

# Thermal Analysis

Combined analysis using a variety of methods is now common in industry

This presentation discusses

Applications of TGA combined with other methods, MS, DSC, and FTIR

**NC State University**

# Thermal Analysis

Thermal analysis consists of the use of several methods to analyze material properties as a function of temperature.

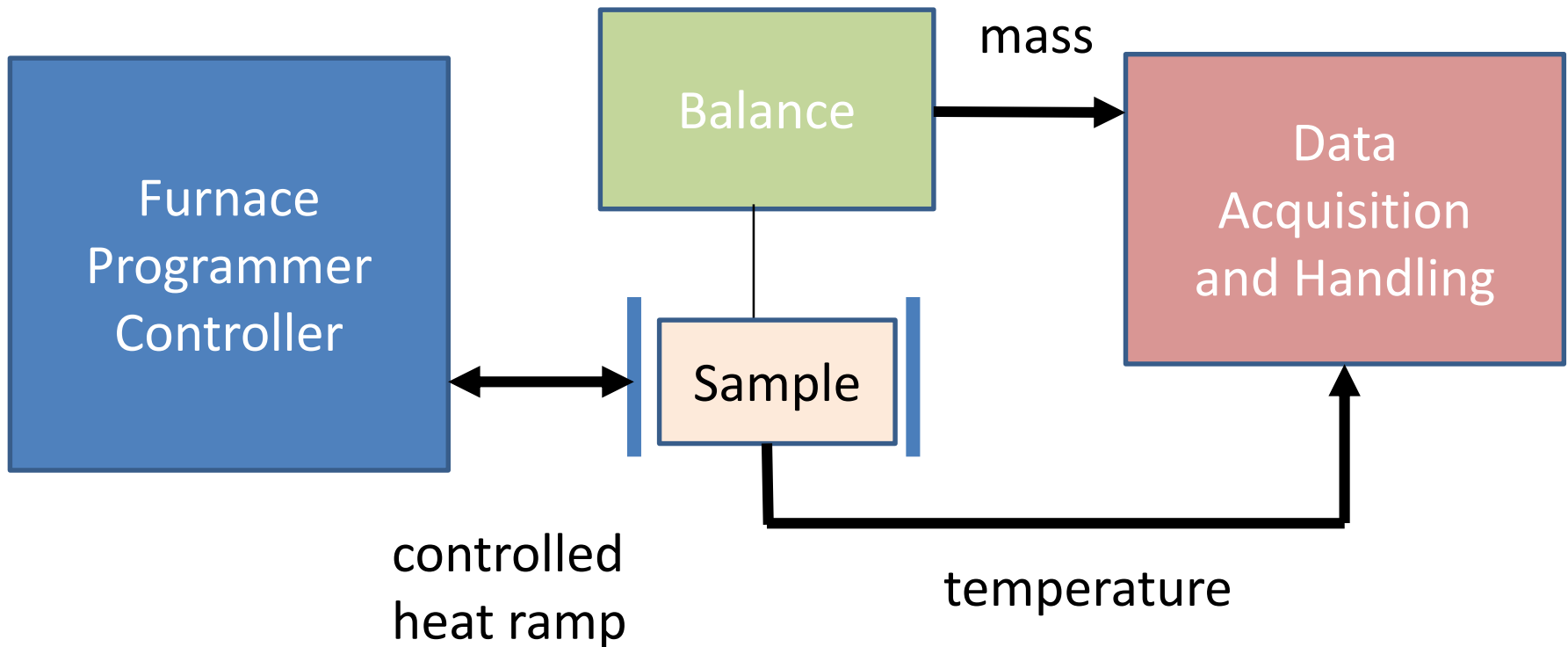
The main techniques are:

1. Thermogravimetry TG/TGA (mass change vs. T)
2. Differential thermal analysis DTA/DSC (heat flux vs. T)
3. Evolved gas analysis (volatiles vs. T)

These techniques can be combined with analysis using FTIR spectroscopy or mass spectrometry off line, meaning that the temperature ramp is interrupted and the sample is analyzed at the desired point in the thermal trace.

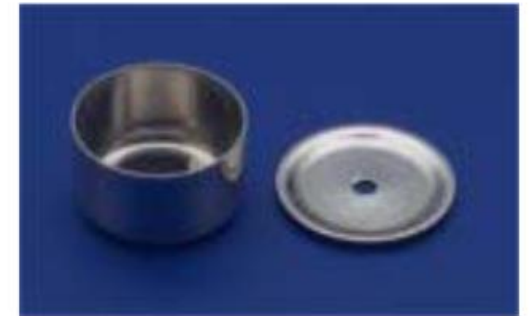
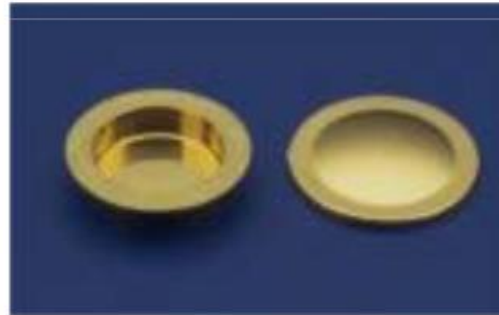
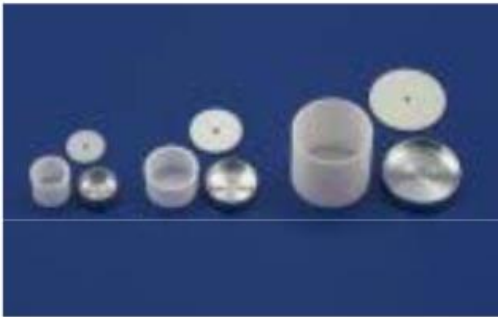
# Thermogravimetry

Thermogravimetry is based on the use of a thermobalance. The schematic below shows the components used to heat the sample, record the mass and then feed those observables to a computer for storage and analysis.



# Thermal analysis crucibles

Pans made of alumina, Pt, Cu or Au are used to hold the substrate. They must be able to withstand heating to 1100 °C.



# TGA; Phenomena causing mass changes

## Physical

Gas adsorption

Gas desorption

Phase transitions

- Vaporization
- Sublimation

## Chemical

Decomposition

Break down reactions

Gas reactions

Chemisorption

(adsorption by means of chemical instead of physical forces)



# TGA, Basics

Measures changes in weight in relation to changes in temperature.

The measured weight loss curve gives information on:

- changes in sample composition
- thermal stability
- kinetic parameters for chemical reactions in the sample

A *derivative weight loss curve* can be used to tell the point at which weight loss is most apparent



# Examples of TGA samples

Common gaseous components originating from inorganic materials that decompose before the melting point:

$\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{Cl}_2$ ,  $\text{F}_2$ ,  $\text{CH}_3\text{OH}$ , etc.

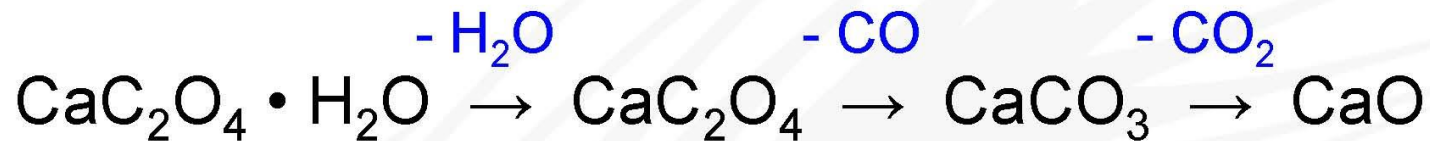
Also some chemical reactions in solid phase result in gaseous weight loss ex.



# TGA

Ex. Decomposition of calcium oxalate monohydrate

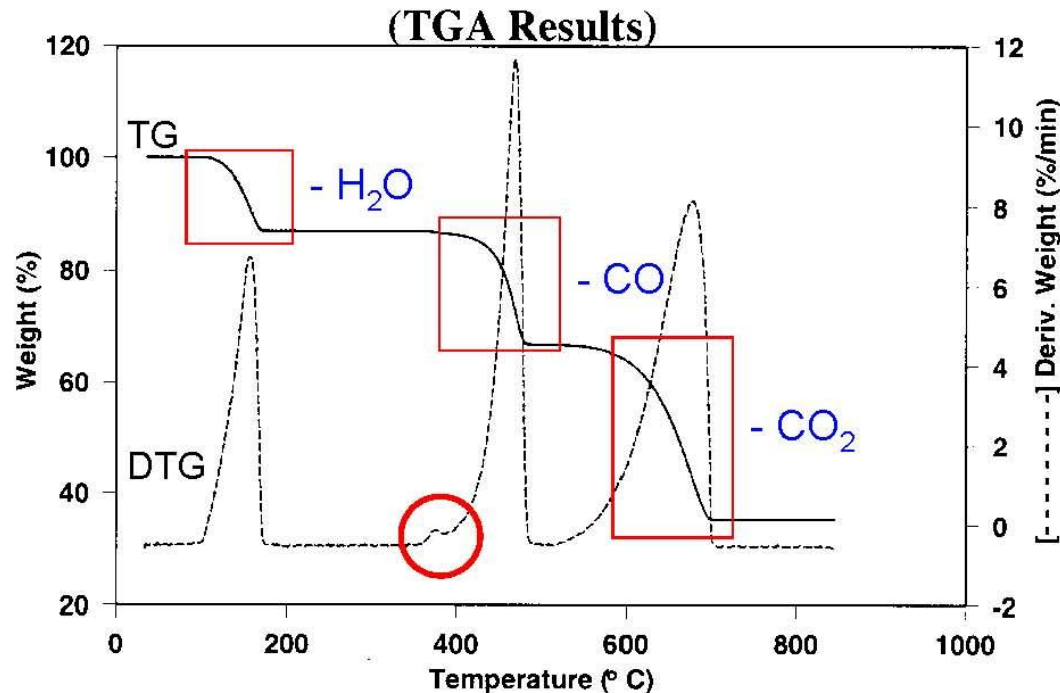
- Calcium oxalate monohydrate, a standard material often used to demonstrate TGA performance.
- Exhibits three weight losses with temperature in an inert atmosphere (e.g. N<sub>2</sub>).





# TGA

Ex. Decomposition of calcium oxalate monohydrate

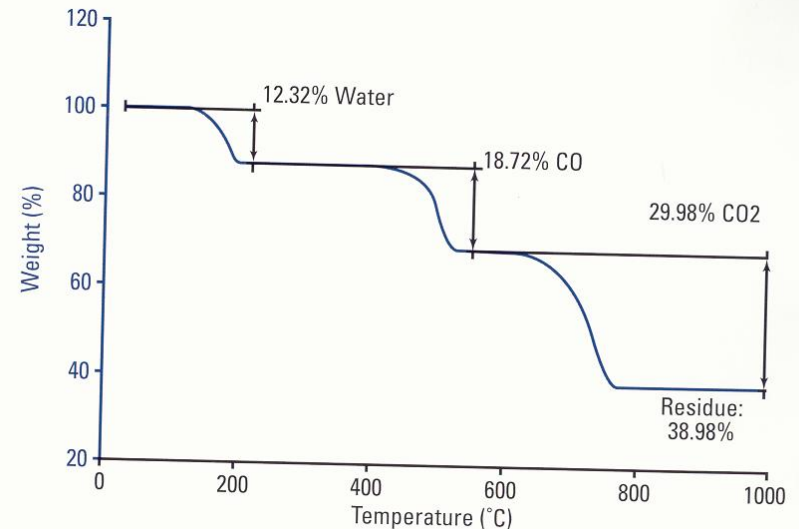


Absolute confirmation of the decomposition process is possible when the gaseous by products are identified as they evolve, eg. by mass spectrometry (MS).

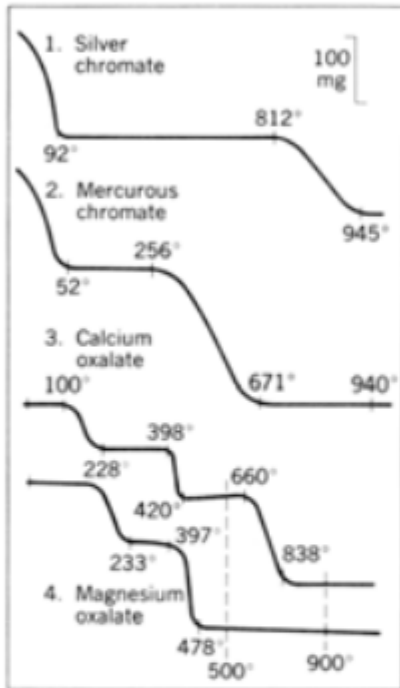
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# TGA summary

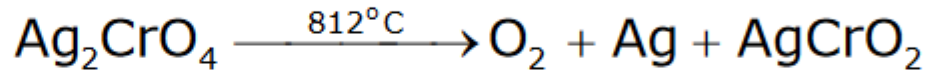
- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate ( $^{\circ}$  C/min)
- Data
  - Weight vs Time
  - Weight vs Temp.
- Differential This Data (DTG)



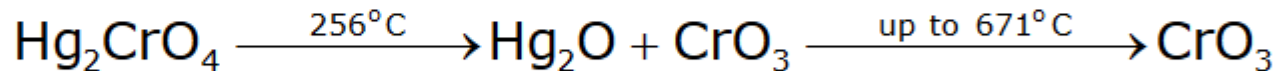
# Application to decomposition



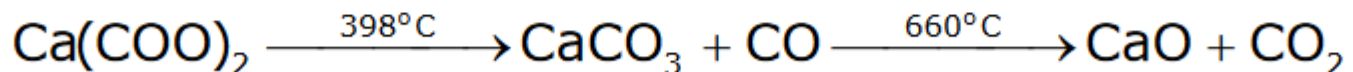
**Curve 1:** initial loss of excess wash water of the precipitate, then constant weight up to 812°C when oxygen release starts



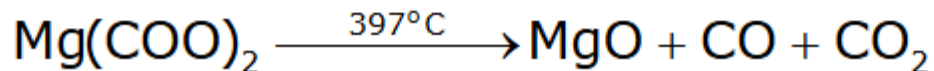
**Curve 2:** loss of wash water, then decomposition from 256°C on, then sublimation of  $\text{Hg}_2\text{O}$



**Curve 3:** Hydrate water release and then decomposition in two steps:

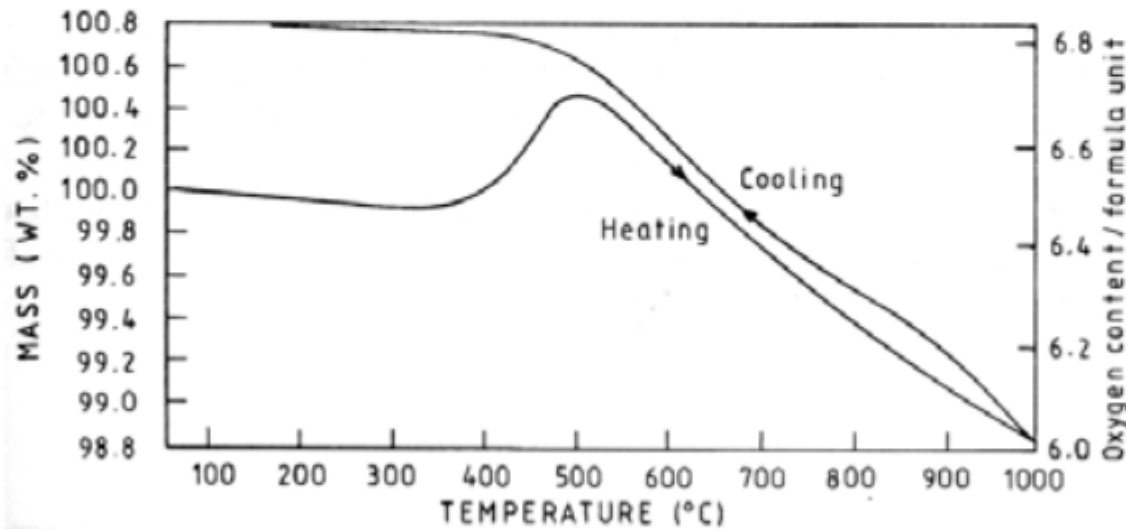


**Curve 4:** Hydrate water release and then decomposition in one step:

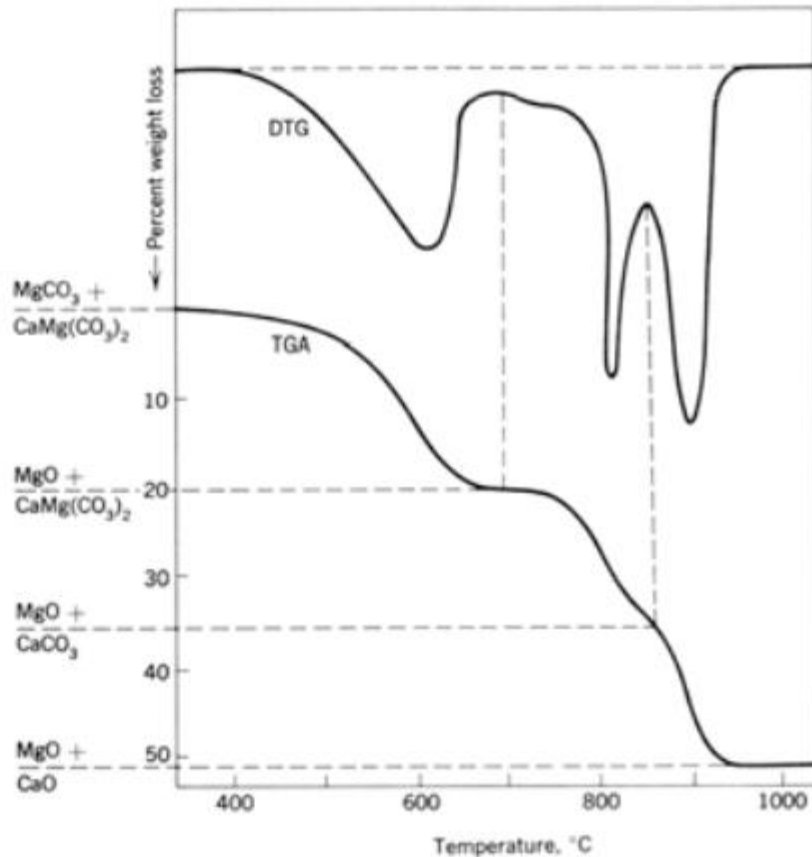


# Synthesis of semiconductors

In this example, the controlled synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  is performed/monitored by slowly heating and then cooling the superconductor in air. The material loses oxygen upon heating and then takes it up upon cooling. The oxygen content of this type of superconductors largely determines the critical temperature.



# Differential thermogravimetry (DTG)

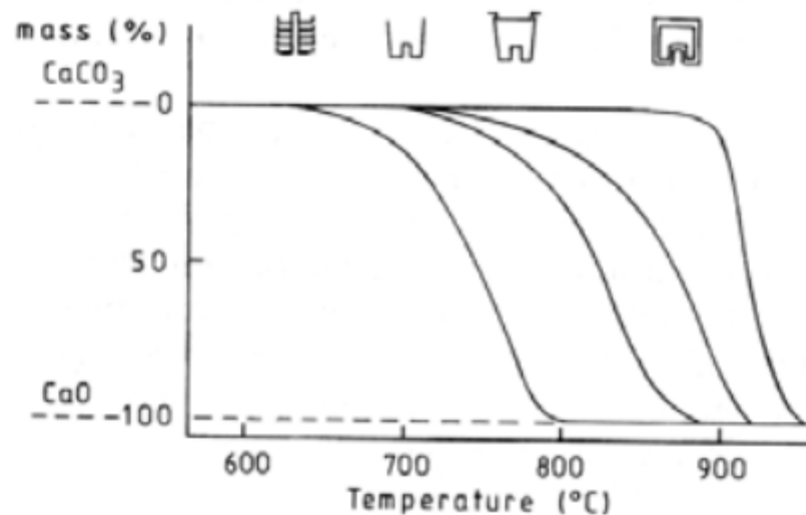


It is very useful to record the first derivative of the TG/TGA curve (DTG) also, because it makes the noticing small features/boulders on the curve much easier (they appear as peaks).

See, for example, the graph on the left that shows the TG/DTG of a mixed carbonate sample. The boulders of the TG curve at around 850°C can hardly be seen, so the corresponding temperatures are difficult to determine. It is much easier done using the DTG curve.

# Potential artifacts

Great care needs to be exercised while loading and operating the instrument if the TG curve is intended to be accurate. Potential sources of error include the effect of heating rate, the geometry of the crucible (see below), gas flow, electrostatic forces, etc.



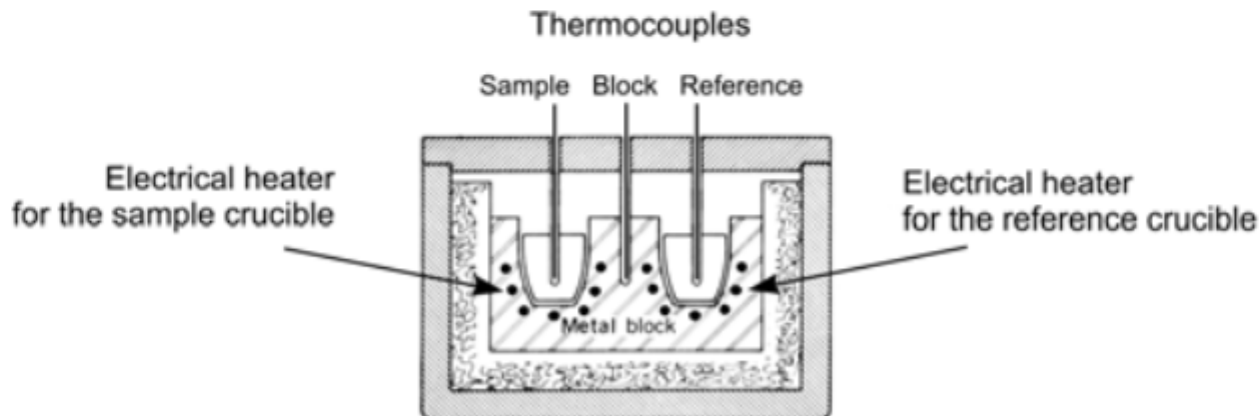
The geometry of the crucible affects the escape of CO<sub>2</sub> and thus influences characteristic temperature values

# Differential thermal analysis (DTA)

## Differential scanning calorimetry (DSC)

**DTA:** follows the temperature difference between sample and reference upon heating or cooling. If there is some endothermic chemical reaction then the temperature of the sample will lag behind the temperature of the reference. If the reaction is exothermic, then the situation is the opposite. In the schematic below, the two heaters are driven commonly.

**DSC:** follows the electrical power (heat) needed to keep the sample and reference at the same temperature. This is the more accurate one. In the schematic below, the heaters are controlled and driven separately.



# Introduction to DSC

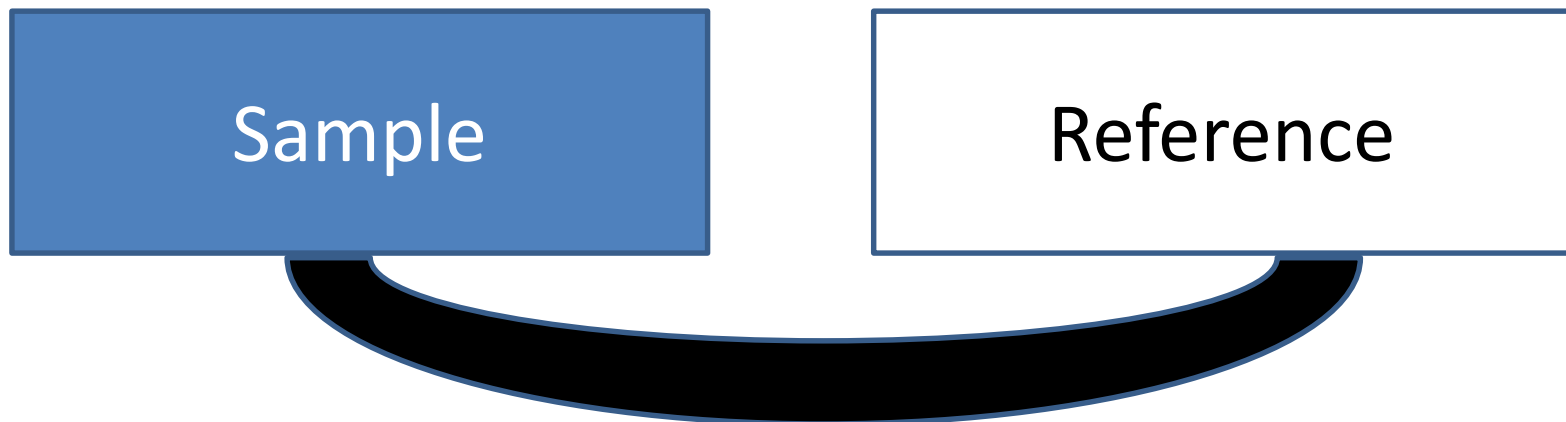
The technique of differential scanning calorimetry (DSC) is based on a comparison of the response of a sample compared to a reference as a heat ramp is applied. The heat, or energy, is measured as the current flowing across a resistor that heats the sample. The response is measured as a change in temperature as a function of heat input. The load of the sample is the heat capacity. Therefore, the slope of the measurement is the heat capacity.

Phase changes in the sample introduce non-linearity, which inform us on the magnitude of latent heat and the nature of heat capacity changes in glass transitions. Thus, not only can we distinguish different types of phase transition (first and second order), but also the magnitudes of the changes.



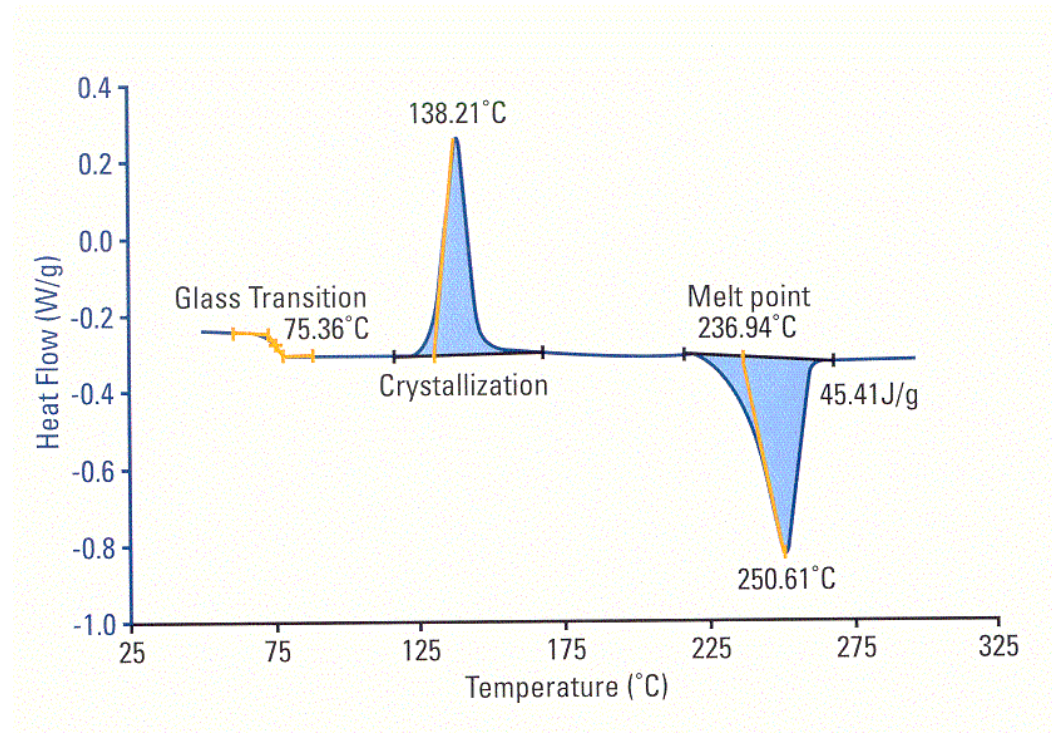
# DSC: The power-compensation principle

With power-compensation DSC, the sample and the reference material are placed in independent furnaces. When the temperature rises or falls in the sample energy is applied or removed from the calorimeter to compensate for the sample energy. As a result, the system is maintained at a “thermal null” state at all times. The amount of power required to maintain system equilibrium is directly proportional to the energy changes occurring in the sample. No complex heat-flux equations are necessary with a power-compensation DSC because the system directly measures the heat flow to and from the sample.



# DSC measurement of phase changes

- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate ( $^{\circ}$  C/min)
- Data
  - Heat flow to sample minus Heat flow to reference vs Time (Temp.)
- Measures heat of crystallization or melting



Polymer without weight change in this temperature range

# Application of DSC to polymer melting

A laboratory experiment is described that uses modulated differential scanning calorimetry (MDSC) to elucidate the differences between crystalline and glassy polymers. The example chosen for study is a comparison of polyethylene glycol (PEG) and atactic polypropylene glycol (PPG). The experiment demonstrates differences in the reversing part of the heat flow for phase transitions of these two materials. The reversing heat flow of glassy PPG has a sigmoidal shape indicative of a transition that has no latent heat. By contrast, the phase transition of PEG has the form of a first order phase transition with an instantaneous change in both heat capacity and enthalpy due to the loss of crystalline order. The laboratory is easily performed in one afternoon and is an excellent demonstration of the thermodynamics of phase transitions and the concept of reversibility.

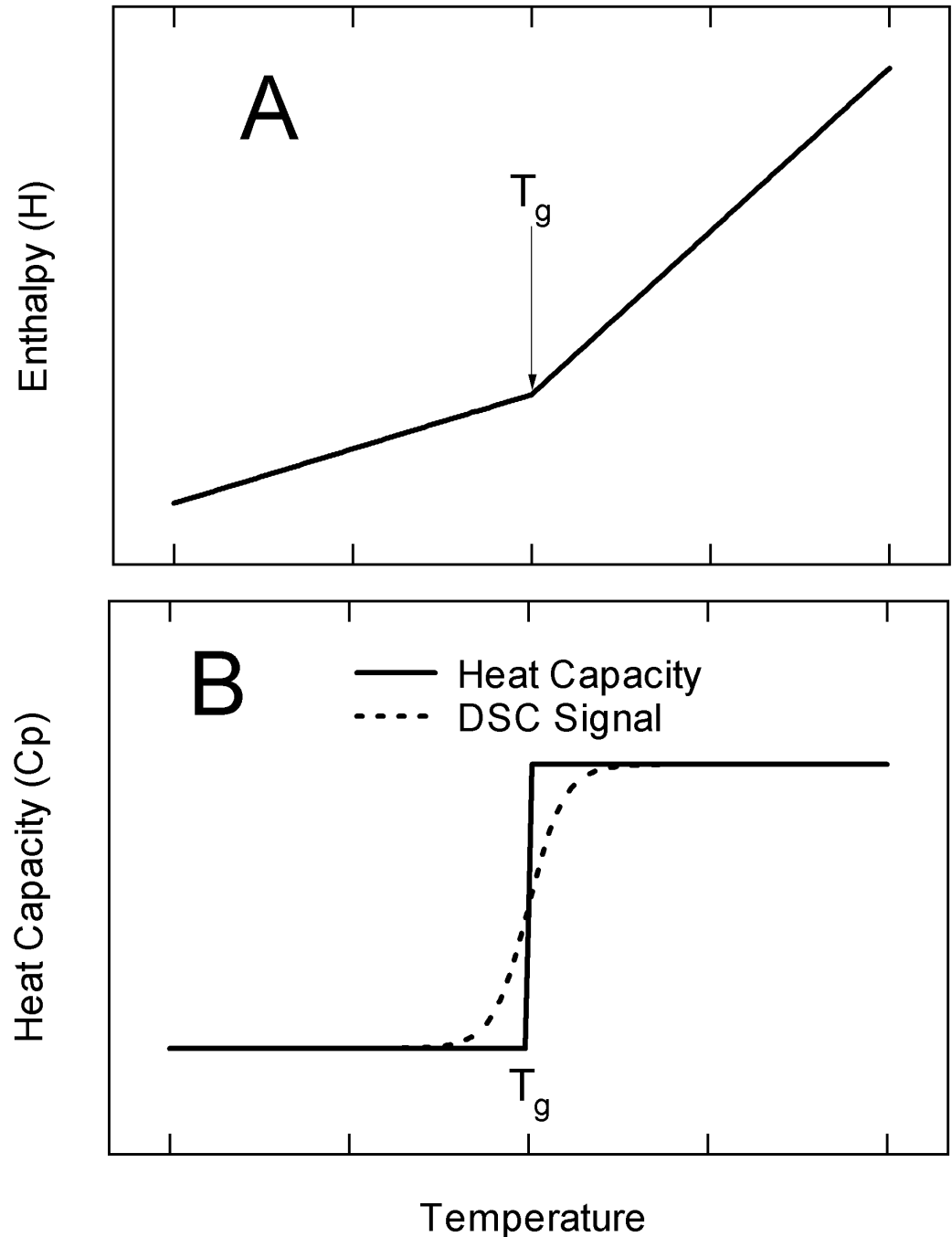
# Introduction to polymer DSC

The theory behind the use of modulated differential scanning calorimetry (MDSC) has been discussed in an accompanying manuscript <sup>1</sup>. The heat flow in a MDSC experiment can be converted to a heat capacity plot to determine the difference between crystallization and vitrification (glass formation). First order phase transitions are observed in MDSC as an instrument broadened peak in the heat capacity vs. temperature plot that arises from the discontinuity in the enthalpy function due to the latent heat of transition in crystallization. Glass transitions only have a change in heat capacity. They present a sigmoidal curve in the heat capacity vs. temperature plot obtained in a MDSC experiment . The current laboratory experiment illustrates these different types of transitions using two polyglycols as examples; polyethylene glycol PEG and polypropylene glycol PPG.

# Glass Transitions

Figure 1. A schematic diagram for the enthalpy and heat capacity as function of temperature for a glass transition.

A. The slope of the  $H$  vs.  $T$  changes at the glass transition temperature. This results in a sudden change in the heat capacity. B.  $C_p$  is shown for an instantaneous change (solid line) and with inclusion of a kinetic term (dashed line).



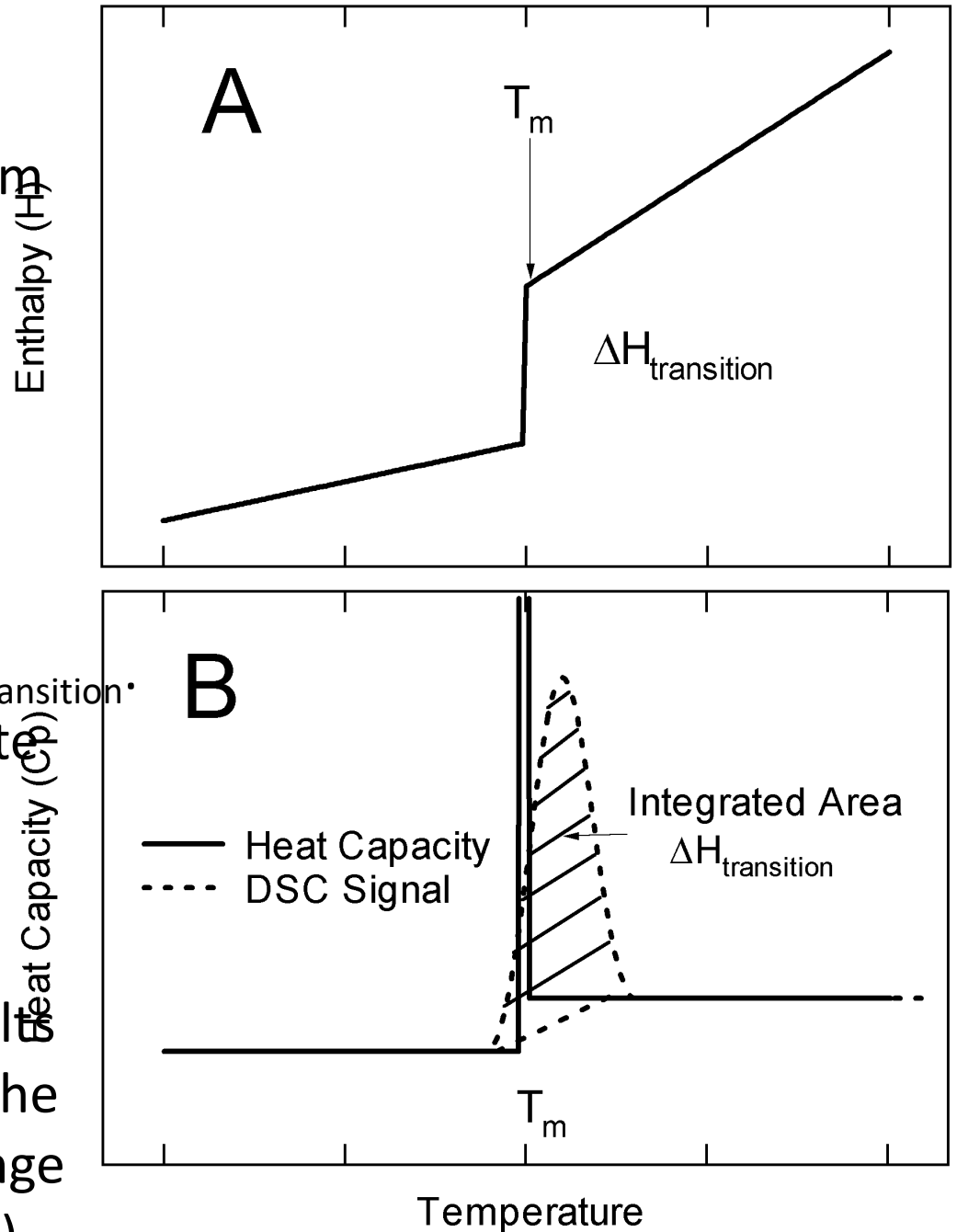
# Crystallization

Figure 2. A schematic diagram for H and Cp as function of temperature during a crystalline melting event.

A. The latent heat of the phase transition is manifest as a sudden change in the enthalpy,  $\Delta H_{\text{transition}}$ .

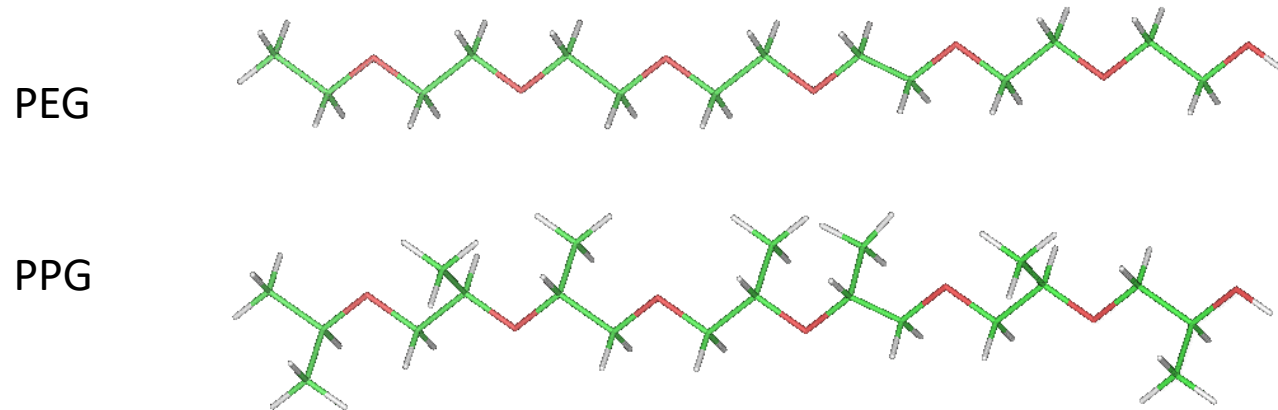
B. The heat capacity is infinite at the phase transition since the enthalpy function is discontinuous (solid line).

The kinetic term in DSC results in a shift and smoothing of the observed heat capacity change upon transition (dashed line).



# Polyglycols

The first subject of the present laboratory study consists of a glass transition of a liquid polymer, polypropylene glycol (PPG) by means of MDSC. PPG is chosen mainly because its physical (thermal) behavior is in such stark contrast to that of polyethylene glycol PEG. The structure of these two polymers is shown below. The synthesis of PEG typically starts with glycerol or another polyfunctional alcohol, a sugar molecule for example. The monomeric building block is ethylene oxide, which reacts under ring opening to add to the  $-OH$  groups of the original alcohol. The result is a polyether chain ending in a  $-OH$  functionality. PPG is synthesized in a similar way using propylene oxide instead of ethylene oxide as the monomer. This can lead to different isomeric products because one of the two carbon atoms of the monomer unit will carry a methyl side group as shown below.



# Isotactic and Atactic PPG

Depending on the specifics of the polymerization the branch groups can all be on the same carbon atom (isotactic PPG) or can be randomly distributed over both atoms (atactic PPG). The industrial product is usually atactic. Atactic PPG is represented on the previous slide with a random distribution of methyl groups.

Chemically, the difference between PPG and PPG resides in the methyl branch group only. Nevertheless, the difference in properties is striking. PEG is a crystalline solid, a white powder with a melting point of typically  $+60^{\circ}\text{C}$ . As usual in polymers the material is actually semicrystalline. Its crystallinity never reaches 100%, but can be quite high. By contrast, atactic PPG shows no crystalline order at all, it remains a viscous liquid until it vitrifies at temperatures as low as  $-70^{\circ}\text{C}$ . The steric hindrance from the methyl side group is quite effective in making the ordering of the molecules into a crystalline lattice an unattractive proposition, at least in the atactic form. On the other hand, the isotactic form does crystallize.



# Experimental

Laboratory calorimetric experiments will be performed on a TA Instruments Q100 MDSC system, with a propane, ethane and propylene driven Refrigeration Cooling System, allowing scans from  $-100^{\circ}\text{C}$  to ca.  $400^{\circ}\text{C}$ . Polyglycols are commercially available in a wide range of molecular weights. For the laboratory module described here PEG 8000 from FisherBiotech and PPG 1000 from AlfaAesar will be used as obtained. The polymers are widely used in cosmetic products and present little hazard. The samples will be placed in aluminum pans that can be hermetically sealed using a crimping device. Filling the pans requires some precision and it is also a useful exercise in handling small quantities of material. For PEG typically 3-5 mg powder suffices. For PPG 10  $\mu\text{L}$  of liquid is enough. We use a 25  $\mu\text{l}$  Hamilton syringe, which needs to be clean and dry. Cleaning with first water and then a small amount of acetone works well, provided the piston is removed and the acetone evaporated, e.g. by blowing air or nitrogen through the syringe. Traces of solvent can otherwise work as a plasticizer and lower the glass transition temperature below the instrumental limit of  $-100^{\circ}\text{C}$ .

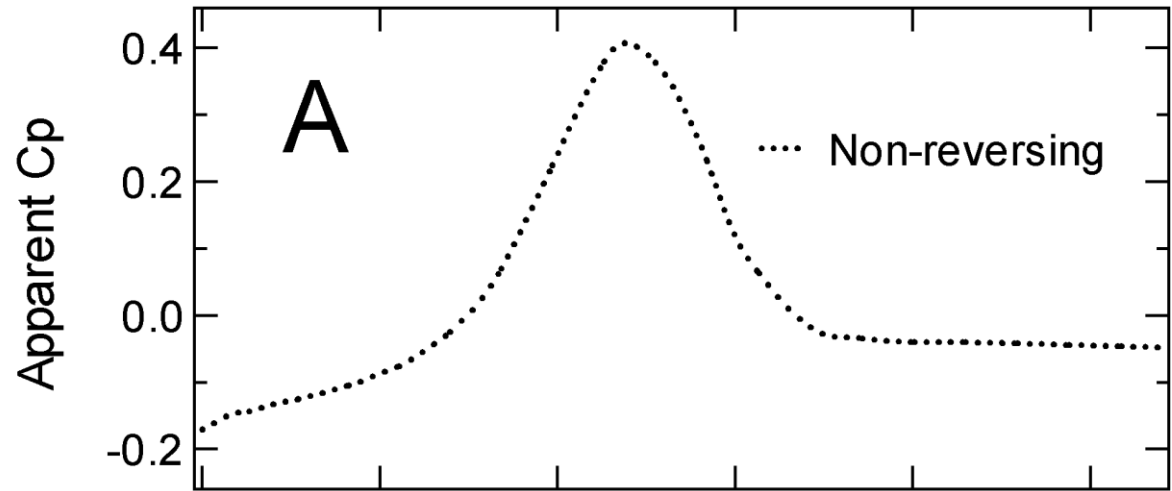
# Main Objective of the Laboratory

You should complete three runs from  $-90^{\circ}\text{C}$  to  $-45^{\circ}\text{C}$  on PPG under slightly varying conditions (different frequency,  $\omega$  or scan rate,  $\beta$  or different aging times). A typical MDSC scan is shown for PPG after allowing it to age for 5 minutes at  $T = -90^{\circ}\text{C}$ . ( $\beta = 5\text{K}/\text{min}$ ,  $\alpha = 0.5\text{K}$ ,  $\omega = 2\pi/40\text{ s}^{-1}$ ). This is shown in the next slide. Note the sigmoidal shape of the reversing part of the heat capacity. For the PPG data that you obtain, determine the glass transition temperature and the  $\Delta C_p$  from the reversing (sigmoidal) part of the glass transition and the  $\Delta H$  of recovery from the non-reversing part. <sup>1</sup>

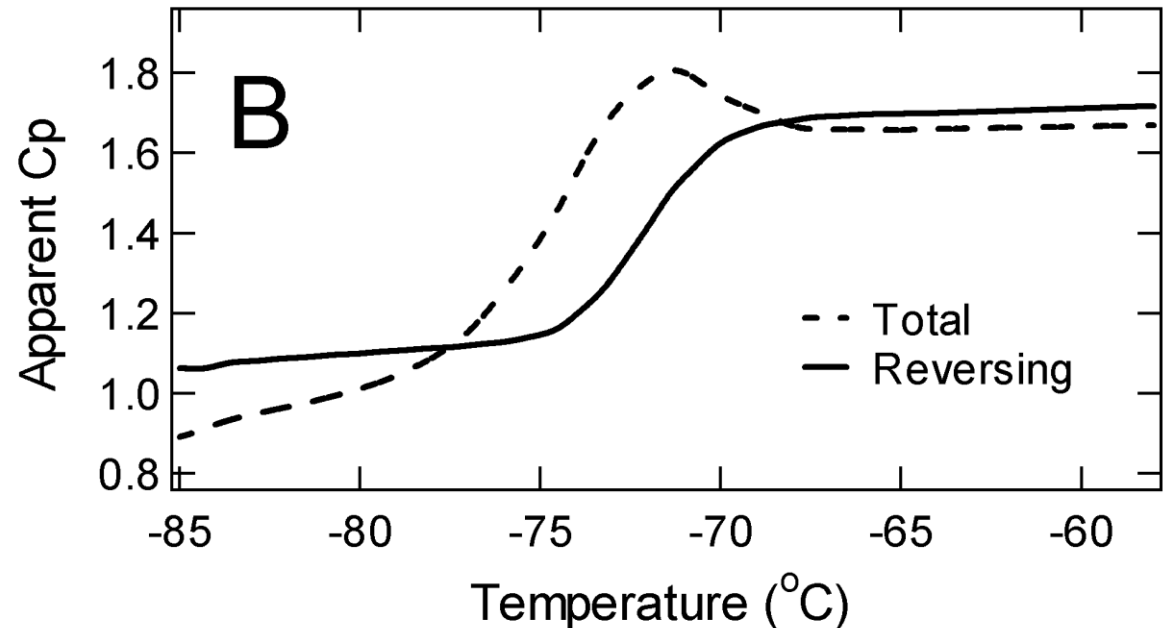
# Results for PPG

Panel A.

The total heat capacity for a PPG glass transition.



Panel B. The resolution of the total heat capacity into a sigmoidal reversing part (bold curve) and a non-reversing part (dashed curve). The latter shows the peak due to the enthalpy of recovery.



# The PEG Comparison

A useful comparison to the study of the PPG glass transition is obtained by running a melting curve on PEG from +25°C to +85°C. The MDSC data for the total heat flow of the phase transition of PEG are shown in the Figure on the next slide . There will always be an enthalpic peak because of  $\Delta_{\text{fus}}H$  for a crystalline material such as PEG (see Figure 1). As stated above the reversible signal for the glass transition on PPG is sigmoidal.

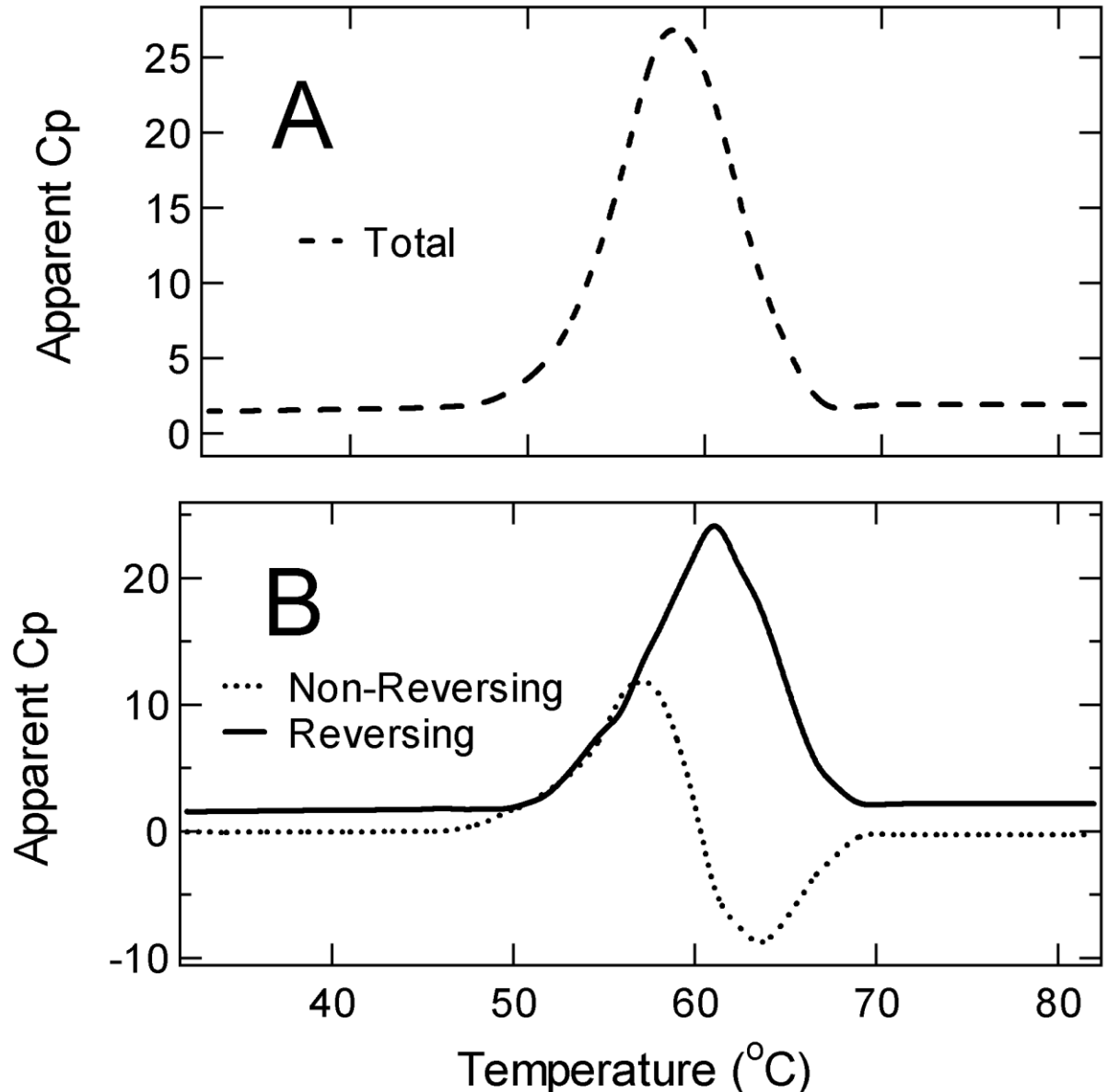
By contrast, the PEG signal shown in the next slide does not even resemble a sigmoid . Note also that the reversing part of PPG transition is much larger than the non-reversing part, while the magnitude of these contributions is of the same order of magnitude.

# Results for PEG

The (apparent) total Cp of PEG during the melting endotherm.

The onset temperature is 52.0 °C and the peak temperature is 58.2 °C. The total Cp signal is in Panel A.

The reversing and non-reversing components of Cp are shown in panel B. Note the non-sigmoidal shape of the reversing signal.



# Analysis

When the experimental measurements are complete analysis is carried out in the following steps:

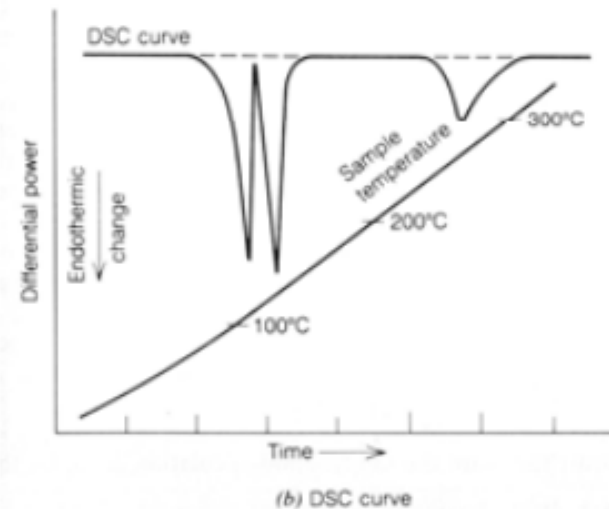
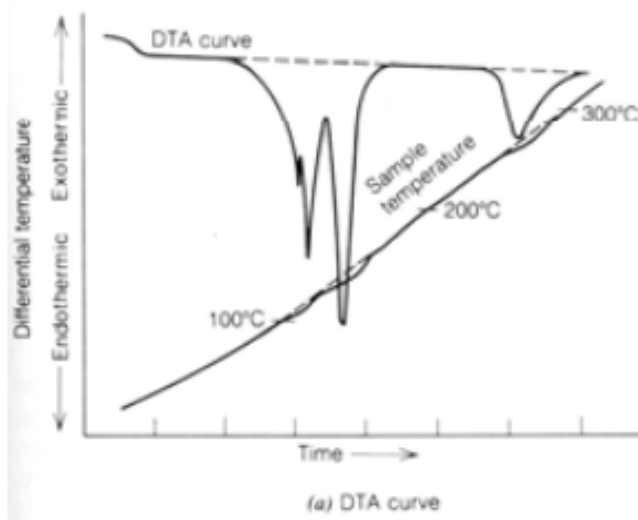
1. Using the instrument software, perform the peak integration on the total PEG signal shown in the previous slide to establish  $T_m$  and  $\Delta H$  fusion from the total heat flow signal. Using these values, calculate  $\Delta S$ .
2. Draw schematic diagrams of  $H$  and  $C_p$  versus  $T$  for both PEG and PPG.
3. For PEG, why is the reversing signal not sigmoidal in shape?
4. Tabulate relevant numbers that were measured for PPG and PEG. Use the diagrams to represent as many values for the thermodynamic quantities that you have measured as you can. How large is the jump? The slope? at what temperature does it happen? Etc.
5. Show that  $H$  and  $S$  are first order derivatives of the Gibbs free energy while  $C_p$  is a second derivative.

# Conclusion

The MDSC experiment presented here involves the glass transition of polypropylene glycol and the melting of polyethylene glycol. These experiments provide an excellent opportunity to reinforce a number of important thermodynamic concepts. First, we have examined reversibility. Glass transitions exhibit aging phenomena, and although they have a great deal in common with second-order phase transitions, the involvement of time as a variable in the formation of the glassy state (i.e. cooling rate) brings a new dimension into materials calorimetry that is of wide interest in science and technology. The functions  $G$ ,  $H$ ,  $S$  and  $C_p$ , are involved in the derivations of the discontinuities in the phase transitions. These topics are reviewed in a companion paper on the theory of MDSC. <sup>1</sup>

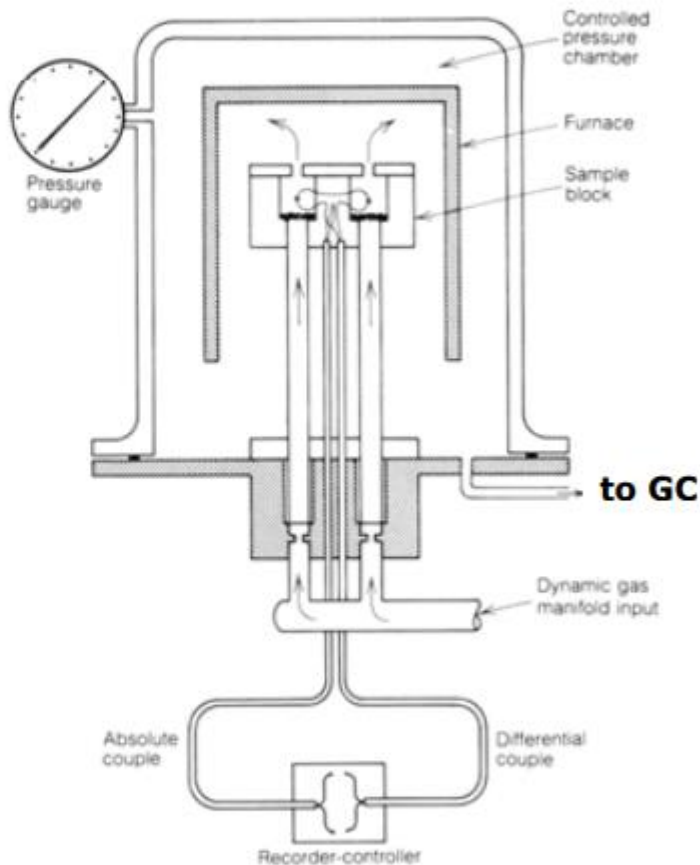
# Comparison of DTA and DSC

This example DTA/DSC of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  shows the superiority of DSC. Peak areas are more accurate and the temperature ramp is less disturbed by thermal events in the sample (e.g. differences in specific heats and thermal conductivities between the sample and reference). In the curves below, the peaks correspond to the loss of two, two and finally one molecule of  $\text{H}_2\text{O}$ .





# Evolved gas analysis (EGA)

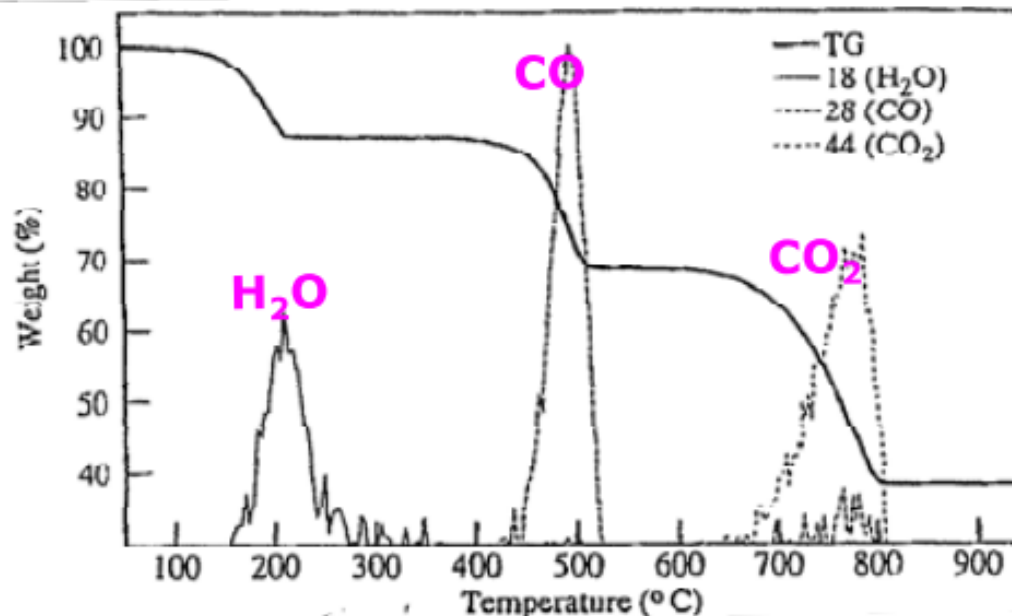


The concept behind evolved gas analysis is that the study of unknown materials and/or thermal processes is much easier if we also use a detector to selectively identify the released compounds and byproducts (volatiles, combustion products, etc.). This can be done by coupling the gas output of a TG or DTA instrument to a selective detector, such as a spectrometer or a gas chromatograph. This is exemplified in the schematic on the left for a DTA-GC combination.

# Evolved gas analysis (EGA)

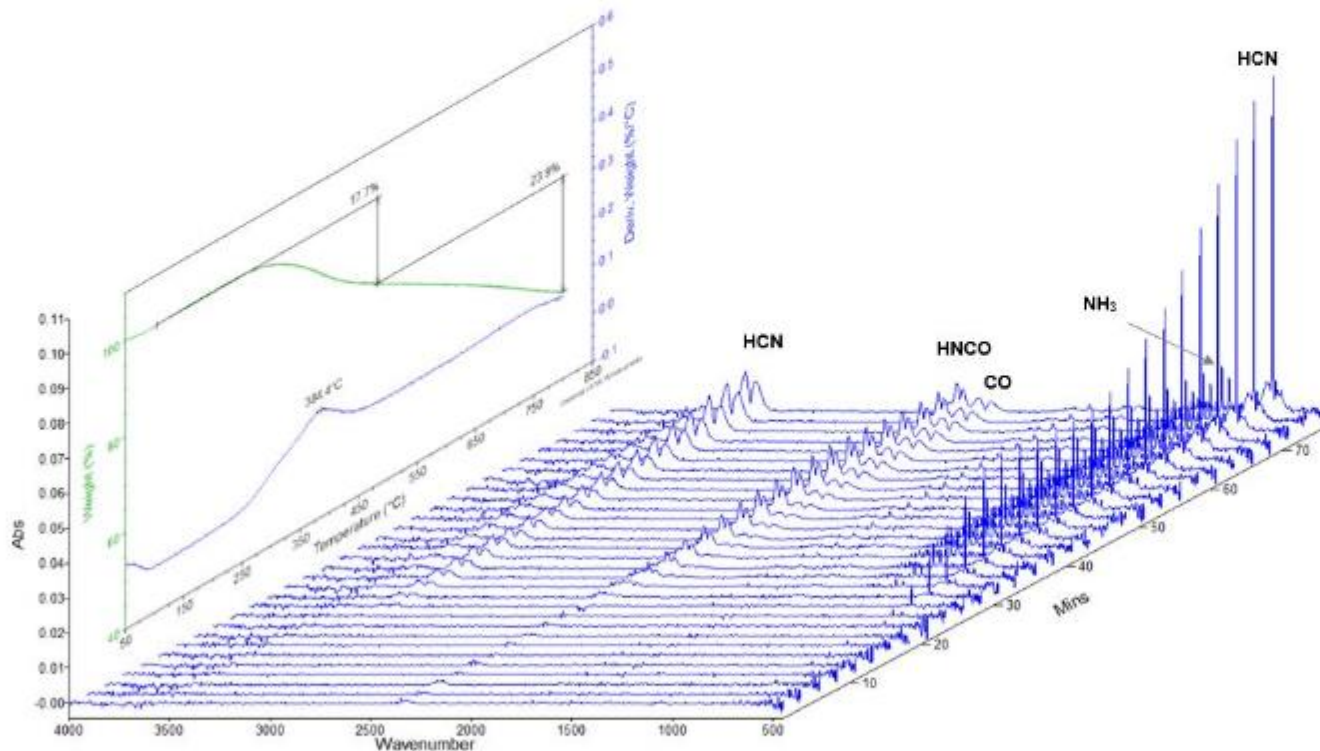
## Calcium oxalate example

The information content of an EGA measurement is illustrated in this example for the decomposition of hydrate water containing Ca-oxalate. The detector was a mass spectrometer in this instance (TG-MS), but could have also been e.g. an FTIR spectrometer (TG-FTIR), or a gas chromatograph (TG-GC).

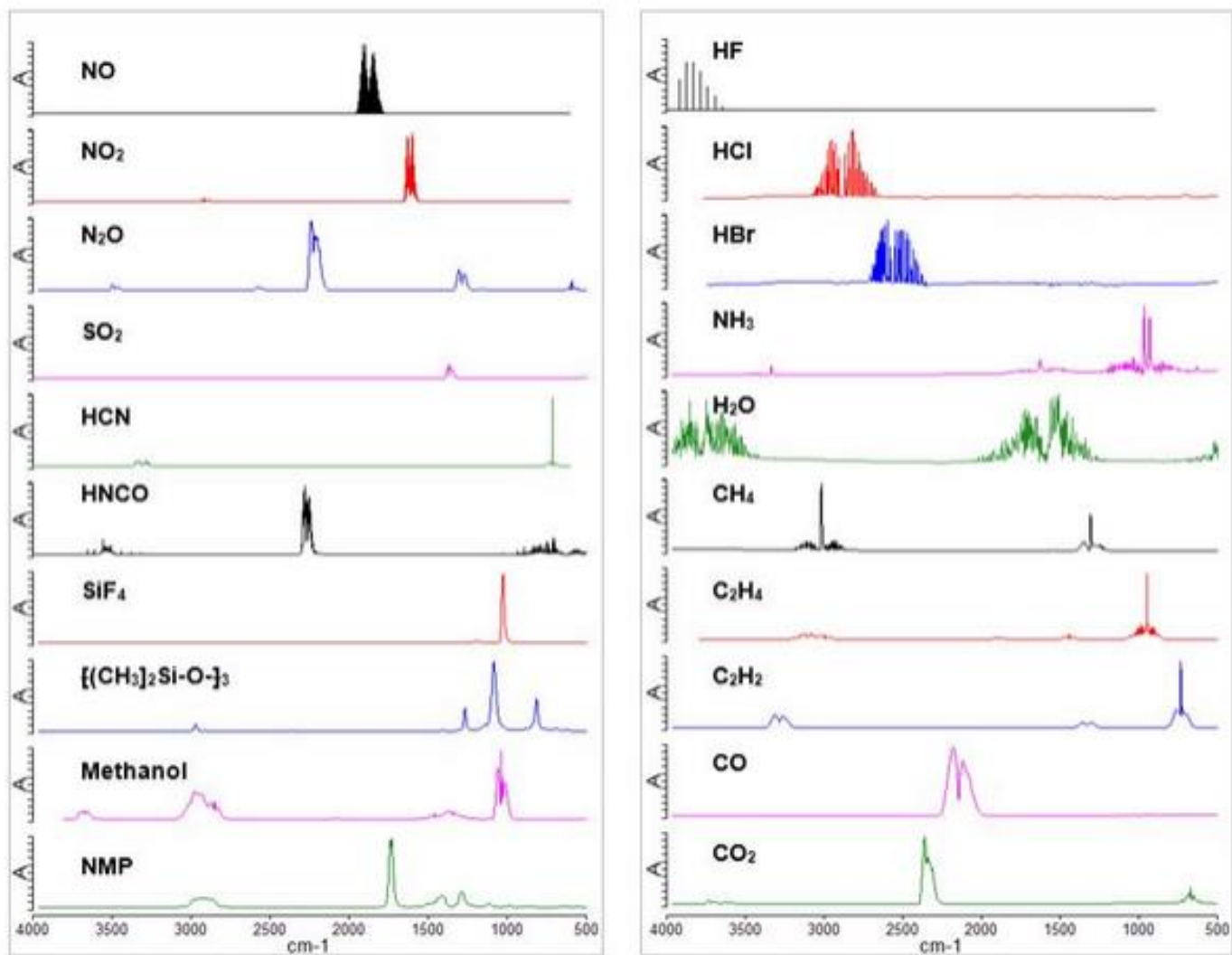


# Evolved gas analysis (EGA) extends to FTIR and Mass Spec

A more specific way to monitor decomposition reactions involves Use of spectroscopic techniques to determine the identity of Gas molecules generated by thermal processes in a TGA. The figure shows the decomposition of polyacrylonitrile in a time-series.



# FTIR spectra of common outgassing species



# References

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*Journal of Chemical Education* **2001**, submitted.
- 2) Gill, P. S.; Sauerbrunn, S. R.; Reading, M.  
*Journal of Thermal Analysis* **1993**, *40*, 931-939.
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