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USE OF GASIMETRIC, TIME-TO-EXPLOSION AND ISOTHERMAL DIFFERENTIAL SCANNING CALORIMETRY TO ASSESS COMPATIBILITY OF DOUBLE-BASE PROPELLANTS AND EPOXY RESIN SYSTEMS

Dennis J. Caldwell, Jeffery B. Edwards, John R. Keifer - Hercules Incorporated, Bacchus Works, Magna, Utah.

Raymond N. Rogers, Los Alamos National Laboratory, Los Alamos, New Mexico.

ABSTRACT

Hercules Incorporated has successfully used a compatibility screening system to ensure safe manufacture of rocket motors for the past 25 years. Recent compatibility tests of double-base propellant and certain epoxy resin mixtures utilized in rocket motor manufacture indicated significant incompatibility although the materials have been used together successfully for some time. In an effort to more fully define the actual thermal hazard of such systems, gasimetric data were generated. These data plus the use of chemical kinetic methods led to the construction of a worst-case situation. Further data were gathered using isothermal differential scanning calorimetry and Henkin time-to-explosion testing to determine the potential for catastrophic self-heating leading to a fire or explosion. The use of isothermal DSC and Henkin data is shown to be a valuable method for assessment of compatibility and thermal hazards of similar processing materials and to define design solutions as needed.

INTRODUCTION

A compatibility screening system has been successfully used by Hercules Incorporated for the past several years. The system is designed to determine the compatibility of any material that may come in contact with double-base propellants or propellant ingredients before the materials reach the processing environment. This system relies heavily on a screening system based on short-term data gathered with the Modified Taliani apparatus (see description below). Experience has shown that this system works well as way of assuring long-term stability and preventing short-term hazards. This topic has been well treated in previous ADPA conferences (see references 1 and 2).

Recent compatibility tests using the Modified Taliani with a double-base propellant and an amine-cured epoxy resin system showed what appeared to be significant incompatibility by producing large amounts of gas. This data seemed to be in conflict with the long-term stability of the two materials which had been used successfully together for nearly 20 years. Further investigation was warranted because the materials were program-critical, and the Modified Taliani data was considered very conservative. Thus it was

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decided that a more comprehensive study was needed which utilized other methods to define the actual hazard of incompatibility.

EXPERIMENTAL

The data presented herein were gathered using four different experimental techniques: the Modified Taliani test, an "off-gas" collection and analysis system, the Modified Henkin test and Isothermal Differential Scanning Calorimetry. A description of each technique will be useful.

Modified Taliani

The Modified Taliani test is a variation of the well-established stability test used in the explosives industry. The test is performed in a Taliani apparatus as shown in Figure 1. A sample of a material of unknown compatibility (test material) is mixed in a 1:1 weight ratio with a known explosive (control material - i.e. propellant or energetic ingredient). Obviously, sample preparation is important and must be consistent to give somewhat uniform data. All solid materials (whether test or control) are ground to approximately 20 mesh where possible. Liquids are introduced neat. The mixture is well stirred by hand to insure as much uniformity as possible.

The mixture is introduced into the glass sample tube which is fitted with a glass helix tube and placed in a heated aluminum block. The helix tube is connected to a valve system which allows for evacuation and purging of the tubes with nitrogen and connection with a pressure transducer (in this case a mercury manometer). In the traditional version of the test, the sample block heater is maintained at 93.3°C (200°F) for 23 hours during the Modified Taliani test.

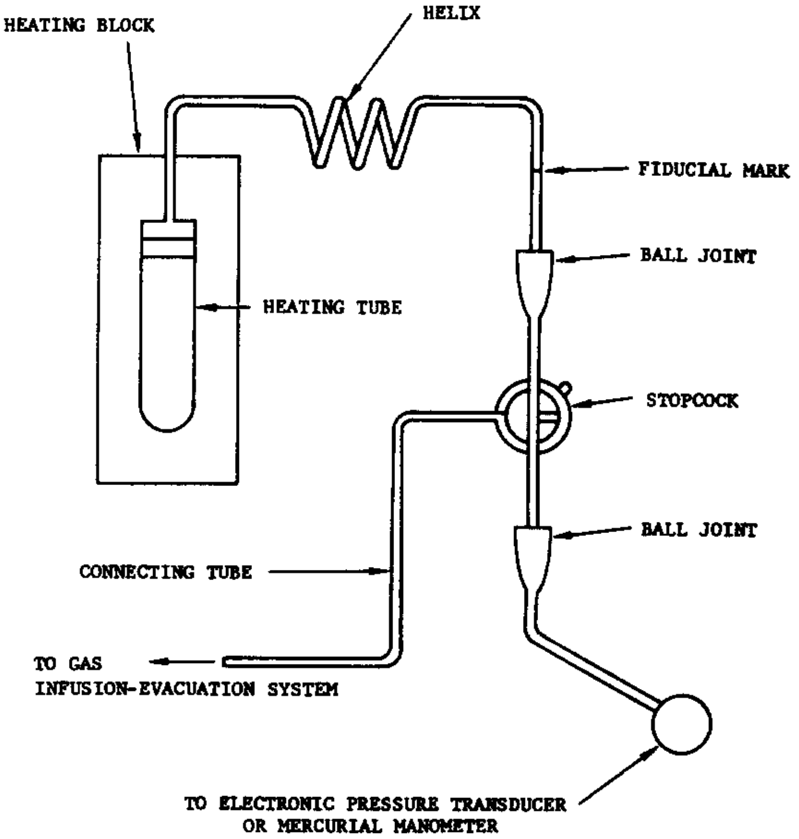

Figure 1: Taliani Apparatus Configuration

Since the test was designed for use with nitrate-ester containing materials, acceptance criteria for this test have been established largely based on past experience. Mixtures which show a pressure rise of more than 200 mm Hg during the 23-hour test period are defined to be incompatible. As mentioned previously, identification of many incompatible materials has been made with this system and serious consequences avoided.

The materials in question were producing gas at pressures well in excess of the 200 mm mark and, in some cases, explosions of sample containers were occurring. However, it was known that the Modified Taliani test conditions are intentionally severe. The time/temperature condition is designed to approach the normal expected safe life of double-base propellants if normal activation energies prevail. Also, the concentration of test material in the control material is a 50/50 ratio.

In the light of the questions about conventional test data, a generalization of the method has been introduced in which the test period was extended (in some cases to as long as 120 hours) and pressure readings taken at 1/2 to 1 hour intervals. This was done for a series of temperatures: 40°C (105°F), 49°C (120°F), 64°C (148°F), 70°C (158°F). In this way, a pressure vs. time curve can be established at a variety of temperatures. Two control materials were used, a double-base propellant and a high concentration nitroglycerin solution. Figure 2 shows the curves for the propellant/epoxy mixture at several temperatures.

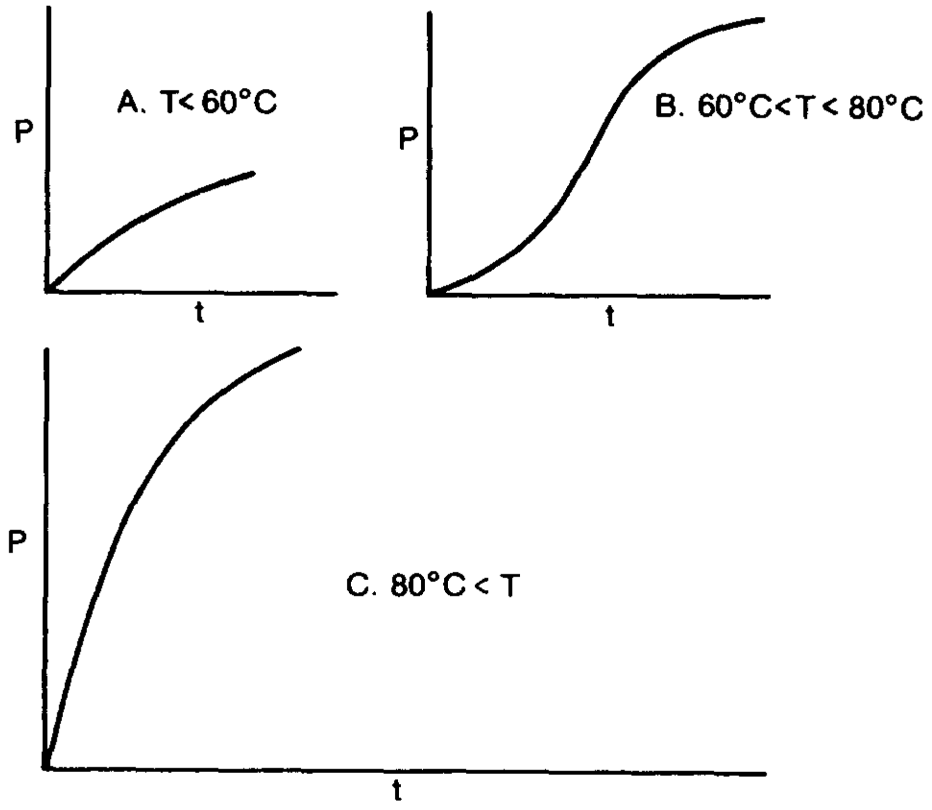

Figure 2: Behavior Patterns for Pressure -Time Plots in Different Temperature Regions

Off-Gas Tests

In addition to the Taliani test, attempts were made to measure the "off-gas" concentration and composition from double-base samples in contact with the adhesive in question to confirm the gasimetric data obtained from the Taliani.

The experimental plan consisted of the determination of rates of gas evolution from propellant samples in sealed tubes at four temperatures: 70°C (158°F), 64°C (148°F), 49°C (120°F), and 40°C (105°F). Samples consisted of slivers of propellant of dimensions 1.5 x 2.0 x 12 mm. Case bond samples were prepared by cutting perpendicular to the plane of the case bond so that the case bond components remained attached to one end of the sliver. Thus each case bond sample consisted of a sliver of propellant 1.5 x 2.0 x 12 mm, one end of which contained the case bond components of embedment resin/embedment granules. Bulk propellant samples were obtained from propellant at a distance greater than 1 in. (2.5 cm) from the case bond.

A weighed portion (1.1 to 1.3 g) of sample slivers was loaded into each off gas ampoule (a glass tube 5 mm (ID) x 155 mm). In order to minimize the free volume, a glass rod was inserted into each tube on top of the sample. The filled tubes were evacuated for 1 hour during which time they were purged with helium three times and then the ampoules were sealed under vacuum. The finished length of each sealed tube was 100 to 105 mm. The ratio of free volume to propellant volume was estimated as 2.5 ± 0.5. The gases generated by the propellant in the sealed ampoules were analyzed by gas chromatography on a column of Porapak Q. Gases analyzed were N_2, NO, CO, CO_2, and N_2O.

The gasimetric data collected using the Taliani apparatus and the off-gas methods were analyzed using a two-stage model wherein the gas producing reaction is diffusion limited. Essentially two types of behavior patterns were observed: for temperatures in the range of 60° to 80°C, a sigmoid pattern was displayed (Figure 2B), while below and above this region a simple exponential type of behavior was observed (Figures 2A, 2C).

The plots of degree of reaction (as followed by pressure) vs time displayed qualitatively different patterns, depending upon the relative rates of diffusion and reaction. When the two rates differ by more than an order of magnitude, the slower process is rate limiting, and the reaction curve resembles a simple exponential law. When the two constants are nearly equal, the curve is sigmoid in shape, characteristic of a process involving intermediates.

In order to assess the hazards associated with this system, rate constants were obtained for both the diffusion and reaction processes. This allowed a comprehensive analysis of practically important nonuniform conditions, where the diffusion process first goes to completion followed by chemical reaction at a higher temperature. This method has been well explained in Reference 4.

Modified Henkin

The modified Henkin time-to-explosion test (Ref. 5) is designed to determine the critical temperature (Ref. 6, 7) for a known size and shape of any material capable of catastrophic self-heating.

Solid samples can be prepared as discs that have as uniform a thickness as possible and a diameter of 6.25 mm. A thickness of about 1 mm is suitable for most explosives and propellants when the test is run in a normal laboratory. The samples are placed in empty aluminum blasting-cap shells (DuPont E-83, approximately 6.25-mm i.d. by 41.3-mm long), and they are confined with a hollow aluminum plug. Approximately 40-mg samples of powders can be pressed directly into the cell under the plug, and plugs can be seated over liquids by using a spacer of suitable thickness. A crimp is rolled around the cell just above the plug to maintain constant dimensions during testing, but the crimp is not intended to provide a positive seal.

Cells are remotely lowered into a preheated Woods Metal bath, and time to explosion is recorded at that temperature. Fresh samples are tested at lower temperatures until no explosions are obtained. The lowest temperature giving catastrophic self-heating is the critical temperature (T_c) for the specific size and shape sample tested.

Explosions are often obvious; however, catastrophic self-heating may be difficult to detect with some materials at temperatures close to the critical temperature. In such cases, we watch for motion in a wire-stemmed "flag" that is in contact with the aluminum plug.

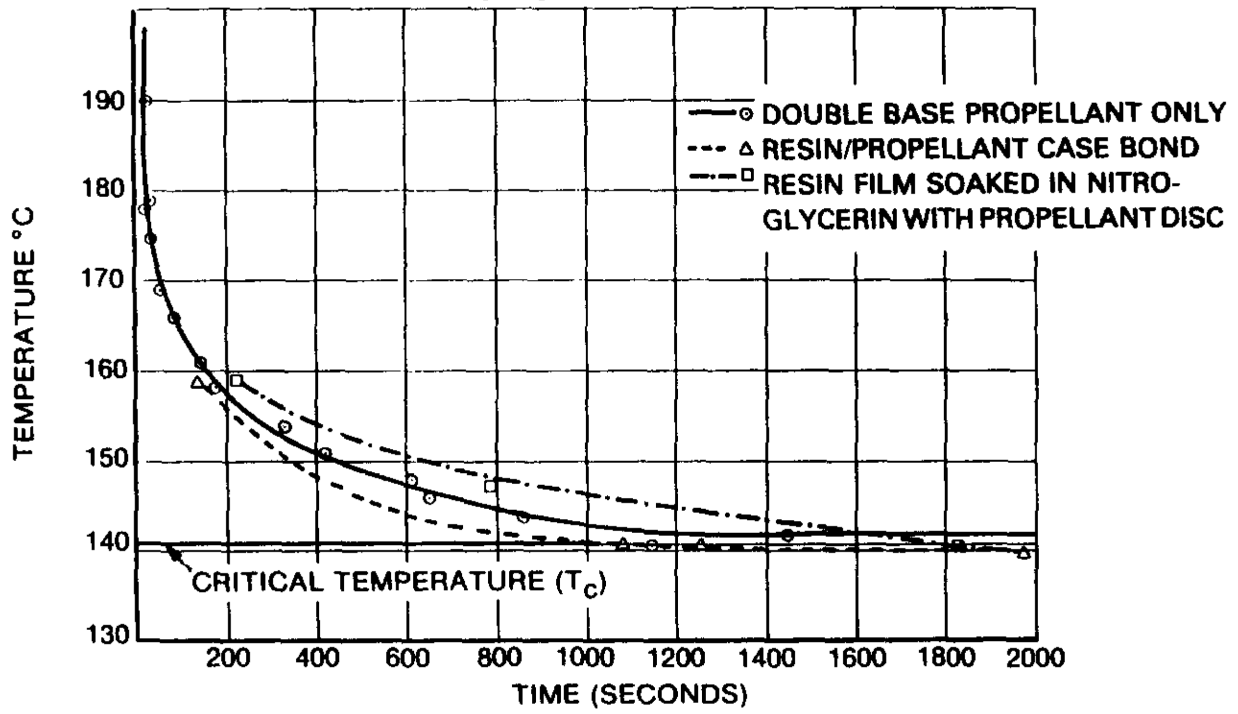

Figure 3: Henkin Time-to-Explosion and Critical Temperature Data

Time-to-explosion tends to increase rapidly as the temperature is decreased, and the curve stops or levels off at the critical temperature (Figure 3). Figure 3 also shows that the critical temperature for a 1.1-mm-thick sample of the double-base propellant in this study is about 140°C. When the propellant was tested in combination with an amine-cured resin that showed incompatibility by gas evolution, the T_c did not decrease significantly. This result shows that no significant self-heating hazard results from the observed incompatibility.

Isothermal DSC

Isothermal differential scanning calorimetry (DSC) testing of the propellant and epoxy/amine combination were carried out. Figure 4 shows the main points of an isothermal DSC scan (See references 8, 9, 10). An empty pan placed in the sample holder at the temperature of interest yields a zero reaction baseline. Once the empty pan is removed and the sample is placed in the holder, any deviations from this baseline indicate exothermic or endothermic processes occurring in the sample. The areas enclosed by the peak and baseline are proportional to the energy given off or taken up by the process.

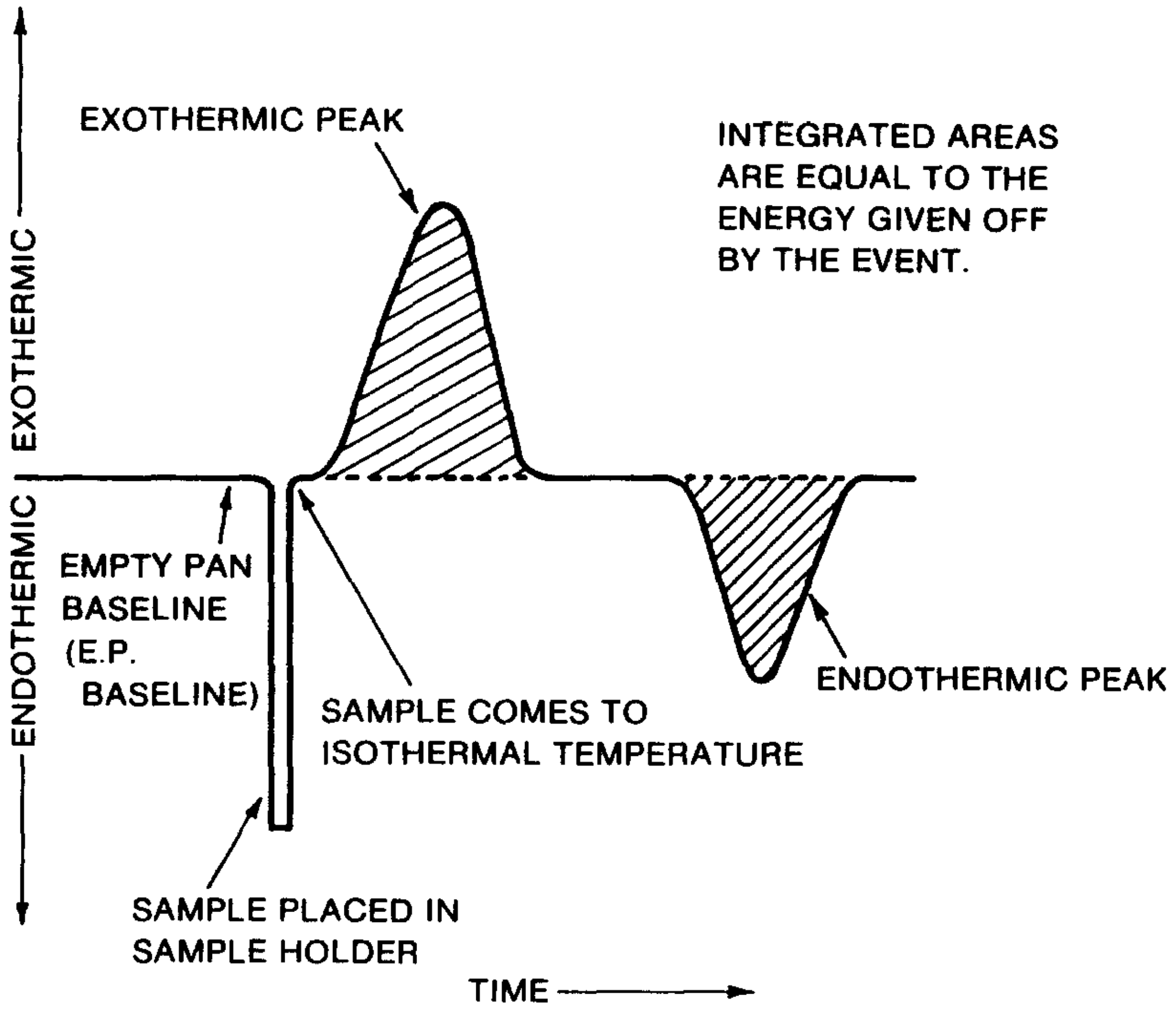

Figure 4: Isothermal DSC Exotherms and Endotherms

For purposes of this study, reaction types were designated as either Nth order or autocatalytic. Figure 5 shows an Nth order reaction as one whose rate is a maximum when time = 0 and decreases. Figure 5 also shows autocatalytic reactions in which the rate increases with time usually rising exponentially after some induction time at the given temperature. As used here, "autocatalytic" indicates the time dependent generation of some reacting species as well as the production of a true catalyst.

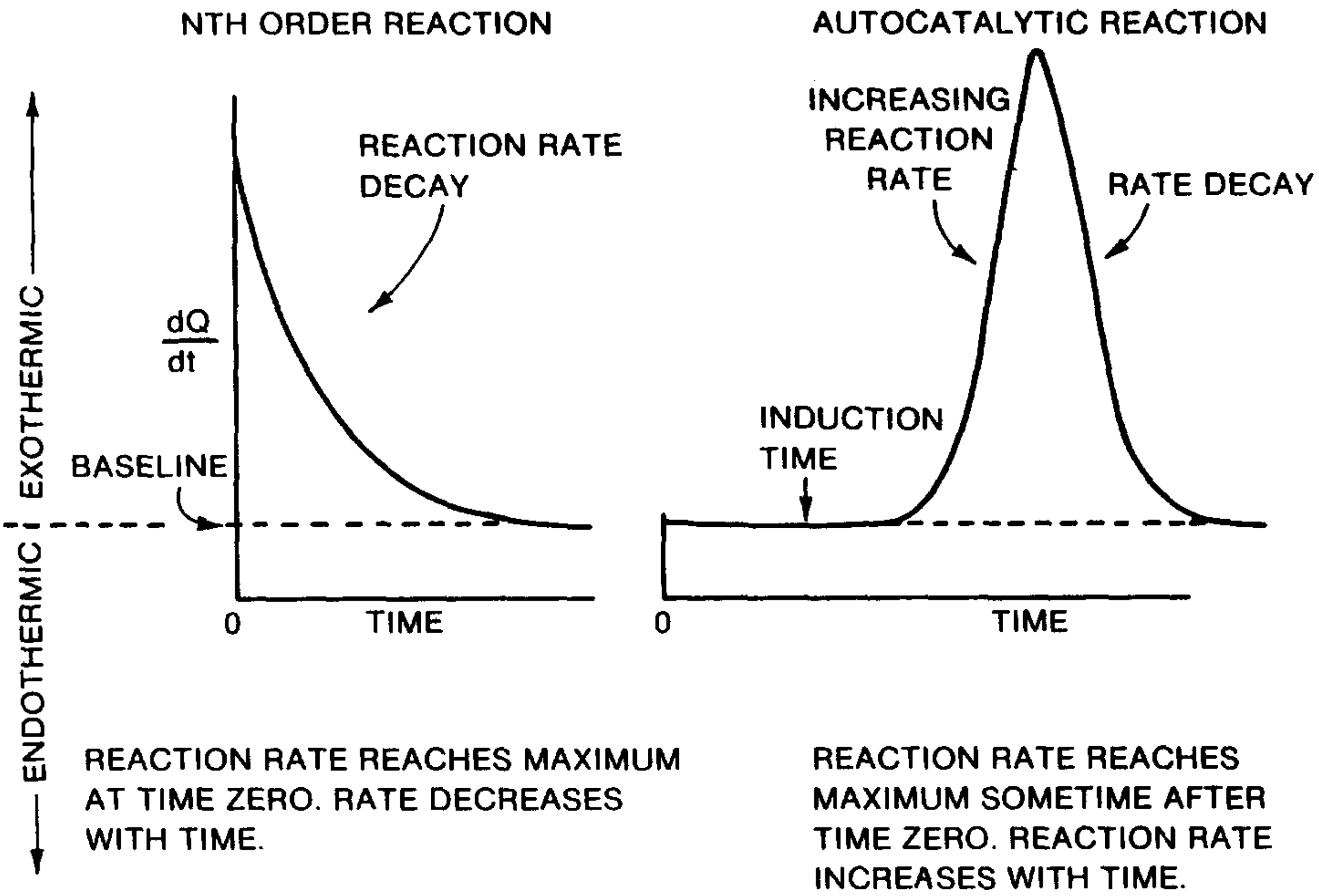

Figure 5: Reaction Type Identification Using Isothermal DSC

DSC sample holder options are important. The different DSC sample pan options can significantly change qualitative and quantitative aspects of the DSC scan. The basic configuration in the top of Figure 6 shows the sample pan and lid which contain the sample. These are cold welded or pressed together and are capable of withstanding small amounts of off gas pressure before rupture. Large or small holes placed in the lid with a dissecting needle will vent any gases produced, and aluminum spacers may be used in the holder to reduce sample dead volume and slow the diffusion of gases from the sample surface.

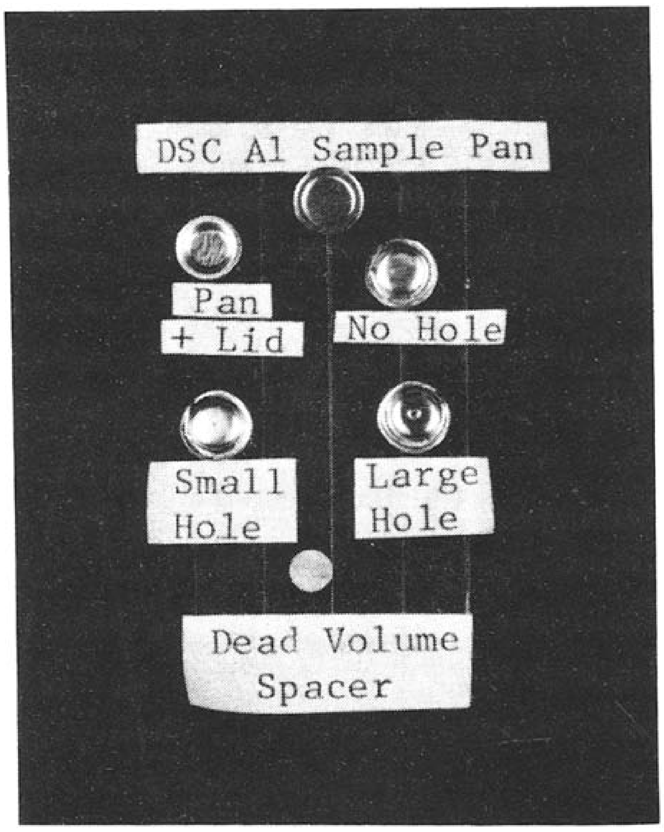

Figure 6: DSC Sample Holder Options

Figure 7 shows how DSC scans of the double-based propellant are affected by sample pan configuration. Although only autocatalytic behavior is seen for the propellant at temperatures below 170°C, two autocatalytic plans are observed in the scans, the second being very steep and thus generating energy at very high rates.

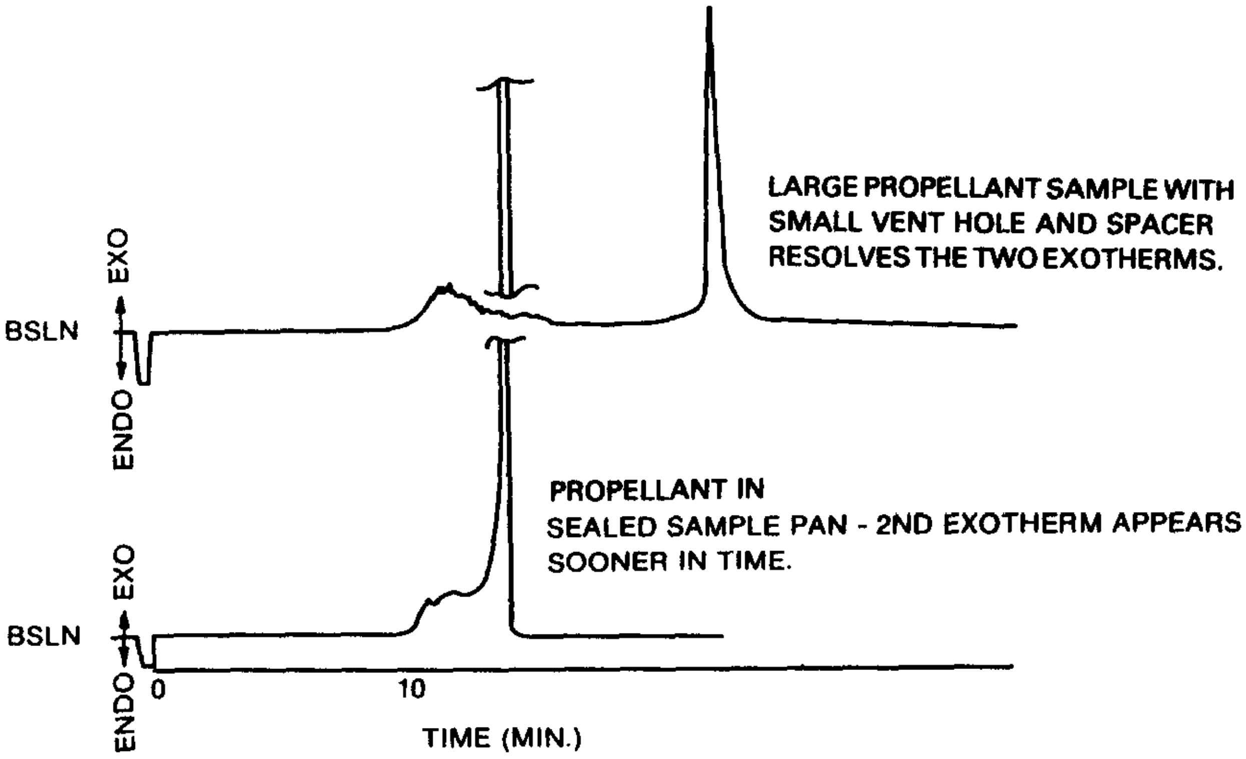

Figure 7: Influence of Gas on DSC Traces

The scan in Figure 7 represents a sample holder configuration where a hole in the sample lid prevents gas pressure buildup, but a spacer on the sample slows the diffusion of gas from the sample surface. In this scan, the two exotherms are resolved with the sharp second peak occurring later in time than the first broad peak. The scan in Figure 8 represents the same propellant without the hole or spacer. Gas generated in this case was totally contained around the sample during the induction time. The second sharp exothermic peak occurs much sooner in time and is not resolved from the first exotherm. Thus the time of occurrence of this second exotherm is extremely sensitive to the ability of the sample holder to contain the gas produced. When propellant samples are run with no lids, the second sharp exotherm will not usually appear at all. By varying the sample pan's ability to contain gas, this second peak can be made to correspond with the times to explosion seen for the propellant on the Henkin test which has a reproducible, although not controlled, gas containment configuration. We have tentatively associated the second exotherm in the DSC scan with explosive behavior in the modified Henkin.

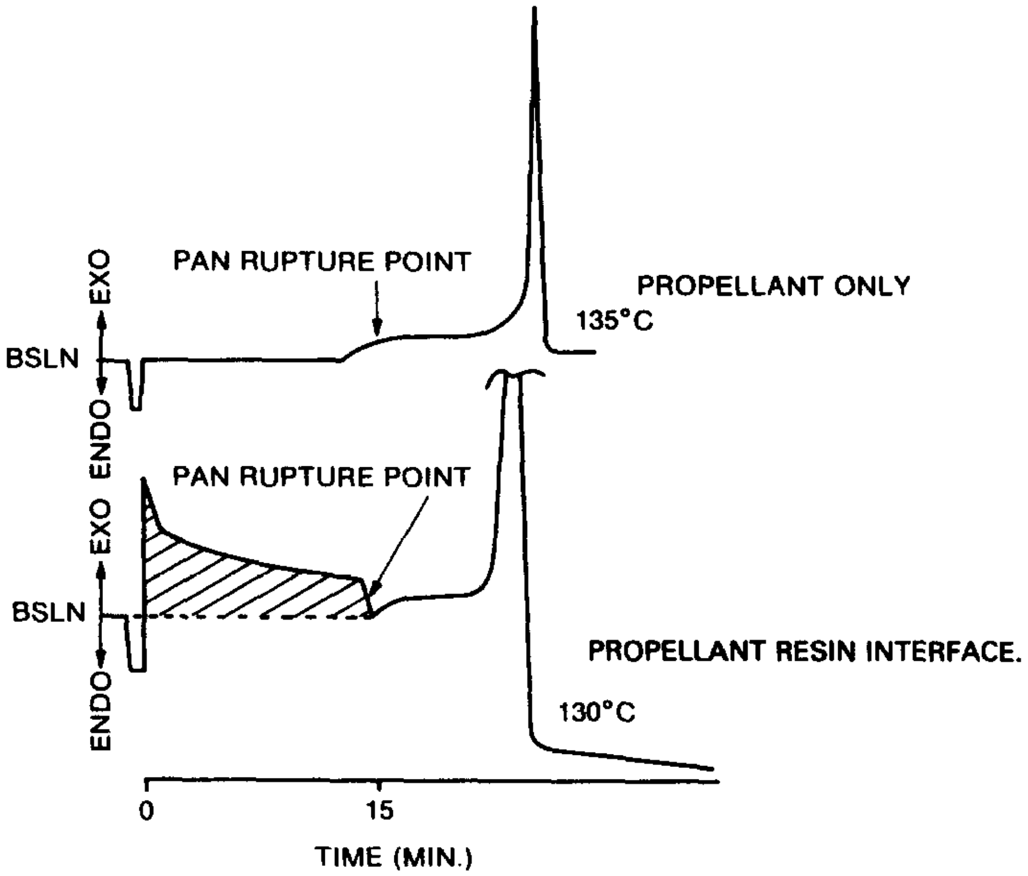

Figure 8: DSC Scan of Propellant and Propellant/Epoxy Interface Traces

Figure 8 compares a sealed sample pan scan of propellant in contact with the amine epoxy system. The purely autocatalytic nature of the propellant is changed in the presence of the resin to include an Nth order contribution. However, the sample pan rupture points from gas pressure as indicated in Figure 8 show that very little gas is produced from this Nth order contribution. The resin propellant system delivers approximately ten times the energy that the propellant alone delivers before pan rupture occurs. Thus although the resin propellant system releases large amounts of energy, the gas production contribution due to the Nth order process is not significant and the induction time of the second exotherm is essentially unaffected by it under the isothermal conditions of the DSC. As expected, the rate of production of gas increases with increasing temperature. As a result, the induction time of the first and second exotherm as well as the Henkin time to explosion decreases with increasing temperature. If the system is thus unable to dissipate the large amount of heat generated by the Nth order incompatibility, a temperature rise would result in an increase in gas production rate which should shorten the induction time and increase the intensity of the Henkin test explosion and the DSC second exotherm. It is important to analyze each testing system's selective ability to dissipate the Nth order heat contribution.

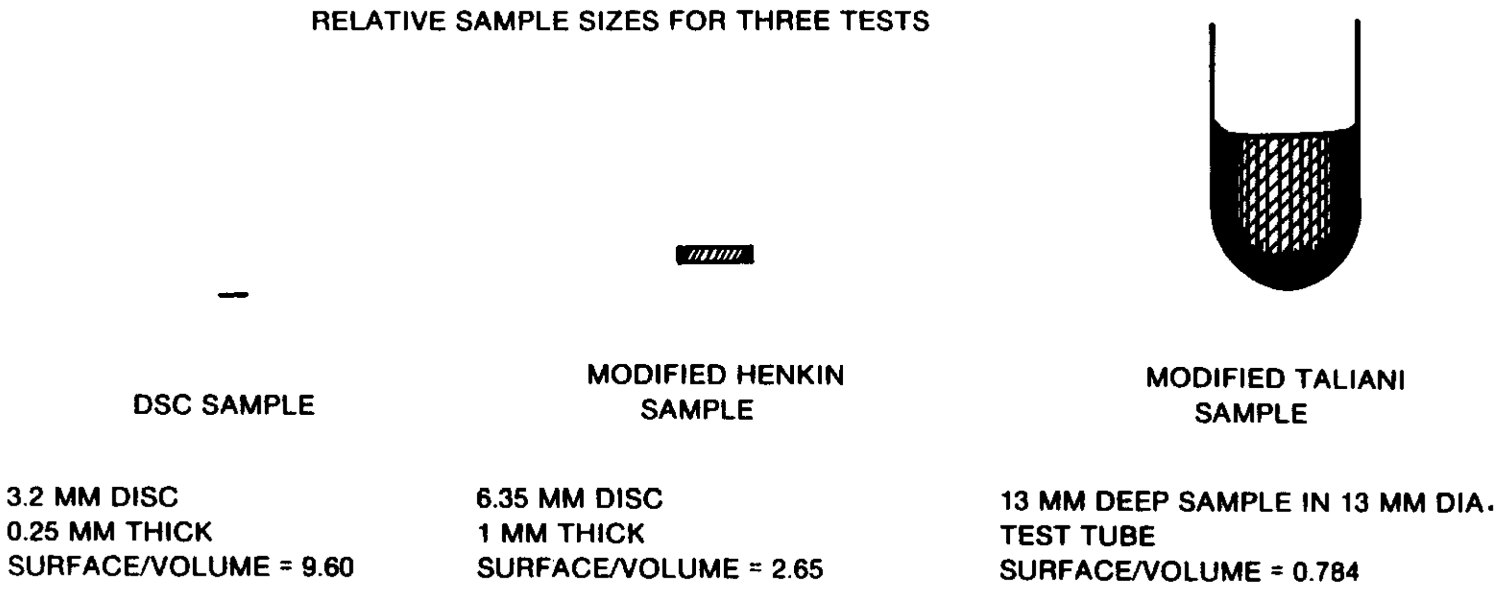

Figure 9: Comparison of Sample Sizes -
DSC, Henkin and Taliani Tests

Figure 9 shows the selective sizes and shapes of the three test configurations used. Since generated heat in the sample can escape only through the surface, the surface-to-volume ratio of the sample is a critical parameter in determining the temperature rise. The DSC has the largest surface area to volume ratio of the three tests (9.6). A large metal heat sink in contact with the sample helps to ensure that isothermal conditions exist. Although the DSC clearly reveals the resin incompatibility as a high energy Nth order process, the sample environment removes this energy, maintaining isothermal conditions. Thus, propellant gas production is apparently the same as without the resin present. The Modified Henkin test is similar where a large sample surface-to-volume ratio (2.6) is in contact with a large metal heat sink. Efficient sample heat dissipation to the heat sink again ensures minimal temperature increases negating the effects of the resin incompatibility on the propellant's explosive behavior.

Since the appearance time of the second propellant exotherm on DSC can be made to correspond with the time to explosion on the Henkin test, it is possible that these events are closely related. This would imply that thermally induced explosions in double-based propellant are primarily determined by the off gas concentration in and around the propellant matrix. Thus, the temperature is important only as far as determining the rate of off gas production during the induction time. The sample environment in the Modified Taliani test allows for very little sample heat dissipation. The selectively small surface-to-volume ratio (0.78) permits less heat to escape than in the other methods. The sample is in turn surrounded by glass and air which are relatively good insulators. Temperature measurements on the outside of the Taliani tube during testing have confirmed that the heat of reaction from the incompatibility can raise the temperature much higher than the initial set temperature of the test, as determined by the sample heater. Thus the high energy Nth order incompatibility would be expected to affect off-gassing rates by raising the temperature of the sample in the more adiabatic environment. However, the thickness of the incompatible system in the actual product has a small surface-to-volume ratio similar to the DSC sample, which is more than ten times that of the Modified Henkin.

DISCUSSION

The diverse experimental techniques found in the DSC, Henkin, and gassing procedures provide data which can in principle be used to obtain rate laws for a given temperature range. A recurring problem of practical interest is to determine the critical temperatures and safe lives for given sample sizes. When the dimension is small, the simplest procedure is to carry out a direct measurement via the Henkin test. With a sufficient amount of effort one may establish the safety margin for samples temporarily elevated above the critical temperature.

The Taliani test has traditionally been used to assess the gross features of potential incompatibility of materials with propellant by measuring the amount of gas produced by a given weight in a prescribed period (Ca. 24 hrs.). This provides a single point in the decomposition curve, which is usually inadequate for making judgements on overall hazard possibilities.

The data illustrated in Figure 2 represent a case in point. At low temperatures, a simple curve is seen and also at high, while within a certain range an inflection point is observed. The analysis of the phenomenon has been reported in Reference 4. The essential feature was the recognition of a two-stage process consisting of diffusion of the active ingredient NG into the resin followed by its reaction there.

Here the model used was the simple two-step process:

$$\begin{aligned} &A \longrightarrow B_1 \qquad && k_1 \\ &B_1 \longrightarrow B_2 \qquad && k_2, \end{aligned} \tag{1}$$

where A represents NG in the propellant.

B_1 is NG diffused into the resin, and B_2 represents the final gaseous products of the reaction. The intermediate "product" B_1 satisfies the equation,

$$\frac{dB_1}{dt} = k_1A - k_2B. \tag{2}$$

When the entire system is solved, one finds that the pressure should satisfy the relation,

$$P = P_{max} \left[\frac{1}{(k_2 - k_1)} \left[k_1 \exp(-k_2t) - k_2 \exp(-k_1t) \right] + 1 \right] \tag{3}$$

When k_1/k_2 differs greatly from 1.0, this displays a simple exponential behavior, while for values between 0.1 and 10.0, a pronounced inflection point is observed. For $k_1 = k_2$, this occurs at $t = 1/k_1$. It was possible to fit the data to this particular model and obtain both rate constants. A lnk vs. 1/T plot gave straight lines for k_1 and k_2 with activation energies, $E_1 = 7880$ cal and $E_2 = 34{,}900$ cal. This confirmed the interpretation of the first as a diffusion process and the second as a nitrate ester decomposition. From these constants, it was possible to make worst case predictions on half lives at low temperatures beyond the range of the DSC.

Predictions for critical size were more problematical, since it is necessary to know something about the heat producing step. There is reason to suspect that the gassing reaction at lower temperatures, while relevant to shelf life, is not the key step in the final approach to cook-off. This emphasizes the need for interplay among the various experimental methods in analyzing propellant hazards and safe life.

In many cases, either time or funds preclude a sufficiently thorough investigation to directly establish the thermal hazards of large samples and other approaches must be brought to bear. It should first be emphasized that the extrapolation of data to larger sizes is subject to many pitfalls.

If the thermal production process can be described by a single global reaction and there is no mechanism change over the temperature region of interest, the critical temperature data can be fitted to the relation:

$$a^2 = fRT_c \; k \; \exp(E/RT_c)/ \;\; AE(\Delta H/C_p) \qquad (4)$$

where T_c = critical temperature, k = thermal diffusivity, A, E = rate constant parameters, f = shape factor, and a = dimension of sample. In addition, there are general relations for extrapolating the times to explosion for different size samples (Ref. 11).

In some cases when the temperature is lowered, safe life can be much shorter than predicted due to a change of mechanism to one associated with lower activation energy. (This would correspond to the extrapolation from small to large-sized samples).

Unfortunately, the DSC tends to give data only in relatively high temperature ranges; however, the direct measurement of heats of reaction provides this instrument with a unique advantage. It is possible with suitable assumptions to predict critical temperatures and times to explosion from DSC data. If these correspond well with the measured values, one has at least established a plausible model to cover the range of temperatures employed in the experiments.

If the DSC were sensitive enough to detect heat generation at low temperatures, it could similarly be used to extend the predictions of critical temperatures beyond the range of the Hazards tests. In order to gauge the reliability of extrapolations of DSC and/or Henkin data, it is clear that measurements of some effect of the reaction are needed in the appropriate temperature interval.

In many respects gassing data performs a complimentary function to the thermal. It has the advantage that one may go down to relatively low temperatures. On the other hand, no thermal data is forthcoming; however, in conjunction with a model formulated from the high temperature DSC and Henkin data, the gassing data imposes requirements from which a reasonable estimate to the low temperature heat generation rate may be made. In particular, if a break in the rate constant curve for gassing is observed, it is reasonable to expect similar behavior in the critical temperature curve, and the model can be adjusted to reflect this.

One of the most crucial aspects of converting isothermal data into predictions of adiabatic behavior is the continuity of the mechanism during the induction period. In the practically important case in which heat dissipation is involved, typically the temperature rises about 10°-20° in a time period which is about 95% of the total time to explosion. This does not rule out the possibility that the critical region extends to a somewhat higher temperature. There is an incentive for seeking a multistage mechanism in which the induction region (I) is intimately bound up with the thermally active regions (II and III). As an example, consider the two-step chain process:

$$A \longrightarrow X + A' \qquad k_1 \qquad (5)$$

$$X + A \longrightarrow 2X + A'' \qquad k_2$$

This is described by the differential equation system,

$$\frac{dA}{dt} = -k_1A - k_2AX \qquad (6)$$

$$\frac{dX}{dt} = k_1A + k_2AX$$

In a normalized system this has the solution,

$$A + X = 1 \qquad (7)$$

$$A = \left[\frac{\frac{k^*}{k_1}}{\frac{k_2}{k_1} + e^{k^*t}}\right]$$

where $k^* = k_1 + k_2$

If $k_1 > > k_2$, this reduces to the simple first order solution,

$A = e^{-k_1t}$. For $k_2 > > k_1$, the denominator and hence A remains approximately at a constant value until $\exp(k^*t) = \left(\frac{k_2}{k_1}\right)$, which corresponds to a time $t_{ind} = \frac{1}{k^*} \ln\left(\frac{k_2}{k_1}\right)$ (8)

At this point the reaction rate increases dramatically and goes essentially to completion in a relatively short time. (See Figure 10). The width of the reaction zone can be found from the relation, $\Delta t = \left[\left(\frac{dA}{dt}\right)_{inf}\right]^{-1}$ where the derivative is evaluated at the inflection point. This is found by setting $\frac{d^2A}{dt^2} = 0$. A simple calculation gives $t_{inf} = \ln\left(\frac{k_2}{k_1}\right)/k^*$, from which one finds $t = 4k_2/(k^*)^2$.

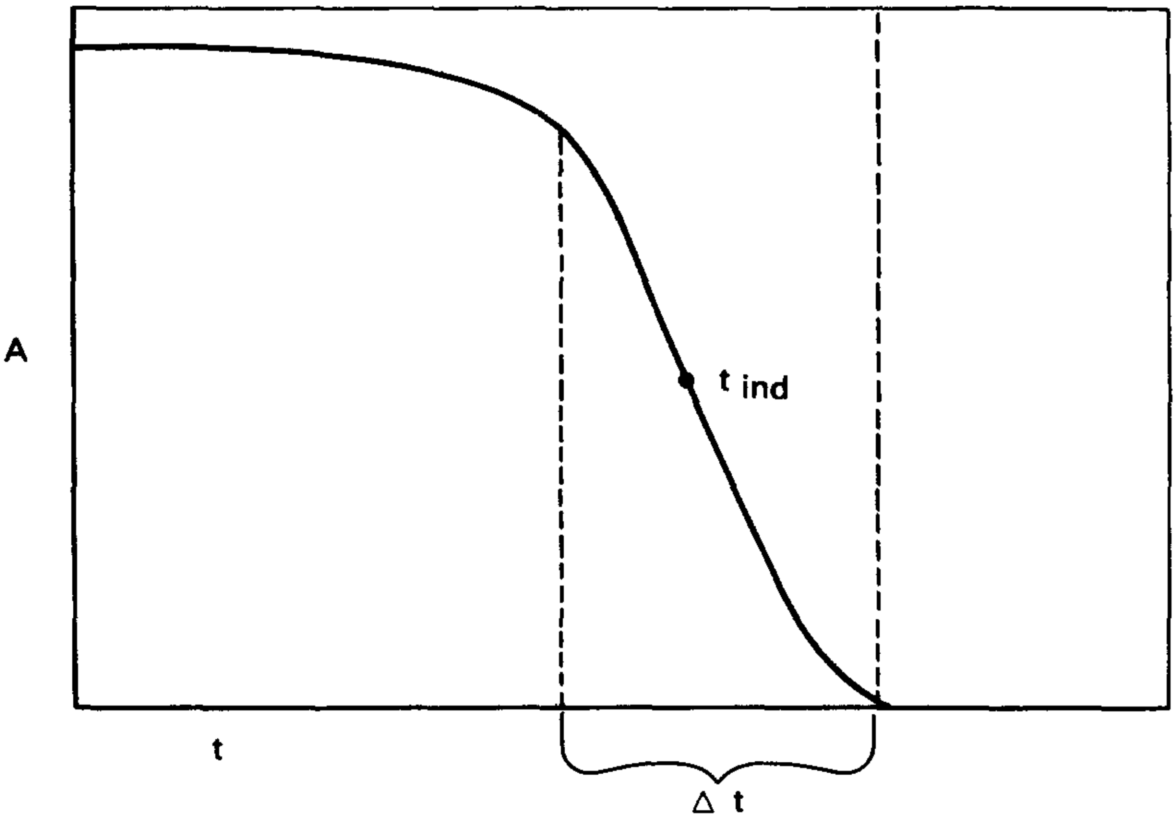

Figure 10: Time Dependence of a Chain Reaction

The ratio of the reaction time Δt to the induction time t_{ind} is given by

$$\frac{\Delta t}{t_{ind}} = \frac{4\ k_2}{k^* \ln\left(\frac{k_1}{k_2}\right)} \cong 4\left[\ln\left(\frac{k_2}{k_1}\right)\right]^{-1} \qquad (9)$$

If one of the constants k_1 is known from the behavior of the normal reaction carried out under conditions where the chain propagating intermediate X is suppressed, the second constant k_2 can be found from the relation for t_{ind}.

It is evident that the data from DSC experiments can be used to calculate thermal parameters from which predictions can be made on the behavior of a system under general non-isothermal conditions.

In principle gassing data, as obtained from the Taliani and off-gas tests, can provide reaction rate information, from which pre-exponential factors and activation energies can be obtained. This can provide important supplementary information in regions not accessible to the DSC. In propellant work the cutoff point for the latter is around 100°C or greater, while gassing data can be obtained well below this temperature. One may use the more detailed information from the high temperature DSC work to formulate a model and extend it to lower temperatures with corrections to the rate as indicated by the gassing data.

As an example of the interplay between the two methods, we outline an investigative technique for assessing the thermal properties of propellants. In certain cases it is of practical importance to predict the behavior of large quantities of material from that of much smaller samples. If the decomposition process followed a one-step rate law over the entire temperature interval of interest, then one could simply use equation (1) to extrapolate from the small size to the larger and obtain a value for T_c, the critical temperature. Below T_c self-heating would be forestalled by conduction, while for temperatures somewhat above T_c the time to ignition can be reasonably well estimated from an equation similar to (1). For temperatures very close to T_c, the time to ignition can be made arbitrarily long; however, a fraction of a degree rise will drastically lower the time or a small decrease may postpone ignition indefinitely.

In actual fact, the situation is not so simple, and the decomposition mechanism cannot be described by a single equation. For example, the safelife of certain propellants is prolonged by the addition of stabilizers which allow operations in regimes above the critical temperature for a time. In some temperature intervals, the stabilizer reaction will suppress the faster of the decomposition reactions, leaving the slower as the rate controlling step. At higher temperatures the stabilizer can no longer accomplish this and the faster decomposition mechanism takes over.

This situation is then described by augmenting the two-step model in equations (7) with a third reaction. The overall scheme is:

$$(10)\qquad \begin{array}{ll} A \longrightarrow X + A' & k_1 = A_1 \exp(-E_1/RT) \\ X + A \longrightarrow 2X + A'' & k_2 = A_2 \exp(-E_2/RT) \\ X + S \longrightarrow S' & k_3 = A_3 \exp(-E_3/RT) \end{array}$$

Where S is the stabilizer.

At low temperatures $k_3 > > k_2$ and the first reaction is rate controlling. Accordingly, k_1 can be directly assessed in this region. At high temperatures it generally happens that $k_3 < < k_2$ and the first two reactions predominate. With k_1 considered as known, k_2 can be found from equation (4) once the induction time has been measured. The last rate constant can be found by fitting the data over the entire temperature region.

Were it not for the possible complication of a mechanism change affecting the individual steps above, this procedure would provide the background for successfully extrapolating high temperature ignition data to larger sizes and lower temperatures. Single reaction mechanism changes are quite common for energetic materials, it is generally necessary to acquire a more direct measurement of rates at lower temperatures. This can be partially accomplished by gassing experiments. Any change in mechanism will be reflected by a change in activation energy in the lnk vs 1/T plot of the rate constants associated with the pressure-time curves. This will allow corrections to be made in the rate constant for the appropriate step through the relation:

$$\frac{A_I}{A_{II}} = \exp \quad -(E_I - E_{II})/RT^* \qquad (11)$$

where A_I, E_I are known at the higher temperature from DSC data, E_{II} is obtained from the gassing data, and T* is the cross-over temperature.

CONCLUSION

We have presented an outline for using diverse forms of data to assess the thermal properties of energetic materials. The key elements in this method are summarized as follows:

1. Multistage reactions are modeled in conjunction with gassing, Henkin, and DSC data in order to obtain a comprehensive picture of a process which displays many facets in different temperature intervals.
2. The DSC is reserved to formulate a high temperature mechanism (above 100°C), from which cook-off data can be assessed in this region, while the gassing data provides supplemental information on possible mechanism changes in the lower temperature regions of practical interest.

3. The best way to obtain cook-off data for small-sized systems is direct measurement via the Henkin test. For large motor-size samples, one must use a combination of all the experimental methods.

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