Predicting DSC Measurements: Preliminary Work

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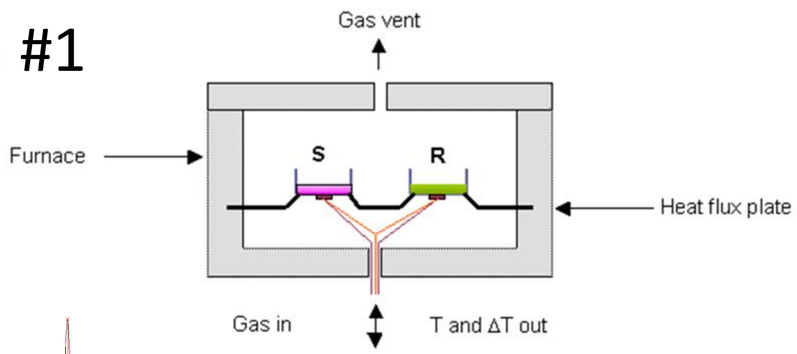
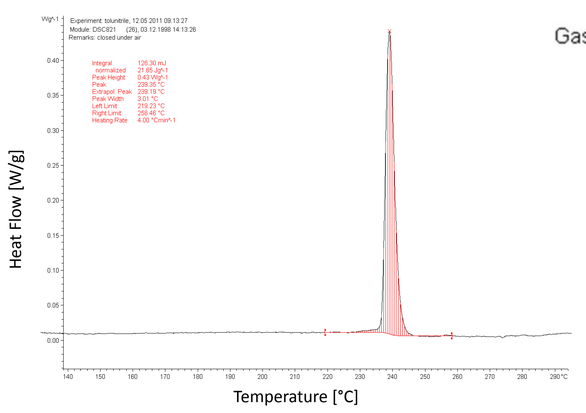
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

DSC Lesson #1





1. Submit sample to heating
2. Compare sample vs reference ΔT
3. Obtain heat flow
4. Analyse it

Purpose of the work

The purpose of this work is to predict DSC thermograms. This requires knowing:

1. The factors that influences DSC measurements
2. How to characterize a thermogram

1. Assessing which parameters influence the DSC measures will allow:

→ Better understanding of thermograms

→ More accurate analysis and interpretation

→ Future experiments on optimal conditions for particular investigations

2. Characterizing properly the thermograms will allow:

→ Extracting more information

→ Performing fittings and predictions of thermograms

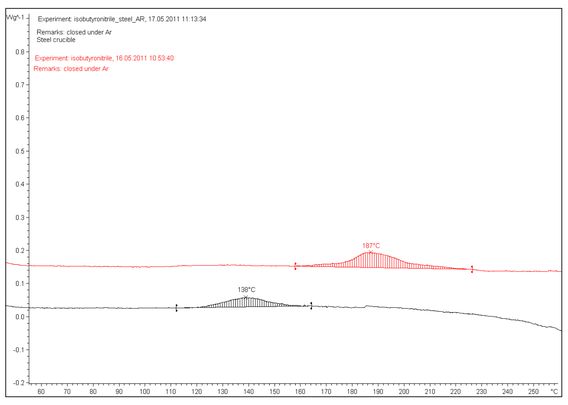
The various parameters and their effects:

1. Experimental Factors

1.1. Coating Material:

Gold (in red) vs Steel (in black)

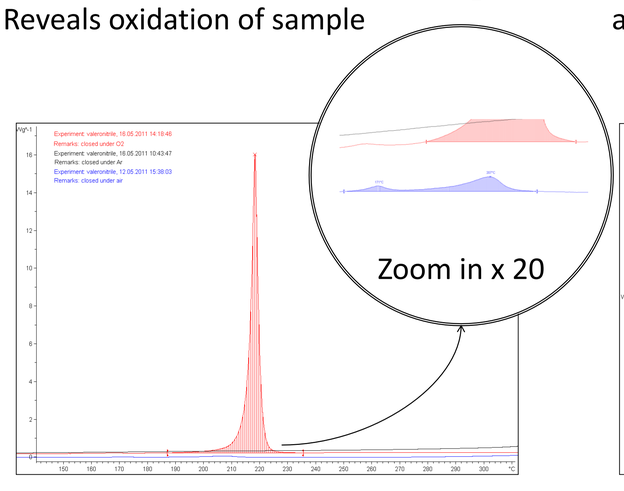
Possible catalytic effect revealed by peak shift



1.2. Atmosphere within crucible

Thermograms for pentanenitrile enclosed under air (in blue), Ar (black), and O_2 (red):

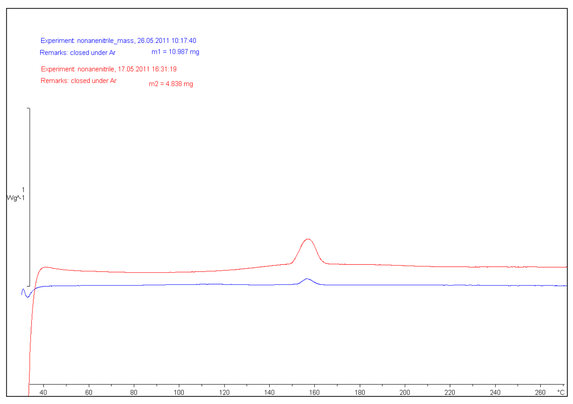
Reveals oxidation of sample



1.3. Sample Weight

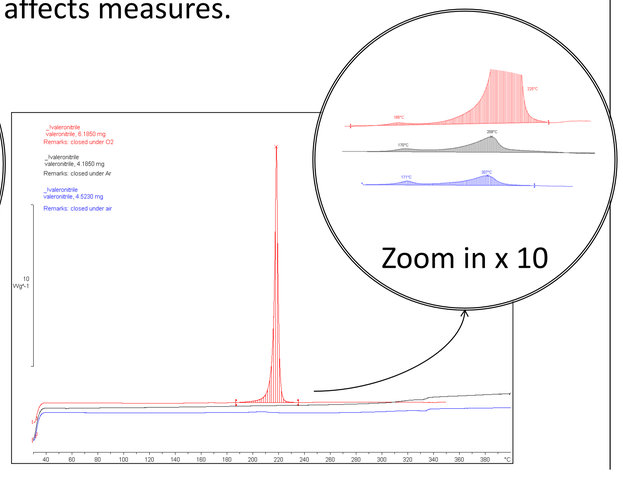
Reaction enthalpies calculated relative to sample mass. High masses can blur results.

No noticeable temperature shifts.



1.4. Pressure

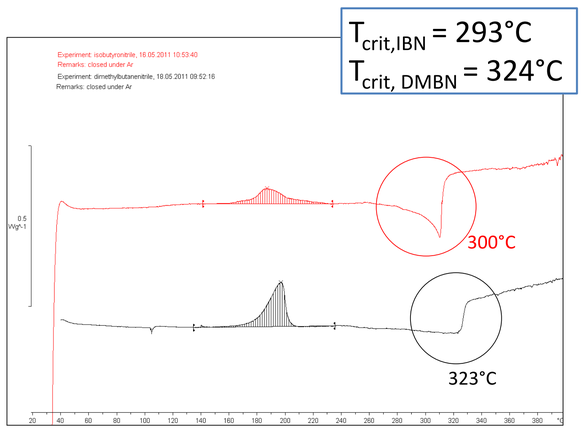
If compounds react to enclosing atmosphere, pressure shifts the equilibrium, and thus affects measures.



2. Physico-Chemical Factors

2.1. Critical Point

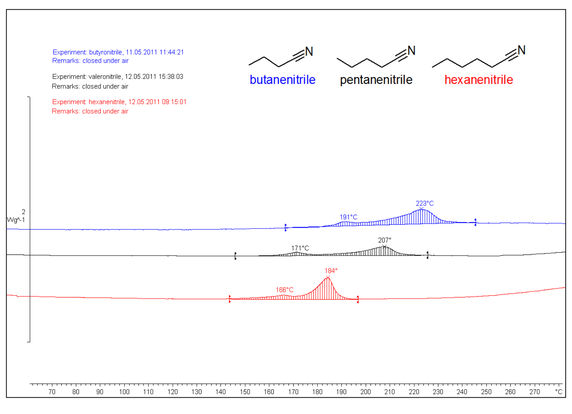
Shifts in baseline due to sudden change of Cp at $T \approx T_{crit}$.



2.2. Molecular Structure: Chain Length

Thermograms for butane-, pentane- and hexanenitrile

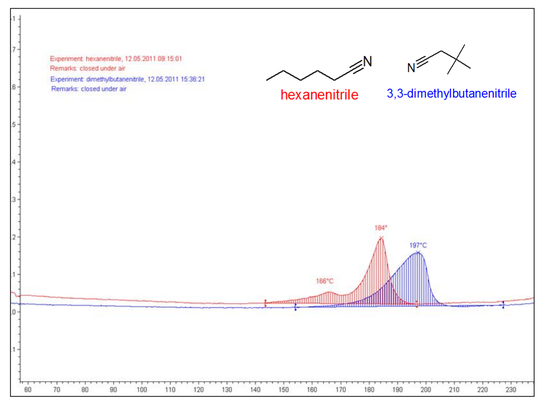
Longer chain = similar reactivity, lower T_{onset}



2.3. Molecular Structure: Branching

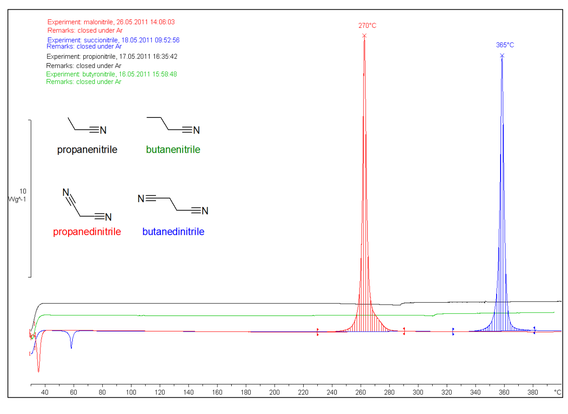
$C_6H_{11}N$ isomers present different thermograms

Branching enhances thermal stability



2.4. Molecular Structure: Number of Functional Groups

Different shape and T_{onset} reveal different reactivity

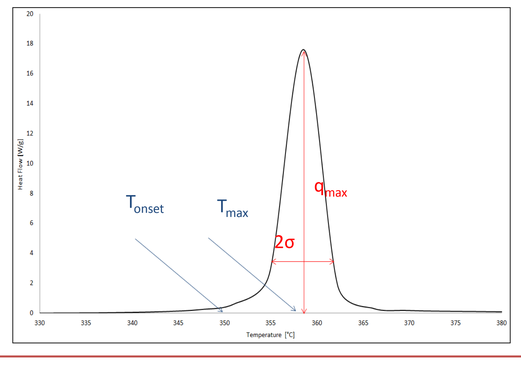


Fitting & simulating a thermogram

Principal properties that describe DSC thermogram:

→ T_{onset}, T_{max}, peak height and width

→ Area under the curve



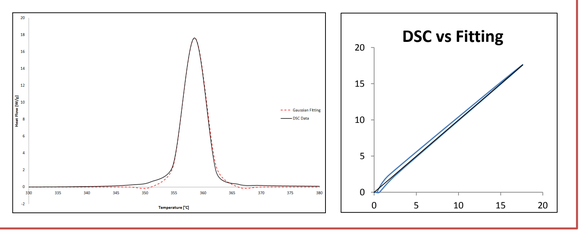
To simulate this peak use a Gaussian curve:

$$f(T) = h \cdot \exp\left(\frac{-(T - T_{max})^2}{2\sigma^2}\right)$$

Results:

Simulation fits thermograms properly

→ R^2=0.996



Conclusions & Outlook

- Study of the influences of 8 parameters on DSC due to

→ Experimental conditions

→ Physico-Chemical properties of compounds

- Simulation of DSC thermograms with known mathematical model

Future work: To develop QSPR-models describing DSC thermograms

References:

http://www.anasys.co.uk/library/dsc1.htm

A. Felinger: Data analysis and signal processing in chromatography

M.E. Brown: Introduction to thermal analysis

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Preliminary Work

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Keywords: Differential Scanning Calorimetry (DSC), Predictions, DSC- influencing Parameters, Fittings.

Most of the industrial chemical compounds are in a metastable state and might decompose, releasing significant amounts of energy. Therefore, a deep knowledge of the reactions' characteristics is required in order to properly assess the process risks and design suitable safety measures that are to be taken to minimize the related hazards. The energy and the kinetic of a decomposition reaction can be determined experimentally by different thermal analysis methods. The presented work is based on Differential Scanning Calorimetry (DSC) experiments.

The output of a DSC measurement is a thermogram from which several key information can be taken such as the onset temperature at which a thermal event starts, the heat release or consumption due to that event, the peak temperature (temperature of maximum heat flux). All these parameters allow assessing the thermal stability of the considered compounds. However before doing so, two preliminary questions shall be answered:

1. Which factors influence these parameters acquired from DSC measures?
2. If these parameters are available, how can the thermogram be modeled?

In the first part of the presented work, the influence of four experimental factors (i.e. coating material, sample mass, sealing atmosphere and pressure) and four physico-chemical factors (i.e. critical point, branching, alkyl chain and functional groups) are detailed.

Here are some observations that were interesting to note: the coating material of the crucibles should not react with the sample or catalyze its decomposition; the sample weight can affect the results due to accuracy loss because of a change in the heat transfer area; the atmosphere under which the crucibles are sealed can have a crucial role if the compounds react with it (observed oxidation instead of thermal decomposition). Besides, it was also noticeable that when reaching critical point, the heat capacity would suffer a sudden change revealed by baseline shifts.

Finally, some molecular structure characteristics seem also to have important influence on the DSC, as for example the alkyl chain length, the branching or the number of functional groups.

In the second part, the possibility to fit thermograms with known mathematical models was investigated. It appears that in order to approximate a DSC peak by a Gaussian curve, only three characteristic values are required: the peak height (q_{max}) and the position of its maximum (T_{max}), and the standard deviation (σ). Even though the Gaussian equation is not the optimal model to describe complex peaks, the fittings are satisfactory and present results that correlate well to the experimental data for simple DSC thermograms.

Finally, it can be concluded that for predicting DSC thermograms, QSPR -models are to be built in order to determine these three parameters (q_{max}, T_{max}, and σ) using results obtained from DSC measurements. The conditions of these DSC measurements are to be set wisely in order to avoid any external influence or blurring of the actual thermal stability of the considered compounds.

This kind of prediction would represent a useful 'desktop method' in chemical hazards assessment as it could offer an easy manner for first evaluation before complete experimental investigations.

References:

[1] Anasys Thermal Method Consultancy, Introduction to DSC and DTA, http://www.anasys.co.uk/library/dsc1.htm

[2] A. Felinger, Data analysis and signal processing in chromatography. *Elsevier,* 1998. 5-43, 114-119.

[3] M.E. Brown, Introduction to thermal analysis, Techniques and Applications. *Kluwer Academic Publishers,*1987. 55-89.