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A Second Appraisal of Methods for Estimating Self-Reaction Hazards

Eugene S. Domalski

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
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Interim Report for Period January - December 1975

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U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, ***Secretary***

Dr. Betsy Ancker-Johnson, ***Assistant Secretary for Science and Technology***

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Acting Director***

Foreword

The work reported here represents a second attempt to appraise methods employed for the estimation of self-reaction hazards for the Office of Hazardous Materials Operations of the U. S. Department of Transportation during calendar year 1975. During the course of this effort, expertise from various sectors of the National Bureau of Standards was enlisted. A clearer and more quantitative definition and identification of thermal instability was sought with an outlook toward establishing a reactivity scale for materials with a tendency to self-decompose.

An assessment of the accidental polymerization of bulk chemicals was provided by Mr. Daniel W. Brown and Dr. Roland E. Florin of the NBS Polymer Stability and Reactivity Section. Assistance was obtained through the NBS Center for Fire Research from Dr. Andrej Macek. Dr. Bert R. Staples of the NBS Chemical Process Data Evaluation Section helped in the collection and formating of the physical test methods, and in the compilation of the corresponding bibliography. Dr. Kenneth L. Churney of the NBS Thermochemical Standards and Measurements Section studied relationships between the physical test methods and the fundamental concepts of thermal explosion theory. Technical contributions were obtained in the area of chemical kinetics from Drs. Wing Tsang, Michael J. Kurylo and Alan H. Laufer of the NBS Physical Chemistry Division.

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I. Introduction

The need to find a clear definition and a more quantitative identification of the property known as thermal instability (self-reactivity) of chemical substances was the goal of the efforts put forward in the Physical Chemistry Division of the National Bureau of Standards (NBS) during the calendar year 1975. This need is acknowledged by groups within various sectors involved in the production, handling, and transport of hazardous materials. The Office of Hazardous Materials Operations of the U. S. Department of Transportation (DOT) has supported this investigation as part of its own program to review the hazard classification system, to re-examine regulations for hazardous cargoes, and to implement an emergency response system.

A previous evaluation program [1][†] for DOT performed by NBS in 1974 examined predictive schemes and physical test data to determine if correlations could be made between the test data and various thermochemical and kinetic parameters which would allow the establishment of a ranking of substances on the basis of their chemical reactivity. Included in this previous program was an attempt to derive a better idea of how thermal instability could be defined. However, because the correlations obtained were not definitive and because only qualitative relationships were apparent, an improved definition or identification of thermal instability did not emerge.

[†] Numbers appearing in brackets refer to references at the end of this report.

Our efforts for DOT during calendar year 1975, to appraise thermal instability concepts and to seek a better definition and identification of self-reactivity as a function of increasing temperature, pursued the following areas: (1) an evaluation of the literature which reported explosive sensitivity test methods and the corresponding test data, (2) an examination of hazards caused by monomer polymerizability, and (3) the re-examination of the predictive schemes.

Although a large array of test methods and test data were found as a result of performing the literature survey, we were not able to establish a reliable reactivity ranking which could be applied to chemical substances as a whole. Some of the test methods and test data are very empirical in nature, however, others could be linked to fundamental concepts involving thermal explosion theory. The broad spectrum of data required to cover the range of reactivity from nitroglycerine to sand were either unavailable or were present in a form which could not be merged easily with other related information. We found that it was difficult to reduce the data obtained from different test methods to a common level for comparison because of the inherent dissimilarities in the kinds of methods employed and parameters measured.

Development of the predictive schemes to accommodate various reaction mechanisms remains a difficult task because of the overall empirical, and in part arbitrary, character of their formulation. Reaction mechanisms are established best by performing reaction-rate experiments on the systems under question. Without experimental kinetic data, prediction of reaction mechanism is subject to considerable risk.

From the evaluation of the test methods and the re-examination of the predictive schemes, it appears that a calorimetric approach has promise of providing part of the necessary information and support for concepts from which a reactivity scheme could be developed. One of the serious difficiencies of many of the existing test methods and the predictive schemes is their overall empirical nature. A firmer foundation for a definition of thermal instability and for a method to rank chemical reactivity could be obtained from the theory of thermal explosion as put forward many years ago by Semenov [2, 3] and by Frank-Kamenetskii [4, 5], and studied more recently by Merzhanov and his co-workers [6].

The calorimetric approach offers the advantage of permitting simultaneous determination of thermochemical, kinetic, and heat transfer parameters from experimental measurements performed on a specific thermal decomposition process. The need to calculate these parameters from the same reacting system, thus providing a common base for comparison, appears to be an important feature. The fact that the calorimetric approach should provide the parameters embodied in the theory of thermal explosion suggests that a ranking for chemical reactivity could be developed from such investigations.

II. A More Detailed Statement of the Problem

The U. S. Department of Transportation is responsible for the effective administration and coordination of the transportation programs of the Federal Government. The safe transportation of hazardous materials is included in these programs. On January 3, 1975 the Hazardous Materials Transportation Safety Act (Public Law 93-633) was passed [7]. This legislation repealed and superseded the Hazardous Materials Transportation Control Act of 1970 (Public Law 91-458). Under both Acts the Secretary of Transportation must prepare and submit to the President for transmittal to the Congress on or before May 1 of each year a comprehensive report on the transportation of hazardous materials during the preceding calendar year. Included in this report is a thorough statistical compilation of any accidents and casualties involving the transportation of hazardous materials, and a list and summary of applicable Federal regulations, criteria, orders, and exemptions in effect.

An area within the existing code of Federal regulations which needs clearer definition and identification is the characterization of thermally unstable materials. The regulations which cover the hazardous materials occasionally classify certain chemicals which are thermally unstable in categories not indicating this property because the other hazard classification is more outstanding. For example, picric acid (with not less than 10 percent water) is listed under

"Flammable Solids"; anhydrous hydrazine is classed as a "Flammable Liquid"; and chloropicrin is identified as a "Class B Poison". These chemicals are all potentially capable of thermal decomposition.

As a result of situations such as those cited above in which only a partially classification of the hazard potential of a chemical is provided, the DOT Office of Hazardous Materials Operations has sought to improve the systematization of its regulations of hazardous materials as part of a long-range research and development effort. New regulations and amendments to existing regulations are published on a yearly basis and should be helpful to shippers and carriers in expediting the transport of hazardous cargoes.

Expertise in the areas of thermochemistry and chemical kinetics which are in the NBS Physical Chemistry Division has been employed in seeking a clearer definition and identification of thermal instability. Both data analysts and experimentalists in this Division have been helpful in providing their appraisals of various aspects of thermal instability, chemical reactivity, self-decomposition, and the examination of other factors which render a chemical as hazardous. In conjunction with these appraisals, the files of the Chemical Thermodynamics Data Center and the Chemical Kinetics Information Center were made available so that the information at hand was as current as possible.

The problem of defining and identifying thermal instability in a quantitative manner is linked to the collection of an array of data, from either the literature and/or the laboratory, from which a mathematical correlation can be derived. Correlatable parameters are obtained from test methods for explosive sensitivity and enthalpies of decomposition, activation energies, and frequency factors which have been determined from thermochemical and kinetic studies. Ideally, the correlation should be able to rank all substances between nitroglycerine and sand in a quantitative manner according to their chemical reactivity. The correlation should have a good theoretical foundation and not be strictly empirical. Our previous attempts to correlate enthalpies of decomposition with impact test data could only provide us with a qualitative relationship because the enthalpies of decomposition used were for other processes than those taking place at impact as imposed by the falling weight. The impact test is useful and has its place in hazard evaluation, but is for the most part empirical in origin, fundamentally difficult to interpret, and limited in the degree to which it can be applied in certain correlations.

We are hopeful that within the theory of thermal explosion and the measurement of parameters contained in the self-heating expressions of that theory, the proper combination of factors necessary to provide a ranking for a chemical reactivity scale will be found. After a sufficient number of experiments have been conducted and parameters calculated, we feel a quantitative relationship can be obtained which will be useful in defining and identifying thermal instability. The problem of scaling to large samples must also be examined as well as changes in the ambient conditions to which the chemical is subjected during handling and shipment.

III. Conclusions and Recommendations

Our general conclusions and recommendations are as follows:

1. Test Methods and Test Data

Thermal tests which provide information about the critical conditions for thermal explosion are valuable because they give quantitative data identifying the limit of thermal stability for a specified material. Examples of such thermal tests are: the JANAF Thermal Stability Test, the ASTM E-476-73 Confinement Test, the Thermal Surge Test, and the Explosion Temperature Test. The adiabatic and isothermal storage tests are useful in estimating the induction time prior to explosion for a material.

Detonability tests apply only to sensitive explosives, and hence, give negative results for materials of lesser sensitivity to initiation. The impact test is probable the most versatile and most widely used of the compression tests. It usually can give reasonable reactivity ranking for explosives. Inversions in rank can occur when impact data from different apparatuses are examined.

The air-blast test is an important test which provides data on the energy release of explosive materials. It is applicable to both detonative and sub-detonative explosives.

2. Predictive Schemes

Attempts were made to develop separate predictive schemes which were oriented toward handling particular reaction mechanisms. We found that it was not possible to devise or formulate separate schemes. Realistic enthalpies of decomposition could not be predicted independent of experimental measurement.

A hazard evaluation study of some selected materials, which are commonly considered safe, showed that the CHETAH program is likely to err in labelling safe materials as being hazardous.

The CHETAH program does not appear to provide a clear-cut ranking of hazards related to polymerization.

3. Accidental Polymerization of Bulk Chemicals

Free radical polymerization involving olefins is the kind of polymerization process most likely to occur inadvertently during transport. Peroxides are the probable source of initiation. Information regarding the identification of the type of inhibitors and their required concentrations which would prevent the accummulation of serious amounts of peroxides is considered important.

4. Thermal Explosion Theory and Hazard Evaluation

From an examination of reports of experimental investigations of hazardous materials and the elements of thermal explosion theory, a calormetric experiment appeared to offer a more likely and reasonable recourse to obtain data from which an unambiguous reactivity scheme could be developed. We feel a test procedure for ranking materials consistent with such a reactivity scheme should be derivable having a firm relationship to thermal explosion theory. Properties of materials which are embodied in this theory (such as the enthalpy of decomposition, activation energy, pre-exponential factor, heat transfer coefficient, the temperature below which no violent decomposition will take place, and the induction time prior to explosion) are derivable from scanning calorimetric measurements. The calorimetric approach has the advantage of permitting the simultaneous derivation the above-mentioned properties from the experiments performed on a specific decomposition process.

IV. Collection and Evaluation of Test Methods and Test Data

We acknowledge the assistance of Dr. Andrej Macek* of the NBS Center for Fire Research in the preparation of this section of the report.

The collection and evaluation of test methods and test data have been approached from the standpoint of both the sensitivity to decomposition or explosion, and the damage potential or total energy release which can be expected from a decomposition or explosion. The sensitivity of a material can be related to the minimum amount of thermal excitation necessary to initiate the process. In more fundamental terms, this concept can be associated with the rates and mechanisms of the initial reaction process. In the case of bond-breaking processes, the bond dissociation energy and the activation energy are equivalent, and are useful estimates of material sensitivity for decomposition. On the other hand, the total energy release (or power) of a decomposition reaction is related fundamentally to the thermodynamic aspects of the reaction, and is a function of the reaction's initial and final states.

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A. Sensitivity Tests

There is a wide variety of standardized tests designed to evaluate the sensitivity of self-reacting materials to external stimuli. The tests can be divided conveniently into two classes, thermal and mechanical. Thermal tests measure the inherent stability of materials and thus allow an explanation of the sensitivity to some degree in fundamental terms. Mechanical tests, on the other hand, are very difficult to analyze in fundamental terms, because the stimulus usually is an intricate mixture of several fundamental processes (e.g., compression, friction, viscous flow) none of which is easy to reduce to quantitative values, and all of which are difficult to scale. It is, therefore, clear that, while both types of tests are important, the approach to the problem of evaluation of the two types of tests must be different.

The question of thermal sensitivity can be approached in a general way, so there even appears to be a possibility of specifying a single testing procedure, applicable to all materials. The approach to mechanical tests ought to be much more empirical. The only reasonable procedure at this point is to seek tests which simulate some aspects of the anticipated practical exposure to stimuli. This means that there are two reasons why one should not expect to be able to specify a simple mechanical test for evaluation of sensitivity. First, there is a variety of possible hazardous stimuli. Second, simulation by laboratory tests is never quite satisfactory, so cumulative ratings by several tests are desirable for increased confidence.

1. Thermal Tests

We are concerned only with materials which self-react exothermically when exposed to sufficiently high temperatures. When this happens, the temperature T in the interior of the sample generally increases above the temperature of the surroundings, T_o, and heat is transferred from the sample to the surroundings. Steady states are possible at sufficiently low temperatures. However, if the temperature exceeds a critical value, T_{cr}, the heat generation rate becomes so large that heat loss cannot keep up with it, and catastrophic self-heating ensues, usually ending in an explosion. These processes have been described quantitatively by Semenov, Frank-Kamenetskii, and others [3, 5, 8] and a relatively simple relationship can be derived for the critical temperature from their treatments which is provided below:

$$\frac{E}{T_{cr}} = R\ln\left[\frac{a^2\rho}{(T_{cr})^2\lambda\delta R}\right]$$

where R is the gas constant, a is the radius of a sphere or cylinder or the half-thickness of a slab, ρ is the density, Q is the heat of reaction during the self-heating process, A is the pre-exponential factor and E the activation energy from the Arrhenius expression, λ is the thermal conductivity, and δ is the shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, and 3.32 for spheres). A maximum value for δ can be calculated for each of the three geometries which corresponds to the steady state situation.

An important assumption which is embodied in the latter equation is that the Arrhenius form of expressing rate processes is applicable to the self-heating problem. The assumption is not trivial and can lead to difficulties when experiments are designed poorly. However, if we presume that experiments are designed properly, pre-exponential factors and activation energies can be derived which will lead to a realistic description of the problem.

Test Methods and Test Data

General format for the exposition of the test methods and test data is as follows:

1. Purpose of Test:

A brief identification of the physical property which is being measured is provided, or the parameter which the measurement is directly related to is mentioned.

2. Operating Principle:

The definitive experimental condition is given under which the sample is subject in the test method, or its relationship to the measurable property.

3. Test Description:

A brief description of the test method is provided.

4. Test Evaluation:

This section discusses the advantages, disadvantages, limitations, and outstanding or unique features of the method.

5. Data:

The hazardous compounds studied are listed along with the parameters which were calculated. Individual values are not always supplied. References are always provided, however, in some cases, because of the large amount of data or the complexity of its exposition, only references are supplied.

a. JANAF Thermal Stability Test Number Six for Liquid Propellants [9]

1. Purpose of Test:

To determine the maximum temperatures to which thermally unstable liquids can be subjected for short periods of time without danger of explosive decomposition.

2. Operating Principle:

Under confinement in a microbomb a liquid sample is either heated rapidly and held at a pre-determined temperature for an arbitrary time interval, or heated at a constant rate until evidence of rapid decomposition appears. Spot immersion is also possible, where the microbomb containing the sample is immersed into the bath at some elevated temperature.

3. Test Description:

A microbomb which is drilled and tapped for a thermocouple and burst disc fitting, has an internal volume of 1.3 cm^3. A liquid sample of 0.5 ml volume is used and burst diaphrams ranging from 300 to 8400 psi failure pressure can be used. The microbomb is immersed in a bath containing a bismuth-lead alloy, which melts in the range 150 to 250°F. Maintenance of the bath around 200°F and of the heating rate at 20°F per minute, allows detection of rates of decomposition of 2°-5°F per minute. An air-vibrator is used to agitate the bath and the sample in order to establish the desired heat transfer between bath and sample. The sample temperature and the temperature difference between the bath and sample are recorded as a functions of time. The temperature at which self-decomposition begins and the rate of decomposition can be derived.

4. Test Evaluation:

This test utilizes small samples of material in good thermal contact with thermostatted surroundings. The temperature of the sample can be increased with time at such a slow rate that quasi-steady states are maintained and a relationship identified by the equation on page 10 is applicable.

Rates of decomposition can be estimated from plots of the sample temperature vs. time, and from plots of the temperature difference between the sample and bath vs. time. The slope of the temperature differential curve represents the rate of heat transfer between the sample and the bath. Factors which need to be taken into account are the rate at which the bath is being heated, heating from the self-reaction of the sample, and temperature gradients in the microbomb. From a plot of the self-heating rate of the sample vs. the reciprocal of the temperature, a linear slope proportional to the activation energy should result. The precision of activation energies derived in this manner is about ±15 percent.

5. Data:

The activation energy of nitromethane was calculated to be 51 kcal mol^{-1} [9].

b. ASTM Standard Method of Test E-476-73 [10]

Thermal Instability of Confined Condensed Phase Systems (Confinement Test)

1. Purpose of Test:

To determine the temperature at which a chemical mixture will commence a reaction, liberating appreciable heat or pressure, when subject to a programmed temperature rise. This method applies to solids or liquids in a closed system in air or some other atmosphere present initially under normal laboratory conditions.

2. Operating Principle:

The sample to be tested is confined in closed vessel equipped with a burst diaphram, pressure transducer, and thermocouple. The apparatus is equilibrated in a bath at room temperature and subsequently heated at a constant rate. The temperature difference between the bath and sample, the pressure in the closed vessel, and the bath temperature are recorded continuously during the course of the test.

3. Test Description:

This apparatus is a modification of that described under the JANAF Thermal Stability Test. The sample (300 mg.) is placed in the test cell or vessel (volume ~ 1 cm^3) and is in intimate contact with a thermocouple. The apparatus also has a burst diaphram-vent tube system to release gases formed during decomposition if the pressure reaches too high a value, and a pressure transducer to provide measurement of the total pressure inside the vessel as heat is supplied from a bath at a constant rate. The nominal heating rate of the bath is 8 to 10 °C per minute. Silicone oil is used in the range 0 to 370 °C.

and a low-melting alloy (i.e., Wood's metal) in the range 100° to 500°C. Recorders are used to monitor, first, the difference between the sample temperature, T, and bath temperature, T_o, as a function of bath temperature, and, second, pressure, P, as a function of bath temperature. No agitation to minimize thermal lag is used.

4. Test Evaluation:

The threshold temperature is the lowest temperature at the left-hand base of the positive peak which appears in the plot of $T-T_o$ vs T_o. The threshold temperature is an indication of the onset of thermal instability in the sample. A potential hazard exists, therefore, when the temperature of the sample exceeds this value. The instantaneous rate of pressure rise with bath temperature (dP/dT) can be obtained from the plot of pressure vs. bath temperature. The maximum pressure generated and the rate of pressure rise are useful hazard parameters related to rough approximations of reaction time, and damage potential.

Examination of the rate of temperature rise of the sample, dT/dt, and rate of temperature rise of the bath, dT_o/dt, not only allows an evaluation of the Arrhenius constants, but also provides for arbitrary scaling of the process. A simpler, and probably preferable procedure, may be to record only T_o corresponding to a runaway condition (e.g., a specificed value $dT/dt >> dT_o/dt$, or rupture of a pressure disk; there is some arbitrariness in the definition of the runaway criterion, but this feature may not be serious), and then repeat the experiment with a different sample diameter, d. The Frank-Kamenetskii condition then gives the value of E from

$$(d_1/d_2)^2 = (T_{o1}/T_{o2})^2 \exp[(E/R)\ (1/T_{o1}-1/T_{o2})].$$

This procedure obviates the necessity of evaluating A and λ, and allows immediate scaling to any size.

5. Data:

None provided [10].

c. Self-Heating Adiabatic Test [11]

1. Purpose of Test:

To follow the thermal decomposition of poorly conducting materials (i.e. wood) under conditions such that heat exchange between the sample and its surroundings is kept to a minimum (i.e., adiabatic conditions).

2. Operating Principle:

A furnace is designed with such controls so as to keep the furnace temperature as close to the temperature at the center of the sample as possible. After a sample had been brought into thermal equilibrium at a given temperature, the furnace temperature control system is changed automatically to allow the sample to self-heat up to a temperature of 500°C with minimal heat exchange to the surroundings inside the furnace.

3. Test Description:

The sample is suspended in the furnace by a wire fastened to a strain-gauge dynamometer. Thermocouples are mounted at the center and near the surface of the specimen as well as in the air within the furnace. The operating range of the furnace is from 30° to 500°C. When the temperature of the interior of the sample reaches the air temperature within the furnace and slightly over-shoots this temperature because of self-heating, heat is supplied to the furnace by means of a control system so as to maintain as small a temperature difference as possible between the sample interior and the gases inside the furnace. A recorder provides a continuous record of the furnace temperature, two or more temperatures within the sample, and the weight of the sample.

4. Test Evaluation:

Since there is no heat-transfer balance, no steady-state is possible in the self-heating adiabatic test, and the δ-parameter criterion does not apply directly. This test can be applied in two ways. First, one can measure the time to thermal runaway as a function of T_o. The runaway times so measured will correspond to the predicted behavior of actual materials in the limit of perfect insulation or of very large size. Thus, while the procedure to obtain this information is straightforward in principle, the test will probably be too severe for all but a very few practical situations. The second way is to use the test for measurement of fundamental parameters--λ, A and E--in the manner described by Gross and Robertson [12]. The information so obtained can be used for calculation of Frank-Kamenetskii parameters (δ, critical size as function of T_o).

5. Data:

Values have been reported [12, 13] using a modification of the above apparatus, for the activation energy, heat-generation coefficient (product of the Arrhenius pre-exponential factor and heat of decomposition), thermal conductivity, heat capacity, and density over specific temperature ranges for: wood fiberboard, cotton linters, sugar pine, cork, crepe rubber, GRS rubber, foam rubber, raw linseed oil, rapeseed oil, sperm oil, olive oil, castor oil, neatsfoot oil, ammonium perchlorate, and nitrocellulose plastic.

d. Vacuum Thermal Stability Test [14]

1. Purpose of Test:

To determine the explosive character or tendency toward decomposition of materials at elevated temperatures (200° to 350°C) in vacuum in a storage environment.

2. Operating Principle:

This test measures the amount of gas evolved by a sample at a fixed temperature.

3. Test Description:

The test chamber consists of a cylindrical aluminum block (radius 4", height 12") and contains a sample holder with twelve sample holes some of which are used to accommodate thermocouples, nichrome heating elements, and thermometers. Mullite tubes are used to protect thermometers and other sensing elements. The vacuum stability test chambers are controlled from 35° to 350°C to about ±0.2°C. Continous AC power is attained by adjustment of two variacs for constant temperature. Temperature control is obtained by shorting out a resistor in series with each of two heating elements. Samples (about 0.2 gram each) are sealed in evacuated tubes. Each tube which contains a sealed sample is also connected to a mercury manometer. The enclosed samples and manometer units are placed in the test chamber at 260°C after room temperature and barometer readings are taken. Manometer and barometer readings are taken for a two-hour period. The volume of gas evolved from the thermal decomposition is calculated as ml. of gas per gram of sample per hour at 260°C. The test may be conducted at temperatures as high as 350°C.

4. Test Evaluation:

Evolution of surface moisture or occluded volatile impurities can give higher pressure readings than appropriate for testing the sample especially in the first 20 minutes of readings. Outgassing and drying of samples prior to testing should be given particular attention. Sublimation of the sample to cooler parts of the system can also occur.

5. Data:

Vacuum stability data for 24 explosives are given in reference [19]. Some samples are:

Amatol 50/50:	1 cm^3/40 hrs at 120°C
PETN:	0.5 cm^3/40 hrs at 100°C
Tetryl:	1 cm^3/40 hrs at 120°C
TNT:	0.23 cm^3/40 hrs at 120°C

e. Thermal Surge Test [15]

1. Purpose of Test:

To determine explosion temperatures (temperatures for which there is a delay time of 250 μ sec before explosion).

2. Operating Principle:

The discharge of a capacitor across a thin-walled tube provides the thermal stimulus to initiate explosive decomposition. The time-temperature profile of the decomposition is obtained from oscillographic records. Although the tubes are thin-walled (0.089 mm), they have considerable strength and provide a state of heavy confinement for the explosive or unstable material.

3. Test Description:

A test sample is loaded into hypodermic needle tubing which is heated, essentially instantaneously, by a capacitor discharge. The temperature and time of the explosive event are recorded from a continuous measurement of the electrical resistance of the tubing by means of an oscilloscope. The test is particularly suited to liquid material but solids can also be accommodated by melting prior to their insertion into hypodermic needle tubing. Materials are subject to temperatures in the range of 260° to 1100°C and delay times of 50 m sec to 50 μ sec. The delay time, T is given by A exp (B/RT) where A and B are constants (somewhat related to the Arrhenius pre-exponential factor and activation energy), R is the gas constant, and T is the absolute temperature.

4. Test Evaluation:

The thermal surge test supplies data on explosion temperatures which represent conditions of minimal heat transfer. This test measures the true induction time of an explosive rather than the time required to heat up the sample. Wenograd [15] was able to show a correspondence between the temperature of the system 250 μ sec prior to explosion and impact test data. The activation energy parameter obtained in thermal surge test measurements under dynamic conditions are considerably lower than those determined in other measurements under isothermal conditions. This test is probably one of the best available approximations to a point source heat initiation of an unstable material in a multicomponent system.

5. Data:

Results are provided in reference [15] for the critical temperature for explosion in 250 μ sec., "apparent" activation energy, and "apparent" logarithm of the Arrhenius frequency factor for: nitroglycerine, pentaerythritoltetranitrate (PETN), bis(2,2,2-trinitroethyl) nitramine (BTNEN), 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB), 2,2-dinitropropyl-4,4,4-trinitrobutyrate (DNPTB), tetryl, trinitrobenzene, and trinitrotoluene. More data are available in reference [16] which include some of the above explosives and also: ethyl nitrate chloropicrin, trinitroanisole, 2,4-dinitrophenol, nitrobenzene, acrylonitrile, crotonaldehyde, nitromethane, m-dinitrobenzene, 1,1-dimethylhydrazine, 95% hydrazine, and 85% hydrazine hydrate.

f. Explosion Temperature Test [17]

1. Purpose of Test:

To determine the temperature at which a material explodes, ignites, or decomposes after a five second immersion in a Wood's metal bath.

2. Operating Principle:

This test gives an estimate of how close the explosion temperature is to ambient condition for a material, and, hence, provides a measurable indication of thermal instability.

3. Test Description:

The material to be tested (~ 25 mg.) is placed in a copper test tube (high thermal conductivity) and immersed in a Wood's metal bath. This test is made at a series of bath temperatures, and the time lag prior to explosion at each temperature is recorded. The bath temperature is lowered until a temperature is reached at which explosion ignition, or apparent decomposition does not occur. The bath temperature working range from about 125° to 400°C. The sample is removed from the bath after 5 minutes if no explosion had occurred at 360°C.

4. Test Evaluation:

The explosion time is very nearly independent of sample size provided the sample size is in the range 10 to 40 mg. In this regard, data for all 25 mg samples should be comparable to data for all 3 mg samples. Particle size is also important in providing consistent results for a group of materials. Rapid equilibration of the sample upon contact with the high temperature bath will depend upon the heat capacity and thermal conductivity of the material, and could be a major uncertainty in this test. Explosion temperature data as a function of time serve as useful indicators to assist in maintaining safe thermal condition during handling and transport.

5. Data:

Explosion temperature, explosion times, and activation energies are provided for [17]: trinitrophenylmethylnitramine (tetryl), N,N-dinitro-N,N'-di(β-nitroxyethyl)oxamide, black powder, lead azide, ammonium nitrate, lead styphnate, picric acid, tetramethylolcyclopentanone tetranitrate, ethyltrimethylolmethane trinitrate, pentaerythritol tetranitrate, nitroglycerine, erythritol tetranitrate, tetramethylolcyclohexano pentanitrate, nitrocellulose, mercury fulminate, diazodinitrophenol, and ethylenedinitramine. Considerable explosive temperature-explosive time data are available in reference [18].

g. Adiabatic Storage Test [20]

1. Purpose of Test:

To determine the time interval (induction period) during which the gradual increase of temperature due to self-heating will result in explosion of the material under test.

2. Operating Principle:

A temperature-time profile is obtained for a substance from a preselected starting temperature until rapid exothermic decomposition results. An indication is provided of what constitutes an unfavorable storage environment under adiabatic conditions.

3. Test Description:

A Dewar vessel which can accommodate a sample volume of about one liter is placed inside a furnace chamber. A stainless steel lid, which has a protective insulating material on its inner side, covers the Dewar vessel. The furnace chamber is surrounded by an insulating mantle. A coiled heater is immersed into the sample and raises its temperature to a preselected starting value. The temperature at the center of the sample and at the wall of the furnace chamber are monitored using thermocouples. The temperature difference between the two thermocouples controls the voltage input to the furnace chamber so that the temperature difference is practically reduced to zero for the duration of the test, thus, rendering the Dewar vessel with its sample under adiabatic conditions, i.e., virtually no heat exchange between the sample and its surroundings. Heat effects as small as 10 mW per kg. can be detected. This is equivalent to measuring temperature increments of as little as 0.5°C per day and still maintaining adiabatic conditions.

4. Test Evaluation:

Testing of a sample can take days or weeks if the preselected starting temperature is too low. This situation is difficult to avoid especially if the substance being examined has not been studied before.

5. Data:

The induction period for the adiabatic storage and apparent activation energy of t-butylperbenzoate is given [20].

h. Isothermal Storage Test [20]

1. Purpose of Test:

To determine the heat generation rate as a function of time and an estimate of the induction period at a given temperature for a material.

2. Operating Principle:

A sample begins to self-decompose and to generate heat inside a large aluminum block held at a constant temperature. The heat flow from the sample to the block takes place via a Peltier element which produces an electric signal. The rate of heat generation as a function of time is observed.

3. Test Description:

A large aluminum block is surrounded by an insulating mantle and maintained isothermal via an electrical heater and thermoregulator system. Two sample containers which can hold up to 50 grams are located at the center of the block. An inert material is placed in one of the containers and used as a reference temperature junction. A Peltier element is located below each of the sample containers and heat flow from the sample to the aluminum block takes place via the Peltier element, producing an electric signal. The apparatus is 1 sensitive enough to detect 1 mW per kg.

4. Test Evaluation:

Test can be made with a large variation in sample size (up to 50 grams). The critical radius of the sample can be calculated from the results. This test also allows one to examine the degree of self decomposition as a function of time at a constant temperature.

Testing can take days, weeks, or months depending upon the number and range desired for various parameters.

5. Data:

A plot of the heat generated as a function of time is given for t-butyl perbenzoate at 58.2° and 67.4°C. Mean activation energies are calculated by constructing iso-conversion lines [20].

i. Exothermic Decomposition Meter Test [20]

1. Purpose of Test:

To determine the self-heating of a sample at small to moderate heat generation rates as a function of temperature or time.

2. Operating Principle:

A cylindrical aluminum block contains a cavity which has a Peltier element attached at the bottom and a sample is placed on the Peltier element. Heat flow from the block to sample is measured by means of the Peltier element which provides an electrical signal to a recording device.

3. Test Description:

A sample vessel constructed of stainless steel (volume, $\sim 2\ \text{cm}^3$) is positioned over a Peltier element, and both are housed inside the cavity of a cylindrical aluminum block. This central block is surrounded by mantles containing electrical heating elements in addition to an insulating layer. The electrical input to the block and mantles is maintained in such a manner as to keep the temperature difference between the block and mantles as small as possible while the block is heated linearly at about 10°C per hour. The heat flow from the aluminum block to the sample is measured by the Peltier element. As soon as the sample begins self-reaction the heat flux to the sample starts to decrease. From a plot of the heat generation of the sample vs. the reciprocal of the absolute temperature, the activation energy can be calculated.

4. Test Evaluation:

Changes in the heat capacity of the aluminum block over the temperature range 20° to 200°C will cause the temperature increase over this range to be slightly non-linear. The Peltier element is temperature dependent, and calibration using a pure copper sample having known thermal properties is recommended.

5. Data:

The rate of heat generation as a function of the temperature is shown for t-butylperbenzoate [20].

j. Homogeneous Explosion Test [20]

1. Purpose of Test:

To determine the pressure-time profile of the thermal explosion of solid or liquid materials.

2. Operating Principle:

A sample is heated under adiabatic conditions in a closed vessel until explosion occurs. The maximum rate of pressure rise and the maximum overpressure are measured as a function of time at different heat input rates.

3. Test Description:

About 100 ml of a sample is introduced into the lower part of a stainless steel vessel. The lower section is sealed off from a larger upper section above by a membrane (breaking pressure ~ 1 bar). The larger upper section serves as a free space for the expansion of reactant or product vapors. During the main part of the induction period, pressure equalization is accomplished by a capillary tube connecting the upper and lower sections of the vessel. The two-compartment vessel is placed inside a larger vessel of 20 liter capacity which seals the former from the external surroundings. A heating mantle around latter vessel allow heating of the inner vessel to take place as near to adiabatic conditions as possible. Around the sample vessel there is also an auxiliary heater which heats the sample at a constant (but adiabatic) rate until explosion occurs. When explosion takes place, the membrane is ruptured and expansion into the larger volume takes place. A piezo-electric pressure transducer records the pressure prior to, during, and after explosion.

4. Test Evaluation:

Differentiation of materials which give large rates of pressure rise and overpressures can be singled out from those which give low values. Subsequent precautions for shipping, transport, and storage can be taken.

5. Data:

Maximum rates of pressure rise and maximum overpressures are given for various heat input rates for t-butyl perbenzoate. Similar data for the self-heating process are also provided [20].

k Self-Heating Test for Organic Peroxides [21]

1. Purpose of Test:

To determine the minimum ambient temperatures for the self-heating to explosion of thermally unstable compounds in charges of specified shape but varying size.

2. Operating Principle:

The thermal decomposition of organic peroxides is observed from studying temperature-time plots to obtain the critical temperatures for explosion, heat transfer coefficient data, and apparent activation energies.

A circulating fan located within the working space of the furnace provides temperature control to within ±0.5°C.

3. Test Description:

A cylindrical tube furnace constructed of steel housed an aluminum open-topped cylindrical container which could hold 40 to 60 grams of organic peroxide. The furnace was heated electrically over the range 50° to 350°C and could be maintained at a fixed temperature to within ±0.3°C. The progress of self-heating in the peroxide sample relative to the furnace was observed by using a differential thermocouple at the center of the sample. A second thermocouple attached to the side of the container monitored the surface temperature. Temperature-time plots were recorded for different cylindrical diameters for the samples and critical temperatures were calculated.

Explosion studies were carried out with sample amounts as large as 800 grams using a somewhat modified apparatus, and similar parameters examined.

4. Test Evaluation:

The chief disadvantage of the method is the long period over which readings must be recorded and the long time required for the furnace to stabilize following a large change in operating temperature.

5. Data:

Critical temperatures leading to explosion, heat transfer coefficients, maximum temperature increase due to self-heating (ΔT max) in charges which did not explode are tabulated for various charge diameters for dry benzoyl peroxide and benzoyl peroxide paste (containing 35% dimethyl phthalate) [21].

References [22-25] contain information on reviews of the kinetics of thermal decomposition of organic peroxides, hazard classification of peroxides, and other test methods.

1 Differential Thermal Analysis (DTA) Test

1. Purpose of Test:

To determine exothermic and endothermic reactions in a material as heat is applied at a particular input rate.

2. Operating Principle:

The material under test and a stable reference material are heated simultaneously at the same rate. Exothermic and endothermic traces are measured using a recorder providing a temperature-time plot of the reaction process.

3. Test Description:

The material to be tested (5 to 25 mg) and a reference material (such as alumina or glass beads) are placed into identical compartments in an aluminum block. Heat is supplied to both compartments at the same constant rate of input. Temperatures are measured using thermocouples in conjunction with automatic recording devices so that a plot of temperature vs. time is obtained. A shift in the base line results from a change in the heat capacity or mass of the material under test. Particular care must be given to the type of temperature sensor used and to the choice of its location in the compartment inside the aluminum block. The geometry of the sample and thermal characteristics (such as thermal conductivity) of the sample will affect the shape of the DTA curve.

4. Test Evaluation:

From the exotherms and endotherms of the DTA curve decomposition temperatures corresponding to various rates of temperature rise can be obtained. Kinetic parameters can be calculated as a result of properly varying the heating rates and assuming a constant degree of conversion of reactant when a specific thermal event (such as the peak temperature of a given exotherm) takes place. When the temperature sensors are placed in the path of the heat flow the DTA apparatus can measure the enthalpies of processes such as heats of decomposition or transition.

5. Data:

See references [26-32].

As a specific example, approximate heats of explosion where determined using DTA for the following compounds: trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), pentaerythritol tetranitrate (PETN), Tetryl, nitroglycerine, N-5 Propellant, JPN Propellant, ABL-2056 Propellant, tetranitromethane and some laboratory prepared composite propellants.

m Shock Tube Test [33]

1. Purpose of Test:

To determine the expected linear relationship between the ignition delay time required to detonate fine dusts or sprays of explosives and the reflected shock temperature.

2. Operating Principle:

Liquid or finely divided solid samples are instantaneously subjected to very hot gaseous environments of known composition. The sample is dispersed by the hot flow behind the incident shock and the particles thus formed are ignited with a measurable time delay by the twice-shocked gases behind the reflected shockwave.

3. Test Description:

Finely-ground solid samples (less than 20 μ diam) are supported on a fuse wire coil 6 mm from the end plate of the low pressure channel. Liquids are similarly supported but placed about 50 mm from the end plate to ensure spray formation behind the incident shock wave. The diaphram separating the high pressure section from the low pressure channel of the shock tube is ruptured and the incident shock provided by the driver gas disperses and thereafter ignites the sample. The reflected shock wave temperature is calculated from the velocity of the decelerating incident shock at the end plate. The explosion time is calculated from the oscillograph trigger of the incident shockwave and the photocell trace. Apparent high temperature activation energies are calculated from:

$$\ln(t_e/T_r^2) = A + E/R\, T_r$$

where t_e is the explosion time, T_r is the reflected shock temperature, A is a constant, E is the activation energy, and R is the gas constant.

4. Test Evaluation:

Only a few tests are required to characterize a given sample which needs to be available in only milligram quantities. Environment de-sensitization may be studied using this technique by studying test responses with a variety of channel gases. The shock tube data were shown to correlate well with impact test data.

5. Data:

High temperature activation energies were calculated for: pentaerythritol tetranitrate (PETN), nitroglycerine (NG), lead azide, hydrazine nitrate, lead styphnate, tetracene, and nitrosoguanidine [33].

2. Mechanical Tests

A great many sensitivity tests using mechanical stimuli have been devised, mostly by the military, hence generally intended for the rating of sensitive energetic materials (explosives and propellants). Since we are interested mostly in commercial materials of lower sensitivity (although often shipped in larger amounts), the main problem is to select a few suitable tests from the large number of existing ones.

a. Detonability (Shock-Initiation) Tests

First a word about tests which do not appear particularly relevant. All tests which depend on development of steady-state (Chapman-Jouguet) detonation for a positive result ("Go" in a "Go - No Go" test) are in this class.

Two such tests , the Card-Gap (or "Booster") test [35, 36] and the Critical Detonation Diameter test [40, 41] may illustrate why these are less important in the context of our study. In both tests, the detonation of a standard donor charge transmits a strong shockwave to the test sample, initiating, or failing to initiate, detonation in the latter. In the Card-Gap test, the sample diameter is specified and constant (usually either 1" or 2.5"), and the shock strength from the donor is decreased until detonation fails to develop in the acceptor. In the Critical Detonation Diameter test, the shock strength from the donor is held at the maximum (unattenuated) value, and the sample diameter is decreased until there is no detonation. While the results of both tests are unusually clear-cut and easily interpretable, they apply only to sensitive explosives. For example, three energetic and potentially hazardous materials, ammonium perchlorate, ammonium nitrate and dinitrotoluene, are all rated negative by both tests even under the maximum stimulus (detonation pressure of Tetryl) and largest diameter (2.5") specified by the tests. The tests do not tell anything about detonability in larger geometries, and, what is worse, nothing about the possibility of destructive sub-detonation explosions. Both tests can be scaled up, in principle, but this is not a promising approach for two reasons. First, scaling to practical cargo diameters would be immensely expensive, and could be done only on very large proving grounds; and, second, the specified stimulus is so strong (shock pressure of the order of 10^5 atmospheres) that it can be generated only by detonation of another closely adjacent charge (which could hardly ever arise in the context of problems under this study), or possibly by a high velocity projectile.

a-1 Card-Gap Test (Booster Test) [34, 35, 36, 38, 39]

1. Purpose of Test:

To establish the ease with which a potentially hazardous material will detonate as a result of detonating a Tetryl charge in its proximity.

2. Operating Principle:

The test provides an estimate of the distance a shockwave must travel from a booster charge in a confined steel tube through a series of Plexiglas disks to detonate a potentially explosive material.

3. Test Description:

The working apparatus consists of a confined steel tube. The donor charge consists of two Tetryl pellets (25g. each) and is initiated by a No. 8 electric blasting cap. The shock attenuator has the same diameter as the Tetryl pellets, is made of Plexiglas or cellulose acetate, and separates the booster charge from the material under test. From 25 to 50 test firings are required to determine a reasonable threshold gap value. High-velocity detonations are characterized by means of detonation velocity probes, witness plate damage, and the size of fragments from the steel tube.

4. Test Evaluation:

The card gap test has some application to situations in which a hazardous material in storage is near other hazardous materials more prone to detonation. For such cases, this test serves to compare the relative ease of initiation to detonation and also provides an estimate of the force needed to bring about detonation.

5. Data:

References [18, 34, 35, 36, 38, 39]. This test is applicable to gels, slurries, cast solids, granular mixes, powders, and liquids.

a-2 Critical Diameter and Detonation Velocity Test [40, 41]

1. Purpose of Test:

To determine the critical internal diameter in a given type of metal or plastic tubing below which propagation of stable high velocity detonation will not take place. Detonation rates can also be measured. The test described here is oriented toward liquid samples although solids can be tested provided some modifications in apparatus are implemented.

2. Operating Principle:

A high velocity detonation is initiated from a blasting cap and booster. The detonation is propagated through the material under test which is contained in a tube constructed of a certain material (such as steel, aluminum, plastic, etc.).

3. Test Description:

The apparatus is constructed of stainless steel and consists of three sections; the first section (length 2", diam. 1") contains a high-energy booster (Pentolite) and a No. 8 blasting cap, the second or donor section (length 5", diam. 1") contains the liquid to be tested; the third or "test" section (length 30", diam. variable, 0.125" to 1") also is filled with the liquid under test. The end of the third section is closed by plugging, clamping, or crimping. If, after detonation of the booster, the "test" section of the apparatus is completely fragmented over its entire length, the critical diameter of the tubing has been exceeded. Fragmentation over a short distance indicates that the tubing is less than the critical diameter.

A ten-MHz counter, or an oscilloscope with a 5 microsecond per cm. sweep frequency is used to measure the time of propagation between timing stations which have been set up. Detonation velocities are calculated from the measured time lapses over the distance between stations.

4. Test Evaluation:

Critical diameter values are reported as the largest diameter at which an explosive reaction will not be propagated for an explosive material under certain specified conditions. Application of the data to real situations must be done with care to be sure that conditions are comparable with those present when the test data were determined.

5. Data:

References [40, 41].

b. Compression Tests

Two types of standard tests and one non-standard compression test will be mentioned. The most common among the compression tests are impact (drop-weight) tests, which are used extensively both by military and civilian agencies. An extensive correlation of the results from the Bureau of Mines [42] and the Picatinny Arsenal [43] impact testers has already been made in the first phase of this study [1].

It should be mentioned that the correlation between the results from the two testers is better for liquids than for solids. This is perhaps not surprising, because processes such as crushing of the granules and friction depend crucially on geometrical details and size of the sample. It should also be mentioned that even for liquids, the agreement between laboratories is far from perfect. JANAF Liquid Propellant Test No. 4 is a standardized impact test for liquids [44], and is identical with ASTM Test D 2540-70, Standard Method of Test for Drop-Weight Sensitivity of Liquid Monopropellants [45].

The JANAF Liquid Propellant Test No. 5 [46] is a piston-compression test which may realistically simulate some aspects of accidents (e.g. tank-car collisions). The procedure is to accelerate a liquid sample to a specified velocity and then stagnate it against a target plate. The correspondence of the test stimulus to anticipated realistic conditions remains to be determined. The equipment for this test is elaborate and probably expensive.

b-1 Impact Test

1. Purpose of Test:

To determine the minimum drop height of a falling weight which strikes an explosive material and produces either a mild or violent decomposition reaction. Both falling weight and explosive material have a fixed and constant mass.

2. Operating Principle:

Impact energy is supplied to an explosive by a weight of constant mass which is dropped from varying heights to establish the minimum height to provide detonation, decomposition, or charring. The impact provides rapid compression and crushing of the sample (which may involve a frictional component of crystals rubbing against crystals) and detonation ensues.

3. Test Description:

The two most prevalent impact tests are those by Picatinny Arsenal (PA) [43] and the Bureau of Mines (BM) [42].

In the PA apparatus a sample is placed in the recess of a small steel die cup, and capped with a thin brass cover. A cylindrical steel plug is placed in the center of the cover, which contains a slotted-vent and the impact of the 2 kilogram weight is transferred to the steel plug.

In the BM apparatus a 20 mg. weight is always employed while the PA sample size may be varied for each experiment. The explosive sample is held between two flat parallel plates made of hardened steel and impact is transmitted to the sample by means of the upper plate. Sample decomposition is detectable by audible, visual or other sensory means.

In an apparatus used by the Bureau of Explosives (part of the Association of American Railroads) and cited in Title 49 CFR (DOT Hazardous Materials Regulations) a falling weight is guided by a pair of rigid uprights into a hammer-anvil assembly containing a 10 mg. sample of explosive. Reproducibility can become a problem here because of a non-ideal collisions between the drop weight and the impact hammer since only a fraction of the drop-weight energy is transmitted to the sample.

4. Test Evaluation:

Greater confinement of the sample will limit the translational component of the impulse to a smaller area as is the case with the PA apparatus. Factors which play an influential role in the test are: materials of construction, sample thickness, sample density, hammer geometry, mass of drop weight, impact area, surface finish, the surrounding atmosphere, temperature, and pressure. Modifications can also be made to accommodate cast and liquid samples.

Impact tests suffer from the drawback that the fundamental processes leading to energy release are complicated and poorly understood. Failure of good agreement between various impact tests shows that these tests contain uncontrolled parameters. On the other hand, (1) partial correlations do exist, (2) the history of the test indicates rough agreement with field experience, (3) the stimulus is of reasonable severity, (4) the tests are widely known and relatively easy to use. These facts make them useful for a partial definition of hazards.

5. Data:

Impact test data can be found in the following references: [8, 18, 19, 36, 42, 43, 44, 47, 48, 49, 52, 54, 55, 56].

b-2 Adiabatic Compression Sensitivity Test [46]

1. Purpose of Test:

To determine the sensitivity of hazardous liquids to the initiation of decomposition in the presence of rapidly compressed gas bubbles.

2. Operating Principle:

A gas bubble in contact with a liquid is compressed rapidly by a gas driven piston. The minimum kinetic energy input per unit volume of gas bubble which is needed to initiate decomposition of the liquid is measured.

3. Test Description:

The apparatus consists of two cylinders with mechanically-coupled pistons axially alligned. Pressure multiplication is achieved by having a small piston in the test chamber cylinder and a large piston area in the driving gas cylinder. When the apparatus is fired, gas from a high pressure tank is admitted to the cylinder thereby driving the end of the small piston against the liquid. The area ratio of the pistons is 20:1; maximum working pressure of the apparatus is 20,000 psi.

Instantaneous pressure in the test chamber is measured by a strain guage on the burst diaphram which is used to seal the chamber. The piston movement is recorded by the signal from a linear motion potentiometer on the large end of the driving piston.

4. Test Evaluation:

The sensitivity of liquids to ignition in the presence of a rapidly compressed air bubbles can be used as a sensitivity rating scale. The sensitivity parameter is based on the minimum compression energy per unit volume of gas bubble necessary to bring about gas phase ignition followed by propagation to the liquid. The sensitivity parameter appears to be constant over the range of bubble volumes (0.2 ml to 0.8 ml) tested.

5. Data:

For the materials tested, the sensitivity ratings in the presence of air bubbles are the following [46]:

Liquid	Sensitivity, kg-cm/ml
60% ethyl nitrate, 40% propyl nitrate	4.0 ± 0.8
n-propyl nitrate	6.7 ± 1.2
nitromethane	10.4 ± 1.7
methylacetylene	86 ± 12
hydrogen peroxide	$\geqslant 144$
hydrazine	$\geqslant 144$
unsymmetrical dimethyl hydrazine	$\geqslant 144$
ethylene oxide	>144

Small variation in test temperature did not appear to be an important effect relative to other random experimental errors.

c. Confinement Tests

Among non-standard tests, the Heavy-Confinement Cap Test merits a mention. In this test a blasting cap is set off inside a confined liquid, but the liquid need not, in fact usually does not, detonate. Instead, the occurrence and the extent of energy release is judged. Thus the test combined a sensitivity measurement with power measurement. The main feature of the test is that the stimulus is one of high pressure and short duration.

Heavy Confinement Cap Test [57]

1. Purpose of Test:

To determine the sensitivity of a chemical (liquid or solid) as a result of detonating a blast cap immersed in it under conditions of confinement. Decomposition takes place by a combination of shock, heat, and pressure. A quantitative measured of the energy release is obtained.

2. Operating Principle:

The sensitivity of a chemical to decomposition under confinement leads to an estimate of the energy release obtained by the decomposition. The height to which a weight is impelled is related to the combination of the sensitivity - energy release parameter observed in this test.

3. Test Description:

A cylinder of cold-rolled steel (5 in. diam.; 6 in. high) contains a central borehole (1 in. diam.; 4 in. deep). The top-face of the cylinder is grooved radially by a cut (0.125 in. wide; 0.0625 deep). The sample (~ 4.0 ml, or 4.0 grams) is placed in a Pyrex test tube along with an Atlas no. 8 electric dynamite cap. A cylindrical test weight made of steel and weighting 5 lbs. is placed symmetrically over the borehole containing the test sample. Upon firing the dynamite cap, the test weight is elevated by the explosion and the maximum height is observed visually. Heights above 20 feet are calculated using a stop watch to measure the time of flight of the test weight from explosion to impact on the ground. If tests are conducted between 10° to 30°C, temperature has little effect upon test results.

4. Test Evaluation:

The energy release measured by this test using unreactive materials such as water, cyclohexane, and benzene show some degree of correlation with the enthalpy of vaporization of the compound tested. Heights attained are usually 2 to 5 feet. Reactive materials indicate an energy release which does not correlate with the enthalpy of vaporization, enthalpy of combustion, enthalpy of decomposition, or enthalpy of formation. It appears that decomposition kinetics probably limit the energy release measured.

This test is particularly applicable to compounds yielding a zero card-gap test value, and is useful in initial screening operations of various hazardous or semi-hazardous formulations. Results are believed indicative of adiabatic compression hazard.

5. Data:

Test results for a few common hazardous materials are [57]:

Compound	Quantity, ml.	Height, Feet
Nitromethane	4.0	48
90% Hydrogen Peroxide	4.0	39
Hydrazine	4.0	39
n-Propyl nitrate	4.0	29
Ethylene Oxide	4.0	10
Methyl Acetylene	4.0	8

d. Friction Tests [54, 58, 59, 60, 61]

The existing (military) friction-sensitivity tests are not quite pertinent to our problem, because they give negative results for all but the most sensitive explosives. For example, even such high explosives as TNT and Composition B are unaffected by the Picatinny Arsenal friction test [59]. This is unfortunate, because friction is a common stimulus in realistic accidents, and should not be discounted a priori. However, a realistically severe friction test from which definitive rankings or conclusions can be obtained, appears not yet developed.

B. Power Tests

The sensitivity tests discussed so far deal with the ease of initiation, hence fundamentally with chemical kinetics. Another aspect of the hazards problem is the magnitude of energy release. The distinction between "sensitivity" tests and "power" tests has been stated clearly in our previous report [1]. While the sensitivity tests present a more crucial aspect of the problem, because the objective is to avoid the release of any energy accidentally, the power problem should not be neglected for two reasons. First, a large energy obviously represents a relatively high hazard. Second, the problems of power and sensitivity are coupled: materials having high exothermicity (relative to heat capacity) will self-heat to high temperatures and thereby represent a high sensitivity hazard.

There are great many explosives tests designed to evaluate the energy release (sometimes also the rate of energy release) under detonative conditions. These tests almost invariably give a measure of energy release by the effect on the surroundings: size of crater or dent in a plate generated by detonation, displacement of a target, or generation of a blast wave in air. Among these, the measurement of the blast wave appears especially useful.

Blast-wave measurement has the following advantages: (a) it is simple and relatively inexpensive; it is done by the placement of a piezo-electric gauge at a suitable distance with a suitable readout; (b) the method of interpretation of records is highly developed, and extensive tables and monographs are available relating the energy release to blast parameters (usually in terms of "TNT equivalents"); (c) while the method has been developed primarily for detonative energy release, it is also suitable for subdetonative explosions; (d) the records give some (usually qualitative) information about the rate of energy release; (e) if the material is deficient in oxygen (which many materials are, the notable exceptions being oxidizers or highly oxidized explosives), the measurement will include the involvement of air in the experiment (or accident).

Since power tests deal directly with the <u>effect</u> of explosions and only indirectly with the manner of initiation, the initiation stimulus must be specified separately. It could be almost any technique discussed earlier in this report. For example, blast gauges could be used in conjunction with an impact test, a friction test, the Heavy-Confinement Cap Test, or even thermal tests, to evaluate the extent and the rate of energy release.

a. Plate Dent Test [8, 19]

1. Purpose of Test:

To determine the brisance of an explosive, or its shattering power. This is an intensive property and not depend upon the quantity of explosive.

2. Operating Principle:

The depth of a dent produced in a steel plate is compared to the dent produced by a charge of TNT.

3. Test Description:

An explosive cartridge of a certain diameter is placed on end in contact with a steel plate of given dimensions. The explosive is detonated from the opposite end of the cartridge. The depth of the dent in the plate is measured. The test is repeated using TNT, and the dent produced compared to that made by the test charge.

4. Test Evaluation:

The depth of the dent produced by the detonation is not dependent upon the length (quantity) of the cartridge used in the test and is probably related closely to the detonation pressure.

5. Test Data:

Reference [18].

b. Ballistic Mortar Test [37, 42, 62]

1. Purpose of Test:

To determine the maximum available energy which can be released in an explosion.

2. Operating Principle:

A standard weight of explosive is fired in a suspended mortar with a tightly fitting steel projectile and the angle of recoil of the mortar is measured.

3. Test Description:

The apparatus is a compound pendulum consisting of a mortar supported by a framework. The framework is suspended on knife edges arranged so that the recoil distance of the mortar is automatically recorded. The mortar has two chambers; an outer chamber for the steel projectile; an inner chamber for the explosive charge. The apparatus is arranged so that the center of percussion coincides with the axis of the firing chamber. Three tests are run with the sample and three tests run with a reference (such as TNT). The quantity of explosive being tested which gives the same recoil as 10 grams of TNT is usually used as the basis for expressing the relative power or strength of the explosive sample.

4. Test Evaluation:

Ballistic mortar test data correlate poorly with the heat released during the explosion of the sample. Care must be exercised during interpretation.

5. Test Data:

Reference [18].

c. Air-Blast Test [64, 66, 67]

1. Purpose of Test:

To determine the energy release from an explosive charge from pressure measurements of the resulting shockwave.

2. Operating Principle:

The effectiveness of an explosive charge which has been detonated in air, can be obtained in terms of an equivalent weight of a standard explosive (such as TNT) to produce the same air-blast overpressure as the test explosive. Measurements of the pressure parameters are made at fixed distances from the explosive charges and can be shown to be proportional to the initial energy of the explosive.

3. Test Description:

An explosive charge is detonated in air with piezo-electric pressure transducers placed at suitable distances from the charge. This equipment is in turn connected to oscillographic and recording equipment. As the shockwave generated by an explosive charge travels away from the source, the peak pressure decreases and the pressure behind the shock front falls off in a regular manner. Measurement of the shockwave velocity provides data on the peak pressures and positive impulses. The methods of interpretation of the data are highly developed and extensive tables are available relating the energy release to air-blast overpressures, usually in terms of equivalents of a standard explosive (such as TNT).

4. Test Evaluation:

Peak pressure and impulse data for equivalent weights of a variety of explosives as compared to a standard, such as TNT or TNETB (trinitroethyl trinitrobutyrate) suggest that a direct relationship exists between the equivalent weight and the heat of detonation. Careful examination of blast test data indicate that relatively large post-detonation reactions of the products with the oxygen in the air can take place. The extent of these post-detonation reactions can be estimated from firings of the explosive charge in a nitrogen atmosphere followed by comparison to test data for firings performed in air.

5. Data:

References [18, 47, 64, 66].

d. Underwater-Blast Test [37, 64, 65]

1. Purpose of Test:

To determine explosive performance and energy release as a result of detonating an explosive charge under water and measuring the shock and bubble energies which are produced.

2. Operating Principle:

Shock and bubble pressure are measured by two piezoelectric pressure transducers in the water and attached to signal conditioning equipment and oscilloscopes.

3. Test Description:

About a kilogram charge with a suitable booster is suspended in the center of a pond at a depth of 12 feet. Transducers are placed 12 feet deep and at a horizontal distance 12 feet from the charge. The explosive charge is detonated under water and the shock produced by the detonation front is transmitted to the surrounding water as a pressure discontinuity followed by an exponential pressure decay. The pressure front moves radially outward as a shockwave in the water until its velocity decays to sonic values.

An expanding gas bubble follows the shockwave. This bubble is composed of reaction products under high pressure. Expansion, contraction, and collapse of the gas bubble follow with bubble oscillations emitting secondary pressure pulses. The period of oscillation is related to the internal energy of the gas and the equilibrium pressure.

4. Test Evaluation:

Underwater explosive effects are more difficult to interpret in comparison to those effects obtained in air. The energy release by the detonation of the explosive charge is partitioned into (1) that of the shockwave, (2) that dissipated in the water during of the travel of the shockwave from the charge to the measuring instruments, and (3) and that remaining in the oscillating bubble formed by the detonation products. Comparison of the measured shockwave energy with the detonation energy shows a rough linear relationship; a direct proportion does not appear to exist.

5. Data:

Reference [64].

C. Summary of Tests

An assessment of the relative importance of various tests with respect to establishing and identifying the thermal stability of a material is given below. As stated earlier, the state-of-the-art is such that several tests are desirable for an assessment of sensitivity.

Important

JANAF Thermal Stability Test No. 6
ASTM Standard Method of Test E-476-73
Thermal Surge Test
Explosion Temperature Test
Exothermic Decomposition Meter Test
Adiabatic Storage Test
Differential Thermal Analysis Test
Impact Test
Air-Blast Test

Useful

Self-Heating Adiabatic Test
Isothermal Storage Test
Homogeneous Explosion Test
Vacuum Thermal Stability Test
Self-Heating Test for Organic Peroxides
Adiabatic Compression Sensitivity Test
Underwater-Blast Test

Marginal

Heavy Confinement Cap Test
(Only when used in conjunction with the Air-Blast Test)

Shock Tube Test

Card-Gap Test
(only to determine whether sample is detonable for diameters equal to 2.5 inches)

Friction Test
(Requires further development)

Less Important

Critical Diameter and Detonation Velocity Test

Plate Dent Test

Ballistic Mortar Test

V. Predictive Schemes

A. Expandability of the Predictive Schemes to Specific Reaction Mechanisms

The predictive schemes, which had been examined in detail as part of our research agreement with the DOT Office of Hazardous Materials Operations in 1974 [1], were studied further to seek improvement in their ability to estimate the hazard potential of chemicals. The idea of developing separate schemes which could be associated with different reaction mechanisms such as molecular elimination reactions or bond fission processes, was explored. In this connection, the critical review of kinetic data on thermally induced, unimolecular, homogeneous, gas-phase reactions of molecules and free radicals by Benson and O'Neal [68] was studied and was found to be very helpful. The latter authors provided evaluated kinetic data for over 160 simple bond-fission processes and 150 molecular elimination reactions.

Although self-decomposition reactions are not all unimolecular processes, such processes constitute a desirable focus for this investigation for the following reasons: (1) more information is generally available for unimolecular processes than for other processes, (2) their overall treatment is simpler, and (3) they represent many explosive reactions adequately.

Certain generalizations regarding the gas-phase kinetics of unimolecular reactions are possible. The generalizations are based upon the assumption that the transition state theory is valid and that the thermal contributions from radical recombination reactions are essentially zero. In the case of simple bond-fission processes, the endothermicity of the unimolecular rate-determining process is equivalent to its activation energy. Exothermic effects in such a process results from subsequent fast reactions. Also, the pre-exponential or frequency factor does not appear to vary widely for the types of compounds which had been reviewed. For most reactions, the logarithm of the frequency factor was about 16 ± 1.5.

Some generalizations regarding molecular elimination reactions are also possible. The enthalpy accompanying an elimination reaction appears to be less positive than the corresponding activation energy. In the case of organic chlorine and bromine compounds which have been evaluated by Benson and O'Neal [68], the difference between the reaction heat and the activation energy was usually about 30 to 40 kcal mol^{-1}. The logarithm of the frequency factor was about 13 ± 1.5. The temperature range over which researchers had studied molecular elimination reactions were often 100 to 200 K lower than the range for bond-fission processes.

After spending considerable time in attempting to develop separate schemes for particular reaction mechanisms, and consulting with several experimental kineticists on the feasibility of this effort, we were not able to formulate a procedure which could compute and predict realistic heats of decomposition independent of experimental data. At present, there appears to be no simple substitute for experimental kinetic data.

B. Evaluation of Safe Materials by the CHETAH Program

Our earlier appraisal of the CHETAH and CRUISE programs for estimating the hazard potential of chemicals showed that both programs over-emphasize explosive power as opposed to explosive sensitivity. This over-emphasis is not a serious problem in some cases where the hazardous chemical or material under investigation gives a reasonably larger energy release as a result of decomposition. This is the case with explosives, such as: nitroglycerine, TNT, PETN, and others. Thus, the philosophy of erring on the "safe-side" suggests that it is very likely that these programs will label a hazardous material as being hazardous, and not safe.

In our earlier appraisal we neglected to say much about the prediction capabilities of the programs with respect to safe materials. It is important that a safe compound be labelled as "safe", and not be labelled as a hazardous material. As a model study, we had taken the CHETAH program and have tested its response toward identifying safe materials among the four CHETAH hazard criteria.

A group of 22 compounds have been selected (arbitrarily) which were regarded generally throughout the chemical industry as being safe from any tendency to self-decompose. The group consists of eight CHO compounds, eight CHN compounds, and six CHNO compounds. Certain vulnerabilities have revealed themselves. The information is presented in a series of tables (see Tables 1-16).

Table 1. Decomposition Reactions Computed by the CHETAH Program

A. CHO Compounds

1. formic acid; 46.0259*; ΔHf° = -90.57(**) [69]
   $CH_2O_2 \rightarrow H_2O + 0.5CO_2 + 0.5C(s)$ (***)

2. ethylene glycol; 62.0689; ΔHf° = -93.9 [69]
   $C_2H_6O_2 \rightarrow 2H_2O + 0.5CH_4 + 1.5C(s)$

3. methyl acetate; 74.0798; ΔHf° = -94.9 [68]
   $C_3H_6O_2 \rightarrow 2H_2O + 0.5CH_4 + 2.5C(s)$

4. glycerol; 92.0954; ΔHf° = -139.3 [69]
   $C_3H_8O_3 \rightarrow 3H_2O + 0.5C + 2.5C(s)$

5. ribose; 150.1325; ΔHf° = -232 [72, 112]
   $C_5H_{10}O_5 \rightarrow 5H_2O + 5C(s)$

6. pentaerythritol; 136.1490; ΔHf° = -185.63 [69]
   $C_5H_{12}O_4 \rightarrow 4H_2O + CH_4 + 4C(s)$

7. ascorbic acid; 176.1264; ΔHf° = -257 [72, 112]
   $C_6H_8O_6 \rightarrow 4H_2O + CO_2 + 5C(s)$

8. sucrose; 342.3025; ΔHf° = -505 [72, 112]
   $C_{12}H_{22}O_{11} \rightarrow 11\ H_2O + 12C(s)$

(*) Datum following the compound name is the formula weight.

(**) Values of ΔHf° are in kcal mol^{-1}; 1 kcal mol^{-1} = 4.1840 kJ mol^{-1}.

(***) Formulas in equations represent substances in the gaseous state unless otherwise indicated.

Table 1. Decomposition Reactions Computed by the CHETAH Program

B. CHN compounds

1. acetonitrile; 41.0529; ΔHf° = 15.74 [71]
   $C_2H_3N \rightarrow 0.75CH_4 + 1.25C(s) + 0.5N_2$
2. acrylonitrile; 53.064; ΔHf° = 42.95 [71]
   $C_3H_3N \rightarrow 0.75CH_4 + 2.25C(s) + 0.5N_2$
3. malononitrile; 66.0628; ΔHf° = 63.5 [69]
   $C_3H_2N_2 \rightarrow 0.5CH_4 + 2.5C(s) + N_2$
4. pyrimidine; 80.0899; ΔHf° = 47.0 [69]
   $C_4H_4N_2 \rightarrow CH_4 + 3C(s) + N_2$
5. pyridine; 79.1023; ΔHf° = 34.35 [69]
   $C_5H_5N \rightarrow 1.25CH_4 + 3.75C(s) + 0.5N_2$
6. adiponitrile; 108.1441; ΔHf° = 40.2 [72, 146]
   $C_6H_8N_2 \rightarrow 2CH_4 + 4C(s) + N_2$
7. triethylenediamine; 112.1759; ΔHf° = 11.4 [69]
   $C_6H_{12}N_2 \rightarrow 3CH_4 + 3C(s) + N_2$
8. benzonitrile; 103.1246; ΔHf° = 51.54 [69]
   $C_7H_5N \rightarrow 1.25CH_4 + 5.75C(s) + 0.5N_2$

Table 1. Decomposition Reactions Computed by the CHETAH Program

C. CHNO Compounds

1. formamide; 45.042; $\Delta Hf^\circ = -44.5$ [70]
   $CH_3NO \rightarrow H_2O + 0.25\ CH_4 + 0.75C(s) + 0.5N_2$
2. urea; 60.0558; $\Delta Hf^\circ = -58.7$ [69]
   $CH_4N_2O \rightarrow H_2O + 0.5\ CH_4 + 0.5C(s) + N_2$
3. glycine; 75.0677; $\Delta Hf^\circ = -93.72$ [69]
   $C_2H_5NO_2 \rightarrow 2H_2O + 0.25CH_4 + 1.75C(s) + 0.5N_2$
4. N,N-dimethylformamide; 73.0953; $\Delta Hf^\circ = -45.8$ [69]
   $C_3H_7NO \rightarrow H_2O + 1.25CH_4 + 1.75C(s) + 0.5N_2$
5. dimethylglyoxime; 116.1206; $\Delta Hf^\circ = -19.3$ [69]
   $C_4H_8N_2O_2 \rightarrow 2H_2O + CH_4 + 3C(s) + N_2$
6. ϵ-caprolactam; 113.1607; $\Delta Hf^\circ = -58.8$ [69]
   $C_6H_{11}NO \rightarrow H_2O + 2.25CH_4 + 3.75(s) + 0.5N_2$

Table 2. Maximum Enthalpy of Decomposition

CHO Compounds

Formula	Name	Maximum ΔH(decomposition) kcal mol^{-1}	Maximum ΔH(decomposition) kcal g^{-1}	CHETAH hazard rating
CH_2O_2	formic acid	-14.3	-0.31	medium
$C_2H_6O_2$	ethylene glycol	-30.6	-0.49	medium
$C_3H_6O_2$	methyl acetate	-29.6	-0.40	medium
$C_3H_8O_3$	glycerol	-43.0	-0.47	medium
$C_5H_{10}O_5$	ribose	-57.	-0.38	medium
$C_5H_{12}O_4$	pentaerythritol	-63.5	-0.47	medium
$C_6H_8O_6$	ascorbic acid	-68.2	-0.39	medium
$C_{12}H_{22}O_{11}$	sucrose	-130.8	-0.38	medium

Table 3. Maximum Enthalpy of Decomposition

CHN Compounds

Formula	Name	Maximum ΔH(decomposition)		CHETAH hazard rating
		kcal mol^{-1}	kcal g^{-1}	
C_2H_3N	acetonitrile	-29.2	-0.71	high
C_3H_3N	acrylonitrile	-56.4	-1.06	high
$C_3H_2N_2$	malononitrile	-72.4	-1.10	high
$C_4H_4N_2$	pyrimidine	-64.9	-0.81	high
C_5H_5N	pyridine	-56.7	-0.72	high
$C_6H_8N_2$	adiponitrile	-76.0	-0.70	high
$C_6H_{12}N_2$	triethylenediamine	-65.1	-0.58	medium
C_7H_5N	benzonitrile	-73.9	-0.72	high

Table 4. Maximum Enthalpy of Decomposition

CHNO Compounds

Formula	Name	Maximum ΔH(decomposition)		CHETAH hazard rating
		kcal mol^{-1}	kcal g^{-1}	
CH_3NO	formamide	-17.8	-0.39	medium
CH_4N_2O	urea	-8.0	-0.13	low
$C_2H_5NO_2$	glycine	-26.3	-0.35	medium
C_3H_7NO	N,N-dimethylformamide	-34.4	-0.47	medium
$C_4H_8N_2O_2$	dimethylglyoxime	-114.2	-0.98	high
$C_6H_{11}NO$	ε-caprolactam	-39.2	-0.35	medium

Table 5. ΔH(combustion) - ΔH(decomposition)

CHO Compounds

Formula	Name	$[\Delta H(\text{comb.}) - \Delta H(\text{decomp.})]^*$		CHETAH hazard rating
		kcal mol^{-1}	kcal g^{-1}	
CH_2O_2	formic acid	-47.0	-1.02	high
$C_2H_6O_2$	ethylene glycol	-237.0	-3.82	medium
$C_3H_6O_2$	methyl acetate	-331.0	-4.47	medium
$C_3H_8O_3$	glycerol	-331.0	-3.59	medium
$C_5H_{10}O_5$	ribose	-470.2	-3.13	medium
$C_5H_{12}O_4$	pentaerythritol	-568.0	-4.17	medium
$C_6H_8O_6$	ascorbic acid	-470.3	-2.67	high
$C_{12}H_{22}O_{11}$	sucrose	-1128.6	-3.30	medium

---

[*] Combustion products are in the gaseous state; $CO_2(g)$, $H_2O(g)$

Table 6. ΔH(combustion) - ΔH(decomposition)

CHN Compounds

Formula	Name	$[\Delta H(\text{comb.}) - \Delta H(\text{decomp.})]^*$		CHETAH hazard rating
		kcal mol^{-1}	kcal g^{-1}	
C_2H_3N	acetonitrile	-261.3	-6.37	low
C_3H_3N	acrylonitrile	-355.4	-6.70	low
$C_3H_2N_2$	malononitrile	-331.0	-5.01	low
$C_4H_4N_2$	pyrimidine	-473.9	-5.92	low
C_5H_5N	pyridine	-592.2	-7.49	low
$C_6H_8N_2$	adiponitrile	-759.7	-7.02	low
$C_6H_{12}N_2$	triethylenediamine	-857.4	-7.64	low
C_7H_5N	benzonitrile	-780.5	-7.57	low

---

[*] Combustion products are in the gaseous state; $CO_2(g)$, $H_2O(g)$, $N_2(g)$.

Table 7. ΔH(combustion) - ΔH(decomposition)

CHNO Compounds

Formula	Name	[ΔH(comb.) - ΔH(decomp.)]* kcal mol^{-1}	kcal g^{-1}	CHETAH hazard rating
CH_3NO	formamide	-118.4	-2.63	high
CH_4N_2O	urea	-142.9	-2.38	high
$C_2H_5NO_2$	glycine	-212.5	-2.83	high
C_3H_7NO	N,N-dimethylformamide	-404.2	-5.53	low
$C_4H_8N_2O_2$	dimethylglyoxime	-473.9	-4.08	medium
$C_6H_{11}NO$	ε-caprolactam	-784.2	-6.93	low

---

*Combustion products are in the gaseous state; $CO_2(g)$, $H_2O(g)$, $N_2(g)$

Table 8. Oxygen Balance

CHO Compounds

Formula	Name	Oxygen* Balance	CHETAH hazard rating
CH_2O_2	formic acid	-34.8	high
$C_2H_6O_2$	ethylene glycol	-128.9	medium
$C_3H_6O_2$	methyl acetate	-151.2	medium
$C_3H_8O_3$	glycerol	-121.6	medium
$C_5H_{10}O_5$	ribose	-106.6	medium
$C_5H_{12}O_4$	pentaerythritol	-141.0	medium
$C_6H_8O_6$	ascorbic acid	-90.8	medium
$C_{12}H_{22}O_{11}$	sucrose	-112.2	medium

---

*Oxygen Balance ($C_aH_bO_d$) compounds =
$-[(32)(a + (b/4) - (d/2))](100)/(\text{formula wt.})$

Table 9. Oxygen Balance

CHN Compounds

Formula	Name	Oxygen Balance*	CHETAH hazard rating
C_2H_3N	acetonitrile	-214.3	low
C_3H_3N	acrylonitrile	-226.1	low
$C_3H_2N_2$	malononitrile	-169.5	low
$C_4H_4N_2$	pyrimidine	-199.8	low
C_5H_5N	pyridine	-252.8	low
$C_6H_8N_2$	adiponitrile	-236.7	low
$C_6H_{12}N_2$	triethylenediamine	-256.7	low
C_7H_5N	benzonitrile	-256.0	low

---

*Oxygen Balance ($C_aH_bN_c$) compounds = $-[(32)(a + (b/4))](100)/(\text{formula wt.})$

Table 10. Oxygen Balance

CHNO Compounds

Formula	Name	Oxygen* Balance	CHETAH hazard rating
CH_3NO	formamide	-88.8	medium
CH_4N_2O	urea	-79.9	high
$C_2H_5NO_2$	glycine	-95.9	medium
C_3H_7NO	N,N-dimethylformamide	-186.1	low
$C_4H_8N_2O_2$	dimethylglyoxime	-137.8	medium
$C_6H_{11}NO$	ε-caprolactam	-233.3	low

---

*Oxygen Balance ($C_aH_bN_cO_d$) compounds =
$-[(32)(a + (b/4) - (d/2))](100)/(\text{formula wt.})$

Table 11. Modified Enthalpy of Decomposition Criterion

CHO Compounds

Formula	Name	$Y = (10)(\Delta H_d)^2(W/n)^*$	CHETAH hazard rating
CH_2O_2	formic acid	8.8	low
$C_2H_6O_2$	ethylene glycol	14.9	low
$C_3H_6O_2$	methyl acetate	10.8	low
$C_3H_8O_3$	glycerol	14.5	low
$C_5H_{10}O_5$	ribose	10.8	low
$C_5H_{12}O_4$	pentaerythritol	14.3	low
$C_6H_8O_6$	ascorbic acid	13.4	low
$C_{12}H_{22}O_{11}$	sucrose	11.0	low

---

* ΔH_d is the maximum ΔH(decomposition) in kcal g^{-1}.

W is the formula wt in g mol^{-1}.

n is the total number of atoms in the reactant.

Table 12. Modified Enthalpy of Decomposition Criterion

CHN Compounds

Formula	Name	$Y = (10)(\Delta H_d)^2(W/n)^*$	CHETAH hazard rating
C_2H_3N	acetonitrile	34.5	medium
$C_3H_3N_2$	acrylonitrile	85.2	medium
$C_3H_2N_2$	malononitrile	114.2	high
$C_4H_4N_2$	pyrimidine	52.5	medium
C_5H_5N	pyridine	37.3	medium
$C_6H_8N_2$	adiponitrile	33.1	medium
$C_6H_{12}N_2$	triethylenediamine	18.9	low
C_7H_5N	benzonitrile	41.1	medium

---

[*] ΔH_d is the maximum ΔH(decomposition) in kcal g^{-1}.

W is the formula wt in g mol^{-1}.

n is the total number of atoms in the reactant.

Table 13. Modified Enthalpy of Decomposition Criterion

CHNO Compounds

Formula	Name	$Y = (10)(\Delta H_d)^2(W/n)^*$	CHETAH hazard rating
CH_3NO	formamide	11.4	low
CH_4N_2O	urea	1.3	low
$C_2H_5NO_2$	glycine	9.2	low
C_3H_7NO	N,N-dimethylformamide	13.5	low
$C_4H_8N_2O_2$	dimethylglyoxime	69.7	medium
$C_6H_{11}NO$	ϵ-caprolactam	7.3	low

---

* ΔH_d is the maximum ΔH(decomposition) in kcal g^{-1}.
W is the formula wt in g mol^{-1}.
n is the total number of atoms in the reactant.

Table 14. Summary of CHETAH Hazard Ratings

CHO Compounds

Formula	Name	Hazard Ratings*			
		(1)	(2)	(3)	(4)
CH_2O_2	formic acid	medium	high	high	low
$C_2H_6O_2$	ethylene glycol	medium	medium	medium	low
$C_3H_6O_2$	methyl acetate	medium	medium	medium	low
$C_3H_8O_3$	glycerol	medium	medium	medium	low
$C_5H_{10}O_5$	ribose	medium	medium	medium	low
$C_5H_{12}O_4$	pentaerythritol	medium	medium	medium	low
$C_6H_8O_6$	ascorbic acid	medium	high	medium	low
$C_{12}H_{22}O_{11}$	sucrose	medium	medium	medium	low

---

*(1) Maximum enthalpy of decomposition
(2) ΔH(comb.)-ΔH(decomp.)
(3) Oxygen Balance
(4) Modified enthalpy of decomposition

Table 15. Summary of CHETAH Hazard Ratings

CHN Compounds

Formula	Name	Hazard Ratings*			
		(1)	(2)	(3)	(4)
C_2H_3N	acetonitrile	high	low	low	medium
C_3H_3N	acrylonitrile	high	low	low	medium
$C_3H_2N_2$	malononitrile	high	low	low	high
$C_4H_4N_2$	pyrimidine	high	low	low	medium
C_5H_5N	pyridine	high	low	low	medium
$C_6H_8N_2$	adiponitrile	high	low	low	medium
$C_6H_{12}N_2$	triethylenediamine	medium	low	low	low
C_7H_5N	benzonitrile	high	low	low	medium

---

*(1) Maximum enthalpy of decomposition
(2) ΔH(comb.)-ΔH(decomp.)
(3) Oxygen Balance
(4) Modified enthalpy of decomposition

Table 16. Summary of CHETAH Hazard Ratings

CHNO Compounds

Formula	Name	Hazard Rating*			
		(1)	(2)	(3)	(4)
CH_3NO	formamide	medium	high	medium	low
CH_4N_2O	urea	low	high	high	low
$C_2H_5NO_2$	glycine	medium	high	medium	low
C_3H_7NO	N,N-dimethylformamide	medium	low	low	low
$C_4H_8N_2O_2$	dimethylglyoxime	high	medium	medium	medium
$C_6H_{11}NO$	ε-caprolactam	medium	low	low	low

---

* (1) Maximum enthalpy of decomposition
(2) ΔH(comb.)-ΔH(decomp.)
(3) Oxygen Balance
(4) Modified enthalpy of decomposition

The ratings provided by the four CHETAH hazard criteria are summarized in tables 14, 15, and 16. Although the selection of the 22 compounds was arbitrary, the first impression one probably obtained was that they are all safe compounds. Also, one might feel that the CHETAH program should rate all or most of the compounds as being of low hazard. The end results, however, reveal that none of the 22 compounds were ranked across-the-board by all the CHETAH hazard criteria as being of low hazard. If one were to adopt the general criterion for CHETAH which defines a hazardous material as one having a rating high or medium hazard by the maximum enthalpy of decomposition (criterion 1), enthalpy difference (criterion 2), or oxygen balance (criterion 3), then all of the so-called safe compounds above would be rated as hazardous.

Closer inspection of functional groups or other structural parameters of the compounds selected provides some of the answers as to why certain hazard ratings were obtained.

Compounds of the CHO-type were generally classed as being of medium hazard because of the large percentage of oxygen which makes up their formula weights. The oxygen ends up as gaseous water in the decomposition products making the maximum enthalpy of decomposition high. Organic cyanides, or nitriles, are particularly vulnerable to a rating of high hazard for the maximum enthalpy of decomposition. Nitriles, in general, have a positive enthalpy of formation which makes for a higher than usual maximum enthalpy of decomposition.

The enthalpy difference and oxygen balance criteria come out with a "low" hazard rating for nitriles as expected. The compounds containing the elements CHNO yield hazard ratings showing poor consistency. Formamide and urea are classed as low, medium, and high among the four hazard criteria. Dimethylgloxime should be suspected as being particular hazardous with ratings of: high, medium, medium, and medium. This compound, however, does contain a carbon atom doubly-bonded to a nitrogen atom (> C = N-) which might suggest a hazard. Dimethylglyoxime has been used by chemists for a long time as an analytical reagent for determining nickel. Experience has not identified it as a hazardous compound. Chemists as a whole would identify the 22 compound studied here as safe from self-decomposition, but none have received a hazard rating of "low" for all four hazard criteria.

We feel this study points out the general trend of the CHETAH Program to not necessarily miss identifying a true hazardous compound as being hazardous, i.e., never giving such a compound a rating of "low" under all four criteria. However, we find an over-emphasis of hazard affecting the ratings for safe compounds. Hence, CHETAH will probably identify a hazard compound as such, but there is a reasonably high probability that CHETAH will indicate a large number of safe compounds as being hazardous.

C. CHETAH Calculation of Enthalpies of Polymerization

We have examined ten olefinic monomers commonly produced in large volume which are routinely polymerized to yield products for various applications. In table 17, we have listed the reaction for the process: monomer (gas) → polymer (solid), the respective enthalpies of formation at 298.15 K and corresponding references, and the resulting enthalpies of polymerization. In table 18, we have tabulated the enthalpies of polymerization of the ten olefinic monomers and ranked them in a manner equivalent to the ranking used for the CHETAH maximum enthalpy of decomposition. The usual four CHETAH hazard criteria were used to calculate the hazard ratings for the monomers in tables 19 through 22.

An examination of the CHETAH hazard ratings for the olefinic monomers shows that collectively all of the monomers could be classified as hazardous if either a ranking of high or medium is sufficient to denote hazard. However, the monomers each have received a ranking of low hazard by one of the four CHETAH hazard criteria. except for vinylidene chloride. A weak relationship can be implied between the hazard rating imposed in table 18 upon the enthalpies of polymerization and those in table 19 calculated from the maximum enthalpies of decomposition. Inspection of table 23 in Section VI on Accidental Polymerization of Bulk Chemicals suggests that monomers such as vinyl chloride, vinyl acetate, and methyl acrylate should be suspect of being more polymerizable than the remaining olefins. No inference of this kind is obtained from the CHETAH hazard criteria or their application to the enthalpies of polymerization in table 18. We feel that the CHETAH program does not present a clear-cut view of hazards related to polymerization.

Table 17

Polymerization Processes and Enthalpies at 298.15 K

1. ethylene (f.w. = 28.0536*)
$C_2H_4(g) \rightarrow (C_2H_4)_n$ (solid polymer)
+ 12.50[70] -13.50 [73]
ΔH polym. = -26.0 kcal mol^{-1}
= -0.927 kcal g^{-1}

2. 1,3-butadiene (f.w. = 54.0914)
$C_4H_6(g) \rightarrow (C_4H_6)_n$ (solid polymer)
+ 26.33[70] + 3.3[73]
ΔH polym. = -23.03 kcal mol^{-1}
= -0.426 kcal g^{-1}

3. isoprene (f.w. = 68.1182)
$C_5H_8(g) \rightarrow (C_5H_8)_n$ (solid polymer)
+ 18.10[70] -6.24[73]
ΔH polym. = -24.34 kcal mol^{-1}
= -0.357 kcal g^{-1}

4. styrene (f.w. = 104.1512)
$C_8H_8(g) \rightarrow (C_8H_8)_n$ (solid polymer)
+ 35.22[70] + 7.99[73]
ΔH polym. = -27.23 kcal mol^{-1}
= -0.261 kcal g^{-1}

5. vinyl chloride (f.w. = 62.4987)
$C_2H_3Cl(g) \rightarrow (C_2H_3Cl)_n$ (solid polymer)
+ 8.40[70] -22.5 [73]
ΔH polym. = -30.9 kcal mol^{-1}
= -0.494 kcal g^{-1}

6. vinylidene chloride (f.w. = 96.9438)
$C_2H_2Cl_2(g) \rightarrow (C_2H_2Cl_2)_n$ (solid polymer)
+ 0.3[70] -24.0[73]
ΔH polym. = -24.3 kcal mol^{-1}
= -0.251 kcal g^{-1}

---

[*] f.w. = formula weight, g mol^{-1}

7. acrylonitrile (f.w. = 53.0634)
$C_3H_3N(g) \rightarrow (C_3H_3N)_n$ (solid polymer)
+42.95[71] + 16.86[77]
ΔH polym. = -26.09 kcal mol^{-1}
= -0.492 kcal g^{-1}

8. vinyl acetate (f.w. = 86.0902)
$C_4H_6O_2(g) \rightarrow (C_4H_6O_2)_n$ (solid polymer)
-75.5[69] -105.2[78]
ΔH polym. = -29.7 kcal mol^{-1}
= -0.345 kcal g^{-1}

9. methyl acrylate (f.w. = 86.0902)
$C_4H_6O_2(g) \rightarrow (C_4H_6O_2)_n$ (solid polymer)
-79.6[71] -106.6[78,79)
ΔH polym. = -27.0 kcal mol^{-1}
= -0.314 kcal g^{-1}

10. methyl methacrylate (f.w. = 100.1170)
$C_5H_8O_2(g) \rightarrow (C_5H_8O_2)_n$ (solid polymer)
-81.6[72) -108.2[78,80]
ΔH polym. = -26.6 kcal mol^{-1}
= -0.266kcal g^{-1}

Table 18 Enthalpies of Polymerization

	olefin name formula	ΔH polym. kcal mol^{-1}	ΔH polym. kcal g^{-1}	CHETAH hazard rating*
1.	ethylene C_2H_4	-26.0	-0.927	high
2.	1,3-butadiene C_4H_6	-23.03	-0.426	medium
3.	isoprene C_5H_8	-24.34	-0.357	medium
4.	styrene C_8H_8	27.23	-0.261	low
5.	vinyl chloride C_2H_3Cl	-30.9	-0.494	medium
6.	vinylidene chloride $C_2H_2Cl_2$	-24.3	-0.251	low
7.	acrylonitrile C_3H_3N	-26.19	-0.492	medium
8.	vinyl acetate $C_4H_6O_2$	-29.7	-0.345	medium
9.	methyl acrylate $C_4H_6O_2$	-26.8	-0.314	medium
10.	methyl methacrylate $C_5H_8O_2$	-21.5	-0.266	low

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*The limits for the hazard rating are equivalent to those for the CHETAH criterion for the maximum enthalpy of decomposition.

Table 19 Maximum Enthalpy of Decomposition (Olefins)

	olefin name formula	maximum ΔH (decomposition) kcal mol^{-1}	kcal g^{-1}	CHETAH hazard rating
1.	ethylene C_2H_4	-30.4	-1.08	high
2.	1,3-butadiene C_4H_6	-53.2	-0.98	high
3.	isoprene C_5H_8	-53.9	-0.79	high
4.	styrene C_8H_8	-71.0	-0.68	medium
5.	vinyl chloride* C_2H_3Cl	-39.4	-0.63	medium
6.	vinylidene chloride* $C_2H_2Cl_2$	-44.4	-0.46	medium
7.	acrylonitrile C_3H_3N	-56.4	-1.06	high
8.	vinyl acetate $C_4H_6O_2$	-49.0	-0.57	medium
9.	methyl acrylate $C_4H_6O_2$	-44.94	-0.52	medium
10.	methyl methacrylate $C_5H_8O_2$	-51.9	-0.52	medium

---

*Cl present in decomposition products as: HCl(g).

Table 20 ΔH(combustion) - ΔH(decomposition) (Olefins)

	olefin name formula	ΔH(comb.)* - ΔH(decomp.) kcal mol^{-1}	 kcal g^{-1}	CHETAH hazard rating
1.	ethylene C_2H_4	-285.8	-10.19	low
2.	1,3-butadiene C_4H_6	-522.7	-9.66	low
3.	isoprene C_5H_8	-665.6	-9.77	low
4.	styrene C_8H_8	-947.8	-9.10	low
5.	vinyl chloride C_2H_3Cl	-237.0	-3.79	medium
6.	vinylidene chloride $C_2H_2Cl_2$	-188.1	-1.94	high
7.	acrylonitrile C_3H_3N	-355.4	-6.70	low
8.	vinyl acetate $C_4H_6O_2$	-425.1	-4.94	medium
9.	methyl acrylate $C_4H_6O_2$	-425.1	-4.94	medium
10.	methyl methacrylate $C_5H_8O_2$	-567.9	5.67	low

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*Combustion products are in the gaseous state; CO_2(g), H_2O(g), HCl(g), N_2(g).

Table 21 Oxygen Balance (Olefins)

	olefin name formula	oxygen* balance	CHETAH hazard rating
1.	ethylene C_2H_4	-342.2	low
2.	1,3-butadiene C_4H_6	-325.4	low
3.	isoprene C_5H_8	-328.8	low
4.	styrene C_8H_8	-307.2	low
5.	vinyl chloride C_2H_3Cl	-166.4	low
6.	vinylidene chloride $C_2H_2Cl_2$	-99.0	medium
7.	acrylonitrile C_3H_3N	-226.1	low
8.	vinyl acetate $C_4H_6O_2$	-204.4	low
9.	methyl acrylate $C_4H_6O_2$	-204.4	low
10.	methyl methacrylate $C_5H_8O_2$	-223.7	low

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*oxygen balance ($C_aH_bN_cO_d$) compounds = $-[(32)(a + (b/4) - (d/2))](100)/(\text{formula weight})$.

Table 22 Modified Maximum Enthalpy of Decomposition (Olefins)

	olefin name formula	$y = 10(\Delta H(\text{decomp.}))^2 W/n$*	CHETAH hazard rating
1.	ethylene C_2H_4	54.5	medium
2.	1,3-butadiene C_4H_6	51.9	medium
3.	isoprene C_5H_8	32.7	medium
4.	styrene C_8H_8	30.1	medium
5.	vinyl chloride C_2H_3Cl	41.3	medium
6.	vinylidene chloride $C_2H_2Cl_2$	34.2	medium
7.	acrylonitrile C_3H_3N	85.2	medium
8.	vinyl acetate $C_4H_6O_2$	23.3	low
9.	methyl acrylate $C_4H_6O_2$	19.4	low
10.	methyl methacrylate $C_5H_8O_2$	18.0	low

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*ΔH (decomp.) in kcal g^{-1}
W is the formula weight
n is the number of atoms in the compound

VI. ACCIDENTAL POLYMERIZATION OF BULK CHEMICALS

(prepared by

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A. Introduction

The question of whether or not the shipment of large quantities of bulk chemicals constitutes a hazard because of accidental polymerization deserves serious consideration. These chemicals are mainly conventional monomers but also include other substances that have non-polymeric uses but some polymerization potential. This report assesses polymerizability and identifies radical polymerization of unsaturated monomers as the most likely mechanism of accidental polymerization during transport. Accidental reaction hazards other than polymerization and dimerization were not considered.

B. Polymerization Classifications

At one time polymers were classified as having been formed in condensation or addition polymerizations [81]. In the formation of condensation polymers, a small molecule (frequently water) was split out when larger molecules combined. In addition polymerizations nothing was split out so the elemental composition of polymer and monomer were the same. It is now fairly common to use cyclic monomers to form some polymers that previously were called condensation polymers. Such monomers combine via ring opening reactions and so give polymers having the same elemental composition as the monomer. The classification now used is based on the nature of the intermediate species involved in polymer formation. If such intermediates are essentially small polymers then the polymer is said to have formed in a "step reaction polymerization." If the intermediate is chemically much more reactive and has a very short lifetime as an individual species the polymer is said to have formed in a "chain reaction polymerization."

The different types of intermediate give rise to different polymerization characteristics [82]. In step reaction polymerizations: (1) growth occurs by coupling of any two species (monomer or polymer) (2) the concentration of the monomer decreases markedly before high polymer is formed (3) the molecular weight increases with the extent of reaction; truly high polymer is not formed except at almost complete conversion (4) the rate of polymerization decreases from the start of the reaction. Chain reaction polymerizations have very different characteristics. These are: (1) growth occurs by rapid addition of monomer to a relatively few active centers (2) polymer of very high molecular weight forms almost from the start of the reaction (3) ideally there is little change in the molecular weight of the polymer or of the polymerization rate over much of the reaction period.

C. Step Reaction Polymerization Hazards

Monomers used to form polymers by step reactions are unlikely to be self polymerization hazards. The class includes condensation polymerizations, some of which use different molecular species for reaction. Moreover, these and self condensation reactions are really equilibrium processes that require removal of the molecule eliminated before the reaction can go far. Indeed, substantially all step growth reactions are nearly thermoneutral; this, and the decreasing rate associated with the decrease in the concentration of reactive groups as reaction proceeds limit heat effects. Materials used in step reaction polymerizations include dibasic acids and anhydrides, glycols, ω-hydroxy acids, urea, amino acids, melamine caprolactams, isocyanates, silanes and siloxanes, phenol, dichloroalkanes, polysulfides, aldehydes, bis-phenol A, and phosgene. Of these materials only formaldehyde and some isocyanates could self polymerize rapidly and then only if somehow initiated in chain reaction polymerizations.

D. Chain Reaction Polymerization Hazards

Chain reaction polymerizations often involve high polymerization heats (15 - 25 kcal/mol). Polymer usually is highly favored thermodynamically over monomer. Thus there exists a definite potential hazard. Olefins and oxides are the most common monomers. Some of the former are ethylene, propylene, styrene, butadiene, vinyl chloride, vinyl acetate, vinylidene chloride, acrylonitrile, methyl acrylate, methyl methacrylate, α-methyl styrene, isoprene, tetrafluoroethylene, and chlorotrifluoroethylene. Ethylene and propylene oxides are the most important oxide monomers. The polymerization mechanism of olefinic and oxide type monomers is very different so their polymerization hazards will be discussed separately.

E. Olefin Polymerizability

Olefins are polymerized by mechanisms involving free radicals, cations, anions, and complex heterogeneous organo metallic compounds. The terms describe organic species occurring during the growth of the polymer. Successful polymerization by the last three mechanisms involves very special conditions and catalysts. The activity of these types of catalysts is destroyed by traces of water or alcohols. Uncommon materials make up the catalysts - aluminum chloride, butyl lithium, aluminum alkyls in combination with transition metal compounds. Let us assume for the sake of the present discussion that the possibility of such compounds being introduced during transport in quantities which would polymerize a monomer is unlikely.

Free radical polymerizations involving olefins are the polymerizations thought most likely to occur inadvertently during transport. Thus behavior in free radical polymerizations is germane to the present problem.

The basic mechanism underlying most free radical polymerizations contains three reactions:

Step	Reaction	Rate
Initiation	$I \xrightarrow{fk_d} 2\ R$	$dR/dt = 2k_d f[I]$
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$	$-\frac{dM}{dt} = k_p [M](\sum_1^\infty [R_n])$
Termination	$R_n + R_m \xrightarrow{k_t} P_{n+m}$ or $P_n + P_m$	$-\frac{dR}{dt} = 2\ k_t (\sum_1^\infty [R_n])^2$

Here I, R, M, P, f, and t represent initiator, radicals, monomer, polymer, an efficiency factor, and time respectively. The k's are rate constants; subscripts d, p, and t indicate decomposition, propagation, and termination reactions. Subscripts n and m indicate that there are specific numbers of monomer units in the species being considered.

The mechanism shows initiator I decomposing to give radicals; only a fraction, f, of these are regarded as initiating polymerization. It is only such radicals that are of present interest and their rate of formation is 2 $k_d f$ [I]. Monomer may add to these radicals with a rate constant, k_p, that is independent of the size of the radical. Radicals of any size may terminate, also with a rate constant, k_t, independent of the size of the radical. In real systems, f is very frequently between 0.5 and 1; k_d is much smaller than k_p which is very much smaller than k_t. Consequently a radical is formed, grows for a short while, and then is terminated. Values of initiator concentration and of the k are such that the time between initiation of a growing chain and its termination is between 0.1 and 100 seconds; in this time, perhaps 100 to 10000 monomer units may be added. Thus, conversion of a significant fraction of the total monomer to polymer requires the initiation of many chains and ordinarily is done over several hours.

If k_d is so small that the concentration of initiator changes little with time then the total concentration of radicals becomes nearly constant in times not much longer than the lifetime of a growing chain. Then,

$$\frac{dR}{dt} = 0 = 2k_d f[I] - 2k_t\left(\sum_1^\infty [R_n]\right)^2$$

from which

$$\sum_1^\infty [R_n] = \left(\frac{k_d f[I]}{k_t}\right)^{1/2}$$

and

$$-\frac{dM}{M\,dt} = \left(\frac{k_d f[I]}{k_t}\right)^{1/2} k_p. \qquad (1)$$

Here, $\frac{-\,dM}{M\,dt}$ is the fractional rate of conversion of monomer to polymer. Expressed in this way the instantaneous polymerization rate changes with time only to the extent that the square root of the initiator concentration changes with time. Integration of equation (1), treating the concentration of initiator as a constant, gives

$$\ln([M_o]/[M]) = \left(\frac{k_d f[I]}{k_t}\right)^{1/2} k_p t. \qquad (2)$$

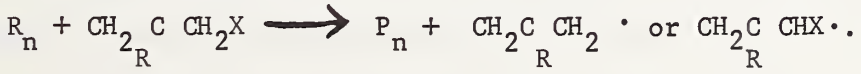
Here $[M_o]$ is the initial monomer concentration.

Conceivably then, substances could be ranked on a polymerizability scale by comparing their polymerization rates in a standard initiating situation. However, even if various special considerations were eliminated, some rates would be too fast or too slow for practical measurement. Another approach is suggested by looking at equation (1) and realizing that only $k_p/k_t^{1/2}$ is a property of the monomer. One can, therefore, choose conditions that give practical rates and calculate $k_p/k_t^{1/2}$ from such rates by using known values of k_d and f. Extrapolation of $k_p/k_t^{1/2}$ to a common temperature then provides a number which can reasonably be considered as the monomer polymerizability at that temperature.

Such values of $k_p/k_t^{1/2}$ are in Table 23 along with the associated activation energy, $E_p - E_t/2$, the heat of polymerization, ΔH_p, and a "Remark" indicating what special considerations are involved. Note that every monomer has such a remark. Most values of $k_p/k_t^{1/2}$ probably required two or more man years of effort per reaction. Furthermore, alternate choices of method give apparent values of $k_p/k_t^{1/2}$ that differ by a factor of five and values of $E_p - E_t/2$ that differ by several kcal/mol. Thus, the ranking is uncertain. Probably the only conclusions justified are that hydrocarbons polymerize less rapidly than electronegatively substituted olefins and that double substitution on the same carbon gives intermediate reactivity. The difficulty is that real polymerizations occur by modifications of the above general mechanism and the methods of compensating for the deviations are imperfect.

Calculation of the polymerization rate from the data of Table 23 is done as follows. Values of k_d have been tabulated for many initiators [83]. 2,2'-Azobisisobutyronitrile has a well known k_d and values of f between 0.5 and 1.0 for several monomers [84]; at 60°C k_d is 10^{-5} sec^{-1}. If f is taken as unity and the concentration of this initiator is made 0.01 molar (about 0.1 mol %) then $(k_d[I]f)^{1/2}$ is 0.3×10^{-3} $(mol/liter, sec)^{1/2}$; this multiplied by the listed value of $k_p/k_t^{1/2}$ gives -dM/Mdt as the fraction of monomer present that is polymerized per second. For the monomers of Table 23 rates range from about 10^{-6} sec^{-1} (isoprene) to 2×10^{-4} sec^{-1} (methyl acrylate) or from 0.4 to 70%/h. The rate of heat release per mole of monomer used is the product of -dM/Mdt and the heat of polymerization. Rates greater than 5% per hour probably cannot be kept isothermal because of this heat release. Therefore, autoacceleration in accord with the Arrhenius equation would be anticipated in the polymerization of methyl acrylate.

Many olefins polymerize too slowly for $k_p/k_t^{1/2}$ to have been measured. For these the polymerizability may be regarded as zero and so the monomers often are not hazardous in ordinary radical reactions. One class of such monomers has abstractable allylic atoms. Examples are α-methyl styrene, propylene and other α-olefins, isobutylene, allyl acetate, and allyl chloride. In radical polymerizations, these monomers undergo transfer reactions that generate stable radicals:



$$R_n + CH_2\underset{R}{C}\,CH_2X \longrightarrow P_n + CH_2\underset{R}{C}\,CH_2\cdot \text{ or } CH_2\underset{R}{C}\,CHX\cdot.$$

Such allylic radicals propagate poorly except at pressures of several thousand atmospheres [85]. However, it should be kept in mind that the presence of abstractable allylic atoms is not a guarantee of non-polymerizability. Both methyl methacrylate and methacrylonitrile polymerize despite having such atoms. Probably polar effects account for their activity. Nevertheless, one should feel that most materials bearing abstractable allylic atoms will not polymerize by ordinary radical reactions.

Internal olefins, including many 1,2 disubstituted ethylenes constitute another group which can ordinarily be regarded as not being polymerization hazards. Many of these bear abstractable atoms one carbon removed from a double bond. However, steric hindrance to propagation is probably the decisive cause of their unpolymerizability. Some internal olefins, maleic anhydride for example, copolymerize (combine with another monomer to form a mixed polymer) readily. Thus, mixtures of monomers might constitute a hazard.

Fluorinated ethylenes are exceptional because of the small size of the fluorine atom. Such highly fluorinated ethylenes as trifluoroethylene, chlorotrifluoroethylene, and tetrafluoroethylene homopolymerize readily. Possibly, this is due to a physical effect described below. At any rate, the polymerizations are too rapid for determination of $k_p/k_t^{1/2}$. Higher perfluoro-α-olefins, however, are polymerized with great difficulty, probably because E_p is large [86]. In passing, it should be noted that organic hydrogen is frequently avoided in polymerizing fluorocarbons because fluororadicals abstract hydrogen and the radical produced may not continue the kinetic chain.

Acetylenes, despite their high energy content, polymerize rather poorly under radical conditions. The triple bond resists radical attack; vinyl acetylene, for example, polymerizes largely through the vinyl group to form a polymer with pendant triple bonds [87]. Thus, it is unlikely that acetylenes themselves are polymerization hazards.

It should be stated that the listed values of $k_p/k_t^{1/2}$ refer to homogeneous polymerizations. These may not be realizable in bulk. Eight monomers in Table 23 may give polymer that is insoluble in the monomer (note a or b). The kinetic consequences of this may be profound. The general result is that the effective termination rate constant is made smaller because the diffusion of large polymeric radicals is restricted in the precipitated phase. Monomer molecules, being small, may still reach these radicals so that the propagation rate constant is affected to a much smaller degree. Thus, as polymer forms and separates from monomer, the number of growing radicals in the system actually increases, leading to an increase in rate. When the rate reaches a value at which effective temperature control is lost, further acceleration occurs in accord with the Arrhenius equation. Extreme temperatures and pressures may result and the character of the reaction may change. The writers (D. W. Brown and R. E. Florin) have seen a copolymerization involving 10 g of tetrafluoroethylene develop 10,000 atm pressure in the course of perhaps 15 seconds. The product was not polymer, but carbon and tetrafluoromethane. On several occasions 15 kilogram vessels, which had been tested to 25,000 atm pressure, were split in the polymerization of 10 g of perfluorocyclobutene. This type of result is not peculiar to fluorocarbons. Vinyl chloride, for example, polymerized in bulk in 50 g quantities in a stirred oil bath, gave dark polymer due to the heat-induced evolution of hydrogen chloride. Nor does the phenomenon of rate acceleration in bulk polymerization even require insolubility of the polymer. Solutions of high polymers containing more than a few percent polymer are exceedingly viscous. With methyl methacrylate, the increase in viscosity with polymer formation causes a several fold decrease in k_t and an increase in -dM/Mdt [88]. Thus, bulk polymerizations may give results grossly inconsistent with Table 23 unless little polymer forms.

Values of $k_p/k_t^{1/2}$ in Table 23 were usually obtained for monomers which give rate accelerations in bulk by working in the presence of a solvent for the polymer. Industrial polymerizations of such monomers are frequently accomplished by suspending the monomer in a large quantity of water and using stirred reactors equipped for cooling.

F. Oxidation

Oxidation of olefins may generate peroxides under ambient conditions [89]. The decomposition of these may initiate polymerization. If allylic hydrogens are present frequently allylic peroxides are formed by a chain reaction:

$$R + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + CH_2\underset{R'}{C}\;CH_2X \longrightarrow RO_2H + R\cdot.$$

As indicated earlier, the polymerization of monomers having allyl hydrogens is generally slow so that further reactions of these peroxides will not be considered.

Olefins which polymerize or copolymerize often form polyperoxides with oxygen by a chain mechanism

$$(RO_2)M\cdot + O_2 \longrightarrow (RO_2)_{n+1}$$

$$(RO_2)_{\dot{n}} + M \longrightarrow (RO_2)\underset{n}{M}\cdot$$

The rate constant for the first of these reactions is so large that the oxygen at low concentrations competes well with the addition of monomer to the same radical. However, only monomer adds to the RO_2 radical and that relatively slowly. Thus, 1:1 copolymers of oxygen and monomer tend to form, although so slowly that oxygen appears to inhibit polymerization. The kinetics and even the nature of the major product depend somewhat on oxygen pressure. As the oxygen is exhausted, the polyperoxides act as sources of free radicals by cleavage of O - O bonds. If the temperature is high, a rapid polymerization can result. Peroxidic products of tetrafluoroethylene can induce violent reaction even at room temperature and any contact of oxygen with this monomer is to be avoided. Polyperoxides are formed by styrene [90], methyl methacrylate [90], vinyl acetate [90], methacrylonitrile [91], methyl styrene [92], and isoprene [93]. Methyl acrylate [91], acrylonitrile [91], and chloroprene [94] give chiefly carbonyl products at the temperatures studied, about 60°C. Even if peroxide forms it is not always an effective initiator; vinyl chloride is an example of this [95].

The complicated effect of oxygen in polymerizations suggests that special precautions should be taken in doing experimental work. Most uninhibited monomers will form peroxides on exposure to air. The time of such exposure should be held to a minimum. Before polymerization, the monomer should be frozen, pumped on, and thawed several times in order to remove oxygen. The monomer can then be used as such, but a better practice would be to evaporate it at room temperature and condense it directly into a reaction vessel, thus leaving behind any peroxide. Generally, an appreciable portion of monomer is left behind in this step, particularly if peroxide is suspected; some of the latter are explosive when concentrated.

Industrial organizations use nitrogen to purge equipment and monomers and add enough additional catalyst to compensate for residual oxygen and inhibitor.

G. Thermal Initiation

Without the presence of an initiator many monomers will not polymerize but the presence of oxygen may cause some polymerization through peroxide formation, even without purposeful addition of initiator. With methyl methacrylate there may be thermal polymerization, but there is evidence that exposure to visible light forms an initiator and observed polymerizations may result from this [96]. Styrenes are probably the only monomers in which true thermal initiation is proven. The uncatalyzed polymerization of styrene itself is slow, about 0.1% per hour at 60°C and has an overall activation energy of 21 kcal/mol [97]. Important monomers thought not to polymerize thermally include vinyl acetate [98], methyl acrylate [98], vinyl chloride [99], acrylonitrile [100], and tetrafluoroethylene [101].

H. Inhibition

Free radical polymerizations are relatively easy to inhibit. The most common inhibitors are phenols and quinones. The mechanism of action is apparently rather complex and even the stoichiometry may be uncertain [102]. Kinetically, however, radicals can be pictured as reacting with inhibitor Z to form non-propagating species:

$$R_n + Z \longrightarrow \text{Products},$$

$$-\frac{dR}{dt} = k_Z([Z])\left(\sum_{1}^{\infty}[R_n]\right).$$

Values of k_z/k_p have been tabulated for many inhibitor-monomer systems [103]. From these one can calculate the concentration of inhibitor required to achieve a desired low level of the polymerization rate in the following manner. If reaction with inhibitor stops substantially all the growing chains, then when dR/dt reaches its steady state value

$$2k_d f\,[I] = k_z([Z])\left(\sum_1^\infty [R_n]\right) \tag{3}$$

$$-\frac{dM}{M\,dt} = k_p\left(\sum_1^\infty [R_n]\right) = \frac{2k_p k_d\, f[I]}{k_z[Z]}\,.$$

This may be solved for [Z], the inhibitor concentration.

Relatively low concentrations of inhibitors can be effective. For styrene and benzoquinone k_z/k_p is given as 225 at 60°C [98]. If [Z] is 10^{-2} mol/liter and the initiator is 2,2'azobisisobutyronitrile, also at a concentration of 10^{-2} mol/liter then -dM/Mdt will be 10^{-7} sec^{-1}. The uninhibited rate, calculated from Eq. 1 by use of Table I, would be 60×10^{-7} sec^{-1}. The inhibitor is consumed and if excess initiator is used there will be inhibition first and then a retardation period in which neither equation 1 nor 2 applies. Subsequently, behavior characteristic of the uninhibited reaction will occur. Thus, commercial styrene, inhibited with p-tert butyl catechol, will polymerize after standing at room temperature for a year or so.

The same substances that inhibit polymerization also inhibit oxidation [92]. Since true thermal initiation is rare, polymerization inhibitors may function more by preventing peroxide formation than by interaction with growing radicals. Indeed, it may be desirable to add free radical inhibitors to olefins that do not polymerize in order to prevent their oxidation. The necessity for so doing is not considered here.

I. Recommendations for Olefinic Monomers

In view of the complexity of free radical polymerization it is thought that results of test polymerizations should not be used as a means of rating olefins as to polymerizability during transport. At most such a testing program would tell something about what happens after polymerization has started. Polymerization in bulk in large containers having a low surface to volume ratio, no provision for cooling, and no stirring probably would be substantially adiabatic. Therefore, if polymerization started at anything but a very small rate it would be expected to continue at an increasing rate until limited by (1) initiator depletion, (2) monomer depletion, (3) change in reaction character at high temperature, or (4) venting of the container. Thus, one feels that the important thing to consider is the likelihood of polymerization starting inadvertently. If such polymerization did start peroxides probably would be the likely source of initiation, since thermal initiation of pure monomer is quite rare. Important considerations for each monomer then are whether true thermal initiation occurs and the character of the oxidation--its rate, means of inhibition, what peroxides, if any form, and whether or not their decomposition is likely to initiate polymerization. The general character of the bulk polymerization is worth knowing to judge how severe an accident might be. However, the ultimate intent would be to establish the level of peroxide likely to accumulate in each monomer during transport and specify one or more inhibitors and concentrations that prevent such accumulation. If it can be definitely established that an uncatalyzed polymerization does not occur and that oxidation products do not cause polymerization shipment of uninhibited monomer could be permitted.

The examination of the literature for information on important monomers produced and shipped in large quantities in this country would be a worthwhile activity. Monomers which should be considered are: ethylene, styrene, 1,3-butadiene, vinyl chloride, vinylidene chloride, vinyl acetate, acrylonitrile, chloroprene, methyl acrylate, methyl methacrylate, isoprene, tetrafluorethylene, vinylidene fluoride, and chlorotrifluoroethylene. At present, these monomers constitute the bulk of free radical polymer formers.

Information of particular interest would be descriptions of incidents in which a monomer has polymerized in transit. Data of interest might be: (1) details regarding the type of inhibitor employed and its initial concentration, (2) the time interval before polymerization occurred, and (3) the temperatures prior to and during the polymerization. Depending upon the nature of the literature search, an experimental program might even emerge which would be directed toward the behavior of slightly oxidized monomers and the detection of the initiation of thermal polymerization.

J. Polymerizability of Olefin Oxides

Ethylene oxide and propylene oxide polymerize by anionic and cationic mechanisms and possibly also be step reactions with alcohols [104], but not by free radical mechanisms. A difference from olefins is that catalysts too inactive for olefin polymerization are still capable of polymerizing olefin oxides, for example, the cationic initiators ferric chloride hydrate and activated montmorillonite clay and such anionic initiators as alkali and alkaline earth hydroxides can cause appreciable polymerization in several days at 20 to 100°C [105]. One incident is reported in which calcium hydroxide and water with ethylene oxide led to exothermic polymerization and explosion [105]. Such initiators could possibly occur as a consequence of gross contamination of equipment. The enthalpy of polymerization is large; $-\Delta H_p$ = 22.5 kcal/mole for ethylene oxide [106]. Aldehydes and ketones form polyacetals under special conditions, but the reaction is thermodynamically favored only at low temperature or high pressure, except for formaldehyde. No further action in this field is indicated.

K. Dimer or Trimer Formation

Dimers or trimers, which some persons might class as low polymers, may form in some instances where high polymer does not form. Their formation would usually evolve heat, but would be undetected by ordinary methods except perhaps dilatometry, distillation, or gas chromatographic analysis. Three cases can be distinguished (a) formation from monomers usually considered unpolymerizable because of their structure, (b) formation in inhibited monomer, by molecular mechanisms not susceptible to inhibition, (c) formation as an important part of the polymerization process. Table 24 lists examples.

In most cases only the fact of formation and the identity of the dimer or trimer are known. Rates under conceivable storage conditions are reported only in a few instances (Table 25). In a few more, the enthalpy or free energy changes have been measured or estimated (Table 26).

In many cases, notably acetaldehyde and α-methylstyrene, rapid dimer or trimer formation requires an acid or alkaline catalyst. The dangers associated with dimerization seem at present more potential then real. Where high polymer formation occurs readily, they are already allowed for, except perhaps when there is exposure to very high temperatures in the presence of inhibitors. Where high polymer formation does not occur, the thermal efforts of dimer or trimer formation tend to be small relative to usual polymerization effects.

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Table 23. Olefin Polymerizability at 60°C in Radical Reactions

Olefin	$10^3\ k_p/k_t^{1/2}$ [103] (ℓ/mol, sec)	$E_p - E_t/2$ [103] kcal mol^{-1}	$-\Delta H_p$ [78] kcal mol^{-1}	Remarks*
Ethylene	7	4	25	a
1, 3-Butadiene	7 [107]	-5	17	b
Isoprene	4 [108]	10	17	b
Styrene	20	7	17	c
Vinyl chloride	300	2	22	a
Vinylidene Chloride	30	2	16	a
Acrylonitrile	70	2	18	a
Methacrylonitrile	30	8	14	a
Vinyl acetate	300	4	21	d
Methyl acrylate	700	4	19	b
Methyl methacrylate	90	5	13	c

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*Remarks:
(a) Polymer insoluble in monomer;
(b) Gelation possible;
(c) Thermal initiation possible;
(d) Branched polymer may form.

Table 24. Instances of Dimer or Trimer Formation

	Remarks
Tetrafluoroethylene	b
Chlorotrifluoroethylene	b
1,2-Dichloroethylene	a
Trichloroethylene	a
Propylene	a
Hexafluoropropene	c
Butene-2	a
Isobutene	c
Butadiene	b
2-Chlorobutadiene	b
Isoprene	b
α-Methylstyrene	c
Methyl methacrylate	c
Acetaldehyde → aldol	a
Acetaldehyde → paraldehyde	a
Acetone → diacetone alcohol	a
Acetone → mesityl oxide + water	a
4'4-Diphenylmethane diisocyanate	c
Benzonitrile	a

(a) High polymer does not form at usual temperature and pressure;
(b) Inhibited monomer;
(c) Polymer forms also.

(No attempt has been made to find references to dimers as minor products incidental to formation of high polymer.)

Table 25. Dimer Formation Rates
(wt %/h) x 10^4

Temp °C	1,3-Butadiene[109]	Isoprene[110]
20	1.5	1.17
40	14	1.9
60	130	21
80	1200	230
100	11000	2500

Table 26. Enthalpies for Dimer and Trimer Formation

Reaction	$-\Delta H$ kcal mol^{-1}	Data Source
Propylene, liq → 1/2(4-methyl-1-pentene), liq	10.7	[111]
Propylene, liq → polypropylene, isotactic, c	20.3	[111]
Formaldehyde, liq → 1/3 trioxane, c	13.6	[111]
Formaldehyde, liq → polyoxymethylene, c	13.0	[111]
Acetaldehyde, liq → 1/3 paraldehyde, liq	8.77	[112]

VII. Thermal Analysis and Hazard Evaluation

A. Thermal Explosion Theory

In 1928, Semenov [2, 3] presented the first quantitative treatment of the theory of thermal explosion. In this treatment, the heat generated by a self-reacting material competes with the heat lost from the exothermic process due to transfer to the surroundings. As the temperature of the surroundings increases in a linear fashion, the rate of heat production from self-reaction increases, exponentially, until a temperature is reached above which equilibration is not possible and decomposition takes place rapidly with ignition or explosion.

The theoretical treatment of Semenov provides for the calculation of the critical conditions in excess of which ignition or explosion will take place. Assumptions basic to this treatment state that (1) the self-reacting material maintains a uniform temperature during decomposition, and (2) the Arrhenius rate law is obeyed. Heat transfer to the surroundings is not limited to any one mode. The exact solution of the equations generated in Semenov's model is not possible without making some approximations. Necessary data for certain thermodynamic, kinetic, or heat transfer parameters are also required before an actual solution can be obtained. In the absence of data, estimates are usually made.

In 1939, Frank-Kamenetskii [4] developed the Semenov model to accommodate a distribution of temperatures within the self-reacting material and limited the heat loss process to conduction only. In many instances, the Frank-Kamenetskii model is a closer approximation to the actual situation.

Various refinements have been introduced into the mathematical treatment of the theory of thermal explosion. Articles by Chambré [113], Todes [114, 115], Rice, et al. [116, 117], Zinn and Mader [119] and Enig [120] should be consulted. Thomas [118] compared the Semenov and Frank-Kamenetskii models and showed that both are special cases of a more general model. Useful reviews have been provided by Merzhanov and Dubovitskii [6], and Gray and Lee [121].

In order to facilitate a clearer understanding between the theory of thermal explosion and hazards caused by thermally unstable materials, we shall describe some features of a thermal explosion process. Let us imagine a test tube (constructed of a high thermal conductivity metal), containing an hazardous material, which has been immersed in an oil bath initially at some low temperature, To. A thermocouple imbedded in the material allows a temperature-time record to be taken. (This situation is analogous to one for the Explosion Temperature Test described in Section IV). In the first test, the temperature of the material will be observed to rise to the bath temperature, then slightly surpass the bath temperature, and proceed to level off back down to the bath temperature. During this time, the material undergoes decomposition, and if the reaction products are gaseous, has disappear completely. As the bath temperature is increased in successive steps, a critical temperature will be attained, which will be the maximum temperature for maintaining a steady-state process. At temperatures above the critical temperature, a steady-state cannot be maintained, and ignition, rapid decomposition, or explosion results.

The phenomenon of the induction period begins to emerge at this point. This period is the time interval between immersion of the material in the bath and explosion.

We shall now examine the rate processes taking place during heat generation and heat loss. The self-reacting material produces heat at the rate dq_1/dt, or $\dot{q}_1$, given by:

$$\dot{q}_1 = dq_1/dt = QV\rho A\exp(-E/RT)$$

where Q is the heat of decomposition, V and ρ are the volume and density of the material, respectively, A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature of the material.

The material loses heat to the surrounds at a rate according to Newton's law of cooling:

$\dot{q}_2 = dq_2/dt = hS(T-T_o)$ where

h is a heat transfer coefficient, S is the surface area of the material, and $(T-T_o)$ represents the temperature difference between the material, T, and its surroundings, T_o.

At the critical temperature, a steady-state is reached when the rate of heat generation and heat loss are equal.

$$QV\rho A\exp(-E/RT) = hS(T-T_o)$$

The heat generation rate of the self-reacting material, plotted as a function of temperature, is shown in Figure 1. The heat loss rate corresponds to three straight lines marked as the bath temperatures at 200, 208, and 210 °C. There are three different relationships which are possible between the exponential curve representing the heat production rate, dq_1/dt or $\dot{q}_1$ and the straight lines depicting the heat loss rate, dq_2/dt or $\dot{q}_2$. The net rate at which heat is generated in the self-reacting material is the sum of $\dot{q}_1$ and $\dot{q}_2$, and the rate of temperature rise will be expressed by this sum divided by the heat capacity, C.

If C = mc where m is the mass of material, and c is its specific heat, and if $m = \rho V$, then the rate of temperature rise is given by:

$$CdT/dt = QV\rho \exp(-E/RT) + hS(T-T_o).$$

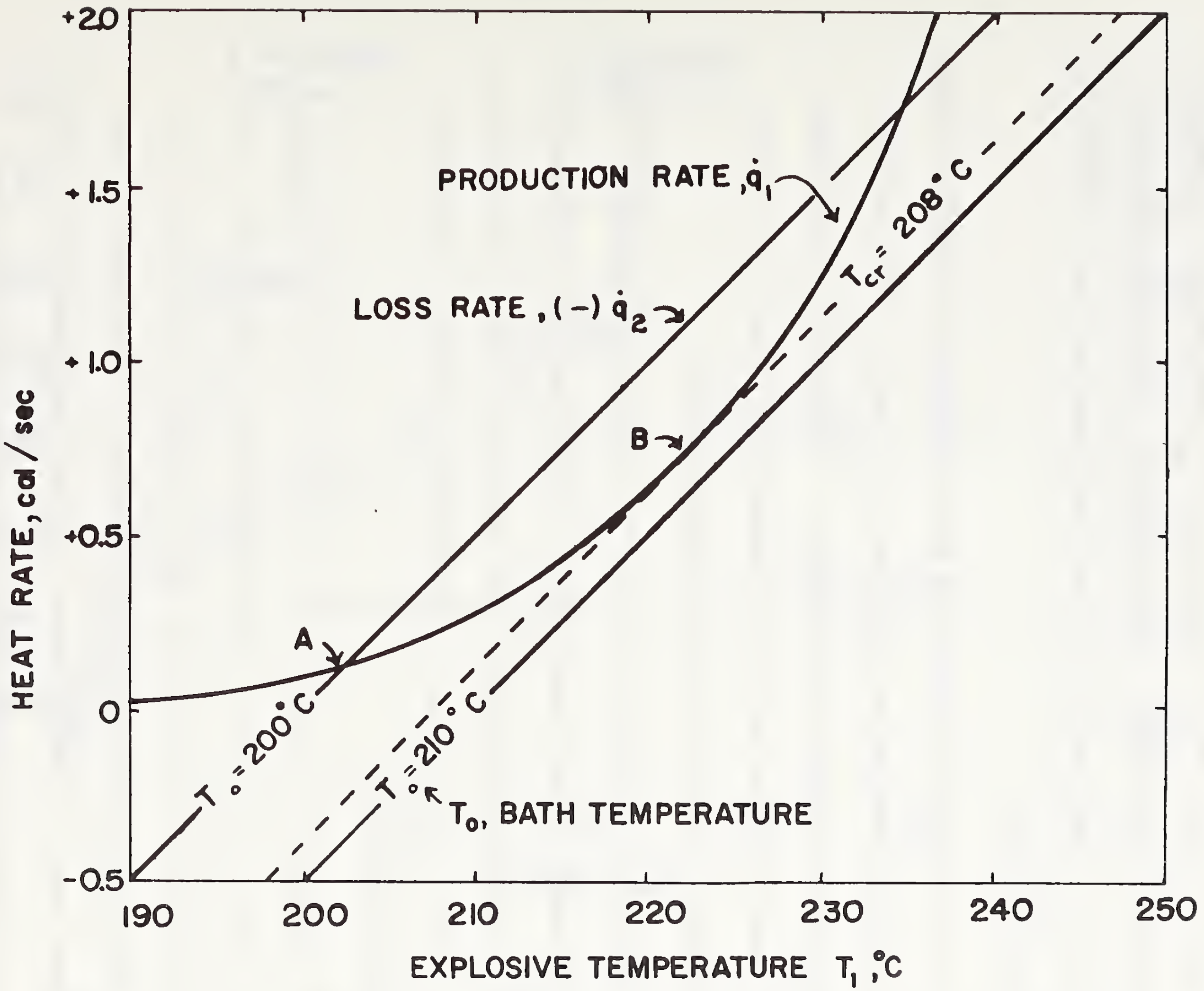

Figure 1 Heat Production and Heat Loss Rates for a Self-Reacting Material

The first relationship shows the curve cutting the straight line at two points. Here, the heat generation rate of the material for a bath temperature of 200°C is greater than the heat loss rate up to point A, where both are equal. This corresponds to a material temperature of about 202°C. Beyond point A, the heat loss rate exceeds that of heat generation and rapid decomposition or explosion does not take place.

In the second situation, the bath temperature is 208°C, which is the critical temperature, T_{cr}, for the material. The curve is tangent to the straight line at point B. The material temperature reaches about 221°C at point B afterwhich sufficient heat loss to the surrounds takes place and no explosion results.

The bath temperature is at 210°C in the third situation. The curve representing heat production via self-reaction of the material and the line representing heat loss do not meet. This temperature, 210°C, is above the critical temperature, T_{cr}, hence, ignition or explosion takes place.

A temperature-time plot for the self-reacting material is shown in Figure 2 for various bath temperatures. Variation in the induction period can be seen as the bath temperature rises above T_{cr}. The induction time prior to explosion is very short as the bath temperature, T_o, exceeds the critical temperature, T_{cr}. The amount of material reacted during the induction period is small. About 4 percent of the material decomposes before explosion when T_o is 210°C and about 2 percent when T_o is 220°C.

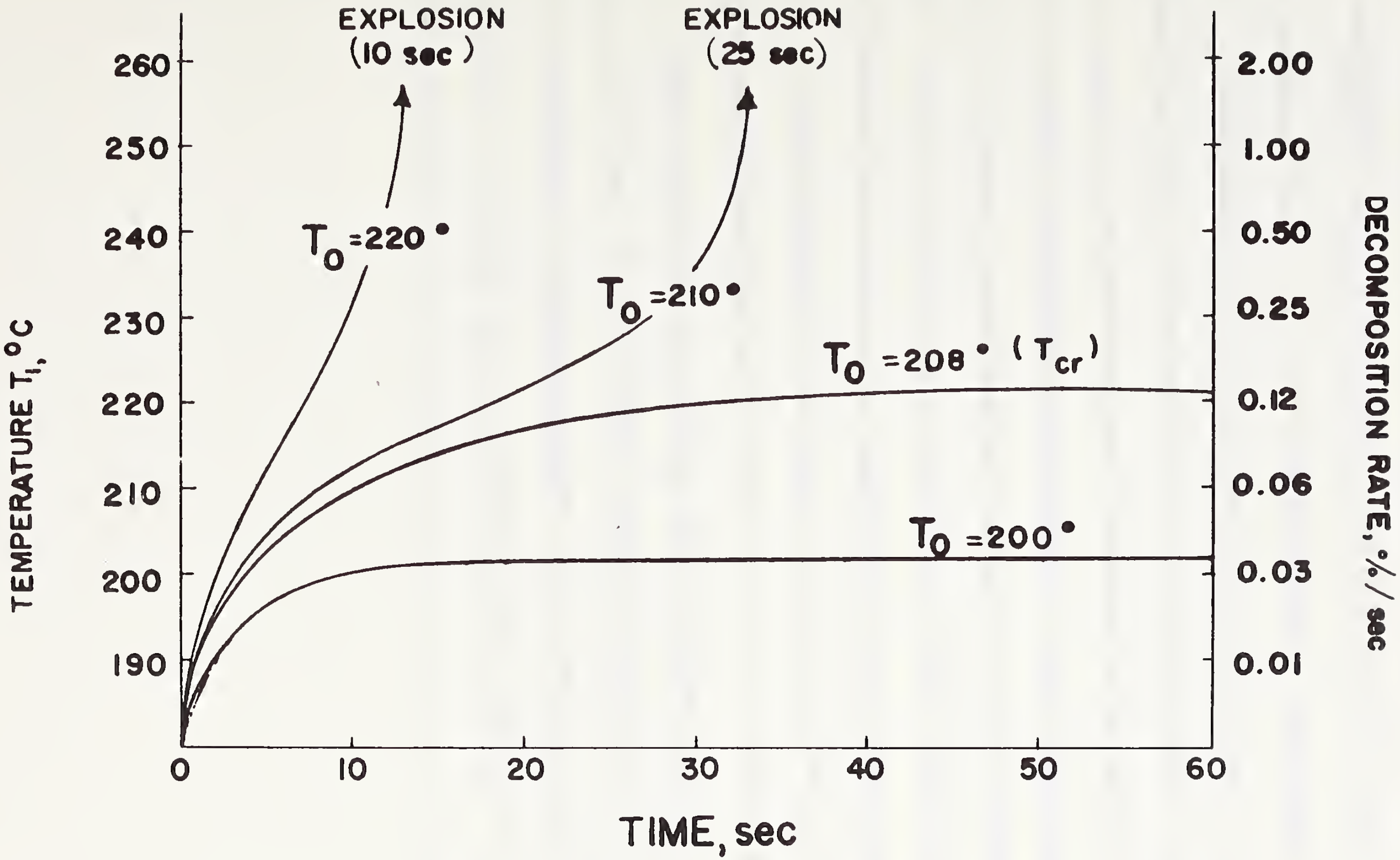

Figure 2 Heating Curves (Temperature - Time Curves) for a Self-Reacting Material

A relationship between the heat transfer coefficient, h, and the surface area, S, of the material, and the induction time seems apparent; both h and S in turn would affect the critical temperature, T_{cr}.

The mathematical treatment of the theory of thermal explosion has been presented adequately by Semenov [3], Frank-Kamenetskii [5], Merzhanov and Dubovitskii [6], and Gray and Lee [121], and hence, will not be delivered in any detail here. An examination of some of the basic objectives of this theory does demonstrate, however, that a fundamental basis for identifying and defining thermal instability are contained in it. These objectives are: (1) to establish what factors determine whether an explosive reaction will occur, (2) to find the conditions under which the reaction will proceed at a steady rate, (3) to determine the temperature distribution in the self-reacting material under steady state conditions, (4) to determine the relationship between temperature and time prior to the attainment of steady state conditions, and (5) to examine conditions which prevail when no steady state is possible.

B. Experimental Studies on Hazardous Materials using DTA, DSC, or Related Measurement Techniques

During the course of examining the literature for physical test methods and test data, we have encountered a large number of articles which report measurements on hazardous materials. Some are studies designed to examine and expand various concepts in thermal explosion theory while others report only thermochemical or kinetic data on a particular decomposition reaction. Many investigators use differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Some researchers have employed the more standard calorimetric or kinetic methods. These articles supplement those mentioned in Section III of this report under Thermal Tests.

Rogers [122-124] has shown that the activation energy and pre-exponential factor can be determined for the decomposition process of many explosives using DSC methods. Critical temperatures can be determined on a routine basis using the method described. Agreement between experimental and calculated values is good for most explosives.

An extensive study of the application of the thermal theory of spontaneous ignition to the explosive decomposition of diethyl peroxide was reported by Fine, Gray, and MacKinven [125]. Thermal explosion theory was able to make quantitative predictions of the maximum temperature rise in the system which just failed to explode and the shape of the temperature profiles for the critical conditions. Experiments were in agreement with predictions.

Merzhanov, Abramov, and Abramova [126] reported a method, based on the heat balance equation, for calculating kinetic constants from a differential thermogram in which non-isothermal kinetic data are reduced to isothermal conditions. The method is demonstrated using the decomposition of tetryl and the polymerization of styrene.

An experimental investigation of the effect of gas removal on the critical conditions for thermal explosion was performed by Samoilenko, Abramov, and Merzhanov [127]. Experiments were performed on compressed pyroxylin samples. Gas removal conditions were varied by changing the pressure of nitrogen in the system. The authors found that as the pressure of the gas over the sample was raised, the critical temperature for thermal explosion fell sharply.

Aleksandrov, Bufetov, Pastukhova, and Tukhtaev [128] reviewed the application of pulsed calorimetry to the determination of thermochemical and kinetics parameters of various explosives. References to studies on the decomposition of nitrocellulose, nitroglycerin powder, ammonium perchlorate, dinitroxydiethylnitramine (DINA) and polymethylmethacrylate were provided.

The thermal stability of tetramethylphosphonium perchlorate, nitrate, and picrate was determined using DTA and TGA techniques by Nambiar and Jain [129]. The thermal stability of these compounds was found to be in the order: perchlorate > nitrate >picrate. The explosive sensitivity of the compounds was determined from explosive delay measurements and indicates the same order as the thermal stability.

The remaining list of articles describing the use of DTA, DSC, TGA, and variation of calorimetric and kinetic measurements to establish the hazardous character of self-reacting materials is still large. We have abbreviated our exposition of this section by providing shorter descriptions of the articles along with the corresponding references.

(1) A study of the energy of combustion of ammonium perchlorate was carried out in a twin-type combustion calorimeter under 11 atm. of helium [130].

(2) DTA, EGA and TGA methods were used to study the decomposition of $KClO_4$-lactose mixtures in the temperature range from room temperature to over 500°C [131].

(3) An automatic TGA apparatus designed for non-isothermal kinetic measurements in the temperature range from 20° to 300°C is described [132]. Heating rates of 1 to 100 deg hr^{-1} are possible for 10g samples.

(4) Thermal decomposition of alkali metal perchlorates were studied by DTA and TGA methods up to 600°C [133].

(5) The compatibility of polymers with explosive materials was determined using DTA methods. [134, 135].

(6) The thermal explosion of lead azide has been studied in vacuum at temperatures high enough for explosion to occur. Reaction rates were measured up to the onset of explosion [136].

(7) A calorimetric determination of the thermal decomposition of a nitroglycine propellant was carried out in vacuum from 70° to 280°C [137].

(8) Heat capacities and phase transitions in HMX were determined using DSC methods [138].

(9) The critical conditions and induction period for the thermal explosion of isopropylbenzene hydroperoxide in a homogeneous flow-through reactor system were determined [139].

(10) Several investigations of the thermal decomposition of dinitroxydiethylnitramine (DINA) have been conducted under various conditions [140-145].

From an examination of thermal explosion theory and experimental studies of hazardous materials by various methods, we felt that a calorimetric approach offered some reasonable promise of providing the necessary information and support for concepts from which an unambiguous reactivity scheme could be developed. A test procedure for ranking materials consistent with such a reactivity scheme should be derivable which has a strong relationship to the theory of thermal explosion. Properties of materials which are embodied in this theory, are obtainable from calorimetric experiments. Moreover, the calorimetric approach has the advantage of permitting the simultaneous derivation of such properties from the experimental measurements performed on a specific decomposition process. The need to calculate thermochemical parameters (such as the energy of decomposition) and kinetic parameters (such as the activation energy of decomposition) from the same reacting system, thus providing the common base for comparison, cannot be overemphasized. This common base has been lacking for most materials. The promise of the calorimetric method to supply the needed ranking for chemical reactivity is based upon its provision of parameters called for by the theory of thermal explosion. One can anticipate further that if self-reacting systems (decomposition and polymerization) are adequately described by this approach, extension to combustion processes should also be possible.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A literature survey was carried out to collect and evaluate test methods and test data on hazardous materials which undergo self-decomposition. Some thermal tests are regarded as valuable because they give quantitative data indicating the limit of thermal stability for specified materials. With the assistance of the CHETAH predictive scheme, a hazard evaluation was conducted on a selected group of compounds normally considered safe. Results showed a tendency to identify these safe materials as hazardous so as not to err in evaluating a truly hazardous compound. In a study of accidental polymerization of bulk chemicals, free radical polymerization involving olefins was considered the polymerization process most likely to occur inadvertently during transport. A calorimetric test procedure appeared to offer the promise of yielding data from which an unambiguous reactivity scale could be developed. The test procedure should have a firm relationship to the theory of thermal explosion.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Accidental polymerization; CHETAH predictive scheme; hazard evaluation; test data; test methods; thermal explosion theory.

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