adiabatic calorimetric and dynamic DSC measurements to estimate time to maximum rate ($TMR_{ad}$).

Estimating reliable kinetic parameters of the main reaction pathway is essential for reactive chemical hazard evaluation. Calorimetric analysis will provide acceptable parameters for homogeneous and one-dimensional chemical systems. However, laboratory investigations are expensive and time-consuming when systems are more complicated. Also, the measured parameters are often not of high accuracy, making reliable thermal hazard evaluation more difficult or impossible [Maria & Heinzle 1998].

Researchers have suggested novel simplification techniques for complex reactions, to reduce the experimental effort. Grewer et al. (1999) discussed the application of calculations based on theoretical models to predict thermodynamic parameters of primary and secondary reactions using the Chemical Thermodynamic and Energy Release Program (CHETAH). Laboratory investigation could then be implemented in case the theoretical approach failed. Maria & Heinzle (1998) suggested those kinetic parameters to be measured from isothermal concentration data and simulated to other kinetic parameters of similar known reactive systems available in databank to help define the reaction pathway. These kinetic parameters could be verified using temperature programmed-DSC. Liaw et al. (2000) developed a mathematical model to predict thermal hazard parameters by simulating adiabatic calorimeter data. Marco et al. (2000) performed isothermal reaction concentration-time experiments and obtained the kinetic equation describing the chemical reaction. The simulation results were compared to temperature-time data for the same reaction obtained from near-adiabatic advanced reactive system screening tool (ARSST) experiment. The combination of isothermal concentration-time results with temperature-time results can help to determine more accurate kinetic parameters and reaction pathways.

Introducing theoretical models of computational chemistry and statistical thermodynamics for predicting thermodynamic parameters was discussed by Bruneton et al. (1997 & 1998). Knowing the system thermodynamics helps focus on the most energetic and therefore the most potentially hazardous reaction pathways.

## SYSTEMATIC APPROACH

An evaluation of chemical reactivity must be based on essential information, which includes:

- process operating conditions
- process chemistry mechanisms
- conditions under which chemical reactive hazards can appear
- parameters for quantifying reactive chemicals hazards

Defining these conditions and parameters helps simulate the chemical process for optimum safe and economical operating conditions. Evaluating this information is not an easy task. Laboratory testing has been the traditional approach to evaluate chemical reactivity. This approach is practical for simple systems, but may not be applicable for more complex systems. Because of the large number of chemical compounds and different reaction scenarios, evaluation can be very expensive and time consuming. Moreover, in case of a complex reactive system, experimental procedures will provide an overall evaluation of system thermodynamics and kinetics data but will not explain reaction pathways. In fact, system analysis is required beyond laboratory measurements.

Discussed in this paper is a systematic approach to chemical reactivity characterization that consists of three levels, as shown in Figure 1. In each level, the reactive system is evaluated to understand the reaction chemistry, identify the possibility of thermal exothermal activity, and quantify the reactive chemical hazards. The three evaluation levels are:

1. screening evaluation
2. computation evaluation
3. experimental analysis

In the screening evaluation level, reactants, products, and operating conditions are identified. Literature and databases are searched for relevant data for the various substances in the chemical system. Relevant data include physical and chemical properties, thermodynamics, kinetics, incidents, and case studies. In addition, in this level, some computations and measurements are made for a preliminary reactivity evaluation. In this evaluation level, some chemicals or reactions that clearly present no hazardous potential can be excluded from further evaluation.

In the second level, all possible reaction pathways are proposed and their feasibility is evaluated based on available information or on predicted properties using numerical techniques such as computational quantum chemistry, statistical thermodynamics, and transition state theory. The non-feasible and non-hazardous reaction pathways are excluded and the remaining ones are tested in the third level of evaluation.

The third level includes experimental analysis. At this level, the numbers of reactions and chemicals to be tested are reduced. More screening tests are performed to exclude more reaction possibilities and to direct the most hazardous reactions to the more advanced experimental techniques. In each of the three evaluation levels, predicting or calculating stoichiometric, thermodynamic, and kinetic parameters are the main objectives and many reaction pathways are thereby excluded from the need for expensive experimental analysis.

Each of these three levels is discussed in the following sections.

## LEVEL 1: SCREENING

The screening level is of great importance for the evaluation of chemical reactivity. Screening may include many simple tools to identify thermal hazards of any chemical. Some of these tools are:

1. literature review
2. oxygen balance criterion
3. molecular structure considerations
4. chemical incompatibility

Determining possible reactants, products, operating temperature and pressure ranges, and any other parameters that may affect the process will identify a reactive system. Once the reactive system is identified, the literature is searched for determining some of the stoichiometric, thermodynamic and kinetic parameters based on previously studied systems with similar components. This information may be used in more advanced evaluation levels. Searching the literature also may yield information about incidents due to the same or similar chemicals.

Oxygen balance calculations are used within the screening level as the amount of oxygen, expressed as weight percent, liberated as a result of complete conversion of the material to relatively simple oxidized molecules. This oxygen balance relates to the number of oxygen and reducing atoms in the substance itself. If all reducing atoms can be oxidized completely without excess oxygen, the oxygen balance is zero, and the energy generation of the substance is maximum and is independent of the external oxygen concentration. For molecules containing the elements carbon, hydrogen, and oxygen, oxygen balance is expressed by:

$$\text{Oxygen Balance} = \frac{-1600\left[2x + \left(\frac{y}{2}\right) - z\right]}{MW}$$

where $x$ is the number of carbon atoms, $y$ is the number of hydrogen atoms, $z$ is the number of oxygen atoms, and $MW$ is the molecular weight.

A criterion for the value of this balance was proposed, because, in some cases the results of this simple tool may be misleading by bearing no necessary relationship to hazard potential. Shanley & Melhem (1995) studied some familiar compounds of known hazard potential, and found that oxygen balance values do not correlate well with the known hazard potential of these compounds. More detailed discussion is provided in [Shanley & Melhem 1995] [CCPS 1995].

The molecular structure of the various components is another screening tool. Some typical structural similarities in high-energy substances are the relative degree of unsaturation, high proportion or high local concentration of nitrogen in the molecular structure, and nitrogen-to-hydrogen bonds [Bretherick 1987]. Some of the well-known molecular structures are used for identifying the presence of reactive chemical hazards, as shown in Tables 1 and 2.

The existence of any of these functional groups and their unstable structure may be an indication for thermal instability, but this is not guaranteed. For example, the presence of a nitro group attached to a long aliphatic chain does not show a thermal hazard possibility, even though the nitro group is one of the unstable structures. On the other hand, the initial absence of unstable groups is no guarantee for long-term stability of the compound. For example, some aldehydes and ethers are easily converted to peroxides by reaction with oxygen from air [CCPS 1995]. The list of unstable structures in Table 1 is not comprehensive, but it is a tool for reactivity indications.

Knowing the molecular structure of each compound in the system may be used for calculating exothermic potential. Various methods have been used such as heat of formation method [CCPS 1995], and average bond energy summation [Craven 1987]. These methods depend on values of heat of formation of various molecules or bond energy, which are often available in the literature. High accuracy is not an objective for these methods, but preliminary evaluations and indications are useful for screening purposes.

The hazards resulting from inadvertent mixing of chemicals such as explosion, fire, excessive increase in pressure or heat or the release of toxic vapors is addressed as chemical incompatibility, which is a well-recognized problem. Much effort was required for developing chemicals incompatibility charts and tables, which are available in the literature [Winder & Zarie 2000] [Hofelich et al. 1994]. Incompatibility is a matter of degree, however, many parameters such as temperature, amount of material, maximum process pressure, and time of mixing may affect the degree of hazard. Hence, when using the available incompatibility charts and tables, system conditions must be specified. In cases where chemicals of interest are not tabulated, a simple mixing test may help provide an indication of incompatibility, which may require advanced testing. More advanced compatibility analysis evaluation methods are available [Hofelich et al. 1994] [Duh et al. 1997].

As shown above, there are many preliminary screening tools. The indications are that these tools should be used with caution. In some cases, the screening level evaluation may result in excluding some obviously safe compounds or reactions from further investigation procedures.

## LEVEL 2: COMPUTATIONAL MODELS

Maintaining the safe operation limits for any chemical process is a primary goal of reactive chemical hazard evaluation. Simulating the dynamic behavior of the process ideally will determine process safe operating conditions. Process simulation is often not possible because of insufficient information. This information includes possible reaction pathways and stoichiometries, thermodynamic parameters, and kinetics of the primary and secondary reactions. However, as shown in the previous section, such information is not usually available in the literature or in databanks, especially, for less common and new systems.

To evaluate the potential of reactive chemical hazards, process parameters must be estimated. An experimental approach, in which the possible exothermic reactions are reproduced in the laboratory, could be taken. However, starting with this approach directly, without additional screening steps was found to be time consuming and expensive, due to the large number of possible reaction pathways, even for relatively simple systems. Also, highly unexpected exothermic secondary reactions may dictate the magnitude and time scales of heat releases during the runaway, and increase the difficulty of interpreting the data of currently used experimental techniques [Bruneton et al. 1998].

In this approach, a computational screening tier is proposed, as illustrated in Figure 2. Identification of the stoichiometries of the reactions that drive thermal instability is a major factor to understanding safety issues of a reactive system. Also, identification of the various possible pathways is the first step to start this computational screening tier.

In most reactive systems, primary reactants and products are known, but products of the secondary reactions are not known. Initially, as shown in Figure 2, a set of possible reaction pathways must be proposed. The basis of this step may vary depending on the system. Available information of similar systems may be used to build this set of possible pathways. Experimental information about the products formed and the subsequent chemistry is another basis for building this set of possible pathways.

The main objective of this computational screening tier is to exclude (eliminate) any infeasible or non-hazardous pathways and to evaluate the reactive chemical hazards for the remaining reactions through the estimated stoichiometries, thermodynamic, and kinetic parameters of the reaction system.

Once the reactants and products are identified or proposed, missing thermodynamic parameters can be estimated using the following numerical methods:

1. molecular group contribution methods
2. statistical thermodynamics combined with computational quantum chemistry methods

Molecular contribution methods are theoretical techniques, which use bond and group contributions in known chemical structures to estimate thermodynamic parameters (e.g. Gibbs free energy, heat of formation and heat of reaction) of the system.

Many different group contribution methods are available; however, the method of Benson (1970) which is used in the CHETAH program is the most widely acceptable one. Molecular group contribution methods are preliminary screening tools to detect sufficiently unstable molecules. Sometimes they are not able to predict the thermodynamics of certain molecules, because some groups are not implemented in these methods [Bruneton et al. 1997]. In fact, these methods are based on correlations obtained from a large number of experimental values of thermodynamic properties for common molecules. Occasionally, these methods are unable to differentiate between the various molecular configurations such as isomers, leading to large deviations in the calculated enthalpies. In such cases, implementation of computational quantum chemistry is the next step for the evaluation of system thermodynamics.

Computational quantum chemistry is based on molecular quantum theory when the motion and distribution of electrons is described in terms of electron probability distributions or molecular orbital [Bruneton et al. 1997]. Numerical techniques have been developed to perform the quantum chemistry calculations. Among the most known techniques are Density Functional Theory (DFT), Hartree-Fock (HF), and semi-empirical parameter techniques. The fundamental quantum chemistry methods, which are also called ab-initio methods, are coupling with statistical thermodynamics to estimate thermodynamic properties, such as enthalpy and entropy of formation of the reactants and products, enthalpy and entropy of the reaction, Gibbs free energy of the ideal gas reaction, and Gibbs free energy of mixing of the reaction.

Predicting thermodynamic information will help, as shown in Figure 2, in excluding infeasible reactions (pathways) and non-hazardous molecules of the proposed pathways. The amount of energy released in any exothermic reaction is not the only key issue in evaluating the hazard of reactive chemicals, although it is essential. The energetic reactions (pathways) will be carried to a more advanced evaluation. The rate (kinetics) at which this energy can be released is the most critical issue. Evaluating the kinetics (activation energy, rate constant) of the reaction system can be challenging or infeasible in case of a complex system of reaction pathways.

A second step of numerical calculations is proposed. Combining computational quantum chemistry (ab-initio methods) with Transition State Theory (TST) calculations is an approach to evaluate reactive system kinetics. Utilizing ab-initio and TST calculations depends on identifying the stoichiometry of the reactions, and then identifying the elementary steps involved in these reactions. The GAUSSIAN package is a commercial software application of ab-initio calculations. More theory and practice of this package is found in [Hinchlifle, 1994]. Unfortunately, applying TST calculations for predicting kinetics may not be useful for some complex systems, but coupling the predicted thermodynamic parameters with concentration-time experimental data is another way to estimate the kinetics of a reactive system.

At the end of this theoretical reactive system evaluation, we conclude that the ability to predict accurate kinetics depends partly on the predicted stoichiometry of the system, which was performed at the beginning and throughout this computational tier. The most exothermic reactions could be further investigated by means of the experimental analysis tier.

## LEVEL 3: EXPERIMENTAL METHODS

Most of the safety and thermal reaction risk estimations are based on the exact characterization of a reaction system, including knowledge of the reaction stoichiometry, thermodynamic, and kinetic parameters.

An exact determination of the reaction parameters by traditional means requires extensive and time-consuming laboratory investigations, which may not be cost-effective for many specialty chemicals or immediately applicable to large-scale production purposes due to the variability in raw materials and operating conditions [Maria & Heinzle 1998]. However, as shown in the previous section, the results using the theoretical computational thermodynamics and kinetics approaches are very dependent on the initial assumptions and process conditions used in the evaluation process. Incorrect assumptions may result in the hazards of the system being greatly over or underestimated. As a result, the parameter prediction process is not safe enough for the most energetic reactions within the system.

In such cases, where the theoretical approach is indicating a potential for exothermal activity (chemical reactivity), a more thorough investigation is required for more exact parameter determinations. Up to this point, theoretical computational methods helped to exclude non-hazardous reaction pathways, indicating the most exothermal reactions, and predicting reliable stoichiometric, thermodynamic, and kinetic parameters. Such knowledge will help to guide the experimental investigations.

For a single reaction, sufficiently accurate estimates of the thermodynamic and kinetic parameters can be achieved by using calorimetric methods [Maria & Heinzle 1998]. However, for more complex reacting systems (more than one reaction), calorimetric methods will provide overall measurements of thermodynamic and kinetic parameters without an explanation of reaction pathways and stoichiometries. Hence, meaningful interpretation of the experimental results based on reaction pathways might be impossible. The previous theoretical approach of reaction pathways and parameter prediction should be performed to develop an approximate model for the reaction mechanism. A reaction mechanism may also be obtained by isothermal time-concentration experiments through a direct measurement of species concentrations and kinetic parameters. Understanding the reacting systems' chemistry is essential for reactivity evaluation, and because of that, a major effort to identify reaction pathways is required by the different means of theoretical approaches, as shown in the previous section, or by experimental approach, as discussed below.

Experimental techniques for chemical reactivity evaluations produce data of varying quality. Mainly, there are four common techniques including temperature-programmed differential scanning calorimeter (DSC), isoperibolic, isothermal, and adiabatic analysis. In this approach these techniques are divided into two levels:

a. screening analysis techniques
b. advanced analysis techniques

Figure 3 illustrates the experimental analysis level of this systematic approach. The screening level contains temperature-programmed DSC and isoperibolic analysis, while the advanced level contains the isothermal and adiabatic analysis techniques. This classification will help to provide the necessary information with the fewest number of expensive and time-consuming experimental analyses.

The screening analysis level will help to meet two objectives:

a. estimation by measurements of the over all heat (energy) released by the system
b. estimation by measurement of the temperature range of exothermal activities

Temperature-programmed DSC is an appropriate beginning for an experimental analysis of a reactive system. In the theoretical part, we may predict a reaction model, but not predict the thermodynamics of this reaction(s), or perhaps be uncertain that the predicted values are accurate enough for reactive chemical assessment. Temperature-programmed DSC, especially the closed cell design, is a screening technique for estimating the energy potential (heat of reaction) of the system by measuring heat flux. This analysis will allow calculation of the adiabatic temperature increase ($\Delta T_{ad}$) according to the following equation:

$$\Delta T_{ad} = \frac{\Delta H}{m\, C_p}$$

where $\Delta H$ is heat of reaction, $m$ is reactant substance mass, and $C_p$ is specific heat of reaction mixture. If this adiabatic temperature increase is not major, and if the system temperature is not above its boiling point, the potential hazard of this system may be excluded.

There are some values of ($\Delta T_{ad}$) used as a rule of thumb; the most common is 50°C [Gygax 1990] [Keller et al. 1997]. In general, as a disadvantage of this technique, the heat flux signals will be slightly distorted which affects the kinetic evaluations but does not affect the overall energy determination [Gygax 1990]. Another disadvantage is that the estimate of ($\Delta T_{ad}$) is considered rough in some cases. Hence the interpretation of ($\Delta T_{ad}$) of a system may not be clear, since at the end 50°C is still a rule of thumb. In such cases another screening test is to be performed to find the range of temperatures within which the system is considered active for unexpected or unwanted reactions. Isoperibolic experiments will give more accurate estimate of the temperature range of reactivity.

Measuring the sample temperature while maintaining the cooling temperature constant is the basis for isoperibolic experiments. The maximum adiabatic rise ($\Delta T_{ad}$) is calculated by:

$$\Delta T_{ad} = \frac{U\, A}{m\, C_p} \int_0^\infty \left(T_s - T_c\right) dt$$

where, $U$ is overall heat transfer coefficient, $A$ is surface area of heat transfer, $T_s$ is reaction mixture temperature, $T_c$ is cooling jacket temperature, and $t$ is time. This estimate will indicate the range of temperatures that should be avoided during chemical processes to eliminate unwanted exothermic reactions. In case the unwanted exothermic reaction initiation temperature is close to or overlapping with the process operating temperature, a more detailed investigation is required.

A more advanced investigation requires the introduction of the thermokinetics approach. On the screening level, knowledge of kinetic parameters was not necessary for reactive chemical evaluation, but in complex systems with many reactions in overlapping temperature ranges, this more elaborate approach is required. This advanced thermokinetics analysis level will help meet three objectives:

a. estimation by measurement of the thermodynamic parameters of the overall reactive system in a more accurate way
b. estimation by measurement of the kinetic parameters of the overall reactive system
c. minimizing the scale-up error factors by using testing conditions that are closer to the actual operating conditions

Although kinetic parameter estimation in these methods is for the overall reactive system, the theoretical approach in predicting the stoichiometery of various pathways can help to reduce the system to simpler and more important reactions for further studies.

Isothermal and adiabatic analyses are two techniques used in very advanced thermal analysis. Isothermal analysis can provide the most accurate heat production rates by maintaining reaction mixture at constant temperature while measuring the heat flux as a function of time. On the other hand, adiabatic analysis is more favored, particularly for large reacting masses. In the real plant situations of thermal runaway, neither the process cooling system, nor the reaction container will be able to dissipate the huge amount of energy released. The increasing reactant mass temperature will increase the rate of reaction exponentially, leading to more heat production while adiabatic conditions are maintained. The data obtained in either the isothermal or adiabatic analysis are then used to calculate the thermodynamic and kinetic parameters of the system. In both analyses, it is difficult to maintain perfect isothermal or adiabatic conditions. This will be reflected on the results, and therefore it should be considered during parameter calculations and reactivity hazard evaluation. Several sophisticated instrumental designs of isothermal and adiabatic reaction calorimeters with advanced features are available. Calculating times to runaway and to maximum rate reactions are possible with this level of thermal analysis data. A detailed discussion of these methods is available in Gygax (1990).

Up to this point, only temperature-time experimental data were used to evaluate reactive chemical hazards. At the beginning of our presentation to this systematic approach, we mentioned the knowledge of reaction pathways for a sufficient understanding of our experimental data. However, accurate determination of kinetic parameters for complex reactive systems may not be possible without isothermal concentration-time experimental data. As shown in Figure 3, experimental concentration-time data will help to characterize reaction pathways and hence verify the proposed pathways. Isothermal concentration-time experimental data can be coupled to experimental thermal analysis data or simulated from other similar systems whose kinetic parameters are known or available in databanks. These simulated systems may help initially to predict the reaction pathways, and hence to increase the confidence in the analysis.

## SUMMARY OF THE PROPOSED SYSTEMATIC METHOD

The proposed systematic approach, as shown in Figure 1, focuses on determining stoichiometric, thermodynamic, and kinetic parameters of any chemical process by utilizing theoretical and experimental methods.

The first level of this approach was to screen the reactive system based on the available information in databanks or literature. Also, simple structure instability and chemical incompatibility considerations were evaluated. Because these considerations are used as a screening tool, the results should be used with caution.

In the second reactivity evaluation level, theoretical methods are used to help find the reaction pathways, and to predict thermodynamic and kinetic parameters. For predicting thermodynamics, two levels of theoretical techniques are discussed: molecular group contribution methods and statistical thermodynamics combined with computational quantum chemistry methods (ab-initio methods). Molecular group contribution methods depend on thermodynamic data available in databanks for similar molecular groups, which makes its usage limited to the available data. Ab-initio methods are more advanced techniques based on quantum molecular theory. These methods may be used to predict thermodynamics if the molecular group contribution methods fail, but more knowledge and experience is needed to utilize ab-initio methods. Predicting system kinetics is possible using computational quantum chemistry with transition state theory. Depending on the complexity of the system, the predicted values may not be accurate enough to be used for reactivity analysis. Experimental analysis should be used for missing parameters or for more accurate measurements.

After excluding non-feasible and non-hazardous pathways based on the theoretical methods, experimental methods are used to complete the reactivity analysis. Temperature-programmed DSC and isoperibolic techniques are used for screening experimental analyses. More advanced analysis of isothermal and adiabatic methods are used for more accurate measurements. System complexity and degree of accuracy are factors affecting the experimental technique selection.

## CONCLUSIONS

Both the ability to evaluate reactive chemical hazards in process chemistry and the ability to determine process safe operating boundaries will enhance not only the safety and operability of processes but will help in determining their optimum operating conditions.

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Table 1. Examples of well-known high energetic compound groups and their unstable structure [CCPS 1995].

| Compound Group | Unstable Structure | Compound Group | Unstable Structure |
|---|---|---|---|
| acetylenic compounds | $-C\equiv C-$ | hydroxylammonium salts | $-N^{+}-OH\ Z^{-}$ |
| azo compounds | $-C-N=N-C-$ | metal acetylides | $-C\equiv C-M$ |
| alkyl nitrites | $-C-O-N=O$ | metal peroxides | $-O-O-M$ |
| alkyl nitrates | $-C-O-NO_2$ | metal fulminates | $-C=N-O-M$ |
| alkyl hydroperoxides | $-C-O-O-C-$ | N-nitroso compounds | $-N-N=O$ |
| aci-nitro salts | $HO-(O=)N=$ | N-nitro compounds | $-N-NO_2$ |
| diazo compounds | $-C-N^{+}=N^{-}$ | N-halogen compounds | $-N-X$ |

Table 2. Examples of well-known high energetic compounds and their heat of formation [CCPS 1995].

| Compound | Unstable Structure | Heat of Formation (kJ/g) |
|---|---|---|
| cyanogen | $N \equiv C - C \equiv N$ | + 5.9 |
| nitrogen trichloride | $NCl_3$ | + 1.9 |
| acetylene | $H - C \equiv C - H$ | + 8.7 |
| hydrogen cyanide | $H - C \equiv N$ | + 4.8 |
| 1, 3 – butadiene | $H_2C = CHCH = CH_2$ | + 2.1 |

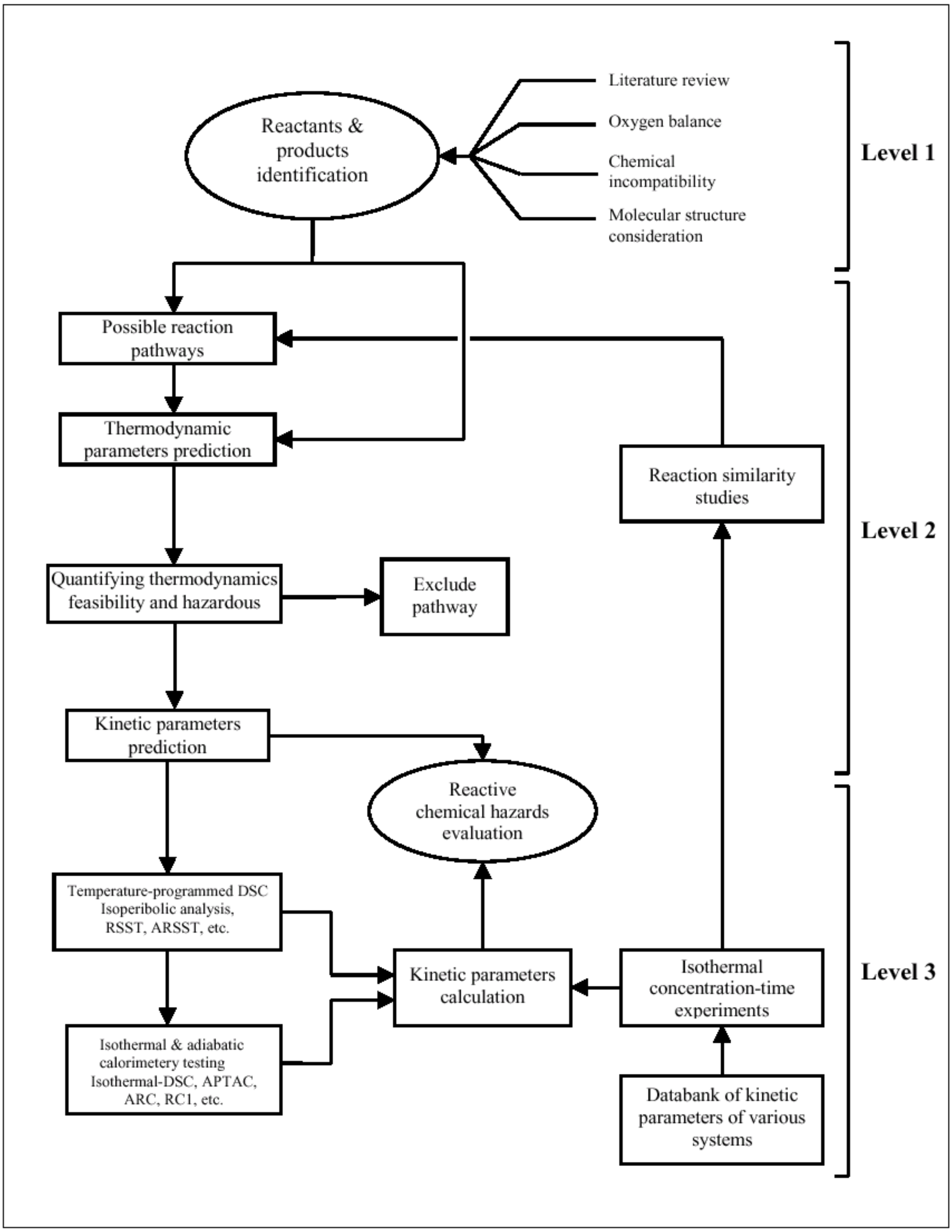

Figure 1: Systematic approach for evaluating chemical reactivity

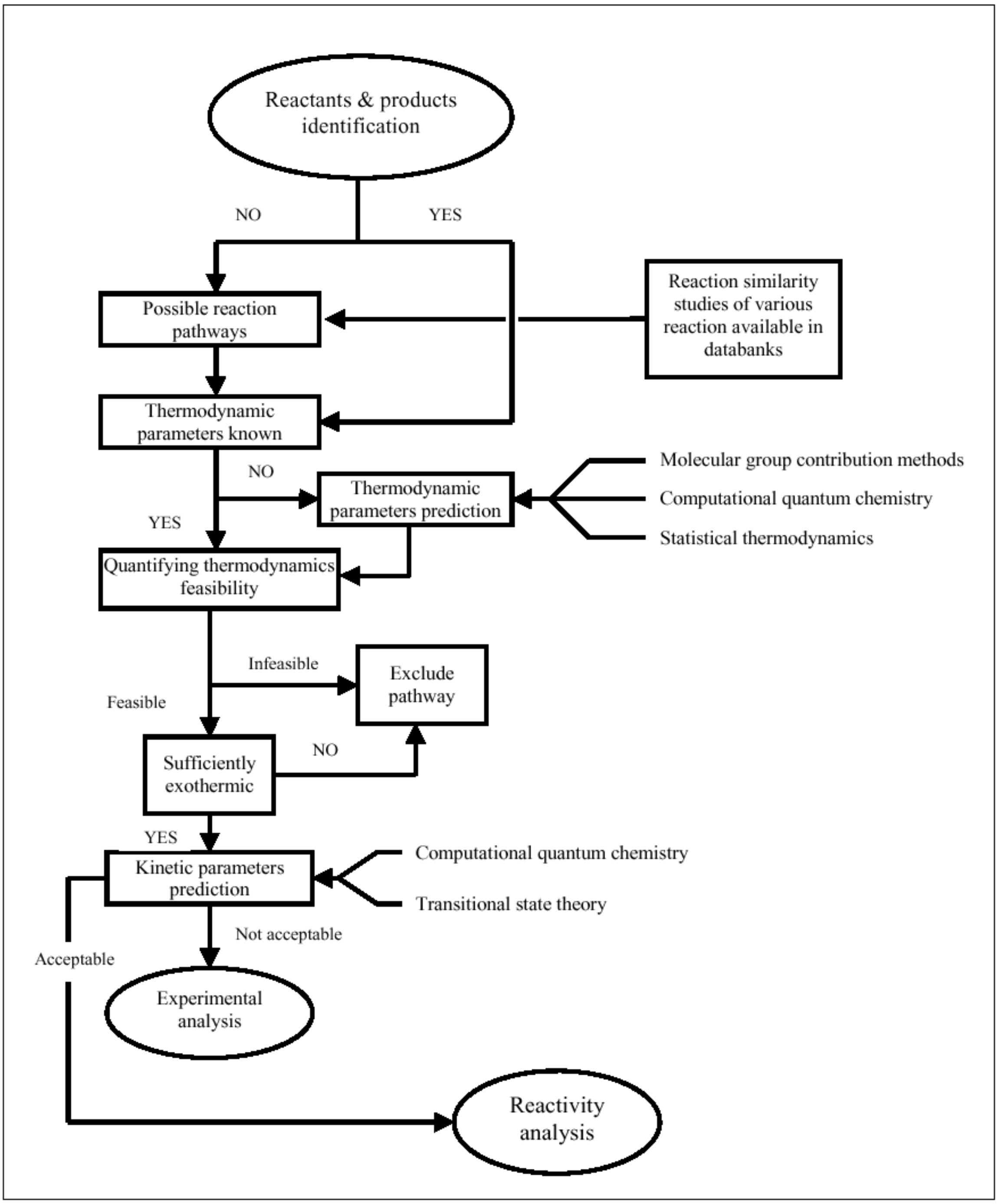

Figure 2: Theoretical methods approach in evaluating reactivity hazard

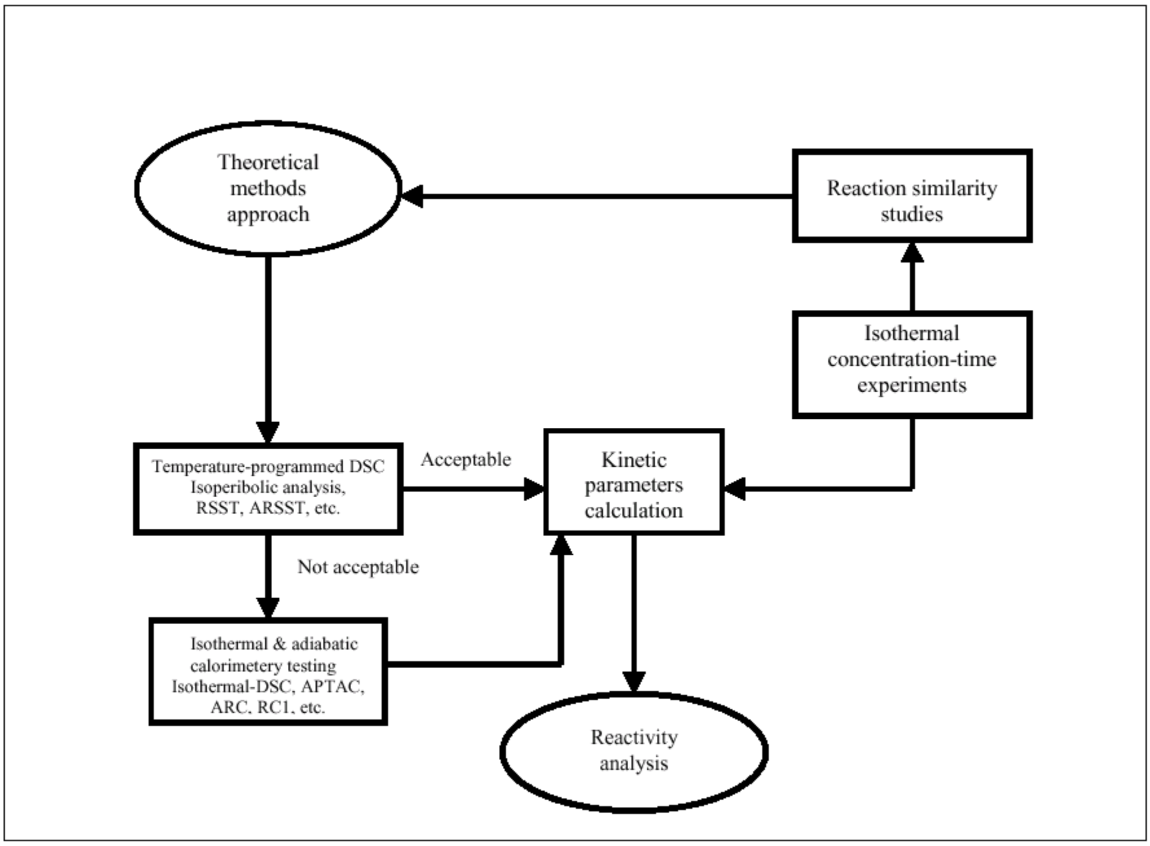

Figure 3: Experimental analysis approach in evaluating reactivity hazard