

Differential Scanning Calorimetry (DSC):

The technique was developed by E.S. Watson and M.J. O'Neill in 1960, and introduced commercially at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in 1963.

A DSC measures the difference in heat flow rate between a sample and inert reference as a function of time and temperature. This technique is used to study what happens to sample upon heating, it is used to study thermal transition of a sample, e.g.; melting of crystalline substance, glass transition and crystallization.

- A *calorimeter* measures the heat into or out of a sample.
- A *differential calorimeter* measures the heat of a sample relative to a reference.
- A *differential scanning calorimeter* does all of the above and heats the sample with a linear temperature ramp.

Principle:

- The sample and reference are maintained at the same temperature, even during a thermal event in the sample.
- The energy required to maintain zero temperature difference between the sample and the reference is measured.
- During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans.

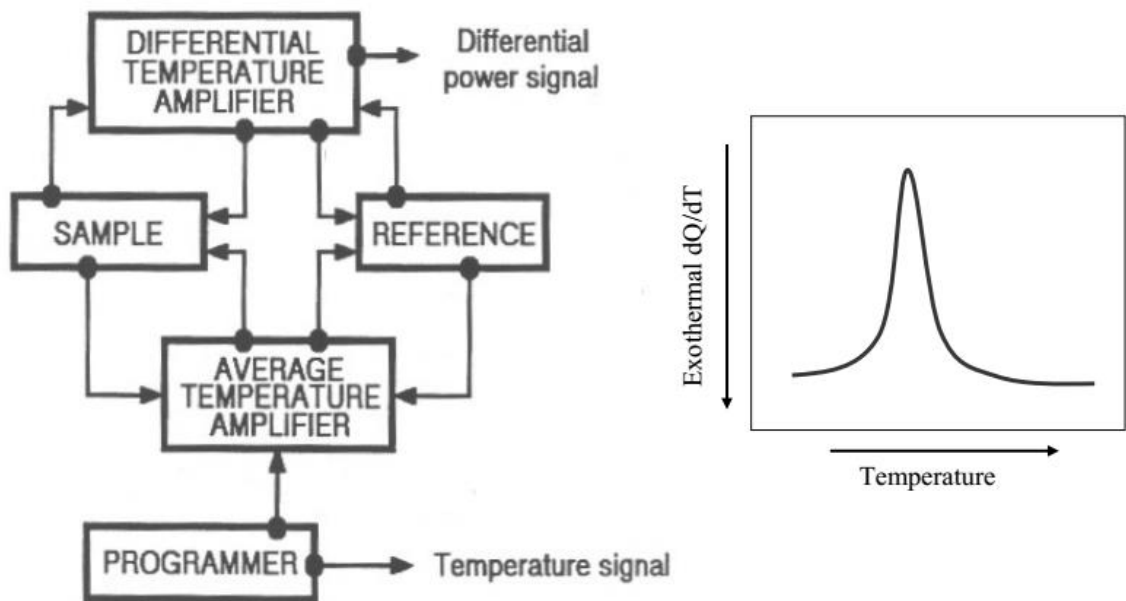
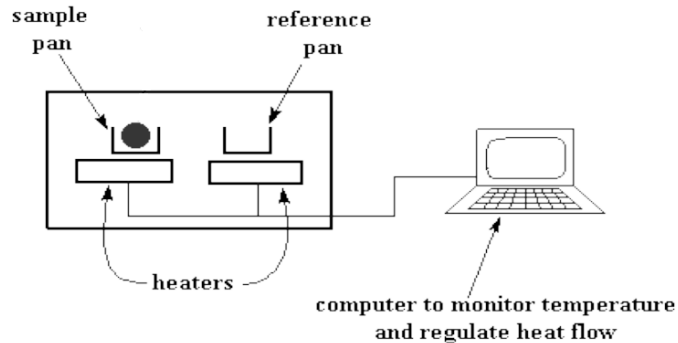
Information Obtained:

- Glass transition temperature
- M. P. and B. P.
- Crystallization time and temperature
- %age crystallinity
- Heat of fusion and reaction
- Specific heat
- Oxidative stability
- Rate and degree of curve
- Reaction kinetics
- Thermal stability

- Purity

What happened to sample when heated:

The sample is heated in the a device that look like something that,



- DSC measures differences in the amount of heat required to increase the temperature of a sample and a reference as a function of temperature

There are two pans, in sample pan, polymer is added, while the other, reference pan is left empty. Each pan sits on top of heaters which are controlled by a computer. The computer turns on heaters, and let them heat the two pans at a specific rate, usually 10°C/min. The computer makes absolutely sure that the heating rate stays exactly the same throughout the experiment.

Sample Preparation:

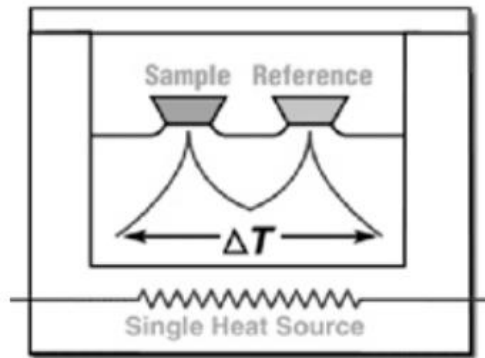
- Accurately-weigh samples (~3-20 mg)
- Small sample pans (0.1 mL) of inert or treated metals (Al, Pt, Ni, etc.)
- Several pan configurations, e.g., open, pinhole, or hermetically-sealed (airtight) pans
- The same material and configuration should be used for the sample and the reference
- Material should completely cover the bottom of the pan to ensure good thermal contact

Types of DSC:

Variants of DSC

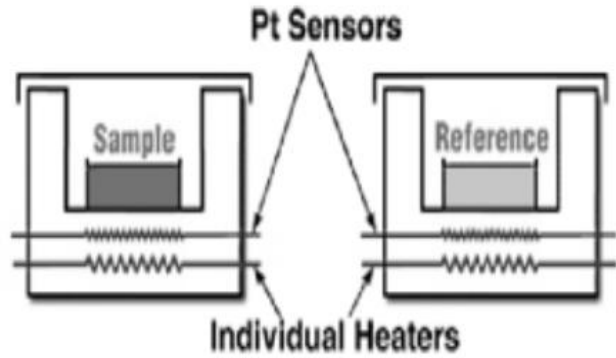
- Heat flux
 - 1955 Boersma
 - 1 large (30 – 100 g) furnace
- Power compensated
 - Separate small (1 g) microheaters for sample and reference
- Hyper DSC
 - Very fast scan rates 500°C/min
 - Mimic processing conditions
- StepScan DSC
 - Short dynamic and isothermal scan steps
 - Separate reversible and irreversible effects

Heat Flux



Same heat flows into both samples; $\Delta T = 0$. When a change occurs (endo or exo) a ΔT signal is generated which is proportional to the heat flow difference.

Power Compensation



When a ΔT is detected, an additional circuit will increase or decrease heating power of sample furnace. This compensating heating power, ΔP , is proportional to heat absorbed or released.

Power Compensation DSC:

Sample holder

- Aluminum or Platinum pans

Sensors

- Platinum resistance thermocouples
- Separate sensors and heaters for the sample and reference

Furnace

- Separate blocks for sample and reference cells

Temperature controller

- Supply the differential thermal power to the heaters to maintain the temperature of the sample and reference at the program value

Heat Flux DSC:

Sample and reference holders

- Al or Pt pans placed on constantan disc
- Sample and reference holders are connected by a low-resistance heat flow path

Sensors

- Chromel (an alloy made of 90% nickel and 10% chromium)-constantan area thermocouples (differential heat flow)
- Chromel -alumel (an alloy consisting of approximately 95% nickel, 2% manganese, 2% aluminium and 1% silicon) thermocouples (sample temperature)

Thermocouple is a junction between two different metals that produces a voltage due to a temperature difference

Furnace

- One block for both sample and reference cells

Temperature controller

- The temperature difference between the sample and reference is converted to differential thermal power, which is supplied to the heaters to maintain the temperature of the sample and reference at the program value

DSC heat flow:

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

$\frac{dH}{dt}$ = DSC heat flow signal

C_p = Sample Heat Capacity
= Sample Specific Heat x Sample Weight

$\frac{dT}{dt}$ = Heating Rate

$f(T, t)$ = Heat flow that is function of time at an absolute temperature (kinetic)

DSC Curve

- The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment.
- This curve can be used to calculate enthalpies of transitions, which is done by integrating the peak corresponding to a given transition. The enthalpy of transition can be expressed using equation:
$$\Delta H = KA$$
- Where ΔH is the enthalpy of transition,
- K is the calorimetric constant,
- A is the area under the peak.
- The calorimetric constant varies from instrument to instrument, and can be determined by analyzing a well-characterized material of known enthalpies of transition.
- Area under the peak is directly proportional to heat absorbed or evolved by the reaction,
- height of the peak is directly proportional to rate of the reaction

Factors affecting DSC curve

Two types of factors effect the DSC curve

1-Instrumental factors

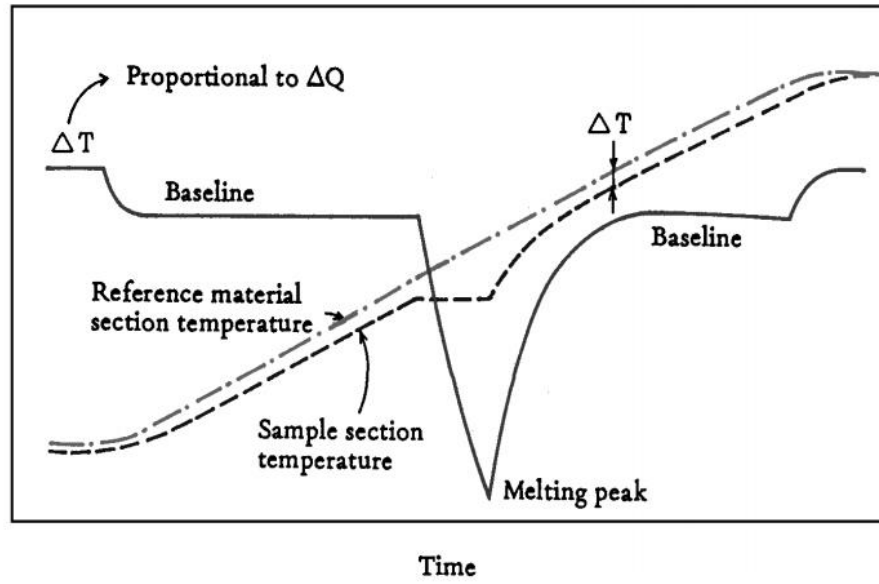
- a- Furnace heating rate
- b- Recording or chart speed
- c- Furnace atmosphere
- d- Geometry of sample holder/location of sensors
- e- Sensitivity of the recoding system
- f-Composition of sample containers

2-Sample characteristics

- a- Amount of sample
- b- Nature of sample
- c- Sample packing
- d- Solubility of evolved gases in the sample
- e- Particle size
- f- Heat of reaction
- g- Thermal conductivity

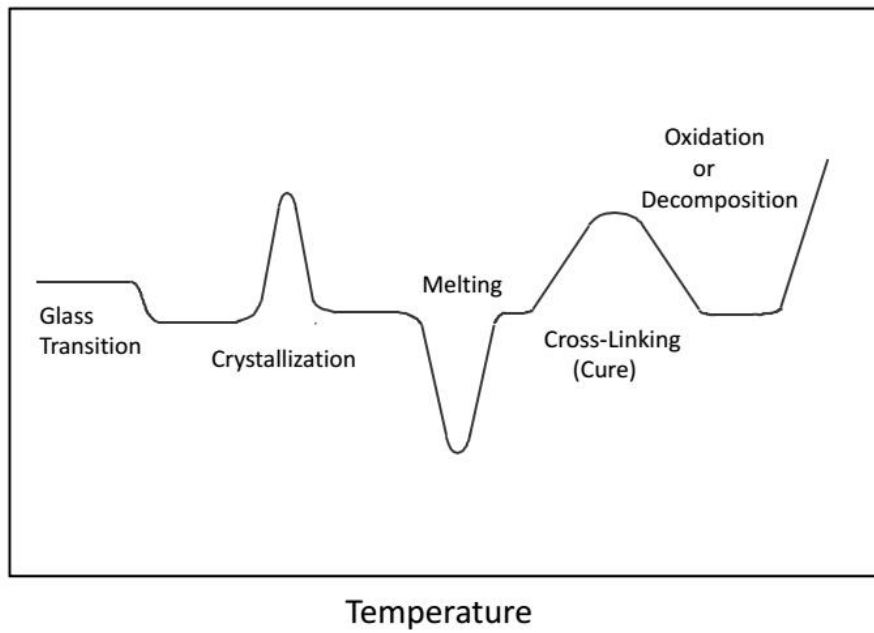
Principle Of DSC

Temperature,
Temperature
difference



SMITHSONIAN TECHNOLOGY EDUCATION

Heat Flow -> exothermic



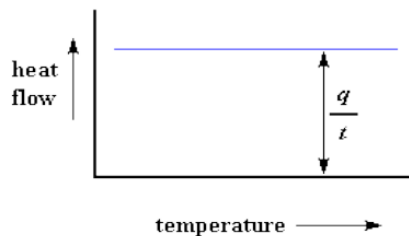
DSC Signals

DSC measures the difference in heat flow rate (mW = mJ/sec) between a sample and inert reference as a function of time and temperature

- Heat Flow
 - Endothermic: heat flows into the sample as a result of either heat capacity (heating) or some endothermic process (T_g , melting, evaporation, etc.)
 - Exothermic: heat flows out of the sample as a result of either heat capacity (cooling) or some exothermic process (crystallization, cure, oxidation, etc.)

Determination of Heat Capacity

- **DSC plot can be used to determine Heat Capacity. Suppose a polymer is being heated. When we start heating two pans, the computer will plot the difference in heat output of the two heaters against temperature that is plot of heat absorbed by the polymer against temperature. The plot will look like this at first.**



- The heat flow is heat (q) supplied per unit time (t), whereas,
- The heating rate is temperature increase (ΔT) per unit time (t)

$$\text{heat flow} = \frac{\text{heat}}{\text{time}} = \frac{q}{t}$$

$$\text{heating rate} = \frac{\text{temperature increase}}{\text{time}} = \frac{\Delta T}{t}$$

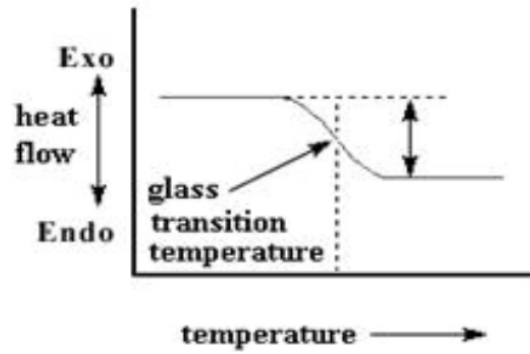
- By dividing heat flow (q/t) by the heating rate ($\Delta T/t$). It ends up with heat supplied divided by the temperature increase, which is called heat capacity.

$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = \text{heat capacity}$$

- When a certain amount of heat is transferred to the sample, its temperature increases by a certain amount, and the amount of heat it takes to get a certain temperature increase is called the heat capacity, or C_p , it can be figured up from the DSC plot

The Glass Transition Temperature

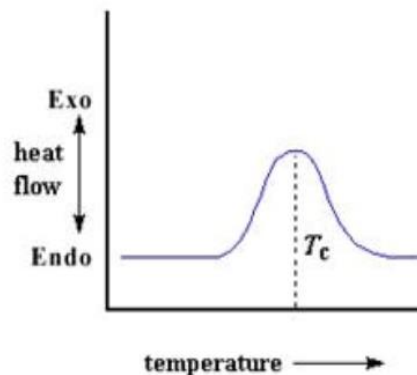
- On further heating the polymer to a certain temperature, plot will shift downward suddenly, like this:



- This means there is more heat flow. There is an increase in the heat capacity of the polymer. This happens because the polymer has just gone through the glass transition. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymer's glass transition temperature.
- Take note that this change doesn't occur suddenly, but takes place over a temperature range. This makes picking one discrete T_g a kind of tricky matter, but we usually just take the middle of the incline to be the T_g .

Crystallization

- After glass transition, the polymers have a lot of mobility. They wiggle and squirm, and never stay in one position for very long time. But when they reach the right temperature, they will give off enough energy to move into very ordered arrangements, which is called crystals.
- When polymers fall into these crystalline arrangements, they give off heat. When this heat is dumped out, it makes the little computer-controlled heater under the sample pan really happy. It's happy because it doesn't have to put out much heat to keep the temperature of the sample pan rising. You can see this drop in the heat flow as a big peak in the plot of heat flow versus temperature



The temperature at the highest point in the peak is usually considered to be the polymer's crystallization temperature, or T_c

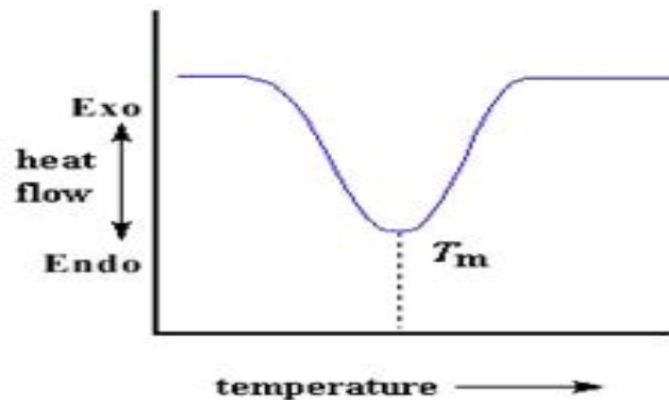
- Also, we can measure the area of the peak, which tells us the latent energy of crystallization of the polymer
- But most importantly, this peak tells us that the polymer can in fact crystallize
- If you analyze a 100% amorphous polymer, like polystyrene, you wouldn't get this peak, because such materials don't crystallize
- Also, because the polymer gives off heat when it crystallizes, we call crystallization is an *exothermic* transition

Melting

- If we heat our polymer past its T_c , eventually we'll reach another thermal transition, called melting. When we reach the polymer's melting temperature, T_m , the polymer crystals begin to fall apart, that is they melt. It comes out of their ordered arrangements, and begin to move around freely that can be spotted on a DSC plot

- Remember, the heat which polymer give off when crystallized is absorbed when reached at T_m . That is a latent heat of melting like latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so. Remember melting is a first order transition. This means that at the melting temperature, the polymer's temperature won't rise until all the crystals have melted.

This means that the little heater under the sample pan has to put a lot of heat into the polymer in order to both melt the crystals *and* keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up as a big dip on DSC plot, like this:



General Experimental Setup

- **Calbration:**
 - Same heating rate as experiment
 - Same atmosphere and purge flow rates(50cc/min)
 - Same temperature range as experiment
- **Pan:**
 - Flat bottom
 - Good sample –to-pan contact
 - Inert to reactive samples
- **Reference:**
 - Same pan as sample, but it should be empty
- **Pan-Cell Contact:**
 - **Symmetric placement of reference and sample**

Reporting DSC Data

- Identification of all substances and their sources
- Details of material histories, pretreatments, purities, etc.
- Calibration procedures, temperatures, cell constants used.
- Details of any preconditioning
- Temperature program
- Method for detrmining Tg, Tm
- Instrument used

Melting and Crystallization

- Melting is the endothermic transition from a crystalline solid to a liquid amorphous state
- Crystallization is the exothermic transition from amorphous to crystalline (normally from liquid to solid during cooling)
- Cold-Crystallization is the exothermic transition during heating from a solid amorphous state to a solid crystalline state.

Measurement of Melting

