Systematic Evaluation of Chemical Reaction Hazards

G. A. MELHEM
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, Massachusetts 02140

ABSTRACT

Effective thermal hazard evaluation requires an integrated approach to assessment of chemical reactivity. A variety of theoretical and experimental methods can be used to determine the thermal stability of specific compounds or reactive systems. Notwithstanding this, recurrent problems occur with materials and/or reactions which are known to be inherently unstable. Correct application of physical tests and interpretation of output data is essential for effective thermal hazard evaluation [1].

This paper provides an integrated approach for the systematic evaluation of thermal hazards and effective scaleup of data for emergency relief system design.

THERMAL HAZARDS ASSESSMENT

In order to develop an effective approach, we need to consider the essential elements which comprise thermal hazard evaluation for pressure relief design purposes. This includes:

1. Screening Checks
2. Data Interpretation
3. Physical Testing

Screening Checks

Before initiating any thermal stability testing program, it is prudent to carry out preliminary screening checks. Complex or unfamiliar materials may exhibit detonation or deflagration properties. In such cases, specialized testing is required. For simple or familiar materials, much

[1]This paper appeared in "International Symposium on Runaway Reactions, Pressure Relief Design, and Effluent Handling", Edited by G. A. Melhem and H. G. Fisher, AIChE, 1998

information can be confidently predicted by theoretical means, thus reducing the need for time consuming and costly testing. Optimization of experimental parameters for subsequent physical tests can increase cost effectiveness of testing programs.

Typical screening checks might include the following three elements, structural analysis, specialized testing (Detonability, etc.) and thermochemical evaluation.

Physical Testing

For thermal analysis in connection with relief system design, we are primarily concerned with the point of incipient instability and with characterization of the runaway process. A variety of calorimetric devices exist which can be used to measure and quantify runaway and/or decomposition phenomena. Other larger-scale devices (e.g. reaction calorimeters) are intended for study of reaction heat release under controlled conditions. Our discussions here will concentrate mainly on the first category above.

A number of practical constraints affect our choice of test methods. Runaway or decomposition phenomena are extremely hazardous, other than on a relatively small scale. Notwithstanding this, generally more representative data can be obtained with increasing experimental sample size. Rapid preliminary screening is often required to target further resources for detailed analysis. Experience indicates that most test methods have inherent advantages and disadvantages.

For purposes of classification, we have defined four generic types of test apparatus.

1. Microthermal Calorimeters
2. Vent Sizing Packages
3. Macrothermal Calorimeters
4. In House Calorimeters

A variety of parameters must be quantified to characterize a runaway or decomposition process for relief system design purposes. These parameters include:

- System Thermal Stability. Nature and the relative magnitude of exothermic/endothermic effects
- Initial decomposition temperature under specified experimental conditions
- Total Heat Release: Reaction heat release per (mass or molar) unit of material
- Rate of Heat Release: Characterized by global kinetic parameters and heat generation as a function of temperature

- Rate of Gas Generation: Volatilization of liquid components, vapor expansion effects, and gaseous decomposition products
- Scaleup/Loading Factors: Physical characteristics of full-scale plant
- Vent Flow Characteristics: Multicomponent/multiphase system properties, continuing chemical reactions, etc.

All of the test methods of interest involve heating a sample of material in a controlled manner and monitoring its thermal behavior, either in absolute terms or with respect to a non-reactive reference (control) sample. Accurate calibration of control and measurement instrumentation is essential to obtain meaningful data. The selected experimental parameters (sample size, containment type, heating rate) can greatly influence results. Understanding of the influence of these parameters is essential for effective experimental implementation and interpretation.

There are four fundamental heating modes which can be employed in thermal analysis experiments of this type. These are illustrated in Figure 1 and include:

1. Scanning
2. Isothermal
3. lsoperibolic
4. Adiabatic

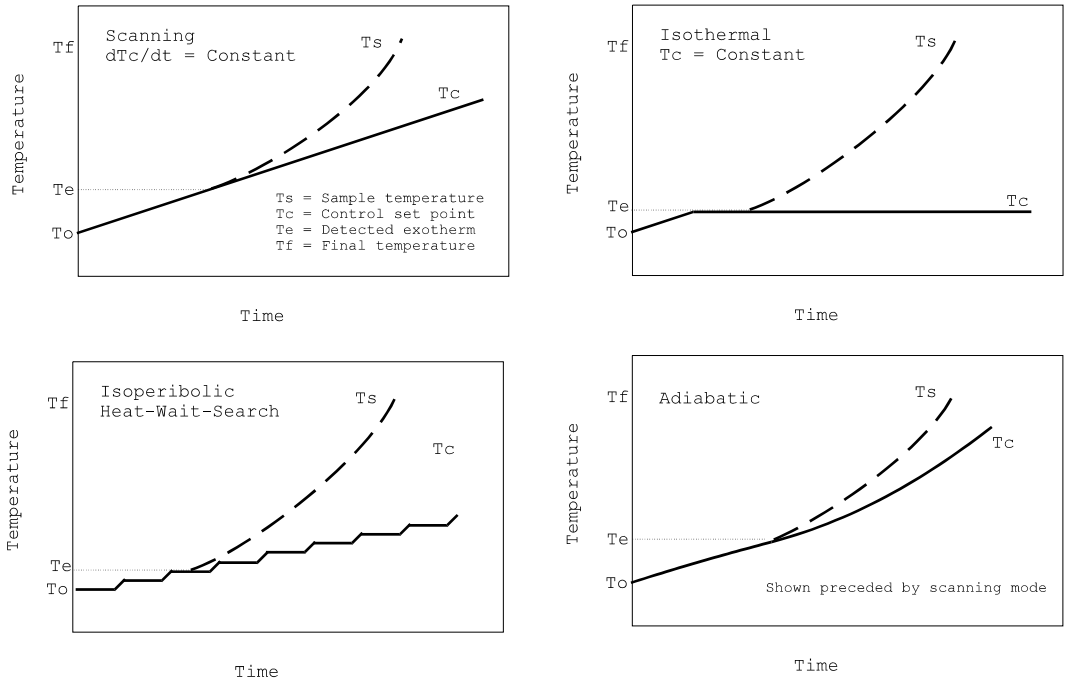
Another important characteristic of any experimental system is thermal inertia. The inertial (or phi) factor tends to unity with increasing reacting mass, for example as encountered in bulk materials. The adiabatic sample self-heating rate (either absolute or relative to an inert reference) can be used to generate pseudo rate data, which in turn yield global kinetic parameters describing the reaction/decomposition process.

Microthermal calorimeters are commercial instruments, primarily developed for other (non-hazardous) thermal analysis purposes. These calorimeters typically employ milligram scale samples (eg., 1-20 mg). They provide 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, noble metal containers (to avoid catalysis/inhibition effects). Heating options include scanning, isothermal, and isoperibolic.

There are three principal types of microthermal calorimetric methods. The operational principle of these devices involves monitoring thermal or physical transitions within the sample as it undergoes a predetermined heating cycle.

- Differential Thermal Analysis (DTA): DTA measures any sample temperature deviations from the programmed temperature profile or with respect to an inert reference (control) sample.

Figure 1: Typical heating modes used in thermal analysis equipment



- Differential Scanning Calorimetry (DSC): DSC measures any decrease in heat input required to maintain a specified temperature profile within the sample, usually compared to an inert reference.
- Thermogravimetric Analysis/Differential: TGA measures weight changes in the thermo-
gravimetry (TGA)sample as a function of temperature, either in absolute terms or with respect to a control reference.

Microthermal methods have a number of inherent advantages and disadvantages.

Advantages

1. Rapid automated screening
2. Low hazard potential due to small sample size
3. Variety of heating modes and heating rates possible
4. Limited sample requirements
5. Useful for characterizing thermal signatures

6. DSC can provide accurate heat of reaction measurement

Disadvantages

1. Representative samples only possible for highly homogenous materials
2. Inertial effects reduce detection sensitivity and can inhibit reaction
3. Rapid loss of sensitivity at high scanning rates
4. No pressure generation measurement possible
5. Kinetic evaluations possible, but frequently misleading for hazard evaluation purposes
6. Heats of reaction misleading if sample containment falls

Macrothermal calorimeters are commercial instruments developed specifically for the study of thermal decomposition processes. These calorimeters typically employ gram scale samples (eg. 1-100g). Improved thermal detection sensitivity is possible due to reduced inertial effects. Experimental options include open and closed, noble metal or glass sample containers, and direct measurement of reaction pressurization effects. Heating options include scanning, isothermal, isoperibolic, adiabatic and combinations. A variety of proprietary instruments of this type have been marketed; for these instruments the operational principle involves programmed heating in conjunction with accurate measurement of sample temperature and/or pressure.

1. Accelerating Rate Calorimeter (ARC): ARC measures sample containment ”bomb” temperature with respect to air jacket temperature
2. Automatic Pressure Tracking Adiabatic Calorimeter (APTAC). APTAC measures the temperature and pressure of the sample containment, while allowing for reagent addition and controller/simple sample venting.
3. Reactive System Screening Tool (RSST): RSST measures sample temperature and self-heating rate during a programmed temperature ramp
4. SEDEX Calorimeter: SEDEX measures sample temperature and/or pressure with respects to surrounding external oven temperature
5. SIKAREX Calorimeter: SIKAREX measures sample temperature with respect to external air jacket temperature

Macrothermal calorimeters have a number of inherent advantages and disadvantages.

Advantages

1. Composition of large sample is more representative in most cases
2. Reduced inertial effects improve relative thermal detection sensitivity
3. Temperature and pressure monitoring possible
4. Variety of heating modes and containment types possible

Disadvantages

1. More onerous and less reproducible experimental parameters (calibration, set up, interpretation, clean up)
2. Increased operator and equipment hazard potential due to increased sample size
3. Robust sample and/or equipment containment necessary to contain pressurization
4. Loss of sample containment probable (potential occupational exposure and disposal liability
5. Can have ”placebo effect” on hazard analysts/management

A number of companies and industry groups have developed their own non-commercial apparatus for thermal hazard evaluation. These calorimeters typically employ gram scale samples (eg. 1 - 100g). They often use common laboratory apparatus such as Dewar vessels, drying or old GC ovens, and standard thermocouples in conjunction with customized sample containers. Published examples include Union Carbide, ICI organics, Sterling Organics, ABPI, and Hoechst.

In house methods have a number of inherent advantages and disadvantages.

Advantages

1. Highly cost effective vs. commercial instruments
2. Can be tailored to suit company products, testing philosophy and data requirements
3. Encourages operator to confront practical limitations on testing and results
4. Has ”researcher appeal” and stimulates continuous improvement

Disadvantages

1. Potentially dangerous (eg. explosion risk, occupational exposure risk)
2. Potentially idiosyncratic, non-user friendly and reliant on frequent calibration/maintenance
3. Requires skilled operator for safety/operability/interpretative purposes
4. Data output nonstandard; difficult for comparative interpretation or demonstrating regulatory compliance

Emergency relief system sizing packages are intended to characterize runaway processes (including vent flow phenomena) directly by means of physical simulation of plant conditions. These tools typically employ 10 - 100 gram reactant. Sample stirring and reactant addition are possible to simulate realistic chemical reaction processes. Inertial effects are reduced by large relative sample size and light (hence mechanically weak) containment construction. Containment integrity is maintained by equalization of external/internal pressure using inert gas padding. A good example of an emergency relief system sizing package is marketed by Arthur D. Little (APTAC) and Fauske and Associates (VSP).

Direct experimental determination of venting behavior and vent sizing parameters has a number of advantages and disadvantages.

Advantages

1. Low thermal inertia (typically circa 1.05) experimental set up, which is comparable to real plant conditions
2. Simulated liquid phase reaction possible
3. Flow regime characterization possible

Disadvantages

1. Equipment complex and relatively expensive
2. Difficult to establish and reproduce experimental conditions/measurements
3. Bulk effects (e.g. transport phenomena, thermal conductivity) may still change the nature of reaction in the full-scale plant

In summary, a number of critical experimental parameters which might constrain or influence testing with a specific instrument.

- Containment Type
- Heating Rate
- Thermal Inertia
- Heating Mode
- Data Interpretation

The selection of instrument type, sample containment type and experimental conditions can strongly influence results. Tempering effects can inhibit reaction in open containers. Potentially dangerous exothermic behavior can be masked by inertial effects and rapid temperature scanning, particularly for samples of limited size. Autocatalytic effects, and catalysis/inhibition by sample containment material, can lead to complex or misleading experimental results. Instrument or software characteristics can produce anomalous results.

This has been demonstrated by comparative testing of controlled samples of a range of reactive materials, each exhibiting different thermal behavior histories prior to decomposition. One such material tested is tertiary butyl peroxybenzoate (TBPB).

This has the advantage of being readily available as technical grade product with high purity specification and also the thermal stability and kinetic data from large-scale tests are available in open literature.

This provides a good comparative basis for instrument comparison with respect to exotherm detection sensitivity and extrapolation of global kinetic parameters (see Table 1).

When developing a rigorous testing strategy for thermal hazard evaluation, similar considerations and constraints exist to those which influence our choice of specific instruments and/or methodologies. The requirements of an effective test strategy include:

- Rapid preliminary screening and effective targeting of experimental resources
- Optimal significance of results with minimal operator risk
- Recognition of inherent strengths and weaknesses of specific methods

In view of this, we propose an integrated, noncommercially aligned approach which incorporates the identified principal requirements: Theoretical/Experimental , Screening Tests, Advanced Numerical and Fluid Dynamic Modeling Techniques, and Detailed Experimental Measurements.

Figure 2 summarizes several popular experimental and theoretical tools that are often used in the characterization of thermal stability, process design data, and runaway reactions. These techniques will be described briefly in the following sections.

Figure 2: Available experimental and theoretical tools for reactive systems characterization

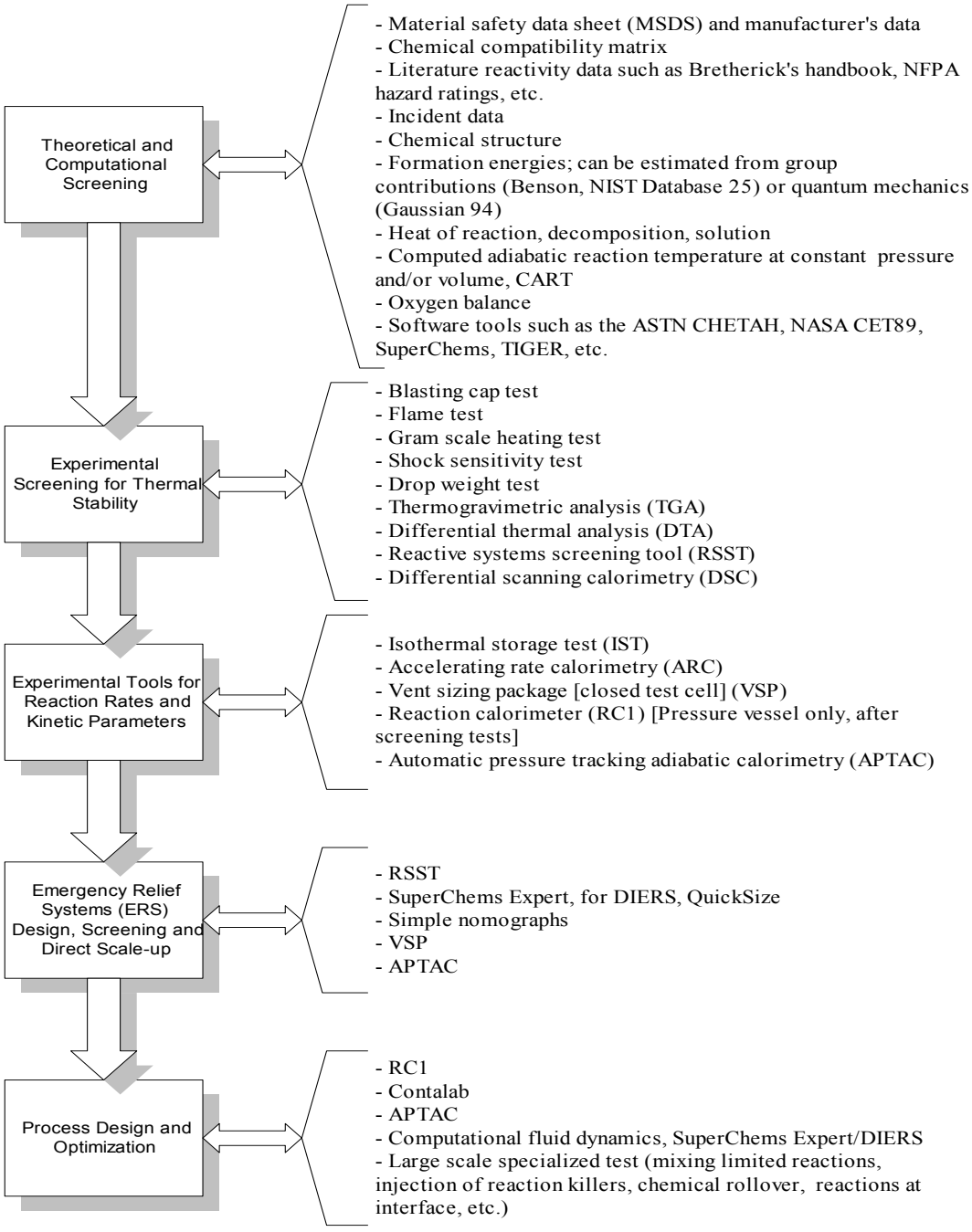


Table 1: Data from various thermal analysis instruments

Test Method	Experimental Parameters	Sample Mass	Detected Onset (C)
DTA	10 C/min	8.1 mg	125
DSC	10 C/min	3.4 mg	122
	5 C/min	4.4 mg	101
	1 C/min	6.4 mg	93
ARC	Start: 50C Heat Step: 10 Wait: 15 min PHI = 2.38	3.5 g	82
SEDEX	0.5 C/min "Scanning"	5.8 g	84
	Experiment	2.0 g	88
SIKAREX	0.125 C/min Scanning	5.0 g	72

THEORETICAL AND COMPUTATIONAL SCREENING

Literature Searches

The first step in analyzing the hazards of a chemical under consideration involves reviewing the literature for any known and available information. Typical literature sources are provided below:

1. The Encyclopedia of Chemical Technology, Kirk-Othmer
2. Handbook of Reactive Chemicals Hazards, 4th Ed., L. Bretherick, Butterworth-Heinemann, Stoneham, MA (1990)
3. National Fire Protection Association, "Manual of Hazardous Chemical Reactions," NFPA, 491M, Quincy, MA (1991)
4. Tokyo Fire Department Compilation: Handbook on Hypergolic Ignition, T. Yoshida (Ed.), Nikkan Kogyo Shinbunsha, Tokyo, Japan (1980).

5. Weast, R. C. (ed.), Handbook of Chemistry and Physics, 66th Edition, CRC Press, Inc. Boca Raton, FL, 1985

Chemical Matrix

Chemical matrices (incompatibility charts) can help in organizing available data on the incompatibilities existing between expected process mixtures. Reference [1] gives one procedure for developing a chemical compatibility chart while describing some of the tools available. Reference [2] also provides a table of known incompatibility hazards.

Data can also be gathered experimentally on the compatibility of materials. Finally, incompatibility charts have been published by both the U.S. Coast Guard [2] and ASTM [3] as well as other industry groups around the world. Again, see Reference [1] for a description of experimental tests and published compatibility charts.

Structural Analysis

From a structural perspective, a number of molecular groupings are recognized as being inherently unstable such as molecules containing $-ONO_2$, -CC-, $N-NO_2$, etc. Table 2 outlines several molecular structures known to be high energy structures.

Oxygen Balance Method

In a 1949 Chemical Reviews article, W. C. Lothrop and G. R. Handrick documented a strong correlation between "oxygen balance" and the explosive performance of organic nitrates and nitro compounds. In this context, an oxygen balance of zero implies an oxygen content just sufficient to convert all carbon to CO_2 and all hydrogen to H_2O. Although valuable and universally used in explosives practice, it has been shown that there is no necessary connection between oxygen balance and self-reactivity in general [3].

[2] "Compatibility of Cargoes," published in 46 CFR Ch. 1 (10-1-93 Edition) - Part 150 with changes that appeared in the Federal Register dated April 11, 1994 as a Final Rule by Coast Guard (CGD 92-100) for Bulk Hazardous Materials. See also: "Compatibility Guide for Adjacent Loading of Bulk Liquid Cargoes (Final Report)", Report No. USCG-D-156-75.

[3] ASTM (American Society of Testing and Materials) Committee D-34 , Proposal-168, "Proposed Guide for Estimating the Incompatibility of Selected Hazardous Wastes Based on Binary Chemical Reactions," and included Minority Report, March 1986. See also: "A Method for Determining the Compatibility of Hazardous Wastes," Hatayama, H.K.; Chen, J.J.; De Vera, E.R.; Stephens, R.D.; Storm, D.L.; CA Dept. Health Serv., Berkeley, (1980) 165 pp. NTIS, SPRINGFIELD VA, PB80-221005. Also published as Report No: EPA-600/2-80-076, April 1980, 165 pages.

Table 2: Typical high energy molecular structures. Taken from Guidelines for Chemical Reactivity Evaluation and Application to Process Design, AIChE/CCPS, 1995.

Definition	*Bond Grouping*	*Definition*	*Bond Grouping*
acetylenic compounds	–C≡C–	tetrazoles; high nitrogen-containing compounds	–N=N–N=N–
haloacetylene derivatives	–C≡C–X	triazines (R=H, –CN, –OH, –NO)	–C–N=N–N(R)–C–
metal acetylides	–C≡C–M	alkyl hydroperoxides; peroxyacids	–C–O–O–H
azo compounds	–C–N=N–C–	peroxides (cyclic, diacyl, dialkyl); peroxyesters	– C–O–O–C–
diazo compounds	–C=N^+=N^-	metal peroxides; peroxoacid salts	–O–O–M
diazeno compounds	–C–N=NH	amine chromium peroxocomplexes	N → Cr–O_2
nitroso compounds	–C–N=O	azides	–N_3
nitroalkanes	–C–NO_2	halogen azides; N–halogen compounds; N–haloimides	–N–X
polynitro alkyl compounds; polynitro aryl compounds	–C(–NO_2)–NO_2	diazonium sulfides and derivatives; "Xanthates"	–C–N=N^+ S^-
acyl or alkyl nitrates	–C–O–NO_2	diazonium carboxylates and salts	–C–N=N^+ Z^-
acyl or alkyl nitrites	–C–O–N=O	amine metal oxo salts	(N → M)$^+$ Z^-
1, 2–epoxides	–C(–O)–C–	N–metal derivatives	–N–M
metal fulminates	–C=N–O–M	halo-aryl metal compounds	Ar–M–X
aci-nitro salts	HO–(O=) N=	hydroxyammonium salts	–N+–OH Z^-
N-nitroso compounds	–N–N=O	arenediazoates	–C–N=N–O–C-
N-nitro compounds	–N–NO_2	arenediazo aryl sulfides	–C–N=N–S–C–
fluoro dinitromethyl compounds	F–C(–NO_2)–NO_2	*bis*-arenediazo oxides	–C–N=N–O–N=N–C–
difluoro amino compounds; N,N,N-trifluoroalkylimidines	–N–F_2	*bis*-arenediazo sulfides	–C–N=N–S–N=N–C–
N-azolium nitroimidates	–N(=)$^+$–N^-–NO_2		

Table 3: Typical high energy molecular structures with positive heat of formation. Taken from Guidelines for Chemical Reactivity Evaluation and Application to Process Design, AIChE/CCPS, 1995.

Compound	*Structure*	ΔH_f°	
		kJ/mol	*kJ/G*
cyanogen	N≡C—C≡N	+308	+5.9
benzotriazole		+250	+2.1
nitrogen trichloride	NCl_3	+230	+1.9
acetylene	HC≡CH	+227	+8.7
allene	$H_2C=C=CH_2$	+192	+4.8
diazomethane	$H_2C=N^+=N^-$	+192	+4.6
hydrogen cyanide	HC≡N	+130	+4.8
1,3-butadiene	$H_2C=CHCH=CH_2$	+112	+2.1

Note: the numbers in the fourth column give a better relative indication of potential energy release than those in the third column.

Indiscriminate use of the oxygen balance criterion can produce misleading hazard assignments.

Enthalpy of Formation

Enthalpy of formation data provide information on thermochemical stability with respect to the elements which make up the composition in question. In fact, most explosives are stable with respect to their elements, but are highly unstable with respect to some set of (usually) simpler reaction products. A positive value of the enthalpy of formation provides an early warning of hazard potential. A negative heat of formation provides no hazard potential guidance.

Table 3 summarizes data pertinent to several chemical structures with positive heat of formation and high energy release potential.

There are several techniques for the estimation of heat of formation data based on molecular structure. The techniques include group contribution methods, quantum mechanical estimates, and heat of combustion data.

Heat of Reaction

The difference between enthalpy of formation of the composition in question and its reaction products represents the enthalpy of reaction. This parameter provides at least a rough guide to the amount of stored chemical energy and, to this extent, to the hazard potential. Note that the specific enthalpy change, as in kJ/gram, is the relevant quantity.

ASTM "CHETAH" Hazard Criteria

The well-known CHETAH program provides a convenient, computerized means for estimating the enthalpy of formation for any composition that can be represented in the Benson group additivity system. CHETAH then uses a linear programming technique to select, from its own data bank, the set of room-temperature reaction products yielding the greatest enthalpy change. The resulting value of $\Delta H(r)$ is reported as CHETAH hazard evaluation Criterion 1. Values of - 2.9 kJ/gram or more negative are taken as indicating "high" hazard potential.

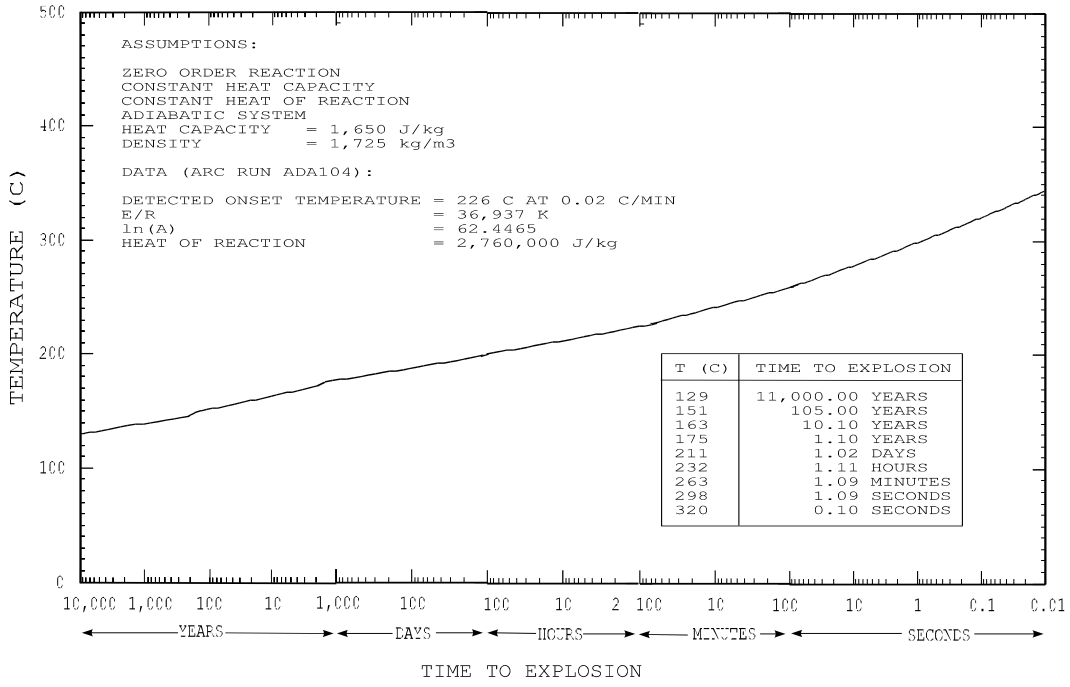
The five additional hazard criteria provided by CHETAH appear to have limited value. A critical review has been published in reference [4].

Computed Adiabatic Reaction Temperature (CART)

As noted above, chemical reactivity hazards originate with stored chemical potential energy. Without stored energy in the form of metastable compositions there would be no self-reactivity hazards. However, it is the rate of energy conversion that distinguishes detonations and fast deflagrations from ordinary chemical reactions. Reaction rates are dominated by temperature, as temperature occurs in the exponent of the rate equation. This effect is well represented by Figure 3. Figure 3 illustrates the impact of temperature on time required for ammonium nitrate to self-heat itself to explosion under adiabatic conditions. For this reason it is to be expected that adiabatic reaction temperature might be useful in hazard prediction. Study of this possibility has been facilitated by the development of computer codes designed to carry out multiphase Gibbs free energy minimization and adiabatic reaction temperature calculations, and by the proliferation of PCs capable of using these codes.

Melhem and Shanley [5] have shown through comparison with experimental data for a wide variety of chemical systems that hazard potential is better predicted with the use of an adiabatic temperature rather than heat of reaction or decomposition. Melhem and Shanley observe that for many materials of interest (including gases, solids and condensed phase) an adiabatic temperature value of 1200 K or more correlated with experimentally established explosive potential. Peroxide and peroxide containing systems are an exception to this criteria. Their explosive potential

Figure 3: Impact of temperature on time to explosion for ammonium nitrate



correlated well with temperature values greater or equal to 800 K.

NIST SP Database 25 Software

The NIST SP Database 25 [6] software is a convenient and user friendly method of applying the Benson group contribution system for the estimation of heats of formation. This tool allows the user to search an existing database or to input data by drawing the particular molecular structure under study. Using this drawing, the program estimates thermodynamic properties, including the heat of formation. The heat of reaction for a balanced chemical reaction can also be estimated.

NIST Chemical Kinetics Database Software

The NIST Chemical Kinetics Database 17 is a database of gas-phase kinetic data. It is a compilation of published kinetic data that can be searched by reactants, products, reactions and authors. It can be obtained by contacting NIST under Standard Reference Data Program, NIST, Bldg. 820, Rm.113. Gaithesburg, MD 20899-0001.

NIST Chemistry WebBook

The NIST Chemistry WebBook provides on-line access to the full array of data compiled and distributed by NIST under the Standard Reference Data Program. Located at $www.webbook.NIST.gov/chemistr$ this website provides on-line access to a large compilation of chemical data, including structural, thermochemical, thermophysical and heat of reaction for over 3000 reactions. Currently NIST is not charging a fee for use of this service. The data can be searched by chemical name, formula, CAS number, molecular weight, ionization energy or proton affinity.

ASTM CHETAH Software

The CHETAH 7.0 [4] program is also a computerized means of applying the Benson system. It is more cumbersome to use than NIST SP; however, CHETAH 7.0 contains many more Benson groups permitting evaluation of many compounds that cannot be modeled in SP. To estimate thermochemical properties using CHETAH, you need to toggle through the various menus of Benson groups, choosing those that apply to the compound of interest. Please see reference [4] for a detailed review of CHETAH 7.

NASA CET89 Software

The NASA-Lewis computer program, CET89, provides convenient means for estimating the adiabatic decomposition temperature (maximum attainable temperature) for most compositions, given the elemental composition and the enthalpy of formation. This program also reports the equilibrium decomposition products at the adiabatic decomposition temperature.

TIGER Software

The TIGER [5] program, developed by the Stanford Research Institute, is capable of calculating the thermodynamic state attained in a heterogeneous system of known atomic composition. The equilibrium state is generated by minimizing the Gibbs free energy of the system at a given temperature and pressure.

[4] CHETAH 7.0, The Chemical Thermodynamic and Energy Hazard Appraisal Program, Version 7

[5] Cowperthwaite, M. and W. H. Zwisler, "TIGER: Computer Program Documentation," Stanford Research Institute, Menlo Park, CA (1973)

SuperChems

SuperChems [7, 8, 9, 10] is an advanced tool for thermal hazards assessment, pressure relief design, and consequence analysis. Developed by Arthur D. Little, Inc. SuperChems™ is available in two editions: Professional and Expert. The Professional Edition consists of a family of rigorous models designed to conduct consequence analysis and hazard modeling. The Expert Edition has been used as an effective design tool with capabilities in multicomponent analysis, transient quasi-three-dimensional heavy gas dispersion, multiphase reaction kinetics, transient gas explosion dynamics with obstructions, transient pipeline flows, and simultaneous phase and chemical equilibrium flash routines.

SuperChems™ is linked to a databank containing over 1200 chemicals with full database functionality, such as the option to add, delete, and modify databank compounds. In addition, several utilities are included to facilitate the manipulation of user-specific data. SuperChems™ Expert handles multicomponent mixtures in every model, using true multi-component phase equilibria, and can perform Vapor/Liquid Equilibrium (VLE), Liquid/Liquid Equilibrium (LLE), Vapor/Liquid/Liquid Equilibrium (VLLE) with or without solids. It can also perform multiphase reversible chemical reaction calculations in vessels and piping.

Two of SuperChems™ capabilities are useful here; they are its properties estimation feature and its ability to reduce and scaleup reactivity data from several different types of calorimeters. This includes detailed methods for extracting stoichiometry data from chemical reactions and decompositions.

Gaussian 94

Gaussian 94 [6] is a connected system of programs for performing a variety of semi-empirical and ab initio molecular orbital (MO) calculations. Gaussian 94 is capable of predicting many properties of molecules and reactions, including:

- Molecular energies and structures
- Energies and structures of transition states
- Vibrational frequencies
- Thermochemical properties
- Bond and reaction energies
- Reaction pathways

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- Molecular orbitals
- Atomic charges
- Multipole moments

Computations can be carried out on systems in the gas phase or in solution, and in their ground state or in an excited state. Thus, Gaussian 94 can serve as a powerful tool for exploring areas of chemical interest like substituent effects, reaction mechanisms, potential energy surfaces, and excitation energies.

HAZARD RANKING

Using the theoretical screening methods discussed in this paper and other recent experimental studies (see reference [11]) we can assign most chemical compositions (condensed phase and gases) to one of three self-reactivity hazard groups, as follows:

1. **NO to LOW self-reactivity hazard group:** Heat of reaction no more negative than -1.2 kJ/gram, and CART no more than 700 K.
2. **INTERMEDIATE group:** Heat of reaction between -1.2 and -3.0 kJ/gram, and CART no higher than 1600 K.
3. **HIGH self-reactivity hazard group:** Heat of reaction more negative than -3.0 kJ/gram, or CART higher than 1600 K.

Compositions falling in the NO to LOW hazard group are usually considered to be suitable for full-scale manufacture and use. Compositions falling in the HIGH hazard category may be regarded as explosive to a practical certainty. Such compositions are usually regarded as unsuitable for manufacture, handling or use under ordinary commercial circumstances.

The intermediate group includes many compositions which are in large-scale commercial use but which may require special care and design to control potential reactivity hazards.

EXPERIMENTAL SCREENING FOR THERMAL STABILITY

Flame Tests

Two small-scale heating tests can provide much insight into the explosive potential of a pure material or reaction/product mixture. The first involves the heating of approximately a 1/10 g

sample on a metallic spatula, for example, by holding the spatula above a small flame. Behavior is rated when the sample is removed from the flame (i.e., flame on spatula slowly heats up sample) and when the sample is directly exposed to the flame. The second test involves the dropping of the same size sample onto a preheated metallic surface (e.g., hot plate). By observing the sample behavior under the three conditions above (slowly heated, immersed in flame, exposed to high heat) judgments can be made as to the explosive potential of the material.

Observations should be made regarding the following behaviors:

- melting
- boiling
- spontaneous ignition
- rapid reaction with sound
- carbonization

Observed burning behavior provides a guide to reactivity and fire hazard potential. Reaction accompanied by noise suggests explosive potential.

Gram-scale Heating Test

A 3-gram sample of liquid or solid composition is placed in a standard 10 ml glass test tube. The test tube is placed in a cavity about 2.5 inches deep bored into the end of a 2-inch diameter length of copper rod about 3-inches long. The copper block also includes a small diameter hole near to and parallel to the test tube cavity. This hole accommodates an unjacketed thermocouple. The copper block is held, cavity end up, in a simple electric furnace which will raise the temperature of the block and the test tube to 300 C in about a half hour. Boiling and decomposition behavior can be viewed through an explosion shield. Heating should be continued until the sample decomposes violently, is completely volatilized, or charred. If no violent decomposition is observed, the test should be repeated by inserting a fresh test tube and sample into the preheated block at about 300 C. Violent decomposition accompanied by noise or vigorous eruption indicates a self-reactivity hazard.

The copper block will contain the worst case violent decomposition to be expected in the case of 3-gram samples of Class 2 materials as described above. Nevertheless, glass fragments may be propelled upward with considerable force. Means for intercepting such fragments should be provided, as well as an explosion shield to protect the observer. In no case should explosives or suspected explosives (class 3 compositions) be subjected to this test in a conventional laboratory setting.

Explosivity and Mechanical Sensitivity Tests

In the processing of chemical compounds it is very important to understand the mechanical sensitivity of a particular substance. Sensitivity tests can be divided into two categories which represent the types of mechanical energy expected to be seen in the process plant. These are mechanical friction (due to materials being wedged between surfaces) and mechanical shock (or impact). Several tests are available for measuring both the sensitivity to friction and impact. These are described in Reference [2, 12]. Two tests for identifying impact sensitive materials are described here. They are the hammer test and the drop weight test. Information concerning additional tests can also be found in Reference [2, 12]. These tests can provide valuable insight into the behavior of a process mixture under extreme process conditions.

Hammer Mechanical Sensitivity Test

In conducting the hammer test, a small amount of sample (approximately 0.1g) is placed on an anvil. The sample is then hit with a hammer and the behavior observed. A comparison of the behavior of a known standard explosive vs. the behavior of a sample can provide insight into the explosive potential of the sample. Hammer tests do not provide a quantitative estimate of the impact sensitivity of the sample; however, they can provide a qualitative assessment of whether or not a particular material will explode under normal operating conditions.

Drop Weight Mechanical Sensitivity Test

Another test for determining mechanical shock sensitivity is the drop weight test. Although, difficult to replicate, behavior in the drop weight test can furnish valuable comparative information about the relative mechanical shock susceptibility of the composition in question as compared with that of better known compounds. The experimental test apparatus is rather straightforward. The sample is placed in a holder designed for the physical state and type of material being tested. A known weight is then allowed to drop from a specified height. After impact the sample is examined for signs of detonation. The weight can be dropped from higher heights if the lower impacts produce no detonation. Typical regulatory agencies require 10 non-detonates out of 10 attempts at a height of 10 inches. A typical testing apparatus has the ability to go to 25 inches in height. Drop weight tests and testing devices are described in further detail in Reference [2]. Care must be taken with these tests as small changes in sample preparation or test setup can greatly affect the results; therefore, drop weight testing is best left to a testing laboratory with experience and equipment to run these tests. Note that both tests described above are conducted in the open and the results may or may not apply to the behavior of the material in a closed system.

Blasting Cap Test

The blasting cap test provides means for assessing the sensitivity of a new composition to relatively intense impact. It may be more appropriate for use in large scaleup problems. However, in selected cases, including the presence of highly energetic groups in the compound, it may prove useful. Advantages to carrying out these type of explosivity tests are that they are inexpensive, fairly easy to carryout and use a small sample size. Despite the fact that they are easy to carry out, current regulations regarding acquisition and use of blasting caps are so restrictive as to discourage in-house use of blasting cap tests.

In the Arthur D. Little Inc. version of this test, a No. 6 blasting cap is detonated while immersed in a column of the composition to be tested. A witness tube provides the means for determining whether or not a propagating explosion was initiated and also provides a means for comparing the energy release behavior of the composition being tested with that of better known compositions. In this manner, it can be determined whether or not a certain sample is expected to propagate a reaction.

Qualitative agreement with CART hazard rankings was reported by Shanley and Myers [11] in a recent experimental blasting cap study conducted at Arthur D. Little Inc.

More than 35 tests were conducted on a wide variety of chemicals ranging from inert substances to known high explosives. The tested materials included water, dodecane, toluene, mononitrotoluene, tetranitromethane (TNM)-toluene mixtures (50/50 and balanced), cumene hydroperoxide 80 %,, Di t-butyl peroxide, benzoyl peroxide, hydrogen peroxide-ethanol mixtures (40/60 and balanced), ammonium nitrate (pure and with dodecane), dinitrotoluene, and urea nitrate.

The test series demonstrated qualitative correlation between CART values and extent of deformation of the blasting cap witness tubes. For example, nine of the ten compositions which produced minimum deformation had CART values below 1700 K. Six of the seven compositions which produced significant or severe deformation of the witness tubes had CART values greater than 1700. All three compositions, which produced severe deformation, had CART values greater than 2100 K. The deformations observed with the two fueled hydrogen peroxide compositions were in good agreement with published findings. H2O2-40 % ethanol is outside the published explosive limits, while H2O2-50 % - ethanol is on the boundary of the explosive region.

The three organic peroxides tested produced minimum deformation of the witness tubes in keeping with their relatively low CART values. The test tube containers are undamaged by these explosions, which suggest a low-rate deflagration rather than a detonation.

In tests conducted as described above, any substantial deformation of the witness tube over and above that produced by firing the cap in an inert composition provides a strong indication of reactivity hazard. Energetic but insensitive compositions such as straight ammonium nitrate and dinitrotoluene provide weak signals (no propagation), while more energetic compositions such as fueled AN and urea nitrate provide strong signals (partial or full propagation). [7]

[7]Note that larger diameter charges or different packing densities (in the case of solid specimens) or different

These experiments demonstrated that the blasting cap can produce valid comparisons between novel compositions and better known materials whose hazardous properties are already established. Such comparisons are useful supplements to evaluations based upon computational methods.

Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry, or DSC, is a micro-calorimetric technique that measures either exothermic or endothermic reactions/phase transitions. Samples on the order of 10 mgs are typical for this technique. The difference in energy required to keep a pan with sample and an empty pan (reference pan) on a specified heating ramp is measured and recorded. The differential technique is used to remove contributions from the pan and to eliminate noise from heater instabilities.

The primary use of the DSC is to obtain information on the thermal behavior of reactive materials. Typical information obtained include sample heat flux as a function of temperature.

A small amount of sample (5-25 mg) is placed in a sample pan which is placed in the calorimeter's cell. The sample is heated or cooled at a specified temperature ramp rate in a temperature range that varies from - 170 C to 500 C and the heat absorption/generation characteristics are compared with an empty reference pan to determine endothermic/exothermic behavior. A variety of gases can be used to pad the sample although the most common gases are nitrogen, air, or oxygen. High pressure conditions up to 1000 psig can also be employed.

Exothermic or endothermic phenomena are evidenced when the DSC trace undergoes a positive or negative excursion, respectively, from the baseline. This type of phenomena includes exothermic or endothermic reactions, melting, evaporation, or phase transitions. Heat capacities of materials can be determined. This is a relatively rapid test which many companies use as the primary screening tool in evaluating the exothermicity of materials.

Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) is another micro-calorimetric technique which closely resembles DSC. Both DSC and DTA measure exotherms and endothermic reactions and phase transitions. Data from both instruments is often very similar. Unlike the DSC, the DTA measures events by monitoring the difference in temperature between a sample pan and a reference pan while both are supplied the same amount of heat energy. DSC is more commonly used and available of the two techniques, however, many high temperature units are DTA based.

initiators for example could produce different effects

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is the oldest and the simplest of the micro-calorimetric techniques used today. Samples up to about 50 mg are placed in an inert pan, usually platinum. The samples are heated at a specified rate and the weight loss of the sample is recorded. A low flow of user selectable gas is used to purge the sample during heating. Inert gases are used to keep the headspace clear of gaseous and sometimes corrosive materials. Other gases, like oxygen, can be used to study the oxidation of materials. Data from this technique is usually plotted as weight loss as a percent or in mg versus temperature.

Reactive Systems Screening Tool (RSST)

The basic operational principle of the RSST [8] involves programmed heating of a sample at a preselected rate (nominally 0-2 C/minute) through a selected temperature range. Exothermic reaction in the sample is identified by positive deviation of the sample temperature rise rate (dT/dt) from the programmed set value. The sample is held in an open glass test cell, although it is possible to operate the test under inert gas pressure. Figure 4 illustrates a recommended test sequence for identification of reactive system type and vent sizing.

The selected heating rate is attained by software controlled switching of a constant voltage supply to the sample heater. The necessary heater switching rate is based on software resident calibration data for a typical organic sample (toluene), presumably under inert gas pressure to suppress boiling. As such, there is no direct control of true sample heating rate or heater power input.

A rudimentary form of on line temperature control/heating drift correction is provided in the form of the heater offset function. This increases the heater voltage pulse rate when negative deviation from the set heating rate is observed. However, the offset function does not correct positive drift, as this could lead to heater cut off during exothermic sample behavior, leading to a rapid loss of heat from the reacting sample. A major problem with this control configuration is that it is not possible to maintain linear temperature ramping for materials which undergo endothermic transitions, during which the heater input power will increase to maintain the set heating rate. When endothermic behavior ceases, the heating rate will remain at an increased level (as negative offset is not possible) unless the heater program is manually interrupted and reset. For materials which exhibit endothermic transition followed rapidly by exothermic reaction (a phenomenon which is not uncommon) it is difficult to envisage how sample thermal behavior can be interpreted.

The slow sampling rate and significant signal disturbance for thermocouple outputs mean that the temperature resolution is estimated to be no better than +/- 0.25 C. Furthermore, the heating rate

[8]The RSST is a trademark of Fauske and Associates Inc.

disturbance at 1 C/minute appears to be approximately +/- 0.2 C/minute. For a sample of a typical organic material with a heat capacity 2.0 J/gm/C and system phi factor 1.05, this corresponds to a detection sensitivity (q_s) given by:

$$q_s = 2 \times \left[\frac{0.2}{60}\right] \times 1.05 = 7 \times 10^{-3} \mathrm{W/g} \text{ or } 7 \text{ W/kg} \quad (1)$$

This sensitivity is comparable to DSC using moderate scanning rates, but is higher than the heat generation levels where spontaneous self heating will occur in an industrial scale plant.

The RSST is very useful for rapid reactivity screening. The performance of the RSST could be improved significantly by externalizing either one or more of the heater power control, temperature program control, or sample temperature monitoring functions.

EXPERIMENTAL TOOLS FOR REACTION RATES AND KINETIC INFORMATION

Accelerating Rate Calorimeter (ARC)

The Accelerating Rate Calorimeter (ARC [9]) is an instrument that can provide adiabatic pressure and temperature time data required for establishing reaction data. The ARC can be used to obtain information on the thermal behavior of reactions and exothermic onset temperatures. The ARC is primarily used for liquid-phase reactive systems. It is also used for safety/performance evaluation of explosives and propellants. Exothermic onset temperatures of 0.01 C/min can be detected. This instrument(see Figure 5)which was developed by Townsend and Tou is known to provide ample thermokinetic data that is applicable to the design and safety/performance evaluation of reactors and storage vessels. Such thermokinetic data includes:

- adiabatic rate of self-heating,
- adiabatic time to explosion,
- rate of pressure rise,
- maximum rate of reaction,
- kinetic data such as activation energy, reaction order and preexponential factor, and
- heat of reaction.

The reaction mixture to be examined is introduced into a spherical cell whose volume is approximately 10 ml. The cell is equipped with a thermocouple mounted on the external wall. The

[9]The ARC is a trademark of Arthur D. Little Inc. and Columbia Scientific Industries.

pressure is recorded by means of a pressure transducer. Various cells can be used which have varying pressure ratings from 4,500 psi to 15,000 psi. As the pressure rating increases, the cell phi factor increases. The ARC is a high thermal inertia instrument whose phi factor is greater than or equal 1.4. The high phi factor requires that the temperature and pressure be corrected by established techniques which requires knowledge of the heat capacity of the reaction mixture and the cell. The significant advantage that the ARC offers over other similar techniques is exothermic onset delectability at 0.01 C/min.

The tracking of temperature and pressure rates is limited to approximately 10 C/min. Temperature drift is not a problem with proper calibration. Operation does not require significant operator supervision. Operator skill is required for proper calibration. The high phi factor can potentially mask exotherms which may occur at higher temperatures.

Vent Sizing Package (VSP)

The primary use of the VSP [10] (see Figure 6) is to obtain information on the thermal behavior of reactions (instrument data and descriptions are taken from reference [13]). It is primarily used on liquid-phase reactive systems. Information obtained includes temperature and pressure profiles. The basic data is manipulated to give self-heat rate, pressure rate, and vapor pressure.

The reaction mixture to be examined is introduced into a thin-walled cylindrical cell whose volume is approximately 110 ml. The cell is equipped with a thermocouple which directly measures the temperature of the reaction mixture. The pressure is measured by means of a pressure transducer. The cell is placed in a high pressure containment vessel. Around the cell there are two sets of heating elements called the auxiliary heater and the guard heater. The auxiliary heater raises the sample to a prescribed set temperature. The guard heater maintains the temperature of the environment around the cell at the same temperature as the cell contents to make the system adiabatic. As pressure develops in the cell, compensating nitrogen is introduced into the containment at a matching rate to prevent cell rupture. The VSP is a low thermal inertia instrument whose phi factor is approximately 1.1. The low phi factor ensures that the experimentally observed temperature and pressure profiles are the same as those which would be experienced in plant process equipment. Temperature and pressure rates as high as 100 to 300 C/min and 20,000 psi/min can be tracked.

The major use of the VSP is in the design of relief vents for runaway exothermic reactions. The vapor pressure behavior of the system can be used to distinguish between tempered, gassy and hybrid systems. The self-heat rate, or rate of adiabatic temperature rise, when coupled with the vapor pressure behavior of the system is used with the DIERS methodology to size emergency relief vents. Heats of reaction can be obtained from the adiabatic temperature rise if the heat capacity of the material is known or can be estimated. Kinetic parameters such as the rate constant and Activation energy can be obtained from the data but apply only for the

[10]The VSP is manufactured by Fauske and Associates Inc.

reaction mixture examined. Blowdown tests can be conducted to characterize the disengagement dynamics of the systems. Rates of inert gas generation can be quantified and with the DIERS methodology, ERS can be designed for gassy systems.

The detection of the exothermic onset temperature is limited to approximately 0.2 to 0.5 C/min. Temperature drift can be a problem unless careful attention is paid to the installation of the insulation. Results can depend upon experimental technique. Operation requires significant operator supervision and skill. Application of the DIERS methodology using data obtained from the VSP or ARC is not recommended for the uninitiated. The kinetic information obtained is applicable only for the particular system tested.

Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

The primary use of the APTAC [11] (see Figure 7) is to obtain information on the thermal behavior of reactions and exothermic onset temperatures. Information obtained includes adiabatic temperature and pressure profiles for reactions. The basic data is manipulated to give self heat rate, pressure rate, and vapor pressure. Exothermic onset temperatures of 0.04 C/min can be detected.

The reaction mixture to be examined is introduced into a spherical cell whose volume is approximately 130 ml . The cell is equipped with a thermocouple which directly measures the temperature of the reaction mixture. The pressure is measured by means of a pressure transducer. The cell is placed in a 4 liter high pressure containment vessel rated to 1900 psig. The pressure is recorded by means of a pressure transducer. Non-isobaric pressure tracking by means of flow control valves prevents the cell from rupturing. Four independent heaters with PID cascaded control maintain adiabatic conditions. Temperature and pressure rates of 400 C/min and 10,000 psi/min can be tracked. The APTAC is a low phi factor instrument (less than 1.15) with exotherm detection capabilities of 0.04 C/min.

The APTAC combines the best features of the VSP (low phi factor and high tracking capabilities) and the ARC (low exotherm onset detection– and low operator attention) into a single instrument. For more information on the APTAC please refer to the paper authored by Chippett et al. in the symposium proceedings.

TNO Isothermal Storage Test (IST)

In the Prins Maurits Laboratory (TNO) Isothermal Storage Test (IST) the heat generated by reacting or decomposing substances at a constant temperature is measured as a function of time.

[11] APTAC is a trademark of Arthur D. Little Inc.

Performance of these measurements at a series of temperatures leads to a quantitative understanding of the relation between temperature and the heat generation of the substance under investigation. The IST is applicable to solids, liquids, pastes and dispersions.

The IST shown in Figure 8 consists of a large heat sink (an aluminum block) which is kept at a constant temperature. In the block are two holes with a very sensitive heat flow meter (e.g., a Peltier element) at the bottom of each hole. Holders are placed on both heat flow meters. These holders are identical. One holder contains the sample, the other an inert substance.

The heat generated by the sample results in a voltage signal from the heat flow meter which is proportional to the heat flow. Random fluctuations in the heat flow are avoided by monitoring the voltage differences between both heat flow meters.

The stainless steel sample holder has a volume of 70 cm^3. The sample mass which depends on the heat generated by the sample, amounts to a maximum of about 20 gram. Measurements can be performed in the temperature range of 250 K to 420 K. Heat generation can be measured between the lower limit of 5 mW/kg and the upper limit of 5 W/kg with an accuracy of at least 30 % in the lower range to 5 % in the higher ranges.

EMERGENCY RELIEF SYSTEMS DESIGN

There are currently two established practices for the design of emergency relief systems:

1. Simplified and direct scaleup methods
2. Detailed computer simulation methods

The simplified and direct scaleup methods are methods that are most applicable to non reactive systems. These methods use direct scaleup techniques to obtain a vent size. The advantages of such techniques are summarized below:

- Simple and easy to use
- Can be used by non-ERS design specialists
- Calculations can be performed using a spreadsheet or charts

The main disadvantages are:

- Scaleup data is only valid for system composition and thermal inertia represented by the small-scale experiments
- Results are often conservative, especially for gassy systems. This can be costly if post release mitigation/effluent handling is required.

- Does not consider the presence of long inlet lines or the impact of downstream equipment on performance of the ERS system
- Little useful information can be obtained for reaction data such as onset temperatures, activation energy, decomposition stoichiometry, etc.
- Fire exposure is difficult to simulate
- Requires an additional experiment per what if scenario for iterative designs

The detailed approach advocates a more fundamental approach to pressure relief design, especially for reactive systems. First, the reaction chemistry is qualified using small-scale experiments and then this data is coupled with fluid dynamics to design the emergency relief system. The main advantages of this approach are:

1. High accuracy
2. Can handle complex systems and systems which interact with other equipment
3. Can be used for iterative design and what-if analyses such as the direct evaluation of the impact of temperature, pressure, composition, fill level, solvent boiling point, reduced charge, etc.
4. In addition to vent sizing information this approach provides insights into process modification and refinement as well as the establishment of a safe operating envelope.
5. Provides necessary flow data for vent containment design (if required), structural support, etc.

The main disadvantages of the detailed methods are:

1. Requires expert skills for establishing kinetic information from test data
2. Requires the use of computer simulation

Figure 9 outlines a recommended general flow chart for selecting appropriate ERS design methods ranging from simple solutions to detailed computer simulations.

FIA Chart

A simple method that can be used for screening is the FIA chart [14]. This chart has been withdrawn as an official document of Industrial Risk Insurers and is not recommended for general

use since it has been shown to be nonconservative for some systems [15] while producing overly conservative results for many others.

The main advantage of the FIA chart is its ease of use. However, the FIA chart is only applicable to tempered reactions with a low relief viscosity in 100 - 125 psig vessels. The chart (see 10) consists of four straight lines drawn on log paper. Reactor volume is plotted on the abscissa, and the required vent area is shown on the ordinate. Each line represents a different class of reaction,

The chart divides reactions into four classes:

1. Class A: Endothermic or very low exothermic reactions.
2. Class B: Reactions with low heat release/volume such as suspension polymerization of vinyl chloride, etc.
3. Class C: Moderately exothermic reactions, such as methyl methacrylate and styrene bulk polymerizations, mono nitration of benzene, toluene, etc., and Friedel-Crafts reactions.
4. Class D: Very high heat release reactions, such as oxidations using nitric acid, bulk polymerization of ethyl acrylate or methyl acrylate, caustic catalyzed phenol-formaldehyde condensation, etc.

Once the reaction class has been selected, the vent area is determined by drawing a vertical line from the vessel charge through the appropriate reaction class line, then extending a horizontal line from the intersection to the vent area axis. For example, a 1,000-gallon vessel running Class C reaction requires 56 square inches of venting capacity (an 8-inch diameter vent) according to the FIA chart.

If measured energy release rate data are available for a reaction, it is possible to draw a new line on the FIA chart to allow interpolation between the reaction categories. The lines for the four categories correspond to these energy levels:

1. Class A: 150 BTU/hr-lb
2. Class B: 608 BTU/hr-lb
3. Class C: 3,040 BTU/hr-lb
4. Class D: 15,200 BTU/hr-1b

The chart can be reduced to a formula that can be easily coded into an electronic spreadsheet, making the vent-sizing process even easier than reading a chart. The formula is:

$$A = (0.0000442)\, E^{0.952} V^{0.93} \tag{2}$$

$$D = 1.128\sqrt{A} \tag{3}$$

where A is the required vent square area in in^2, D is the vent diameter in in, E is the rate of evolution of energy $\mathrm{BTU/lb-hr}$ and V is the vessel volume in (gal).

Simplified Nomograph Method

Boyle [16] developed a simple method for quick estimation/screening of vent area for reactive systems. He defined the required vent area as that size which would empty the reactor before the pressure could rise above some allowable overpressure for a given vessel.

$$A = \frac{V\rho}{G_{2p}\delta t_v} \tag{4}$$

where A is the relief vent area, V is the reactor volume, ρ is the density of the reactants, G_{2p} is the mass flux through the relief device, and δt_v is is the venting time which can be approximated using the following equation:

$$\delta t_v \simeq \frac{\Delta T C_p}{q_s} \tag{5}$$

where ΔT is the temperature rise corresponding to the overpressure ΔP, C_P is the heat capacity, and q_s is the energy release rate per unit mass at the set pressure of the relief system.

Combining the above two equations yields an expression for A which depends on the reactor mass, the reaction energy release rate, allowable overpressure, two-phase mass flux and heat capacity:

$$A = \frac{V\rho q_s}{G_{2p}\Delta T C_p} \tag{6}$$

The two-phase mass flux can be estimated using various methods as illustrated later in this paper. A simple method that is often used is that developed by Fauske which assumes homogeneous equilibrium between the vapor and liquid phases (no slip) and should provide conservative estimates for relief areas (underestimates the actual mass flux which can be higher due to slip, subcooling, etc.):

$$G_{2p} = (0.9)C_d \frac{\lambda}{(V_v - V_l)}\sqrt{\frac{1}{C_{p,l}T_s}} \tag{7}$$

where C_d is the discharge coefficient, λ is the latent heat of vaporization, V_v is the specific vapor volume, V_l is the specific liquid volume, and T_s is the reaction temperature at the set point of the relief device.

The ratio of the latent heat over the specific volume difference can be redefined using the Clausius-Clapeyron equation:

$$\frac{\lambda}{V_v - V_l} = T_s \frac{dP}{dT_s} \tag{8}$$

Substitution of Equations 8 and 7 in Equation 6 yields the following simple equation for estimation of relief area:

$$\frac{A}{M} = \frac{q_s}{(0.9)C_d \Delta P \sqrt{T_s C_{p,l}}} \tag{9}$$

where M is the vessel mass in kilograms, ΔP is the vessel overpressure over the set point in Pascals, T_s is the relief set pressure in Kelvins, q_s is the reaction energy release rate in J/kg/s, and $C_{p,l}$ is the liquid heat capacity in J/kg/K.

Equation 9 provides a conservative estimate of the vent area required. By considering the case of 20 % absolute overpressure, assuming a typical liquid heat capacity of 2,510 J/kg/K for most organics, and assuming a saturated water relationship, the following equation was obtained by Fauske [17]:

$$A \text{ in } (\text{m}^2/1,000 \text{ kg}) = 0.00208 \frac{\frac{dT}{dt}}{P_s} \tag{10}$$

where dT/dt is the reaction energy release rate in (C/min) and P_s is the set pressure in (bar). A simple nomograph of the results can be plotted and is shown in Figure 11. The required vent area is determined simply from the heating rate, the set pressure and the mass of reactants.

The Fauske nomograph is useful for performing quick estimates and checking the results of more rigorous estimates. The nomograph data of Figure 11 applies to a discharge coefficient of 0.5 representing a discharge (L/D) of 400. The nomograph can be used for smaller L/D by multiplying by the ratio (less than 1) of 0.5 over the actual C_d value.

DIERS Methods

Two phase mass flux can be estimated by maximizing an expression involving an overall enthalpy change (stagnation - outlet) as a function of exit pressure and a selected thermodynamic path for determining the outlet vapor quality and temperature:

$$\text{Maximize } G = \rho_m \sqrt{2(H_o - H)} \tag{11}$$

where G is the two-phase mass flux, ρ_m is the mixture density, H_o is a two-phase stagnation enthalpy and H is the enthalpy at exit conditions. Both H_o and H are mixture properties that depend on vapor quality. The vapor quality is typically calculated by assuming an isentropic expansion.

By invoking the thermodynamic relation between entropy and enthalpy under isentropic conditions, nozzle flow can be estimated via an integral equation.

$$TdS = 0 = dH - VdP \tag{12}$$

which leads to:

$$G = \sqrt{2\rho_m \int_P^{P_o} \frac{dP}{\rho}} \tag{13}$$

This expression is integrated from the exit pressure to the stagnation pressure.

Instead of using a detailed equation of state to represent the PVT and phase equilibrium behavior of pure components and/or mixture, DIERS proposed a simple two-parameter equation of state with two adjustable parameters, a and b, that are determined from either isentropic or isenthalpic equilibrium flash calculations:

$$\frac{\rho_o}{\rho} = a\left(\frac{P_o}{P} - 1\right) + b\left(\frac{P_o}{P} - 1\right)^2 \tag{14}$$

The parameters a and b are calculated by fitting the volumetric expansion behavior using two or more flash equilibrium calculations at pressures lower than stagnation. This approach may not work well for mixture with wide boiling point difference such as hydrocarbon mixtures containing hexane and hydrogen, for example. The same concept was extended to pipe flow using homogeneous equilibrium (no slip between the liquid and vapor phases) by DIERS.

Leung's simplification of the DIERS two-parameter equation, the omega method, was introduced in several publications with an overall summary paper published in reference [19].

Leung uses the same DIERS form with $b = 0$ and $a = \omega$:

$$\frac{\rho_o}{\rho} = \omega\left(\frac{P_o}{P} - 1\right) \tag{15}$$

This simplification leads to a generalized form for mass flux for nozzle flow using the ω pressure/volume equation in Equation 14:

$$\frac{G}{\sqrt{P_o\rho_o}} = \frac{\sqrt{-2\left[\omega \ln\left(\frac{P}{P_o}\right) + (\omega - 1)\left(1 - \frac{P}{P_o}\right)\right]}}{1 + \omega\left(\frac{P_o}{P} - 1\right)} \tag{16}$$

This equation can be evaluated for different ratios of P/P_o to find the point at which G is maximum where P ranges from the stagnation conditions to the back pressure imposed on the

system. The critical pressure ratio can also be solved for by setting the first derivative of G with respect to pressure to 0. This is illustrated in Figure .

The value of ω ranges from 0 for all liquid flow, 1 for all vapor/gas flow, greater than 1 for flashing flow and between 0 and 1 for non-flashing flow.

The ω method is simple to evaluate for systems involving pure components and is of limited use for systems involving mixtures with wide boiling point difference or where composition changes are significant due to chemical reaction or large pressure drops. In addition, recent experimental flow data indicate that slip should be considered in estimation of the mass flux, especially for viscous systems. This becomes an issue when designing downstream effluent handling equipment since in many situations the assumption of no slip between the liquid and the vapor phases leads to under estimation of the two-phase mass flux and as a result to a conservative estimate of the required relief area.

Leung provides the following expressions for ω which depend on stagnation properties only.

For flashing systems:

$$\omega = \alpha_o + (1 - \alpha_o)\rho_{m,o}C_pT_oP_o\left(\frac{V_{v,o} - V_{l,o}}{H_{v,o} - H_{l,o}}\right)^2 \tag{17}$$

where α_o is the void fraction at stagnation conditions.

For non-flashing systems:

$$\omega = \alpha_o \tag{18}$$

Leung published many variations on the omega method extending its use to pipe flow, subcooled flow and for the calculation for reaction forces. We find these extensions less useful since they cannot handle inlet piping and outlet piping configurations with multiple segments and elbows, etc. The geometry of the inlet and outlet piping becomes very important for flashing flow, since pressure drop will lead to vapor quality change and will lead to choking at lower mass flow rates. In addition, the omega method is not capable of handling the impact of continuing reactions in piping and vent containment.

Relief Sizing for Gassy Systems Using Direct Scaleup

The volume balance equations represented in the earlier section are most applicable to reaction systems with tempering characteristics, i.e. ”vapor” systems. For gassy systems, the reaction temperature can continue to increase after relief due to negligible tempering effects of noncondensable gas generation. The vent size should be able to handle the maximum rate of gas generation.

The required relief area can be estimated by equating the rate of volume generation due to reaction and the rate of volume discharge from the relief device:

$$\left(\frac{M_o}{M_{cell}}\right)\left(\frac{V_{cell}}{P_o}\right)\left[\frac{dP}{dt}\right]_{max} = \frac{C_d G A_h}{\rho_o} \tag{19}$$

where G is a two-phase mass flux to be computed using the omega method for non-flashing systems:

$$\omega = \alpha_o \tag{20}$$

The pressure rise rate data is typically derived from a suitable open-system calorimeter. P_o is the maximum allowable working pressure of the vessel (MAWP), M_o is the initial vessel charge, V_{cell} and M_{cell} represent the void volume in the test cell and the mass in the test cell.

Solving directly for the relief area, we obtain:

$$A_h = \rho_o \left(\frac{1}{GC_d}\right)\left(\frac{M_o}{M_{cell}}\right)\left(\frac{V_{cell}}{P_o}\right)\left[\frac{dP}{dt}\right]_{max} \tag{21}$$

The estimates of relief areas produced using this equation have been shown to be a factor of five to ten times larger than what is needed (see, for example, paper by A. Chakrabarti in Proceedings of International Symposium on Runaway Reactions and Pressure Relief Design, Boston, 1995, AIChE).

Relief Sizing for Hybrid Systems

Sizing for hybrid systems requires the use of detailed computer simulation methods. However, an estimate of relief area requirement can be obtained by performing the sizing as a vapor system and as a gassy system and selecting the larger of the resulting relief areas.

Direct Scaleup of RSST data

The vent sizing equations used to scaleup RSST data account for two-phase flow. For a gassy system the required vent area is calculated from:

$$A_h = 3 \times 10^{-6} \frac{1}{F} \frac{M}{m} \frac{\dot{P}}{P_{\text{mawp}}^{1.5}} \tag{22}$$

where m is the sample mass, M is the plant vessel contents mass, $\dot{P}$ is the maximum measured pressure rise rate in (psia/min) and F is a flow reduction factor which compensates for vent lines. F can be estimated from:

$$\ln(F) = -0.0408 \left[\frac{L}{d}\right]^{0.554} \tag{23}$$

For a vapor system, the required vent area is calculated from:

$$A_h = 1.5 \times 10^{-5} \frac{M\dot{T}}{FP_{\text{set}}} \tag{24}$$

where $\dot{T}$ is the measured temperature rise rate (C/min) at the vent set pressure, and F is given by:

$$\ln(F) = -0.0125 \left[\frac{L}{d}\right]^{0.671} \tag{25}$$

For hybrid systems the equation is similar to that for a gassy system:

$$A_h = 3 \times 10^{-6} \frac{1}{F} \frac{M}{m} \frac{\dot{P}}{P_{\text{mawp}} \sqrt{P_{\text{mawp}} - P_{\text{set}}}} \tag{26}$$

where F is a flow reduction factor which compensates for vent lines. F can be estimated from:

$$\ln(F) = -0.0408 \left[\frac{L}{d}\right]^{0.554} \tag{27}$$

SuperChems for DIERS

The Design Institute for Emergency Relief Systems (DIERS) Users Group awarded Arthur D. Little, Inc. a contract to provide the next generation computer program for emergency relief system and effluent handling designs.

The new computer program, SuperChems for DIERS [8], is a dynamic simulator, capable of performing emergency relief system and effluent handling designs for complex geometries and multiphase reaction systems. In addition, SuperChems for DIERS is an equation-of-state based program which provides several benefits over existing non-equation-of-state based methods for systems involving supercritical reactions like polymerizations of butadiene and acrylonitrile, solution effects such as HCl/Water, and a priori determination of phase-splitting.

This new computer program allows the user to dynamically simulate several common configurations for vent containment design. For example, the user is able to simulate a vessel discharging

a two-phase mixture into a quench/vent tank where the catch/vent tank will vent to a stack or a scrubber. Effluent handling equipment available includes separators (horizontal and vertical), cyclones, etc. The impact of back pressure and continuing reaction in the vent containment system is accounted for in the dynamic simulations. [12]

SuperChems for DIERS Functionality

Highlights of the new computer program as outlined in the request for proposal are summarized below:

1. Provide a general purpose thermodynamic and transport properties generator with implicit corrections for non-ideal behavior in both the liquid and vapor phase. The properties generator should also be able to provide temperature and pressure dependent derivatives for all properties of interest. The generator should be detailed enough so that heat of solution effects and vapor-liquid non-ideal equilibrium are implicit. This generator should also be able to provide all properties and all derivatives required by the computer models. The generator should be equation of state (EOS) based.

2. Create/design an interface allowing the properties generators to access a thermophysical properties database so that properties do not have to be manually added. A databank manager should be provided in order to allow the users to input/modify their own compounds, if needed.

3. Revise all flow models such that the new computer program will address the following items:

   (a) inclined flow

   (b) subcooled flow

   (c) sudden expansion/contraction

   (d) piping segments with varying diameter and orientation

   (e) viscous two-phase flow through safety relief valves and pipes

   (f) continuing chemical reaction in piping and vent containment systems

   (g) detailed energy balances for vessels and piping

   (h) detailed momentum balance for piping

   (i) implicit vapor-liquid equilibrium relations

   (j) the flow models and the vessel balances should be equation oriented.

[12]This paper appeared in the AIChE Loss Prevention Symposium Proceedings, March 1997, Houston

4. Provide a suitable stiff differential/algebraic (DAE) equation-solver. Proposed schemes should include Gear's or Michelsen's methods.

5. Provide a user-friendly menu-driven interface including graphics plotting capabilities and report generation.

6. Provide required documentation including an Operations Guide, a User's Guide, and a Reference Manual.

7. Validate all new models using experimental data, where available.

Arthur D. Little Inc. (ADL) had already developed a computer program which contained all the above specifications. This program took about five years to develop and is known as SuperChems Expert Version 3. The emergency relief system design portion of SuperChems was customized for the DIERS Users Group and is available for sale from the American Institute of Chemical Engineers (AIChE).

SuperChems for DIERS is an equation-of-state based program which provides several benefits over existing non-equation-of-state based methods for emergency relief system design for systems involving:

1. Reactions with supercritical components such as polymerizations of butadiene, acrylonitrile, etc.

2. Solution effects such as HCl/water, etc.

3. A priori determination of phase-splitting

SuperChems for DIERS contains a databank of more than 3000 binary systems with equation-of-state binary interaction parameters derived from experimental vapor-liquid and liquid-liquid data. There is also a VLE/VLLE data package. This versatile utility allows the estimation of binary interaction parameters for the equation of state composition dependent mixing rule. The source of data can be one of six types:

1. Azeotropic data

2. TPXY measured data (SuperChems for DIERS also includes three thermodynamic consistency utilities for X and Y calculations)

3. Mutual solubility data

4. Henry's law constants (mostly used for gas solubility in liquids)

5. Activity coefficient model parameters

6. Infinite dilution activity coefficients

SuperChems for DIERS has an extensive database with over 1200 chemicals. The database contains 39 thermophysical properties with temperature dependent properties and data quality parameters. The program also has a detailed regression package (linear/non-linear) which allows the reduction of tabular data to equation forms supported by the databanks.

SuperChems for DIERS Computer Implementation

Emergency relief system design does not stop at the estimation of the size of the relief device. The effluent must be treated if it is toxic and/or flammable or if it presents an environmental impact. While homogeneous-equilibrium flow (no slip) is typically used for sizing the relief device, slip-equilibrium flow should be used to establish correct pressure drops and safety/environmental impacts.

SuperChems for DIERS is a computer program which allows the integral evaluation of relief dynamics and downstream effects. For example, using SuperChems for DIERS, we can evaluate the time dependent history of pressure, temperature and composition in a reactor vessel as the relief occurs. Simultaneously, the effluent is discharged, and handled to meet established (regulatory or internal) criteria. Typically, many options are evaluated before a final design is selected. This includes separation equipment, flares, stacks, etc.

The most useful aspect of SuperChems for DIERS is its scenario/object driven architecture. Once an object (such as a vessel or piping configuration) is defined, it can be used by one or more scenarios. Once a scenario is defined, it can be duplicated and used to perform what-if or sensitivity analysis.

The detailed algorithms for SuperChems for DIERS are published in references [9], [10] and [8].

CONCLUSIONS

Our discussions have provided an overview of the range of techniques available for thermal hazard evaluation in connection with relief system design. It is clear that, in practice, a number of (possibly conflicting) factors might influence the precise approach chosen. This includes existing testing regimes, equipment familiarity / availability, regulatory drivers, time pressure, and financial resources.

Ultimately, the main requirement is for a coherent and consistent approach to thermal hazards evaluation using the best means available. All instruments and methodologies have inherent strengths and weaknesses. Diversity of approach stimulates active interpretation and understanding, and avoids common mode errors. Informed interpretation is ultimately more important than quality of hardware.

Figure 4: Reactive System Screening Tool

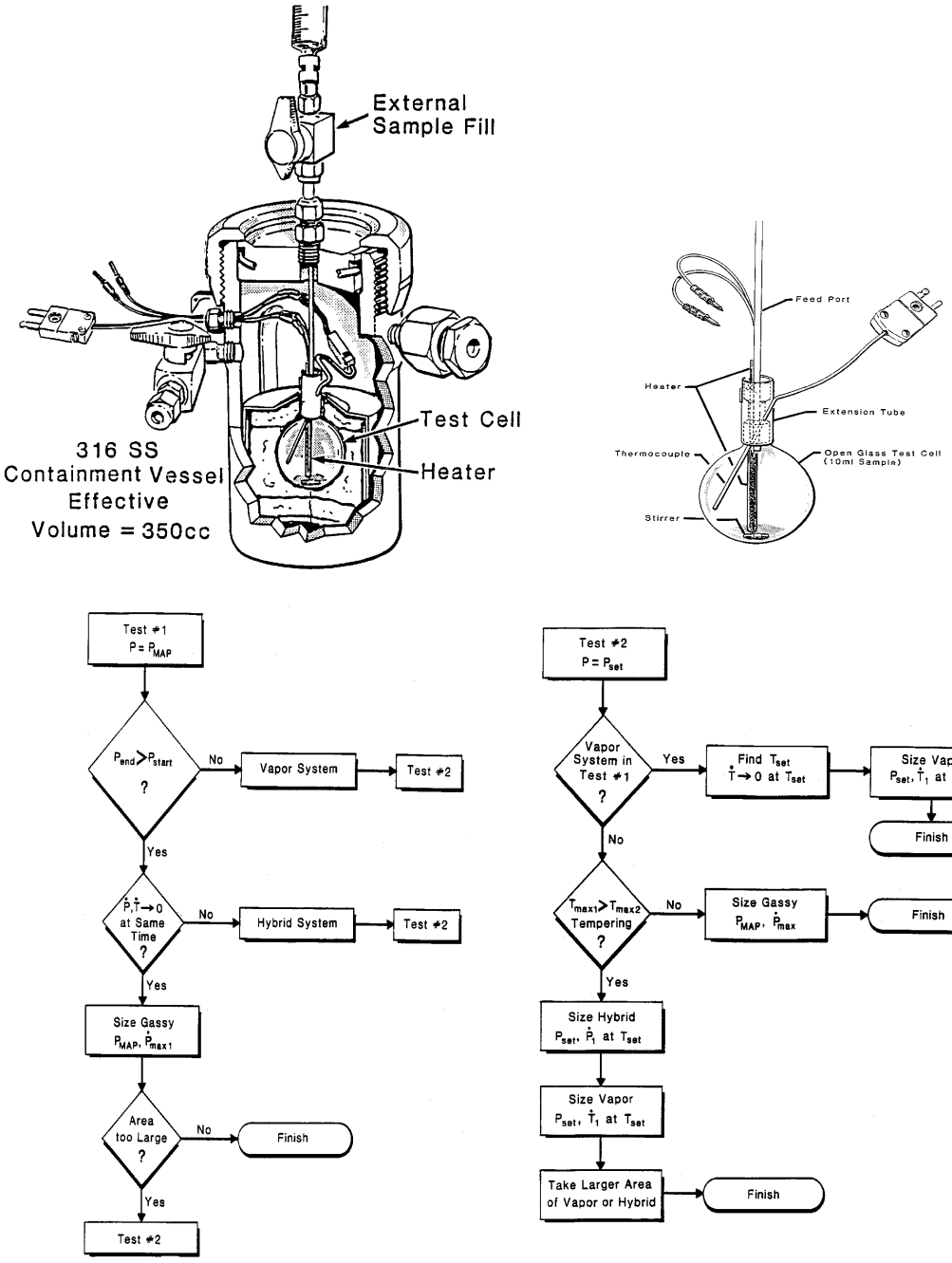


Figure 5: The Accelerating Rate Calorimeter (ARC)

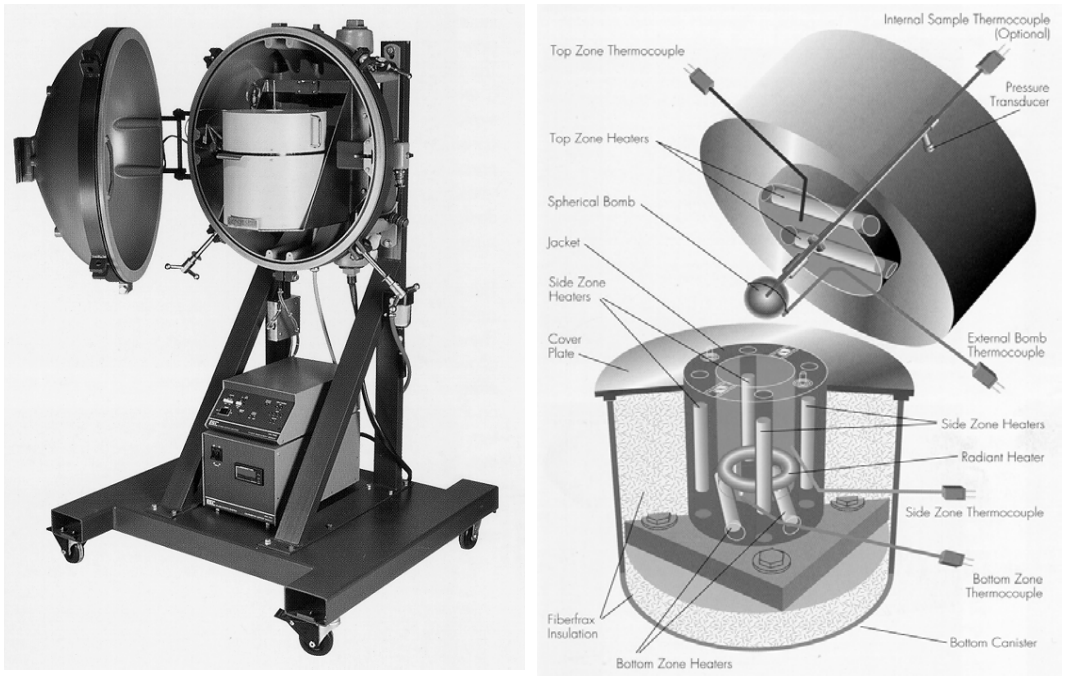


Figure 6: Vent Sizing Package

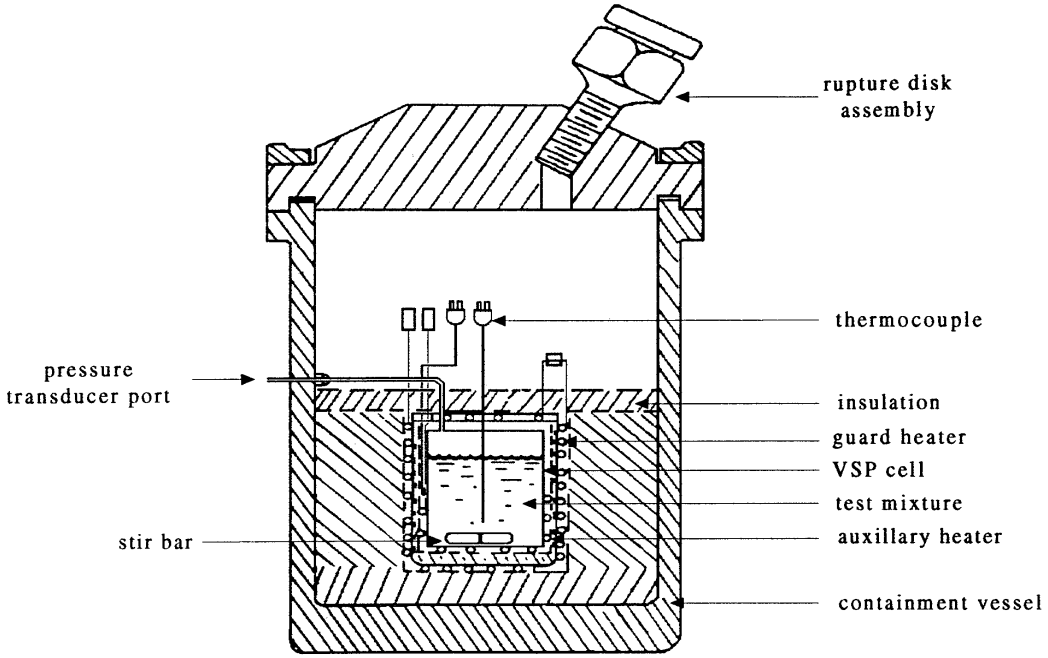


Figure 7: Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

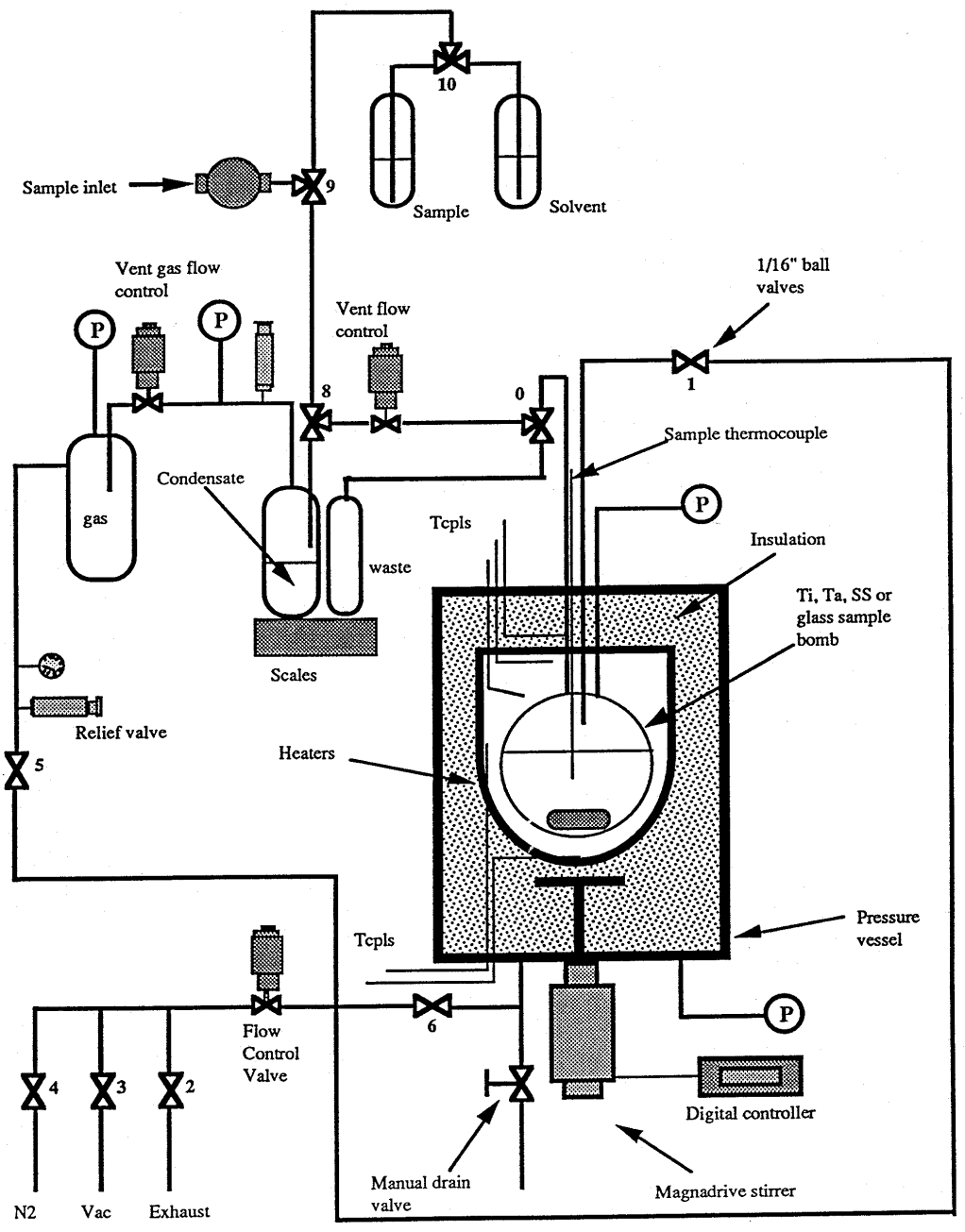
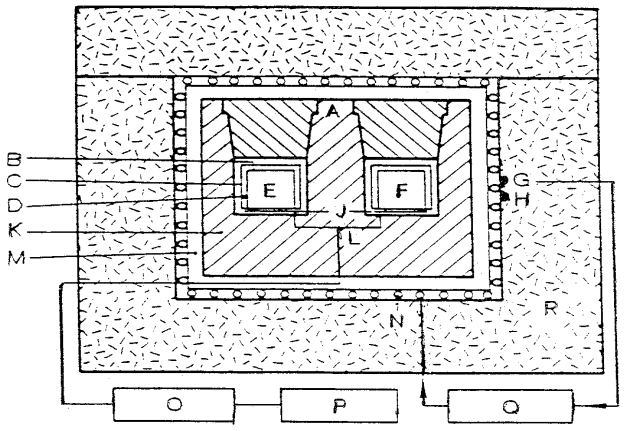


Figure 8: Isothermal Storage Test



(A) PT-thermometer

(B) Sample vessel

(C) Cylindrical holder

(D) Air spaces

(E) Sample

(F) Inert material

(G) PT-sensor for temperature control

(H) PT-sensor for safety control

(J) Peltier elements

(K) Aluminium block

(L) Electric circuit

(M) Air space

(N) Heating wires

(O) Amplifier

(P) Data-registration

(Q) Temperature Controller

(R) Glass wool

Figure 9: A selection chart for ERS design methods

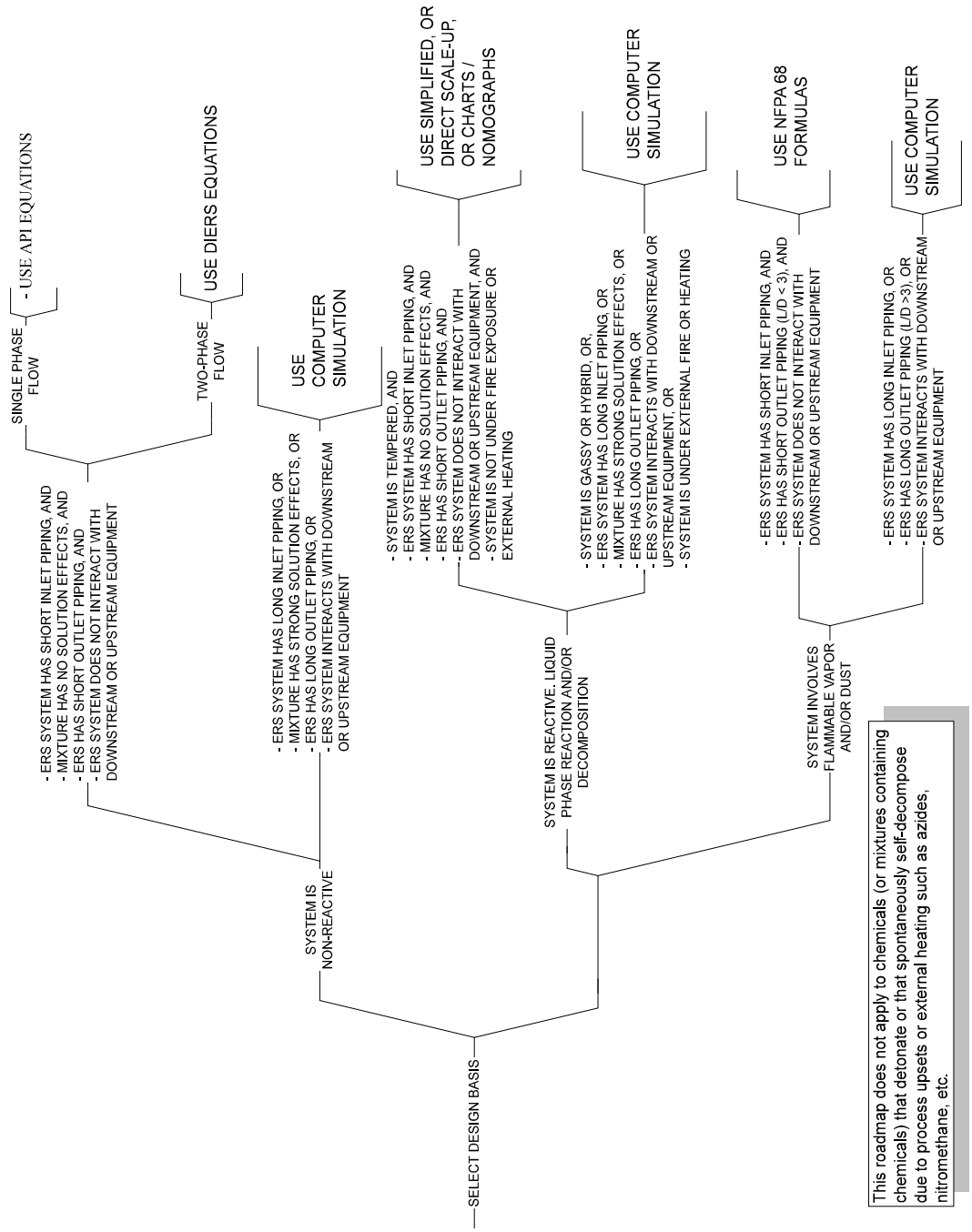
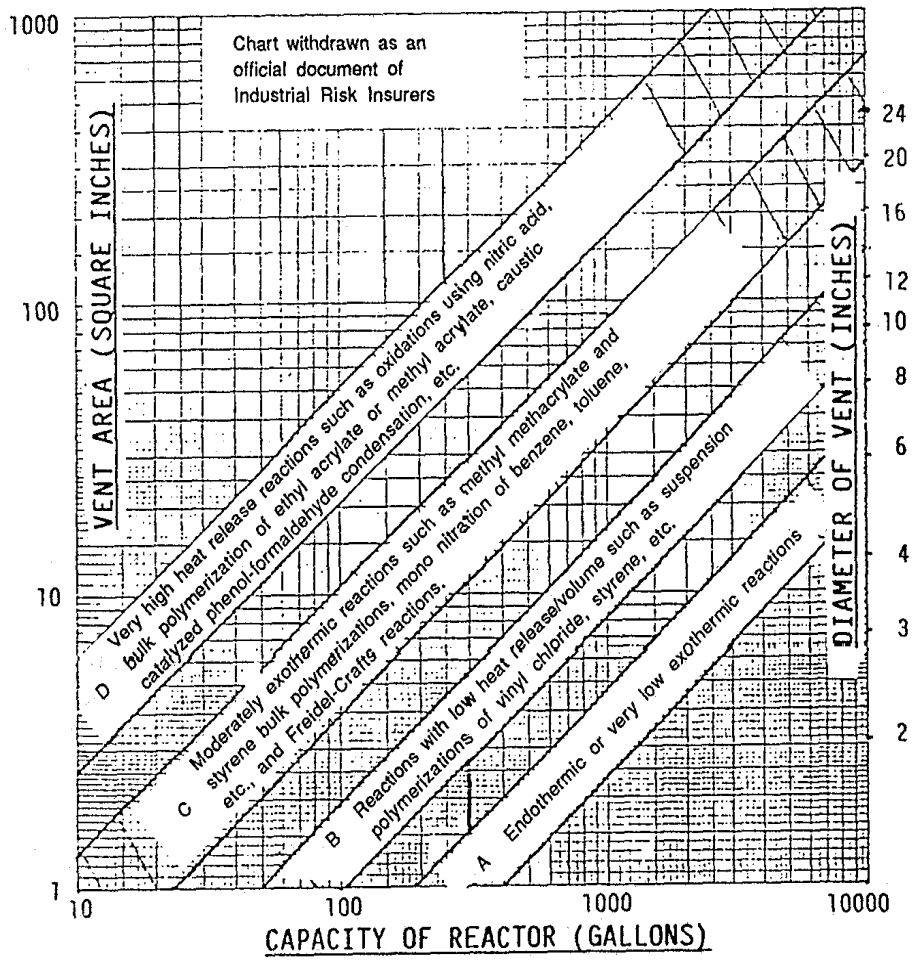


Figure 10: FIA Chart



BASIS: TEMPERED REACTIONS
100-125 PSIG VESSEL PRESSURE
≤ 15 FEET RELIEF LINE LENGTH*
LOW RELIEF VISCOSITY

WARNING: CHART RECOMMENDATIONS ARE NON-CONSERVATIVE FOR SEVERAL OF THE NAMED REACTIONS

*NOTE: RELIEF AREA CAN BE ADJUSTED FOR THE EFFECT OF LINE L/D ON FLOW

Figure 11: Nomograph for sizing two-phase reactor reliefs.

Taken from reference [18].

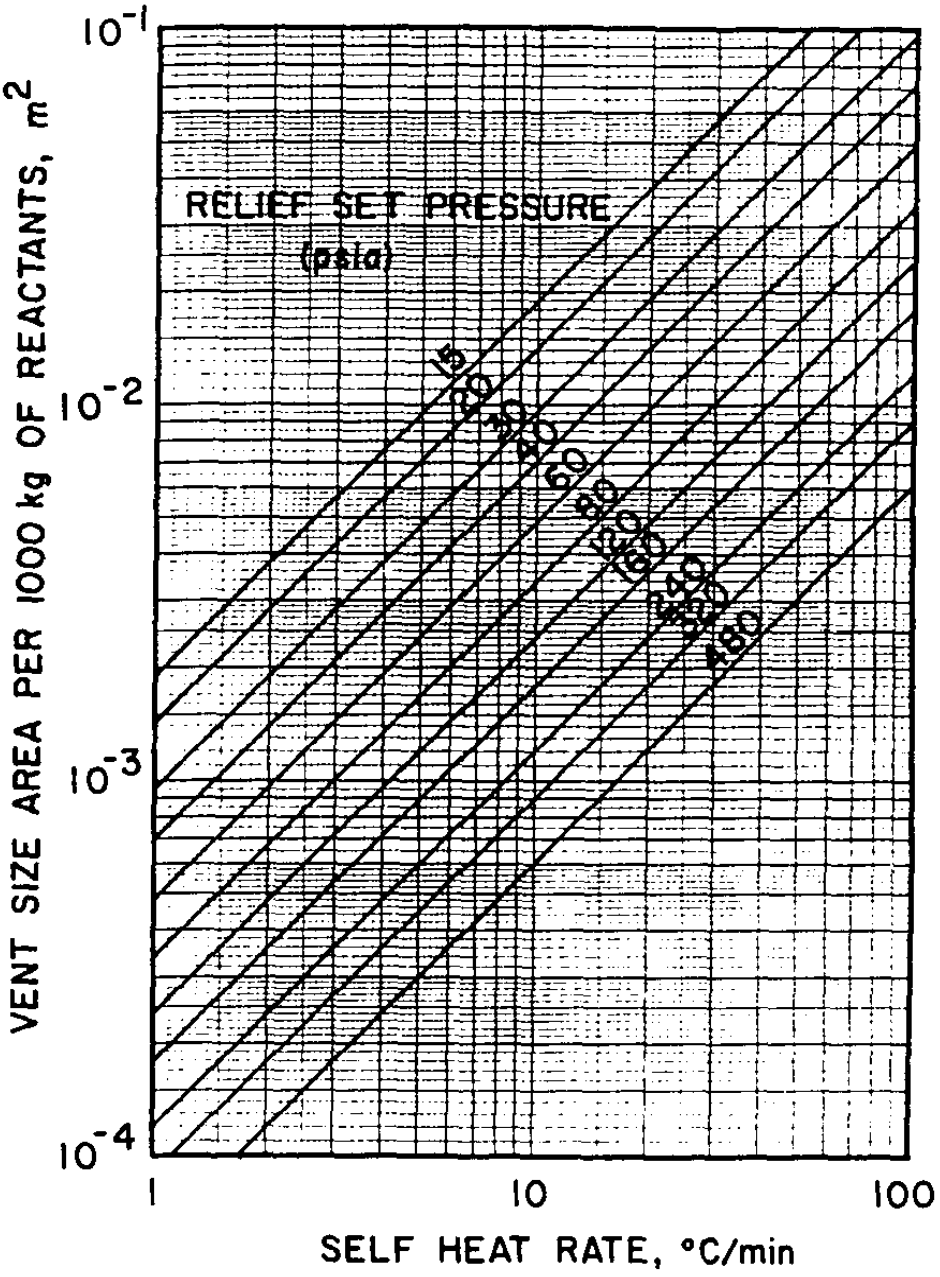
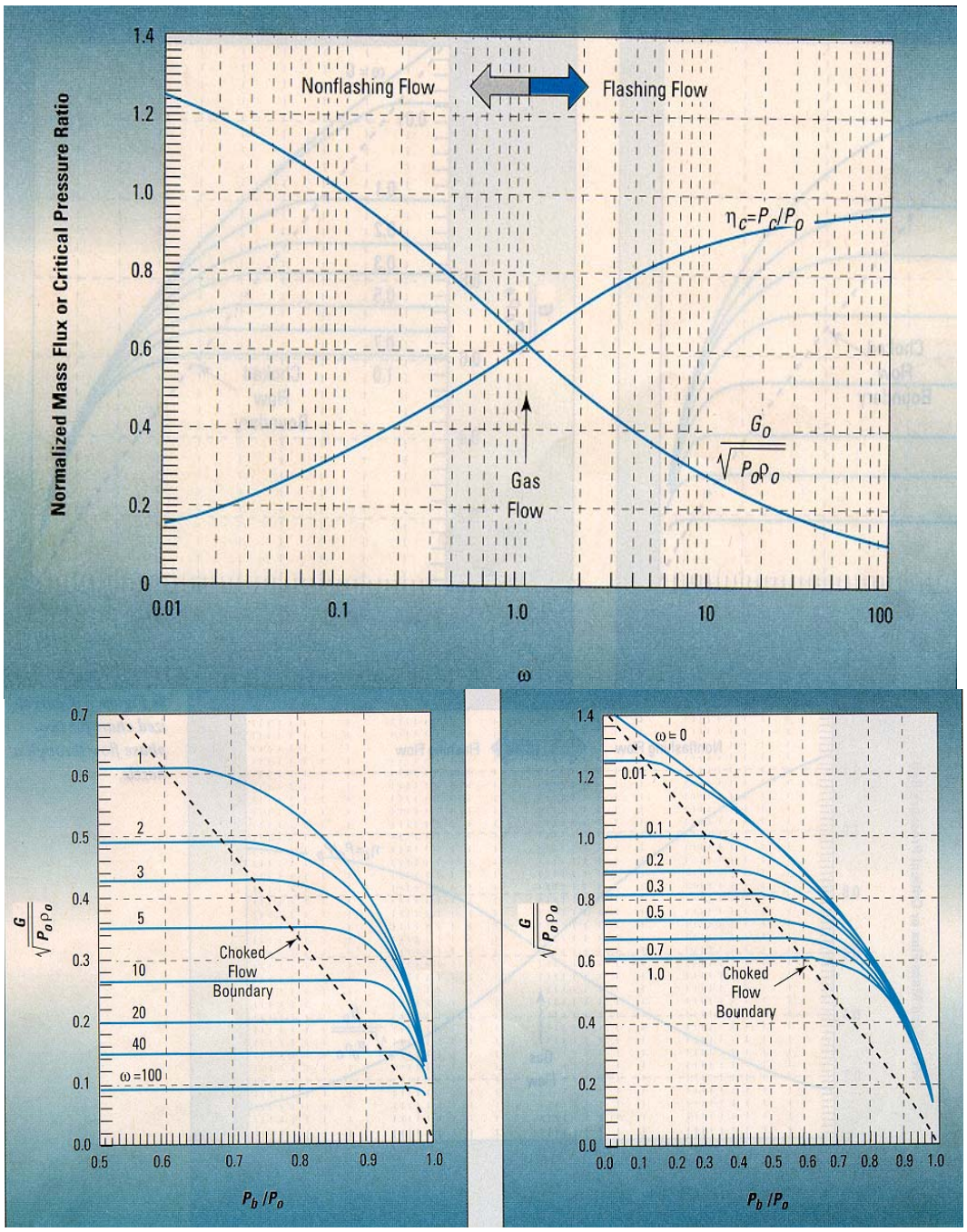


Figure 12: The omega method for estimation of two-phase mass flux and critical pressure ratio. Taken from Chemical Engineering Progress.



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