Energetics

Testing Propellants by Calorimetry

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Fig 1. The French battleship "Liberté" destroyed by a propellant explosion in 1911.

The need to survey the stability and compatibility of explosives in general and propellants in particular is beyond discussion.

During the more than 100 years that nitrocellulose has been in use as a propellant, an enormous number of tests have been devised to survey its stabiliiy. The majority of these tests are rather simple and empirical in nature. During the last decade or so, however, modern analytical methods have been introduced in the explosives field, and are often used in parallel with older methods. Modern methods give real information about the components studied, but the translation of the result into terms of stability, compatibility and remaining stable life of the complex mixture of ingredients in a propellant is no easy task.

Propellants are among the least stable and most difficult explosives to analyse. The main component of propellants is the polymer is nitrocellulose, or, more precisely a deliberate mixture of nitrocelluloses with varying molecular weights and varying of degrees esterification. To determine the molecular weight distribution and also the degree of esterification of the different fractions is of course possible with modern methods. But to carry out such determinations with the high precision needed to detect the small changes associated with a dangerous deterioration of the propellant is a highly demanding task. To turn the determinations into simple routine tests is not possible today. This has led to the

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development of indirect tests of stability instead, such as the determination of stabilizer changes. While stabilizer changes are connected with the nitrocellulose degradation, not all reactions involved in the nitrocellulose decomposition affect the stabilizer. Furthermore the reactions involved are numerous and not fully established.

A way out of these difficulties is to measure the total reaction heat envolved by the different simultaneous and consecutive reactions in the propellant. This idea is not new, though it is not until now that it has become interesting due to the development of very sensitive calorimeters.

Already in 1883 Hess[1] in Germany proposed the study of heats of reaction for the estimation of the stability of explosives, but his equipment (Figure 2) was too crude, and used sample sizes of up to 100 g. Hess's technique was never used to any great extent. The English silvered vessel test is a later adoption of the same principle. In Germany, Siebert took up the method about 50 years after Hess and then inspired a coworker, Frey[2], to develop a microcalorimeter with specially designed sample holders. Van Geel[3] in Holland has also designed a calorimeter particularly for stability studies. The French Calvet calorimeter[4], [5], while constructed for general studies, has also been used for some years for the study of propellants and explosives.
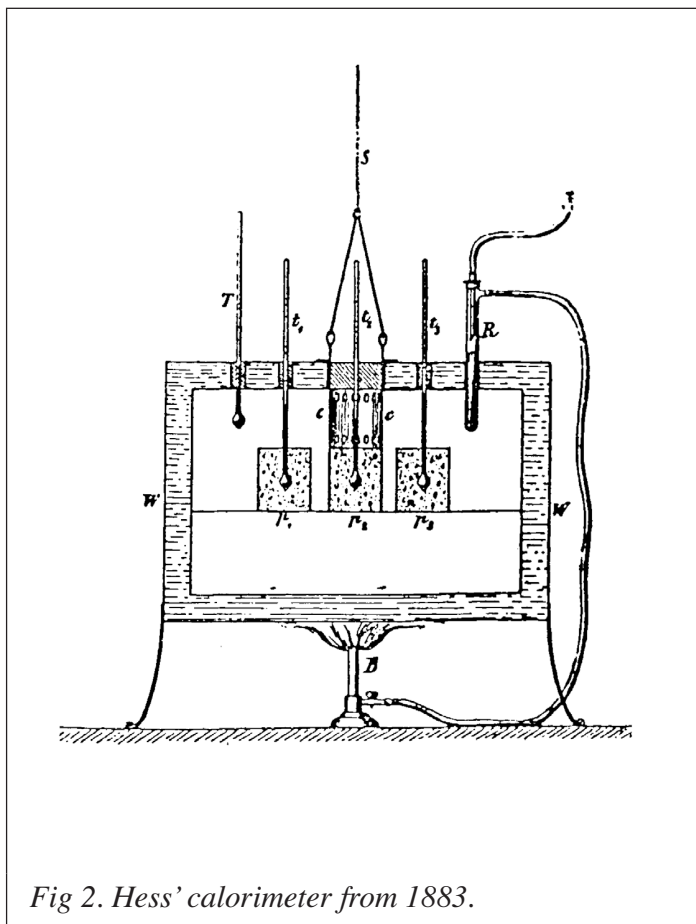

Fig 2. Hess' calorimeter from 1883.

The three last-mentioned calorimeters normally use 25—50 g samples and are mono-calorimeters, i.e. are designed for only one sample at a time. With the LKB 2277 calorimeter[6] used here the sample size can be kept down to 1 g, and four samples can be run at the same time, the latter being interesting for comparative tests. Even four parallell runs is a small number when testing propellants since the decomposition reactions are slow and therefore require long testing times. This necessitates intermittent measurements and storage of the propellants in an oven between runs. Such a procedure is of course much easier if the sample size is small reducing any danger of explosion or evolution of hazardous amounts of nitrogen oxides. Furthermore the LKB calorimeter attains equilibrium within 1 hr or less making it possible to measure initial reactions.

EXPERIMENTAL
Instrument

LKB 2277 Microcalorimetry System with four measuring cylinders. Thermostat bath temperature constancy: ±2 x 10^{-4}°C, according to specification. Measuring precision: ±2 % at the highest sensitivity, corresponding to a full scale deviation of 3 μW, also accord-

ing to specification.

Glass ampoules and stainless steel ampoules with an effective volume of 3 and 5 ml respectively were used. The glass ampoules were sealed with an aluminium cap and rubber and teflon packing. To confirm the tightness of the ampoules they were weighed before and after the runs. Both sample and reference ampoules show a certain weight decrease. The caps of the glass ampoule evidently give a weight loss of a little less than 3 mg that occurs quickly. In addition the sample ampoules give a weight loss through gas leakage of about 50 μg/day/g sample with the propellant used in the runs described here. A leakage of this order does not affect the measurements.

To minimize disturbances the ampoules were introduced into the measuring cylinders by lowering them stepwise over a period of 30 mins. It is probably possible to shorten this time without any disadvantage.

Propellant

A double-base propeltant with the following composition was used:

Nitrocellulose (13.1 %N)	59.6%
Diethyleneglycol dinitrate	39.0%
Ethylcentralite	1.3%
Graphite	0.1%

Reference substance

Fine glass beads dried over silica gel were used as a reference substance in order to give both sample and reference ampoules the same heat capacity. Precise agreement does not seem necessary.

RESULTS

Runs have been made in the range 60 ° C to 80 ° C at 5 ° intervals and with samples from 0.5 to 2.2 g. The registered power output is proportional to the mass of the propellant (see Figure 3).

Figure 4 shows the long-time behaviour of the propellant at 80°C. After an initial, relatively constant phase lasting about one day the heat output decreases to a minimum. There follows a slow increase of about 50–100 nW/g propellant/day. In the case illustrated here the power output had risen to 16.5 μW/g after somewhat more than 90000 mins.

Humidity has naturally a great influence on the degradation of nitrate esters and there-
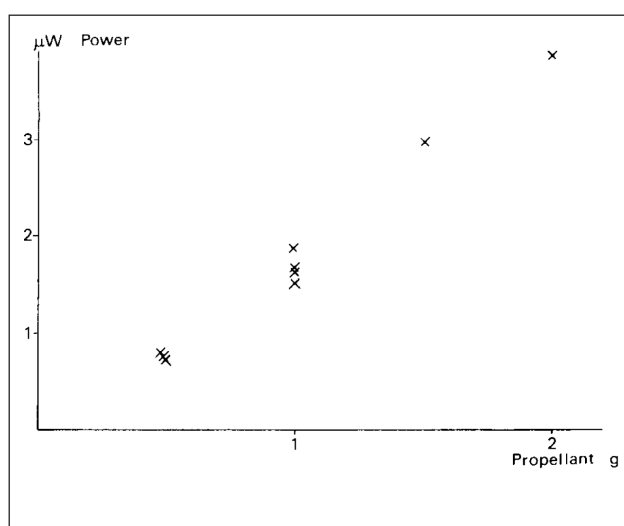

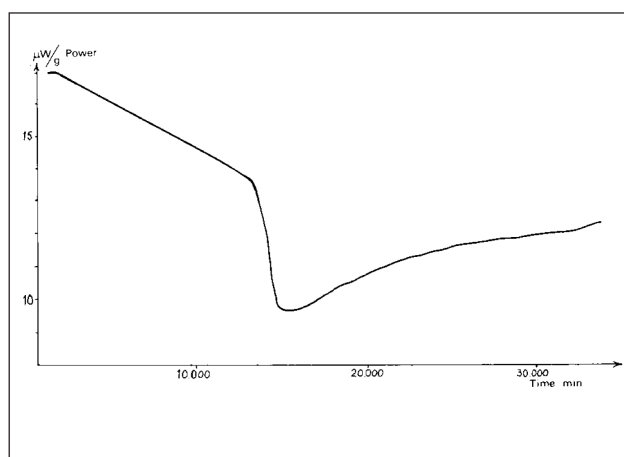Fig 3. Dependance of heat output on sample weight.

Fig 4. Long-time run at 80°C.

fore of propellants. Some runs were made with propellants that had been moistened at 52 % and 100 % RH and with samples dried in an desiccator over silica gel. These treatments cannot be expected to have changed the propellant grains homogeneously, but they affect the initial decomposition stages markedly. Higher humidity gives a higher power output and an earlier occurrence of the minimum. The dried sample shows an accelerating power output during the first two days. All the samples tend to reach the same value as the more or less surface-located changes caused by the preliminary treatments are smoothed out.

Fig 5. Influence of humidity on the initial decomposition stages.

Figure 6 Finally, shows an Arrhenius' plot of runs at five different temperatures between 60 and 80°C, from which an activation energy of about 26 kcal/mole can be calculated.

DISCUSSION

The evaluation of the calorimeter measurements depends on the problem they are used for. The simplest case is compati¬bility studies, not exemplified here, when the behaviour of a mixture can be referred to that of the simple components as standards.

When calorimetry is applied to the study of propellant stability, the ideal case is that concerning a propellant that has been studied a short time after its manufacture and its degradation followed until the end of the induction period. This renders an easy estimation of the remaining stable life possible at later occasions.

With no such initial measurements available, the case becomes more complex. Frey[2] integrates the effect until the end of the induction period, assuming a constant decomposition velocity. From measurements at different temperatures and by extrapolating the over-all reaction velocity to the storage temperature, one can estimate the remaining stable lifetime of the propellant.

Van Geel[3] uses a more complicated approach, which requires a great number of mea-
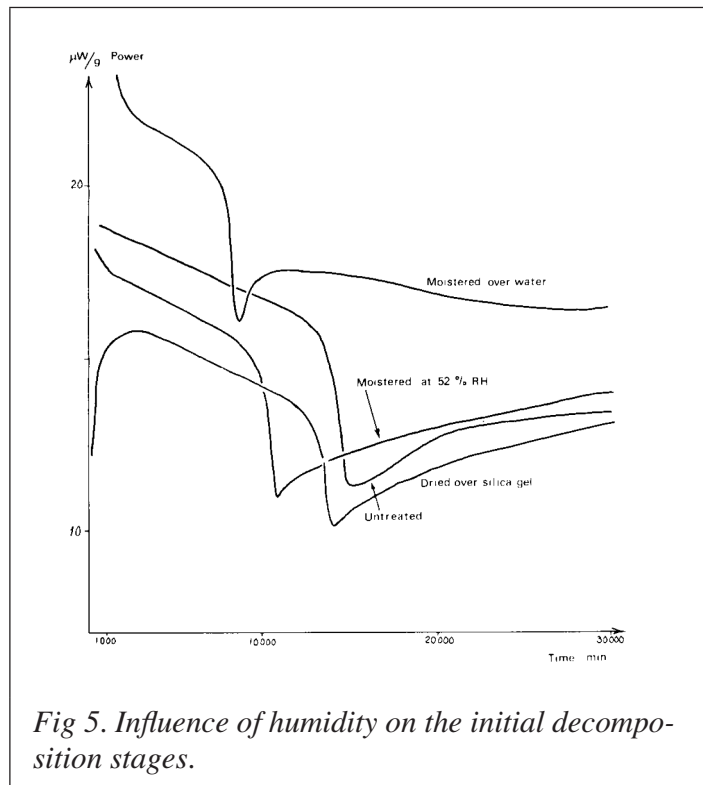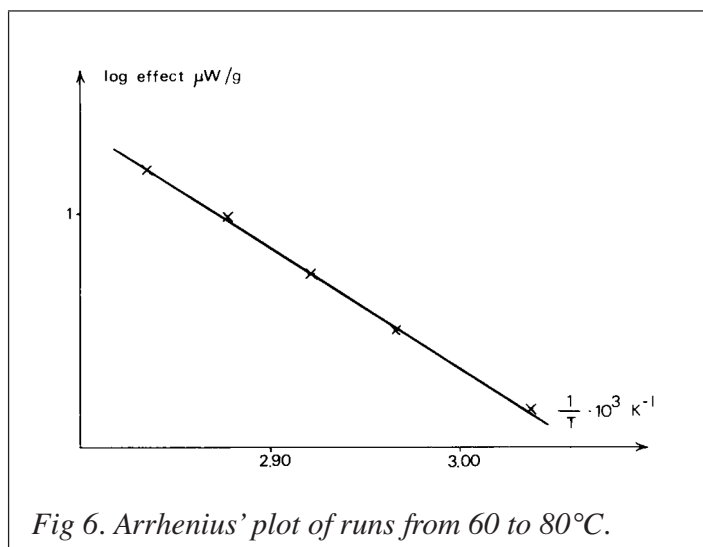

Fig 6. Arrhenius' plot of runs from 60 to 80°C.

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surements. From runs at different temperatures and the proposition

$$q = \frac{dQ}{dt}$$

where q is the power, and Q the total heat evolved by the propellant until time t, he derives activation energies, which he uses to calculate critical values according to Frank-Kamenetskii's thermal explosion theory.

The application of thermal explosion theory is, of course, of great interest and the theory in its simplest forms has been referred to widely. The practical cases, however, present some difficulties not taken into account by the simple Semenov and Frank-Kamenetskii theories, as the explosives or propellants are usually parts of irregular ammunition items and are always packed in boxes and are surrounded by different kinds of more or less heat insulating wrappings. An initial attempt to handle such problems has been made by Boddington, Griffiths, Scott and Hansson[7] and shows an important influence of packing materials on critical sizes, which should be taken into account when dealing with surveillance problems.

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Ampoule Microcalorimetry for Stability and Compatibility Testing of Explosives and Materials

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ABSTRACT

Microcalorimetry is a powerful tool for solving compatibility and stability problems for explosives and other materials. It is a very general method due to the fact that practically all physical and chemical processes are accompanied by heat exchange. The high sensitivity of the method makes it possible to carry out measurements at temperatures close to real conditions and to detect very slow (ageing) reactions. In compatibility studies, the heat flow is measured separately for the two materials and for a mixture of these. The experimental heat flow curve for the mixture is compared with a calculated hypothetical curve for the same mixture with no physical and chemical interactions. An interaction energy is defined as the time integral of the difference between these curves. Heat flow data, interaction energies and physical and chemical properties of the materials are considered in the interpretations. Three different compatibility problems are discussed.

Microcalorimetry yields information about the stability of propellants and high explosives. The heat flow is a measure of the decomposition rate. The difference in stability of a stabilized propellant and the same propellant without stabilizer is demonstrated. It is shown that the lowest decomposition rate that could be detected occurs at a temperature that corresponds to an autocatalysis time of approximately 25 years. Furthermore, microcalorimetry could be used for stability testing of pyrotechnics. An example concerning the oxidation of boron in a pyrotechnic igniting composition is presented. Quantitative considerations show that this oxidation process may become an important ageing effect after long time storage in open air.

INTRODUCTION
Compatibility

High explosives, propellants and pyrotechnics for ammunitions, missiles and similar products are usually exposed to a variety of other materials, e.g. plastics, adhesives, sealants and metals, either by direct contact or via the atmosphere within the product. It is of vital importance that all materials are compatible, i.e. that they do not interact chemically or physically with each other in the product under consideration. Such interactions may give rise to misfunction or safety hazards in handling or reduced shelf life. There is usually a large number of possible material com¬binations, and consequently a multiplicity of different types of possible interactions with a wide range of reaction rates. A suitable analysis technique for com¬patibility studies must therefore be very "general" and also very sensitive. In this paper we show that microcalorimetry is a powerful technique that

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meets these requirements. The generality of the method follows from the fact that practically all physical and chemical processes are accompanied by heat exchange.

The high sensitivity of microcalorimetry to these reactions offers some important advantages compared to standard compatibility testing methods like vacuum stability test (1), DTA (2) and weight loss tests (3):

1. Measurements can be carried out at lower temperatures than used in standard methods. Transformation of the results to normal temperature conditions will thus be more realiable.

2. It is possible to detect even very slow reactions. "Long-term" incompatibility, i.e. interactions of very low rate between materials, that affect safety or functions of a product after several years of storage, may thus be predicted.

Stability

Microcalorimetry is also a suitable method for stability studies of explosives (4, 5) where the heat produced in the decomposition of the materials is measured. Again, the high sensivity of the microcalorime-ter makes it possible to use lower measuring temperatures than employed in e.g. the vacuum stability test. Rate constants, activation energies and other kinetic parameters could thus be obtained for temperatures very close to real conditions.

In order to illustrate the versatility of microcalorimetry in the field of explosives, we present results for a number of stability and compatibility problems representing different physical and chemical conditions. All examples are chosen from routine investigations of explosives and materials.

EXPERIMENTAL

A prototype of a LKB Multi-channel Microcalorimetry System 2277-020 equipped with four ampoule calorimeters 2277-201 was used in this work. All measurements were made at 70°C. The instrument was connected to a minicomputer (ABC 80) in order to facilitate data collection, evaluation and curve plotting. The computer software was developed at AB Bofors, Karlskoga, Sweden.

All materials were used as received, unless otherwise specified. Approximately 1 gram of the samples were packed in 2.5 ml glass ampoules, which were sealed with a glass disc and a UV-curing adhesive (Loctite 358). This sealing technique yields a very tight ampoule with a minimum of polymeric sealant present. 1.5 grams of high purity sea sand was used as the reference sample.

Heat flow data were recorded either continuously or as "single point" measurements. In the former case, the samples were kept in the calorimeter throughout the experiment, and the heat flow was recorded by the computer at fixed time intervals. The "single point" technique was applied to experiments of long duration. In this method, the ampoules were stored in an oven at 70 °C between each measurement point.

All results have been normalized to unit sample weight.

RESULTS AND DISCUSSION
Compatibility studies

Anaerobic adhesives and sealants are frequently used in ammunition, missiles and similar products. These materials contain reactive peroxides and acrylic esters, which could interact with various explosives. A compatibility study of the system Loctite 270/single base propellant (16/84 wt%) is shown in fig. 1.

Curve A represents the heat flow of the propellant alone. Its slightly exothermic behaviour is discussed in detail in a subsequent example. The pure (uncured) Loctite 270,

curve B, has an initial heat production of about 40 μW per gram, which levels off gradually. This heat is ascribable to a slow curing reaction, which is effectively suppressed through interference with the oxygen in the ampoule. Curve C is a calculated theoretical heat flow curve for a 16/84 mixture of adhesive and propellant with no chemical or physical interaction between the components ("non-interaction curve"). It is simply a 16/84% linear combination of B and A. The experimental behaviour of the mixture is illustrated by curve D, which differs markedly from curve C, indicating a certain level of interaction
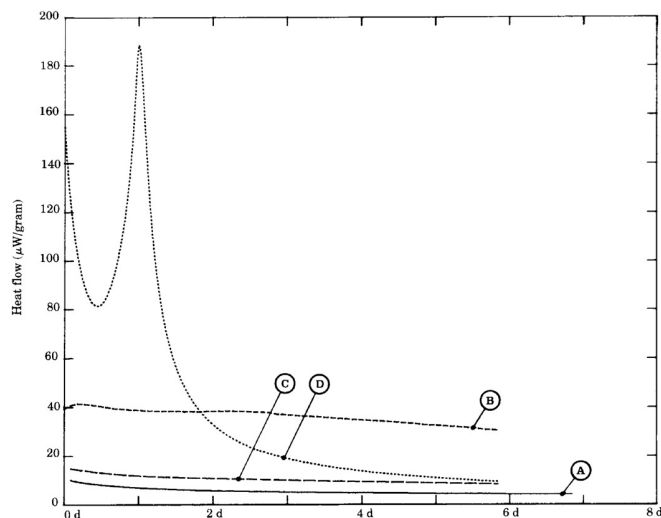

Fig. 1. Calorimetric curves for the system Loctite 2701 single base propellant. (A) propellant, (B) uncured Loctite 270, (C) and (D) "non-interaction" and experimental curves, respectively, for a 16/84 wt% mixture of Loctite and propellant.

between the materials. There are two distinguishable interactions responsible for this discrepancy. First, the sharp peak after approximately 1 day is identified as a complete curing of a small fraction of Loctite, located in the perforations in the propellant grains, and thus protected from exposure to oxygen. Secondly, the shape of the rest of curve D is typical for an absorption process, in this case presumably swelling of the nitro¬cellulose in Loctite. The initital sorption rate is high due to large concentration gradients in the nitrocellu¬lose, but it decreases gradually when the system approaches equilibrium swelling. It is not possible to establish the existence of any chemical interactions accompanying the absorption.

However, the merging curves C and D show that there are no long-term chemical effects of importance in the system.

Integration of the difference between curves D and C with respect to time yields the interaction energy shown in fig. 2.

Interaction energies often provide valuable information about the type of interaction. The curing and "absorption" energies amount to approximately 5 and 10 J/g of mixture, respectively. The former is in good agreement with the calculated curing energy for the small volume of
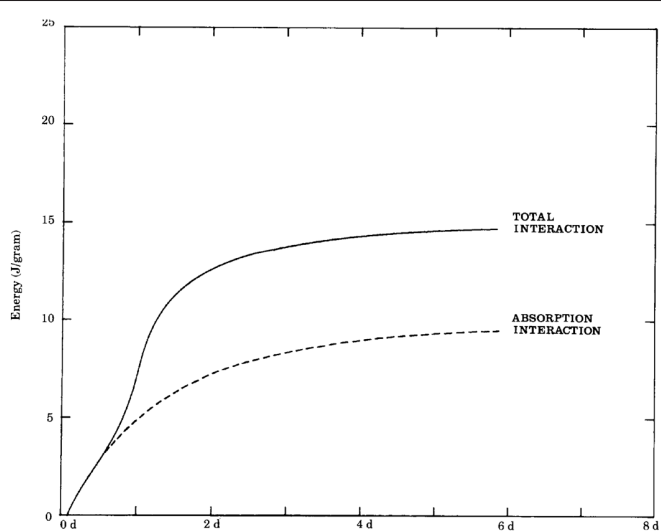

Fig. 2. Interaction energy vs. time for the Loctite 270/ single base propellant system. The dotted line is the estimated curve for the absorption process alone.

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Loctite in the perforations (3-4 J/g), and the latter corresponds to approximately 7 kJ/mole of nitrocellulose (monomer), which is a typical value for a physical absorption process rather than a chemical reaction.

Swelling effects and Loctite curing in perforations are phenomena that clearly affect the mechanical and burning characteristics of the propellant. Strictly according to the definition, the materials should there¬fore be classified as incompatible. We consider however, that this "functional" incompatibility is of little practical importance as long as minor amounts of the adhesive is used. Furthermore, no direct safety hazards are expected when the components are mixed, as indicated by the limited degree of interaction.

Fig. 3 shows a compatibility study of a polyamide (50% glass fiber reinforced)/single base propellant system. In conformity with the first example, a non-interaction curve (dotted line) has been calculated for a 10/90 wt% mixture of finely ground polyamide and propellant. The corresponding experimental curve (C) is about 4 μW higher. This may look like a fairly weak interaction, but it is nevertheless important as it is practically constant over a long period of time. A considerable part
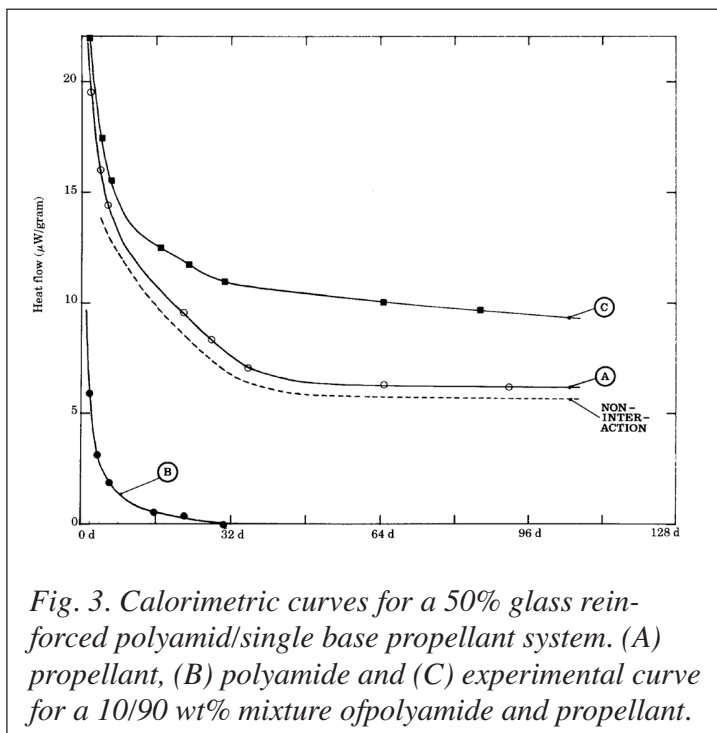

Fig. 3. Calorimetric curves for a 50% glass reinforced polyamid/single base propellant system. (A) propellant, (B) polyamide and (C) experimental curve for a 10/90 wt% mixture ofpolyamide and propellant.

of this interaction is supposed to take place in the polyamide between the amide groups of the polymer and propellant stabilizers absorbed by the polymer. A separate weight test has shown that the polymer increases its weight by 0.7% due to absorption of stabilizers. The stabilizer is a mixture of several nitro derivatives formed during the reaction with NOX in the propellant. In a previous study (5) we have shown calorimetrically that nitro groups may react strongly with amide functional groups. The interaction energy of the first 100 days amounts to approximately 600 J/g of polymer or 150 kJ/mole of monomer. This energy magnitude would correspond to a more or less complete degradation of the polymer if the interaction was mainly arising from a polymer backbone scission process. Since important changes in mechanical properties normally appear after only a few percent degradation, the polyamide must thus be considered as incompatible with this particular propellant.

Stability tests

As mentioned in the introduction, the microcalori-metric method could be used for stability testing of explosives. Some examples are shown in fig. 4.

Curve A represents a standard single base propellant. After approximately 4 days the propellant reaches a steady state at about 3 μW/gram at 70 °C. The heat production arises from the complex decomposition of the nitrate ester and the subsequent reactions between the liberated NOX gas and the stabilizer(s). The initial higher exotherm is presumably caused by interference with oxygen plus a number of equilibration processes when the sample temperature is raised from ambient to 70°C. The NOX concentration increases in

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the propellant when the stabilizer is gradually con¬sumed. This has a catalytic effect on the decompositions rate, and the heat production increases rapidly (autocatalysis). The phenomenon is clearly illustrated by curve B, which represents the same propellant without stabilizer. The catalyzed decomposition becomes evident after only 50 days, while there is practically no sign of increased rate during the first four months for the stabilized material.

The rate constant for the decomposition of a propellant is approximately changed by a factor 3 per

Fig. 4. Calorimetric curves illustrating the decomposition of a single base propellant (A) with and (B) without stabilizer. (C) represents a nitro compound (RDX).

10°C (6). Since the sensitivity of the microcalorimeter is approximately 0.1 μW, it would thus be possible to measure the stability of the propellant in fig. 4 at least at 60°C and possibly even at 50°C, if statistical evaluation methods are employed. The time to autocatalysis for this propellant at 50°C, if statistical evaluation methods are employed. The time to autocatalysis for this propellant at 50°C is typically 25 years. The fact that it is experimentally possible to measure such a slow degradation process with some accuracy clearly demonstrates the excellent sensitivity of the instrument.

For comparison, the heat flow curve of a nitro compound (RDX) is also shown in fig. 4, curve C. This material has a negligable heat production, which indicates a very good stability at 70°C. A similar result has previously been obtained for a TNT sample (5).

Boron is frequently used in pyrotechnic compositions as a reducing agent. The pure material is readily attacked by oxygen (5), forming a layer of B_2O_3 on the surface. The large enthalpy of oxide formation (AH = -1262 kJ/mole) is of course favourable for calorimetric measurements, especially at low oxidation rates. An example of an oxidation process at 70°C in a consolidated igniting composition containing boron is presented in fig. 5.

Curve A represents the sample when exposed to a dry oxygen atmosphere in the ampoule. 3 hours after insertion in the calorimeter, the heat flow reaches a maximum at nearly 1400 μW/gram, followed by an immediate rapid decrease. Curve B illustrates an identical sample under dry nitrogen conditions. This curve exhibits only a small peak, probably due to an oxygen residue present in pores in the sample, or adsorbed on the surface of the components. Integration of the O_2 curve from 0 to 4 days yields a reaction energy equal to 62 J/gram, which corresponds to an oxygen consumption of 1.7 ml. This is approximately equal to the volume of O_2 in the ampoule, i.e. all oxygen has been used in the oxidation process. The heat flow would probably have continued at a high level if an unlimited quantity of oxygen had been accessible to the sample (a flow system must be used to verify this assumption).

A simple calculation shows that a constant heat flow equal to 1400 μW (= peak height) would correspond to oxidation of approximately 1% of the boron per day in O_2 at 70°C. The time for a 1% oxidation in air at room temperature would roughly be 1.5 years. Oxidation of 5-10% of the boron is probably sufficient for unacceptable changes in the
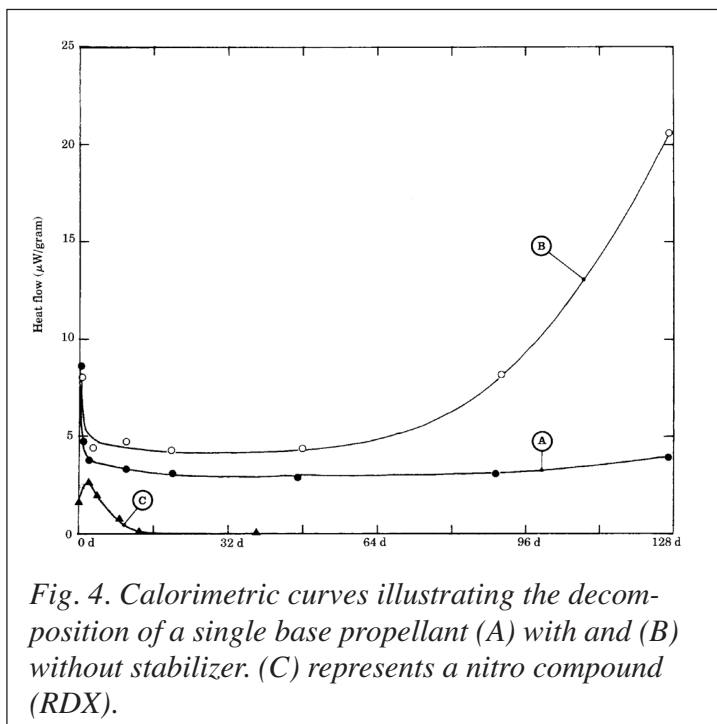
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burning characteristics of the igniting composition. This shows that oxidation processes could be an important ageing factor under special environmental conditions.

CONCLUSIONS

Microcalorimetry is a very general method that could be applied to a variety of compatibility and stability problems of different physical and chemical natures. It offers an excellent sensitivity, which is indispensible e.g. for measurements of propellant decomposition rates at low temperatures and for establishment of long-term incompatibility between materials. In compatibility testing, heat flow data are used together with calculated interaction energies and physical and chemical considerations in the interpretation of in¬teraction phenomena. The microcalorimetric method is also well adapted for studies of oxidation and other surface reactions in pyrotechnic compositions.
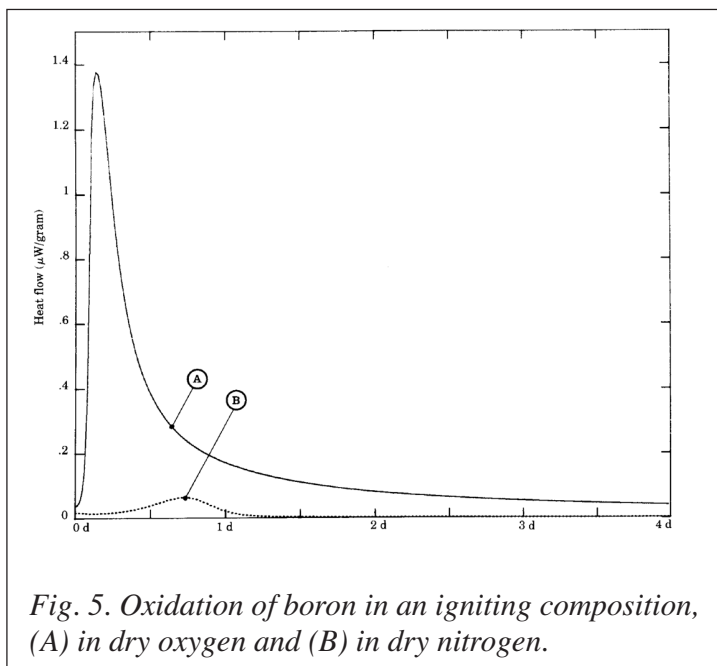

Fig. 5. Oxidation of boron in an igniting composition, (A) in dry oxygen and (B) in dry nitrogen.

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Ampoule Microcalorimetry for the observation of the Curing Process of an Acrylate Binder in a Pyrotechnic Composition
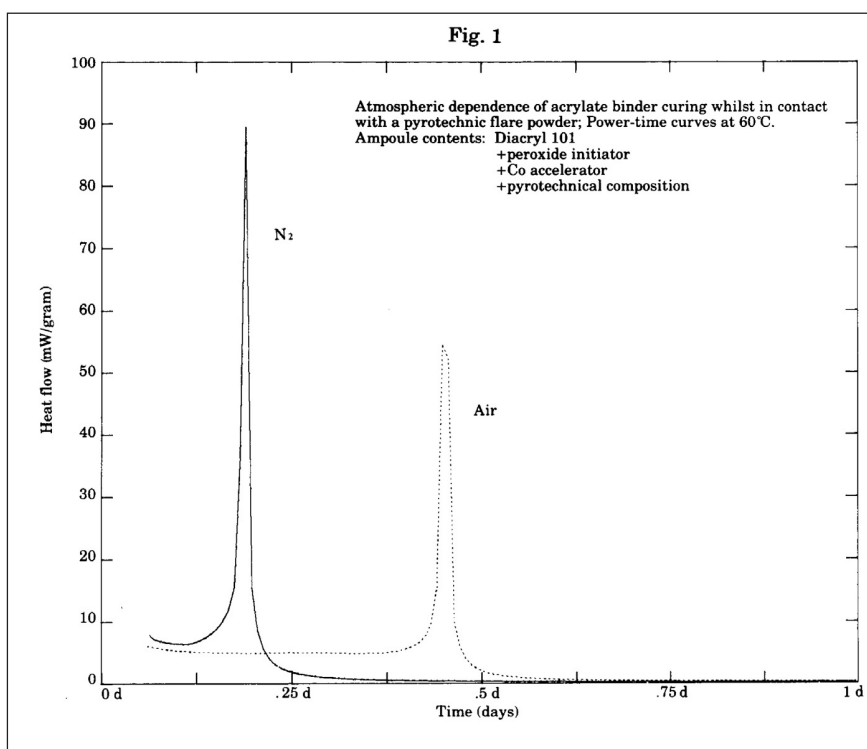
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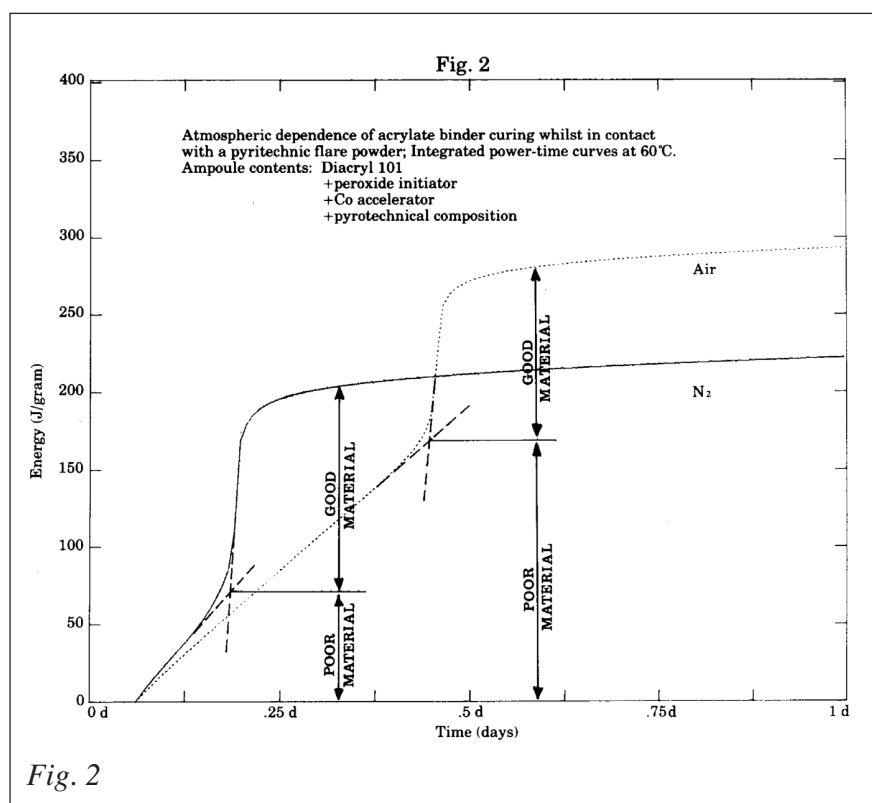Per E. Lagerkvist
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The problem concerned the curing of an oxygen sensitive acrylate binder used in a pyrotechnic flare composition. Since the aerobically cured adhesive was known to give a poor quality bond, it was necessary to assess the progress of the anaerobic and aerobic curing processes in order to optimise production. From the two power time curves (Fig. 1 and 2) it can be seen that curing is rapid once all the oxygen in the sealed ampoule is consumed.

The exotherms prior to the main curing peaks reflect oxygen interference with the curing reactions, which lead to the formation of peroxide links in the polymer. Such links contribute to the poor mechanical properties of the material.

If a nitrogen atmosphere is used, this oxygen is residual and absorbed on the flare composition grains, hence the shorter lag before curing. From the integrated curves (Fig, 2) it is obvious that the fraction of poor polymer is considerably reduced upon the exclusion of atmospheric oxygen.

Fig. 1

Atmospheric dependence of acrylate binder curing whilst in contact with a pyrotechnic flare powder; Power-time curves at 60℃.
Ampoule contents: Diacryl 101
   +peroxide initiator
   +Co accelerator
   +pyrotechnical composition

Fig. 2

Fig. 2

Atmospheric dependence of acrylate binder curing whilst in contact
with a pyritechnic flare powder; Integrated power-time curves at 60°C.
Ampoule contents: Diacryl 101
+peroxide initiator
+Co accelerator
+pyrotechnical composition

Stability Predictions for the Autocatalytic Decomposition of Nitrocellulose in Toluene

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INTRODUCTION

Nitrocellulose with toluene diluent is preferred for the manufacture of furniture coatings and priming inks. However, it is known that replacing the normal alcohol diluent with toluene decreases stability. A number of warehouse fires occurred during storage of the toluene-wet material. Programmed DSC and DTA experiments are normally used to obtain stability data for such energetic materials. However these techniques cannot be used to evaluate the reaction hazard of this system. The use of highly sensitive isothermal microcalorimetric methods were necessary to determine the exact nature of the reaction at close to normal storage conditions.

EXPERIMENTAL

A 2277 Thermal Activity Monitor (TAM) was used for isothermal microcalorimetric measurements between 60 and 75°C. DSC runs were also made on the samples.

STABILITY CALCULATIONS

Plots of times-to-peak and maximum heat rates versus 1/T allowed the calculation of the Arrhenius activation energy, Ea. The maximum safe reactant dimensions (r) for various ambient temperatures (T) and related peak heat rates (q) were then determined using values for Ea, critical shape factor (δ), concentration (C), and thermal conductivity (K), in a form of the well-known Frank-Kamenetskii heat balance equation:

$$r^2 = (\delta\ K\ R\ T^2)/(C\ q\ Ea)$$
where R is the gas constant.

RESULTS AND DISCUSSION

DSC experiments showed single, high temperature decomposition exotherms which could not be related to storage stability (fig 1). In contrast, isothermal microcalorimetric data showed the presence of a low temperature autocatalytic reaction (fig 1). The times to peak height at different temperatures are shown in table 1. The sudden release of the autocatalytic reaction heat was enough to trigger a runaway of the high temperature decomposition reaction. Additional experiments showed that water was not tightly bound to the nitrocellulose and that the water readily migrated from warmer to cooler zones in the container. This subsequently would tend to keep the preparation safe. However, in production lots with higher water and acidity levels, the autocatalytic rate could exceed the water loss rate and the migration mechanism would no longer be protective.
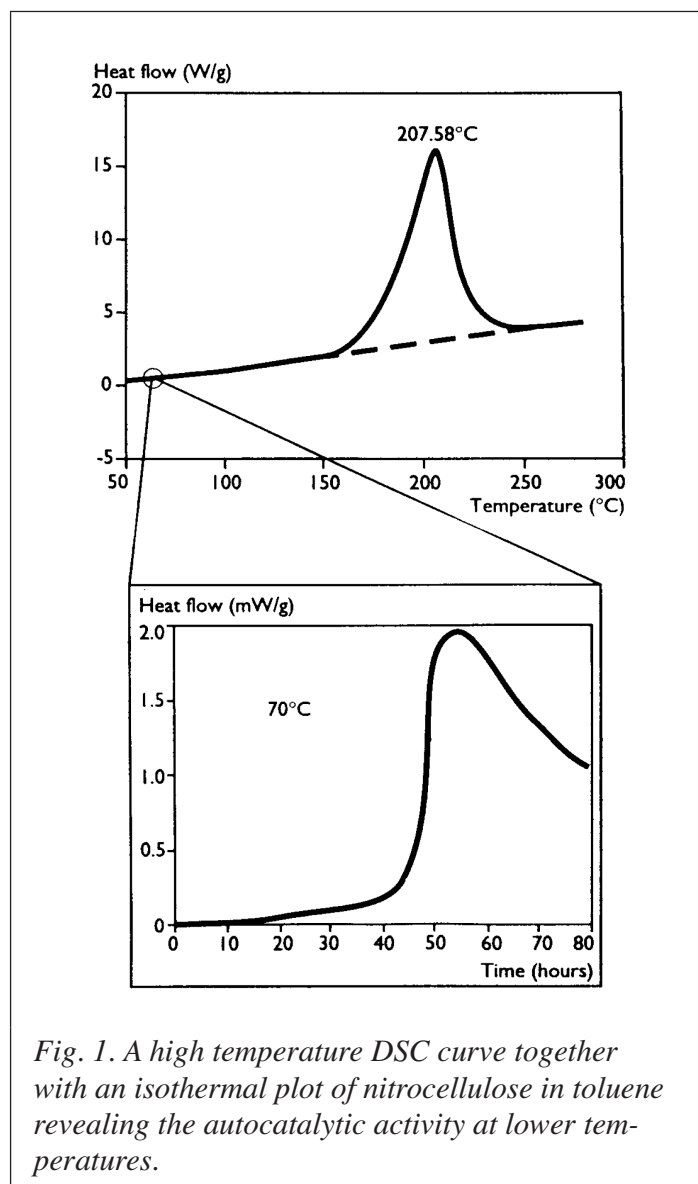
Fig. 1. A high temperature DSC curve together with an isothermal plot of nitrocellulose in toluene revealing the autocatalytic activity at lower temperatures.

Temperature	mWatts/g	Peak Times, Hours
60 °C	880	118.00
65 °C	1500	70.25
70 °C	2600	41.25
75 °C	4500	24.00

CONCLUSION

DSC experiments, while showing the main decomposition exotherm, could not be used to study the autocatalytic reaction responsible for nitrocellulose instability. Indeed, data from isothermal heat conduction microcalorimetry were necessary for determining the product specifications leading to safe storage of toluent-wet nitrocellulose.

NOTE

This application note was written by A. Duswalt (Hercules Inc) and M. Shafiq

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A Microcalorimetric Study of Powder Surface Energetics

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INTRODUCTION

The surface energetics of a powder plays an important role in the ease of preparation, stability and dissolution of pharmaceutical products. Existing techniques for assessing surface energetics of powders (i.e. liquid penetration and contact angles) suffer from practical and theoretical limitations as well as being somewhat subjective.

The objective of this study was to evaluate the data obtained by microcalorimetric techniques from which ΔH and other kinetic parameters of adsorption can be determined. Results were supplemented by data obtained by vacuum microbalance methods.

EXPERIMENTAL

Measurements of the enthalpy of adsorption (ΔH) were undertaken using an LKB 10700 microcalorimeter. A specially constructed calorimeter cell was connected to a vacuum pump and water reservoir. A series of powders was placed in the cell, outgassed and weighed quickly to allow minimal adsorption from the atmosphere. The powders were then assayed under repeated adsorption/desorption experiments in the microcalorimeter. It is important to note that 2277 Thermal Activity Monitor, TAM, the successor to the LKB 10700 has now been used in such studies.

RESULTS
Enthalpy of adsorption

This was calculated by subtraction of the heat flow produced by control experiments and corrected for moles of water adsorbed.

Gibb's function and entropy of adsorption

The standard state is assumed to be the number of moles of water adsorbed [b] per gram of powder at saturated vapour pressure [p] of water. The equilibrium constant is thus defined as:

$k_{ad} = [b]/[p]$

The Gibb's function is obtained by: $\Delta G = -RT\ln k_{ad}$
The entropy of adsorption can then be obtained from:
$\Delta G = \Delta H - T\Delta S$
The thermodynamic parameters are shown in Table 1.

Kinetics of Adsorption

The experiments conducted in this study can be regarded as batch experiments, the excess heat output decay function can thus be compared to the decay from an electrical

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calibration peak. The logarithm of the difference in area under the heat flow curve compared to the calibration curve plotted against time, can give an indication of the kinetics of the reaction; the gradient being equal to the apparent first-order rate constant.

DISCUSSION

Previous studies have shown that the use of contact angles for the determination of ΔG and subsequent calculations of ΔS for wetting processes are not suitable. Microcalorimetric techniques coupled with data from the vacuum microbalance have shown it is possible to obtain direct measurements of ΔH for the adsorption process, and ΔG from a single adsorption isotherm. The combination of methods therefore allows the study of small changes in powder surface energetics which affect the adsorption process.

Values of ΔG were the same for each powder because the same amount of water was adsorbed (Table 1). However, ΔH values were found to differ significantly between each of the powders. Liquid penetration data showed the ranking of powders in terms of hydrophobicity to be different to results from microcalorimetric techniques. Furthermore, microcalorimetric data revealed that wetting of the more hydrophobic powders was enthalpically favoured and this was associated with a large unfavourable entropy term. Thus, previous predictions on the wetting process using enthalpy data derived from classical methods of analysis may not be completely accurate.

Powder	Quantity of Adsorbed Water (mg/10,000 mg)	ΔH_{cal} (kJ - mol⁻¹)	ΔG (kJ - mol⁻¹)	ΔS_{cal} (J - mol⁻¹, mol⁻¹)	ΔH_{iso} (kJ - mol⁻¹)	ΔS_{iso} (J - mol⁻¹, mol⁻¹)
Amylobarbitone	0.080	-25.5	+38.4	-214.4	-66.8	-353.0
Pentobarbitone	0.080	-12.7	+38.4	-171.5	-67.5	-355.4
Phenobarbitone	0.074	-8.1	+38.6	-156.7	-65.2	-348.3
Butobarbitone	0.080	-4.5	+38.4	-144.0	-61.4	-334.9

Table 1. The thermodynamic functions of adsorption at 25°C

CONCLUSION

The combination of microcalorimetric and vacuum microbalance techniques allows the possibility of calculating the thermodynamic parameters associated with the wetting process and in addition, gives insight into the mechanism of wetting.

REFERENCES
1. G. Buckton and A.E. Beezer. *International Journal of Pharmaceutics* 41:139-145 **(1988)**

NOTE
Application Note written by M. Shafiq, Thermo-Metric AB.