

Thermal Analysis

We define thermodynamics... as the investigation of the dynamical and thermal properties of bodies, deduced entirely from the first and second laws of thermodynamics, without speculation as to the molecular constitution.

—J. Clerk Maxwell

Classical thermodynamics... is the only physical theory of universal content which I am convinced... will never be overthrown.

—Albert Einstein

Ice when heated, gives water which on heated boils!

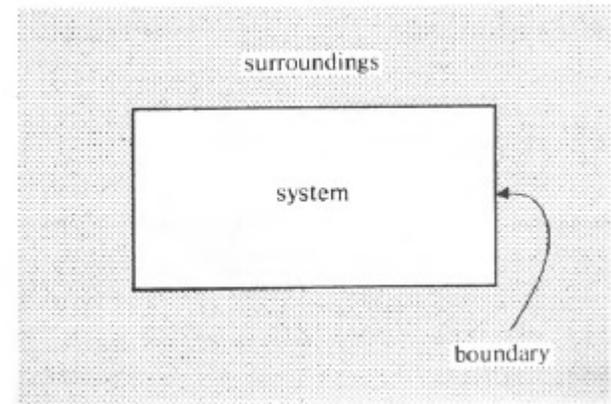
Which can then be cooled to return back to previous states!

Sugar when heated gives a brown caramel.
Heating coal gives gas, tar and coke.

Certain properties are obvious at appearance.

However detailed investigation can reveal interesting properties about material

Thermal properties such as heat capacity, enthalpy, entropy determine physical characteristics



What is Temperature ?

It follows from Zeroth law:

If two systems are in thermal equilibrium with third, then the two must be in thermal equilibrium.

So what is thermal equilibrium ?

For a portion of the universe that concerns us, called system, there exists a set of observables (measurables like pressure, volume, polarizability, displacement,...).

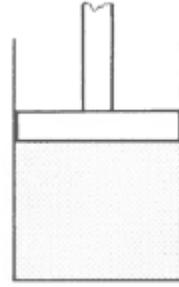
When our system is made to interact/ brought into contact with some surroundings/another system, a change of measurables is set in motion.

A state of thermal equilibrium is reached when the changes die down (No measurable change)

But still, what is temperature ?

Consider the example of frictionless piston P_1

At any time, its state is defined by variables P_1, V_1



The piston contains a fluid with uncountable number of particles. There are two free variables P, V

Imagine a reference piston P_R

We set the piston to a state with P_R, V_R

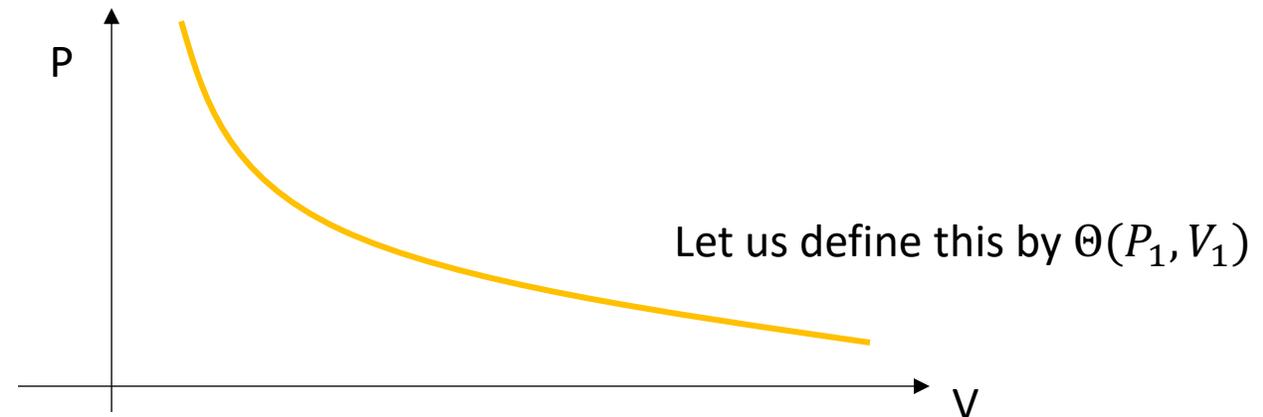
If we enforce thermal equilibrium between the two fluid pistons, then there will be only one free variable. If we take it to be V , then the pressure will be determined by the equilibrium condition

We can draw what are called as Isotherms

At any point on the curve, two systems are in equilibrium.

Each point is uniquely determined by P_1, V_1, P_R, V_R

We can define a function \mathfrak{S}_1 such that $\mathfrak{S}_1(P_1, V_1, V_R) = P_R$ for P_1 and V_1 along the line



Remember, P_2 is also in equilibrium with P_R

So, we can also then find another function $\mathfrak{S}_2(P_2, V_2, V_3) = P_R$

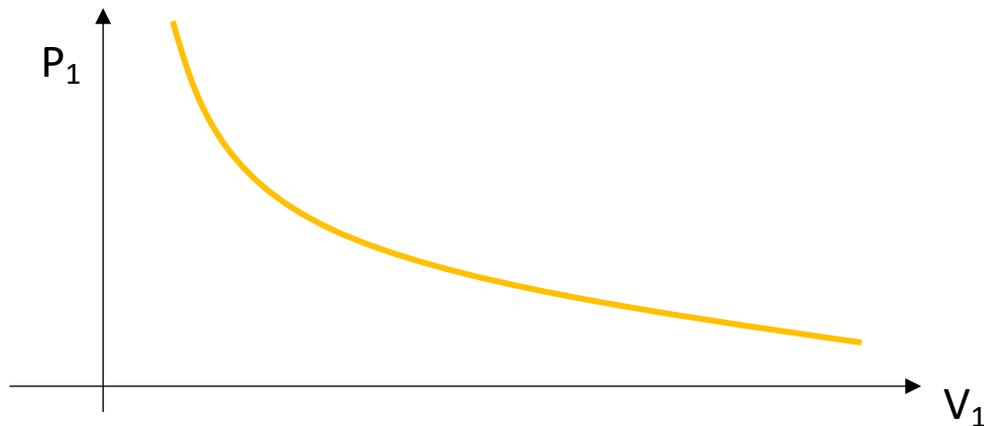
Obviously, $\mathfrak{S}_1(P_1, V_1, V_3) = \mathfrak{S}_2(P_2, V_2, V_3)$

Since, V_3 appears in both equations, coming from similar formulations, it will cancel out, giving you a form

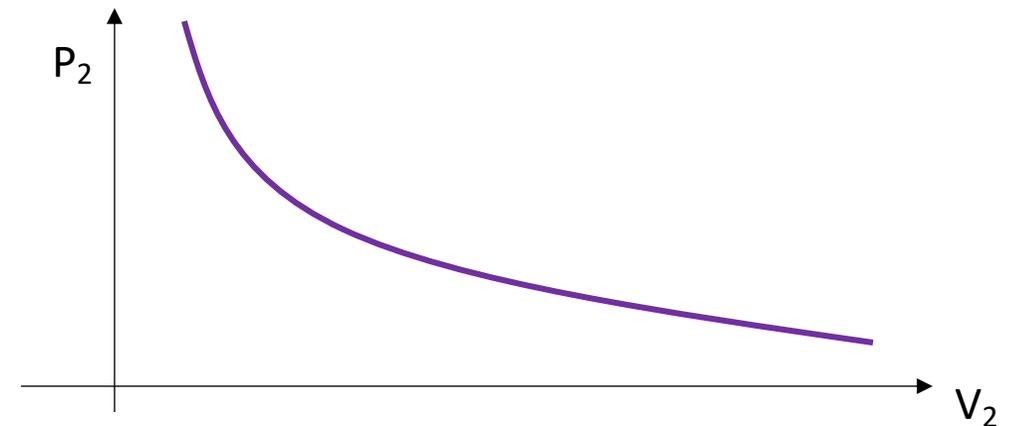
$$\Theta_1(P_1, V_1) = \Theta_2(P_2, V_2)$$

Thus, there exists function of pressure and volume of each systems, which remains the same in both the systems.

We call the function Temperature



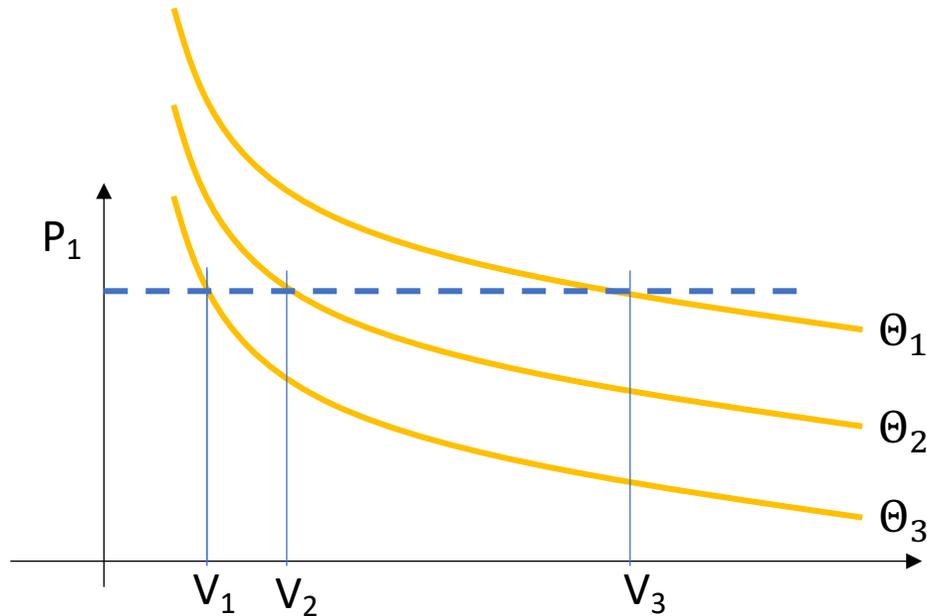
Due to P_1 being in equilibrium



Due to P_2 being in equilibrium

We have still been very vague!

We need a numerical value of 'hotness'



You have three isotherms – defined by the 'invariant function Θ '

A numerical estimate of the function can be obtained as follows:

Take a gas – at low enough pressures, works like ideal gas.

$$\text{We defined } T = \lim_{p \rightarrow 0} \frac{pV}{R}$$

Lord Kelvin: let us choose R , such that at the triple point of water, the thermodynamic temperature $T = 273.16$ K.

The difference between melting point and boiling point of water was needed to be 100 units! (For calibration)

If you are wondering, why such weird number:

The ratio of 'hotness' of triple point to hotness difference from triple point – boiling point – 2.73!

That's why Kelvin's scale is an absolute scale. 0K is the lowest temperature.

Consider a situation when two systems are not in equilibrium and brought to contact.

So, two systems have two different temperatures. Under such situations, there seems to be an exchange – called heat.

Heat is a form of energy that is exchanged.

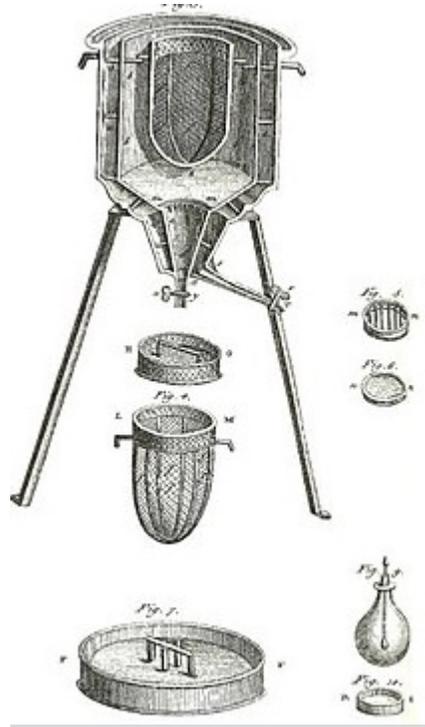
What is heat ?

Two theories existed:

Caloric theory

Heat is an indestructible fluid which permeated matter.
If flowed from hotter bodies to cooler bodies

Black's 1761 experiment:



Molecular motion theory

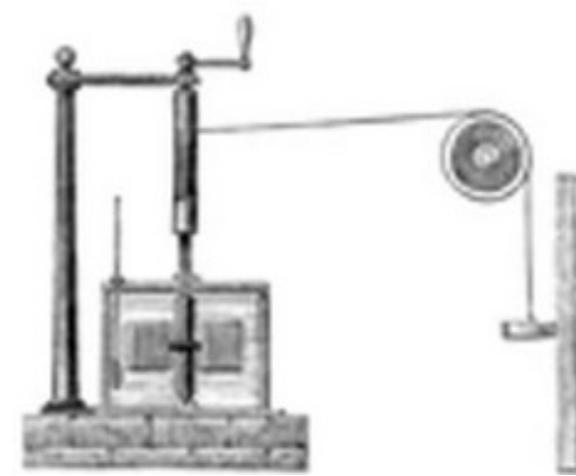
Heat was associated to rapid vibration of molecules.

When ice cold water was kept in hot room, the water temperature raised fast,
If an ice cube is inside the water, the ice cube melted, but the water temperature didn't rise!

If heat flowed from outside to inside, the heat in water should be more than that in the ice?

Joule's Heat (1840)

Heat doesn't have to flow from outside. He took thermally isolated systems and generated heat!

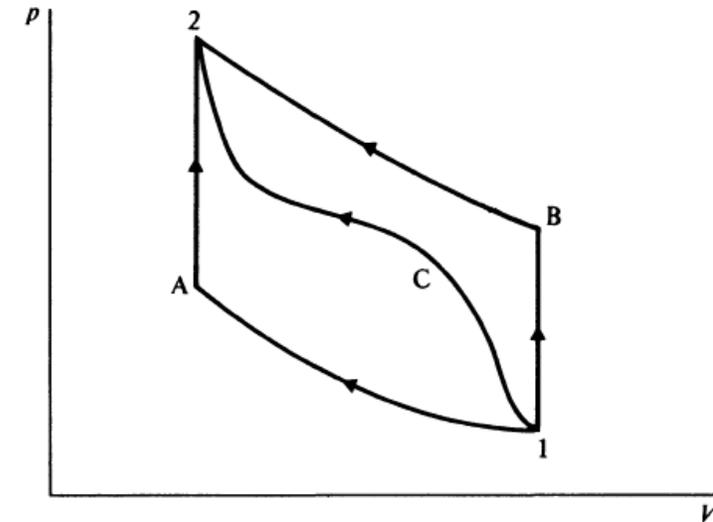


He showed temperature increase in isolated systems by

1. viscous dissipation in liquids
2. Friction in solids
3. Electric heating in wires.

'Work' needs to be done on the system to generate heat \rightarrow rise temperature.

There has to be a proportion between heat and work.



1st law: If the state of an otherwise isolated system is changed by performance of work, the amount of work is solely decided by the change effected – Not by the means of work nor the intermediate stages through which the system passes between its initial and final states.

So, as before, a state of a system is defined by P,V in the simplest case of a piston.

We define U, (Internal Energy) a function of the state,

Such that when work is done **on** the state, there is change in the internal energy

$$\Delta U = W$$

However, this was the case when we used thermally isolated walls. (adiabatic)

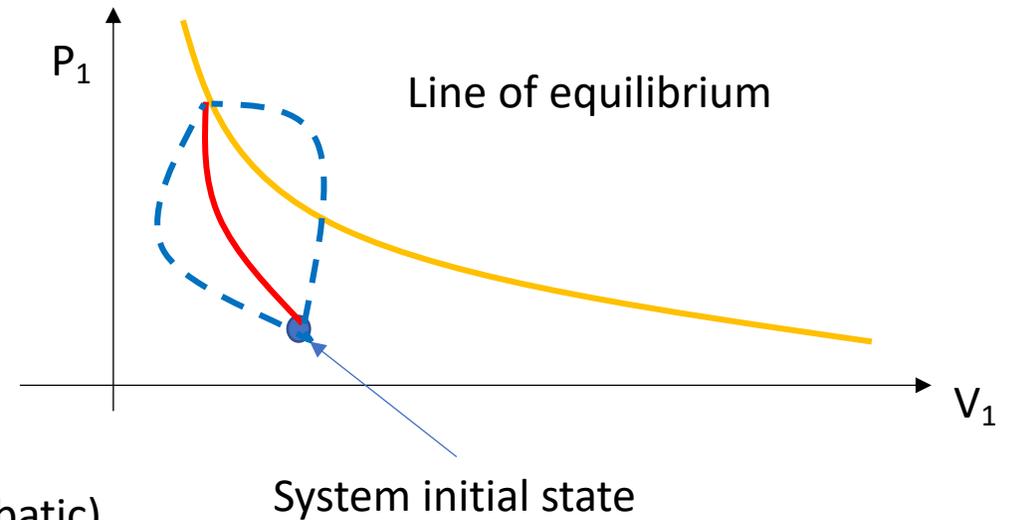
What happens if there can be heat flow (Q) from outside ?

$$\Delta U = Q + W$$

Remember, if work of magnitude W is performed **by** the system $\Delta U = Q - W$

For a small infinitesimal energy change dU can be obtained either from small heat flow dQ or small work dW

$$dU = dQ + dW$$



Examples 1: Work done under hydrostatic pressure

Piston with cross section A .

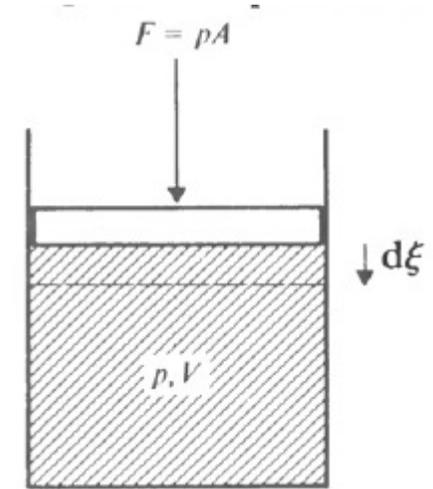
Force on the piston $F = pA$, p is applied pressure

If it causes a displacement $d\xi$, work done

$$dW = Fd\xi$$

Substituting $dW = pAd\xi = pdV$

In decreasing volume, work is done on the fluid, and in other case, work is done by the fluid.

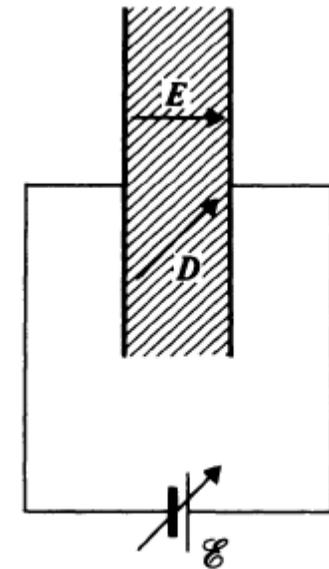


Example 2: Work done under electric field:

If E is the electric field perpendicular to the plates, causing a polarization

P is the dipole moment $p = q * d$ and $dp = q * dd$

Work done is then $dW = E \cdot dp$

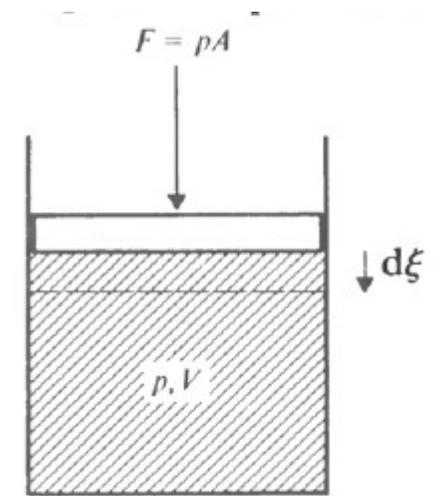


Consider the same hydrostatic pressure system

If a work W is done by the system

$$\Delta U + W = Q$$

In other words, for a work W done by the system, a heat Q is provided by the surroundings



Considering the case in which work is done under constant pressure P

$$W = \int_{V_1}^{V_2} p dV = p(V_2 - V_1)$$

$$Q_{1 \rightarrow 2} = U_2 - U_1 + pV_2 - pV_1$$

$$Q_{1 \rightarrow 2} = U_2 + pV_2 - (U_1 + pV_1) = H_2 - H_1$$

We call this term $H = U + pV$ as Enthalpy

Thus under constant pressure, heat provided to a system (closed) is the Enthalpy change

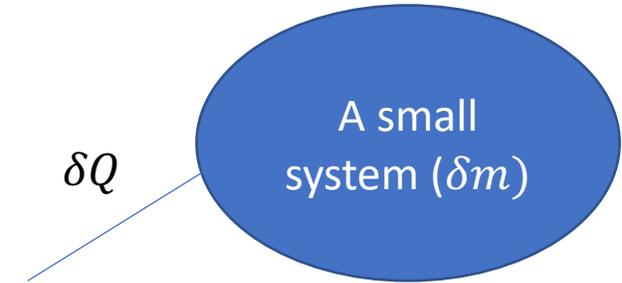
It is to say that if you need to expand (positive V change) under constant pressure, heat has to be supplied to the system.

Microscopically: the molecules now need to hit the walls at higher velocities

Heat Capacity

General heat capacity is the heat energy required to make a small change in a state observable α

$$C^{(\alpha)} = \left. \frac{\partial Q}{\partial \alpha} \right|_{\text{other variables}}$$



A common heat capacity is defined using temperature

$$C^{(T)} = \left. \frac{\partial Q}{\partial T} \right|_{V,P,..}$$

In the same hydrostatic pressure case

$$Q = U + pdV$$

This is not surprising: constant volume means no work is done!

$$C_V^{(T)} = \frac{\partial U}{\partial T}$$

Specific heat capacity at const volume $c_V = \frac{\partial u}{\partial T}$

Where $u = \frac{U}{\delta m}$

In similar ways, we can calculate $C_p^T = \left. \frac{\partial Q}{\partial T} \right|_P = \frac{\partial(U+pdV)}{\partial T} = \frac{\partial(U+pV)}{\partial T} = \frac{\partial H}{\partial T}$

Formal definitions of thermal analysis

Calorimetry:

Is the measurement of heat changes which occur during a process.

If calorimetric measurements are done under constant volume its called bomb calorimeter

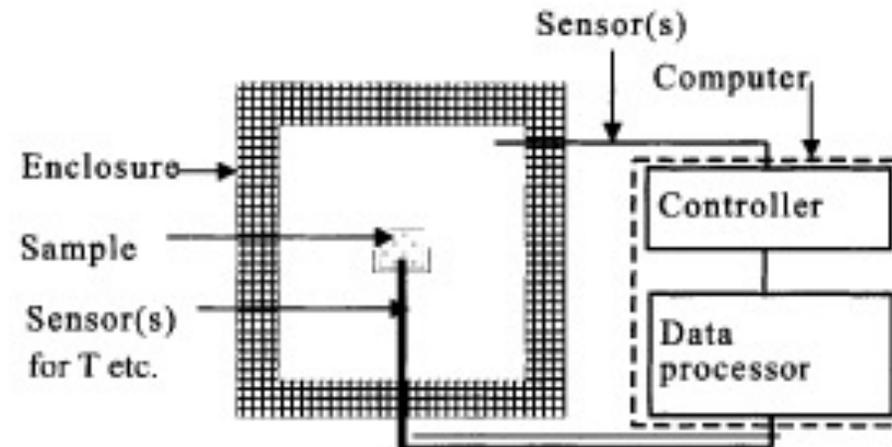
And those under constant temperature are called as isothermal calorimeter.

Thermal Analysis:

Is a group of techniques in which one property is studied as temperature is slowly varied.

1. E.g. sample may be heated or cooled at a fixed rate $\frac{dT}{dt} = \beta$ – eg: 10 K/min

Technique	Abbreviation	Property	Uses
Thermogravimetry or (Thermogravimetric analysis)	TG TGA	Mass	Decompositions Oxidations
Differential thermal analysis	DTA	Temperature difference	Phase changes, reactions
Differential scanning calorimetry	DSC	Power difference or heat flow	Heat capacity, phase changes, reactions
Thermomechanical analysis	TMA	Deformations	Mechanical changes
Dynamic mechanical analysis	DMA	Dimensional change Moduli	Expansion Phase changes, glass transitions, polymer cure as DMA
Dielectric thermal analysis	DETA	Electrical	Decompositions
Evolved gas analysis	EGA	Gases evolved or reacted	
Thermoptometry		Optical	Phase changes, surface reactions, colour changes
<i>Less frequently used methods</i>			
Thermosonimetry	TS	Sound	Mechanical and chemical changes
Thermoluminescence	TL	Light emitted	Oxidation
Thermomagnetometry	TM	Magnetic	Magnetic changes, Curie points



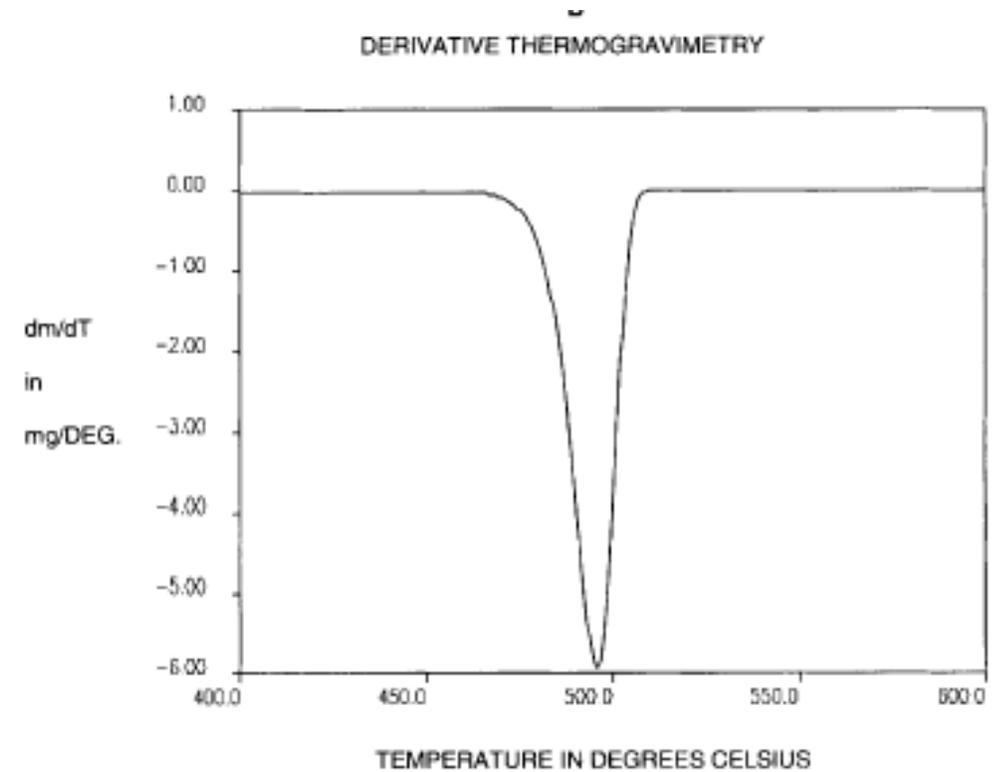
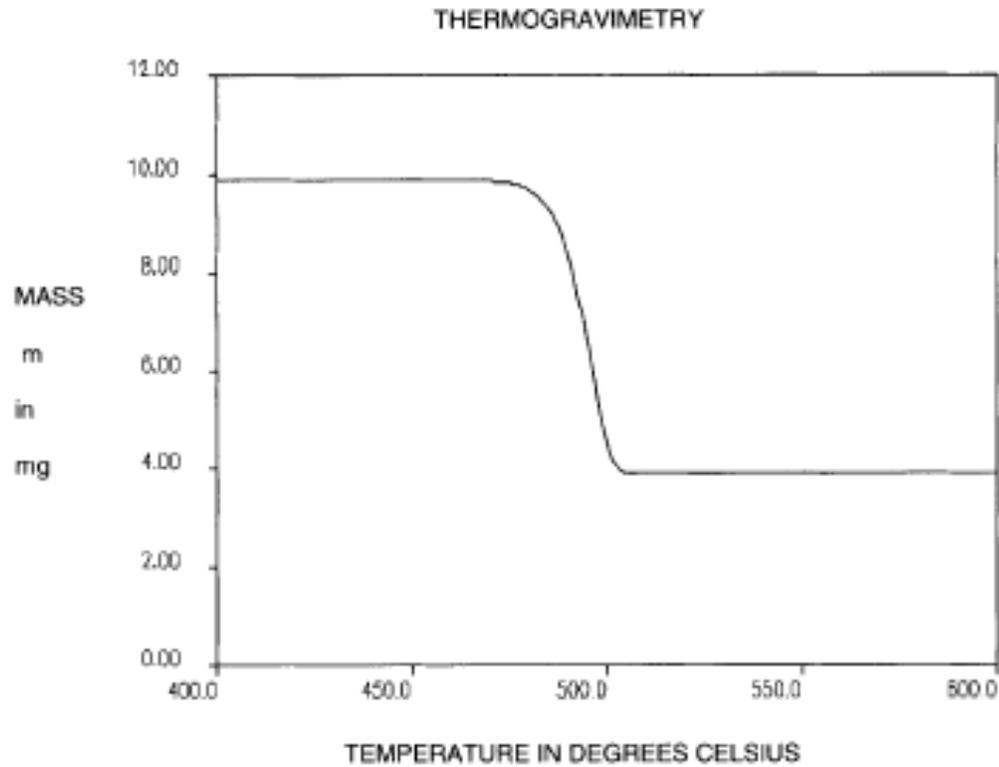
Thermal Transitions

Physical Phenomena	Chemical phenomena
Crystalline transition	Chemisorption
Second order transitions	Desolvation
Fusion	Decomposition
Vaporization	Oxidative transition
Sublimation	
Absorption	Solid-State reaction
Adsorption	Solid-gas reaction
Desorption	

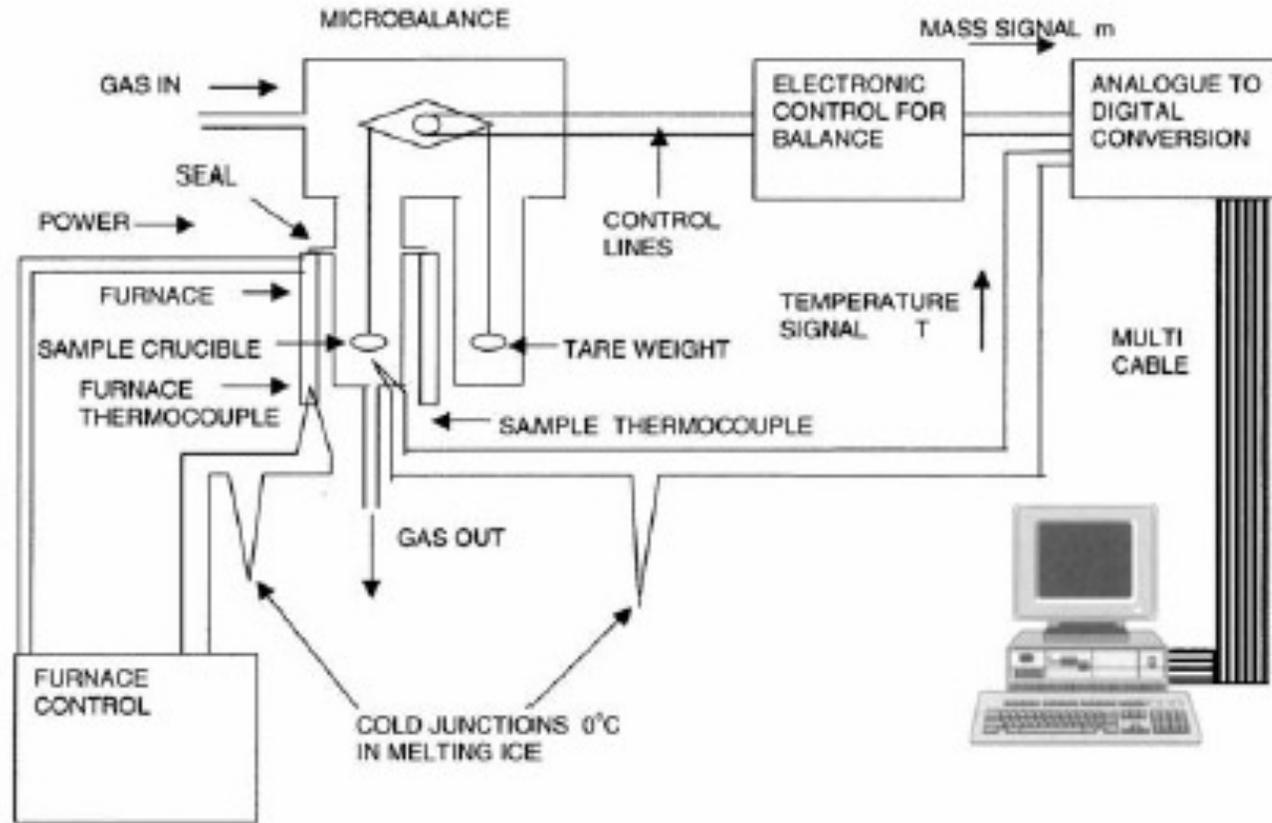
Thermal gravimetry analysis gives information relating to

Thermal Gravimetry:

Mass change of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program.



A typical thermobalance



Microbalance: The accurately measure weight

Furnace: Provide heat controllably
Typically can do $-160 - 1600\text{ }^{\circ}\text{C}$

Atmosphere control: inert gas
ambient/oxidising ambient

Crucibles: Sample holders which doesn't get affected by heat/chemicals

Thermocouples: combination of two metals which provide a EMF based on the temperature.

Temperature control: This is typically using a feed back loop between the furnace and the thermocouples

Data Collection: This is typically computer automated. Measurements are typically made in terms of time or temperature. They are recorded using a computer and plotted as necessary.

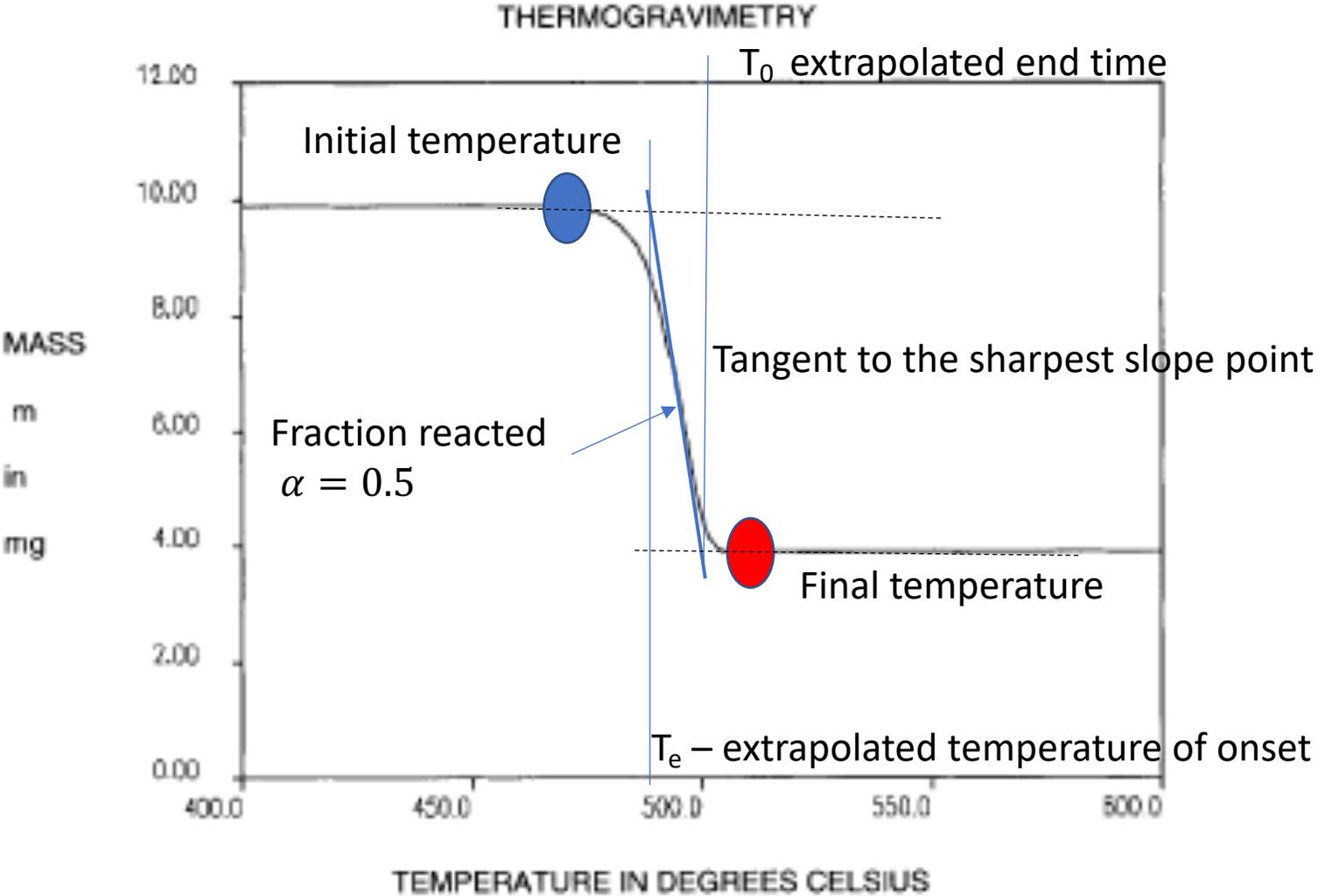
Types of thermogravimeter:

1. isothermal measurements
2. scanning/ramping/rising measurements

Calibration of mass and temperature:

1. Zeroed values: In the absence of the sample, the total mass should fall down to zero. This needs to be corrected before the experiment begins.
2. Calibration: This is typically done using a standard of known mass. The manufacturer of the equipment typically provides the mass standard.
3. For temperature, the thermocouple can be calibrated using different techniques
 1. Look for some known features that occur at predefined temperatures (such as melting of metals at STP)
 2. Calibrate unknown thermocouple with a known thermocouple.
 3. Locate the Curie point of metals – Say Nickel.

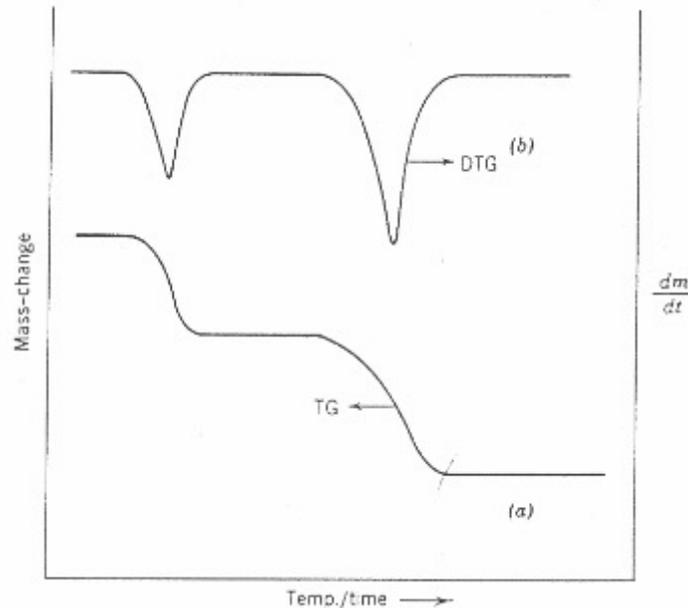
Analysing a measurement:



Differential TG

In traditional TG, mass is recorded as a function of Temp/Time,

$$m = f(T, t)$$



In derivative TG,

$$\frac{dm}{dt} = f(T, t)$$

When there is no mass loss, TG and DTG both have flat lines.

When there is change, peaks are observed in DTG.

The peak position tells you the inflection point – point at which the reaction rate is maximum

The area under the DTG is proportional to the mass change !

TG and DTG are invaluable experiments to observe desorption, decomposition, oxidation processes.

If you want to know the accurate temperatures for drying/dehydration, ignition of precipitates/solvent, TG/DTG is an ideal and simple technique

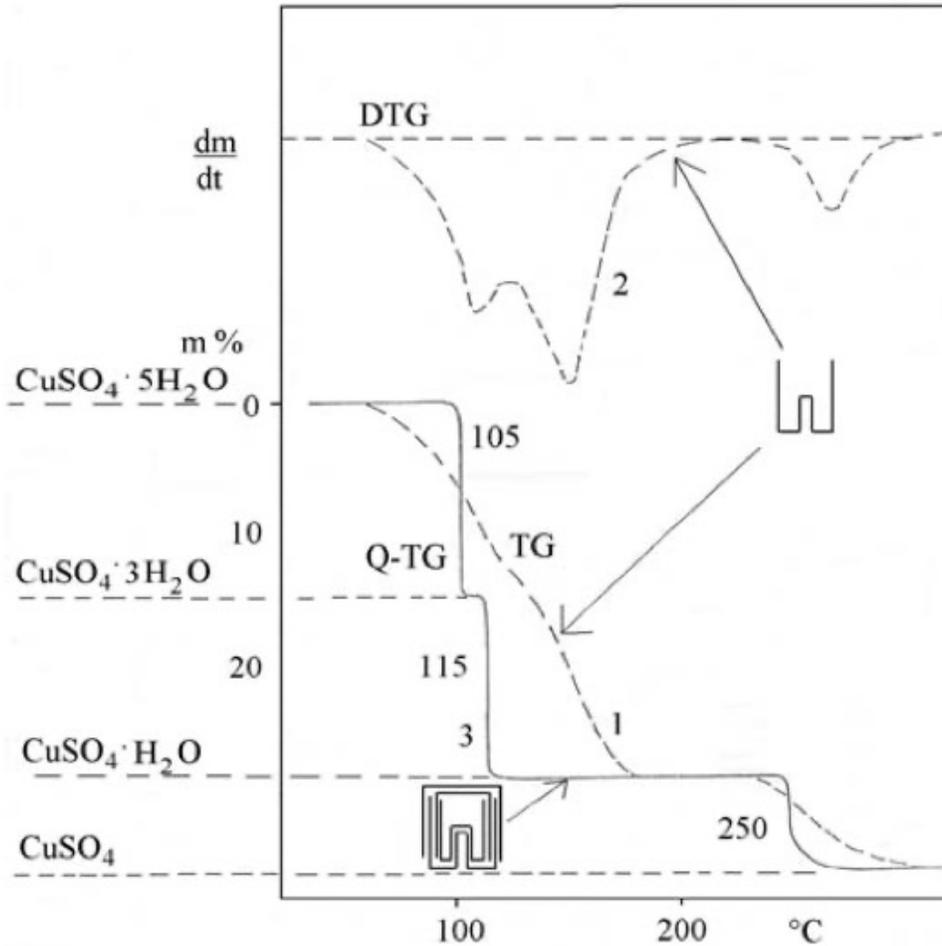
Main applications in characterization of

- Thermal stability
- Material purity
- Determination of humidity

Examination of

- Corrosion
- Gasification
- Kinetic processes

Examples of TGA: Dehydrogenation



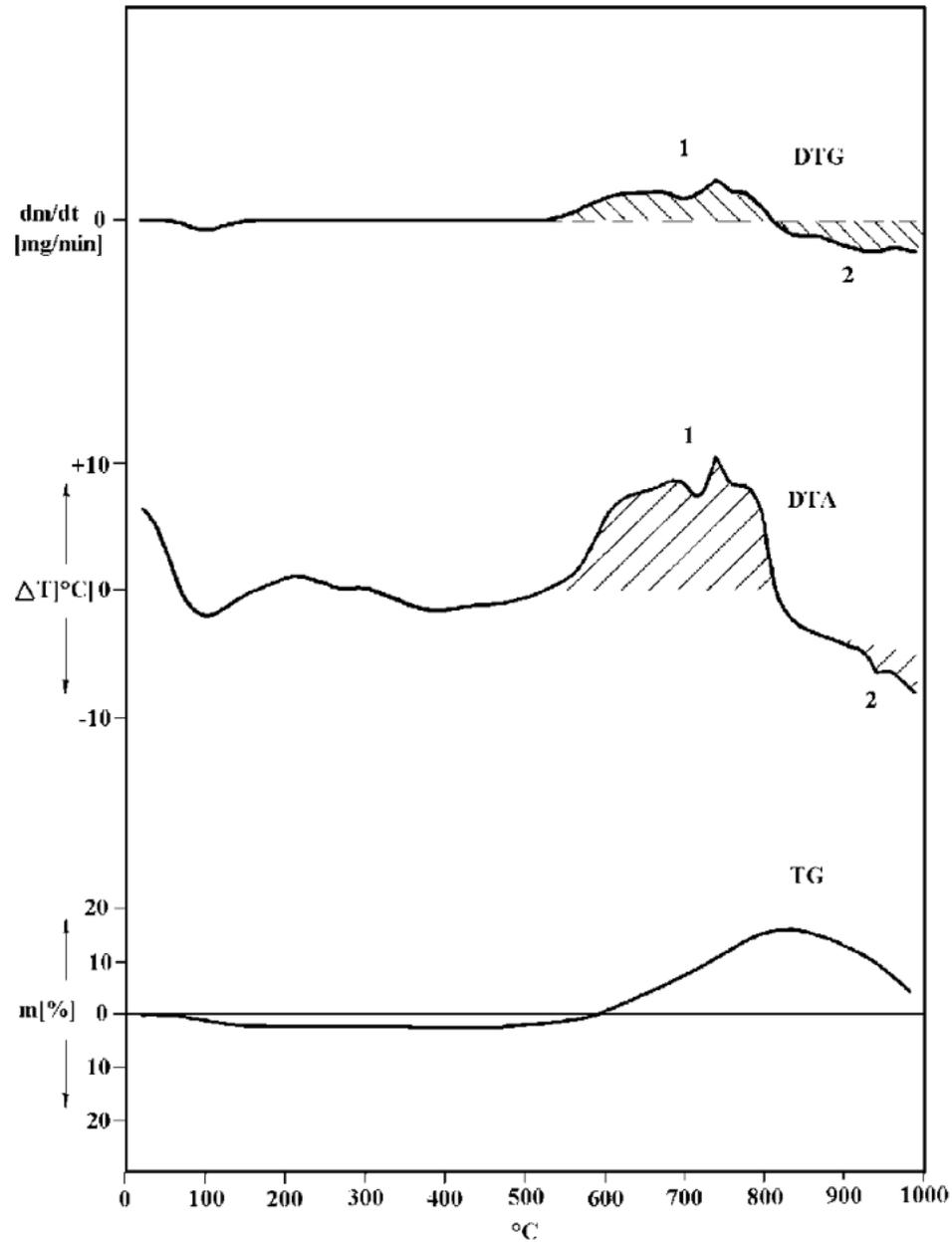
Water molecule coordinated with Cu^{2+} gets desorbed at different temperatures.

While the first two molecules are isothermal – starts almost at the same temperature,

The last molecule of water leaves much higher in temperature!

Reactions:

1. Between 600–820 °C: exothermic: oxidation with different internal products of PbO, PbSO₄, and PbO·PbSO₄.
2. Between 850–1100 °C: thermal decomposition, endothermic:
 $\text{PbSO}_4 \rightarrow \text{PbO} + \text{SO}_3 \uparrow$.

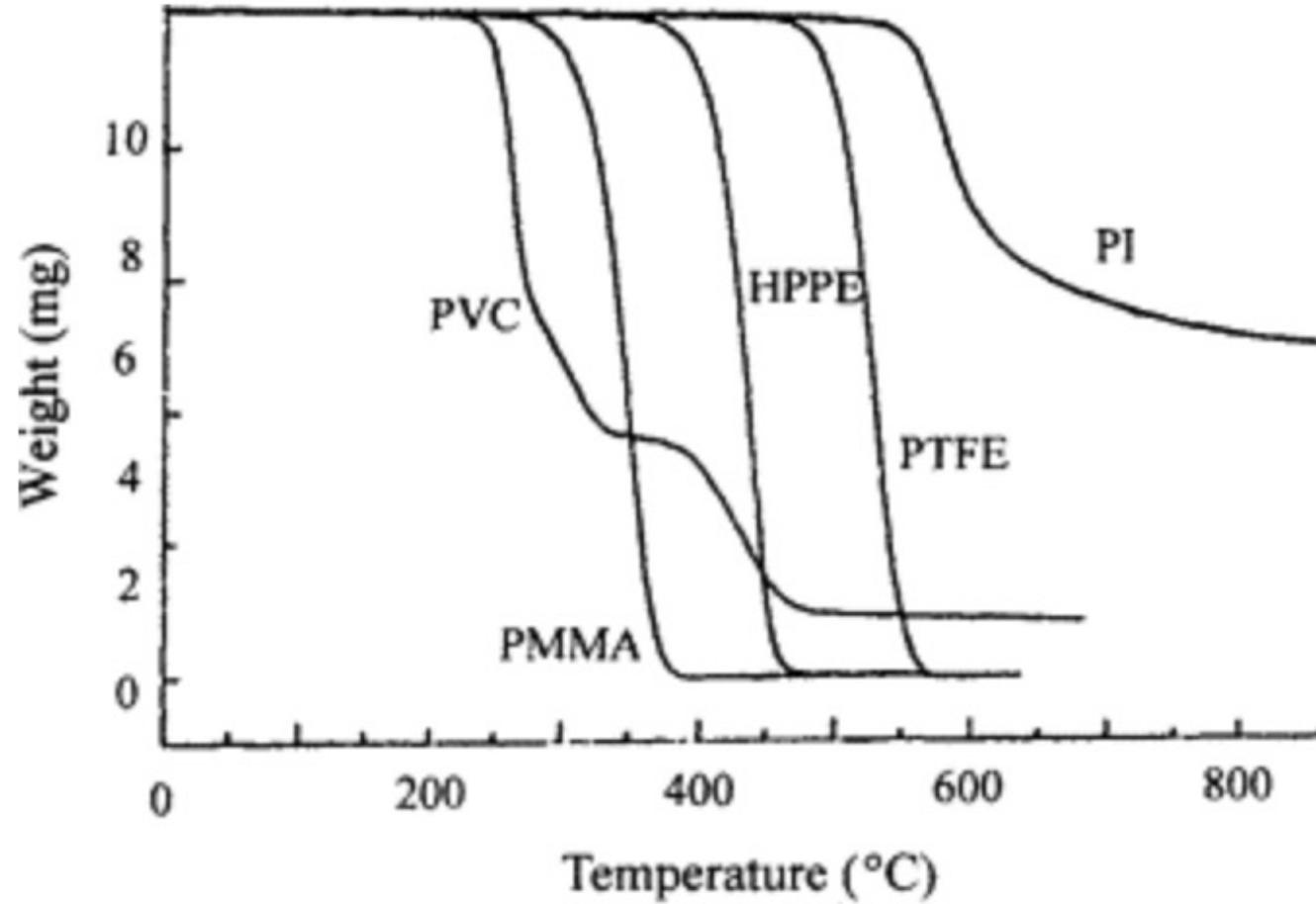


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 $\text{PbSO}_4 \rightarrow \text{PbO} + \text{SO}_3 \uparrow$.

Example degradation of polymers



Factors affecting TGA measurements:

1. Heating Rate: If $T1$ is the reaction starting temperature, and $T2$ – reaction ending temperature

$$(T1)_f > (T1)_s \text{ and } (T2)_f > (T2)_s$$
$$(T2 - T1)_f > (T2 - T1)_s$$

2. Sample related:

Reaction is endothermic/exothermic and its influence on the measurement is impacted by the mass of the sample used.

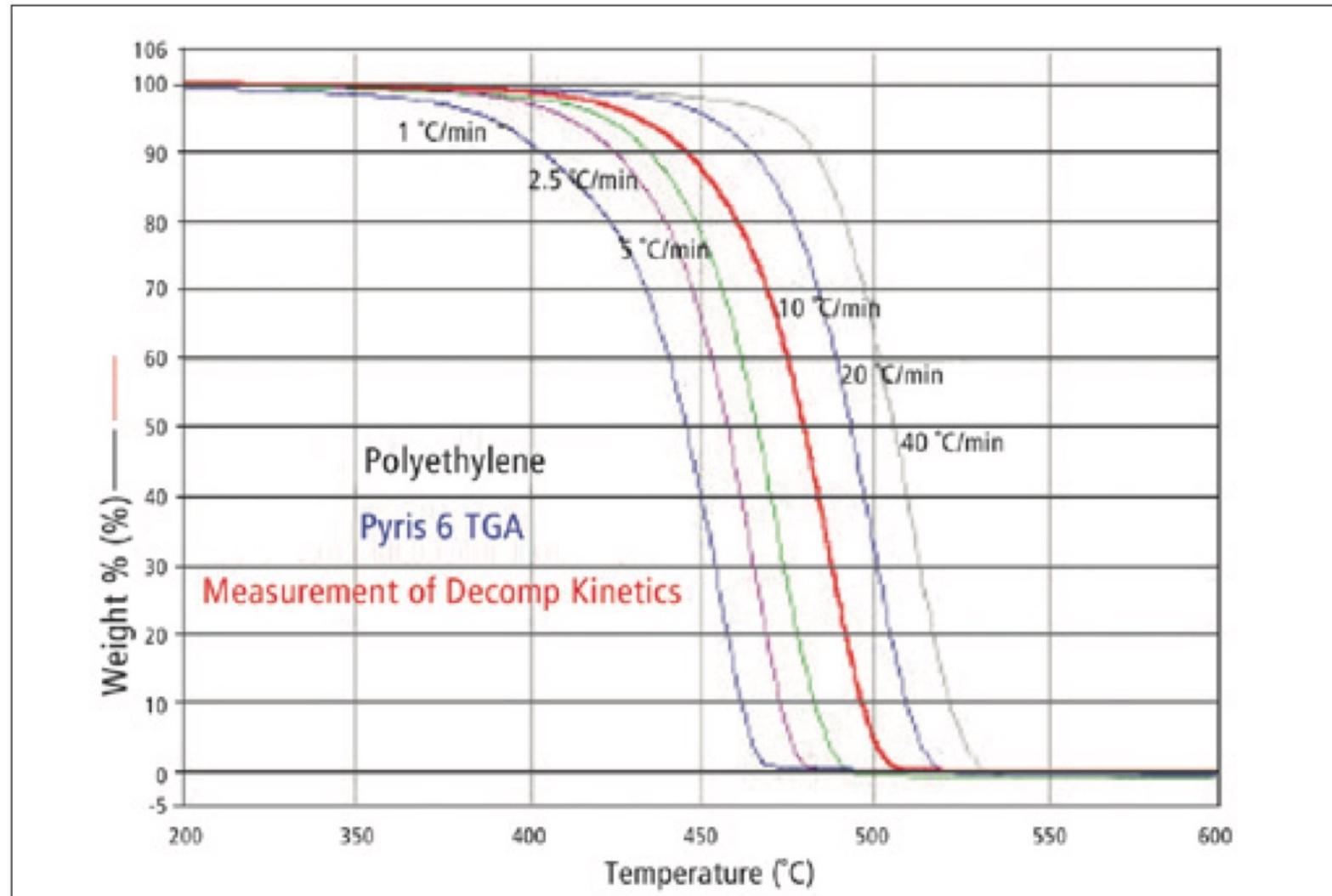
Thermal conductivity of the sample and the gas diffusivity effects the reaction temperature measurements.

Surface to volume rate has a dominant role to play

3. Geometry of the crucible

4. Atmosphere of the reaction

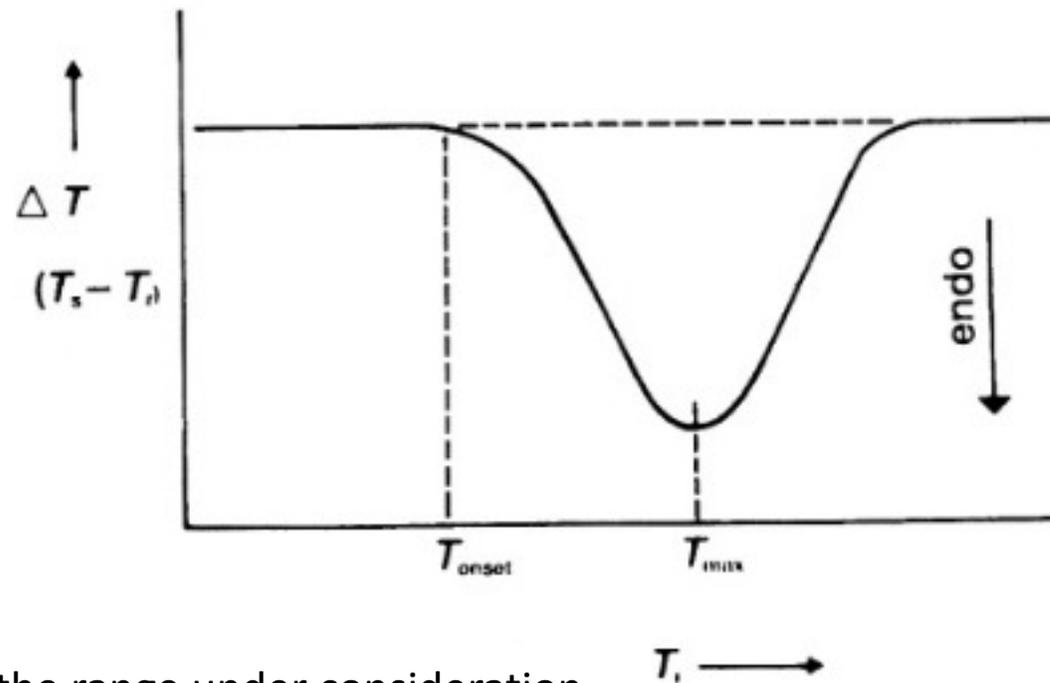
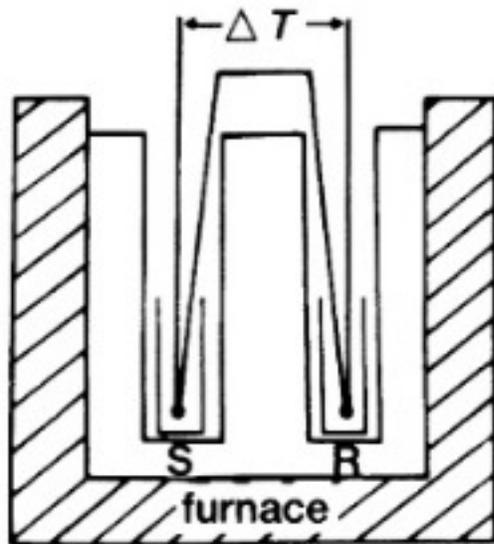
Example of effect of heating rate:



Differential Thermal Analysis and Differential Scanning Calorimetry

Being the most common technique:

It measures the temperature change difference between a sample and reference upon same delivery of heat.



A reference is chosen such that:

1. There should be no thermal event in the range under consideration
2. It shouldn't react with the sample holder/thermocouple
3. The thermal conductivity and heat capacity should be similar to the sample.

Alumina/carborundum are commonly used references

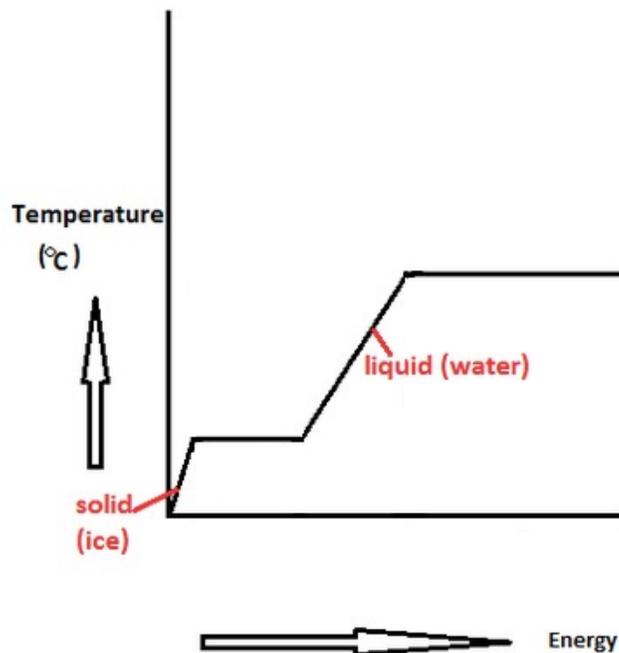
Remember, we defined Enthalpy H , and related $\Delta H = Q$ to the heat supplied to the system.

Take the example of ice



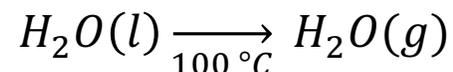
As the heat is supplied to ice, its temperature will rise till very near to zero. Beyond which a mole of water will not change temperature till $\sim 6\text{kJ}$ of heat is provided .

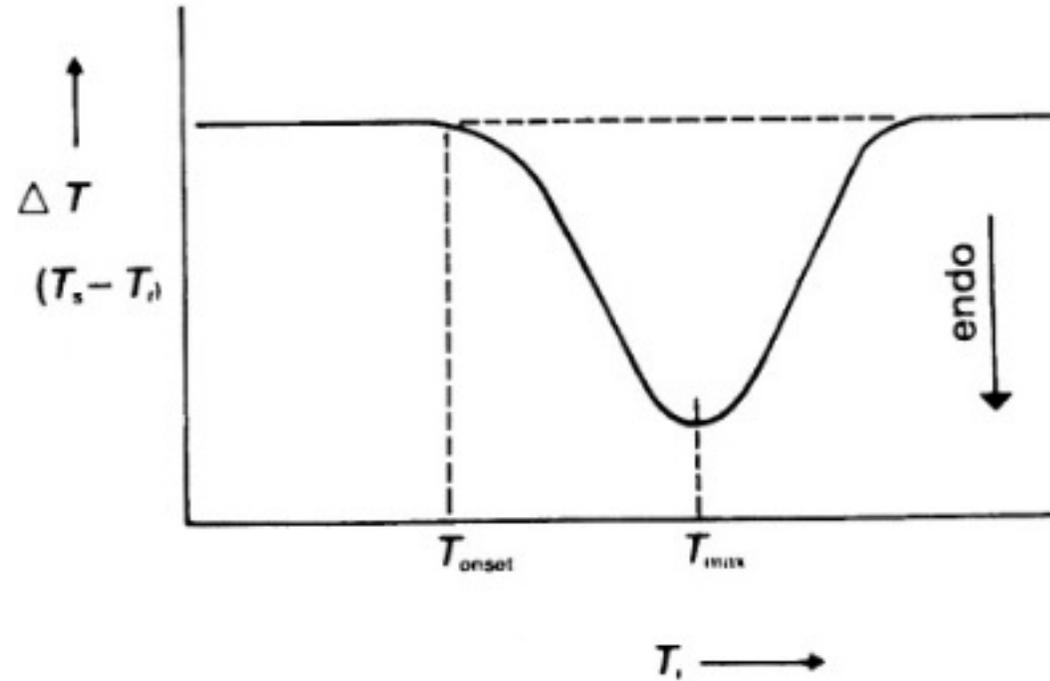
This heat energy, is called as enthalpy of fusion.



A similar transformation is observed when $100^\circ C$ is in vicinity.

A mole of water will not change in temperature for 40.67 kJ , called as enthalpy of vaporization.



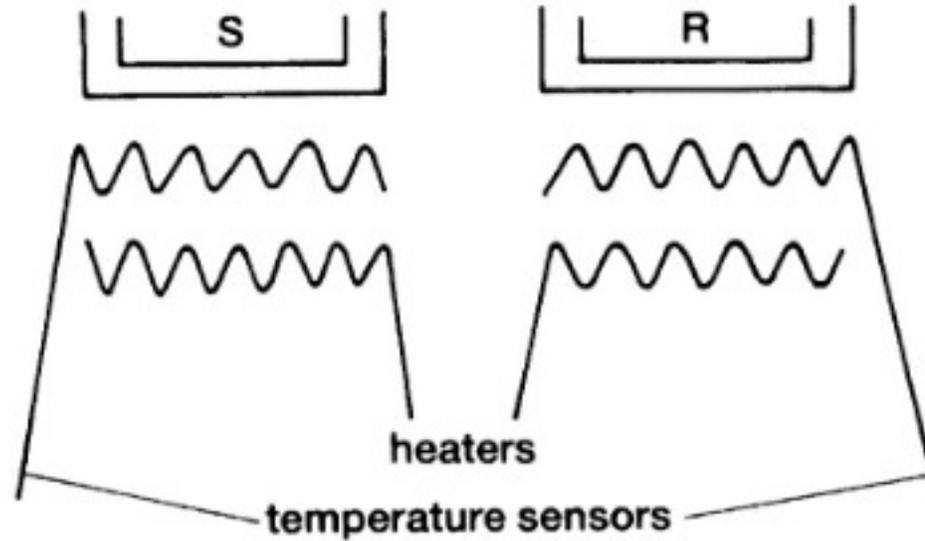


Since, in DTA, the plotted function in y-axis is $\Delta T = T_S - T_R$

When a thermal event such as melting is going to happen, the sample temperature doesn't change. A dip in the plot is obtained.

Since melting is an endothermic reaction in most cases, a dip is associated to endothermic reaction.

Differential Scanning Calorimetry

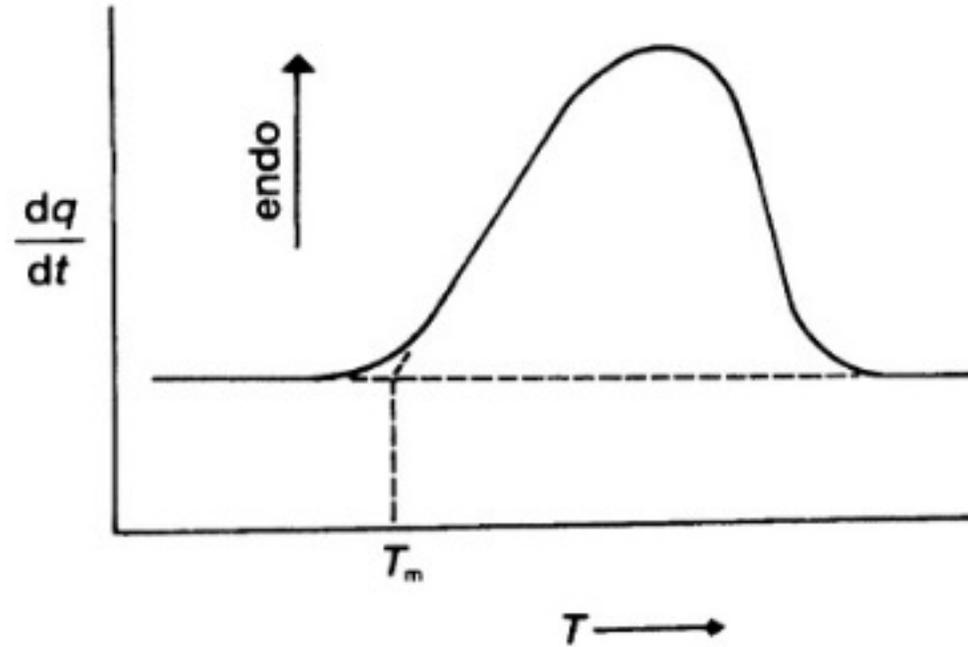


In a calorimetric setup, the heat supplied is measured instead of the temperature. The temperature of the sample and the reference is kept constant.

Such meters are called as power compensated DSCs.

$$\frac{dQ}{dt} = \left(\frac{dT}{dt} \right) (C_S - C_R)$$

A typical DSC plot for endothermic reaction

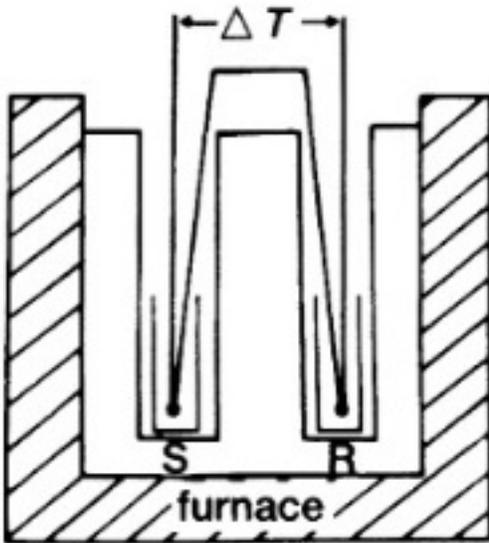


A typical measurement in which a melting transition is observed. Remember, here, again the differential is on the heat! Additional heat is required in the case of transition in the sample marking an endothermic reaction!

The Ohm's law for heat:

$$\Delta T = R * \frac{dq}{dt}$$

R – thermal resistance, q – heat supplied



In classical DTA –

The heat supplied is maintained a constant.

If the thermocouples remain the same in the sample and reference, thermal resistance between the sample and its holder and reference and its holder negligible

$$T_S - T_S^0 = \Delta T_S = R * \left(\frac{dq}{dt}\right) \text{ from the Ohm's law for the sample}$$

$$\frac{dq}{dt} = C_S \frac{dT_S}{dt}$$

$$\Delta T = T_S - T_R = R(C_S - C_R) \frac{dT}{dt}$$

The measured temperature difference depends on

heat capacity difference, heating rate as well as the thermal resistance (R)! R is very system specific!

Power compensated DSC:

The heat is supplied separately to sample and reference!

Such that $T_S = T_R \Rightarrow \Delta T = 0$

$$T_S - T_S^0 = \Delta T_S = R * \left(\frac{dq_S}{dt} \right)$$

$$T_R - T_R^0 = \Delta T_R = R * \left(\frac{dq_R}{dt} \right)$$

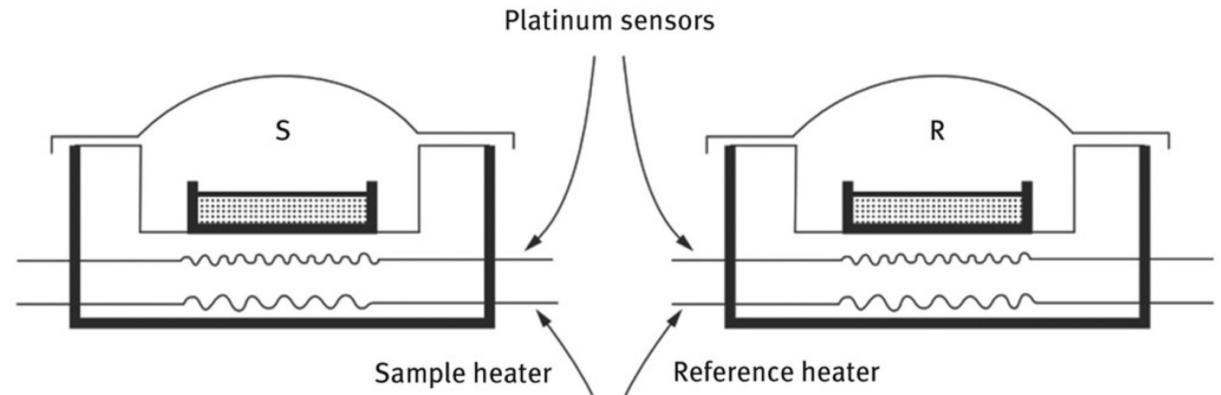
If the power is compensated such $T_S = T_R$,
 $\Delta T = T_S - T_R = 0 \Rightarrow R = 0$

Since the sample and reference are heating with some rate -

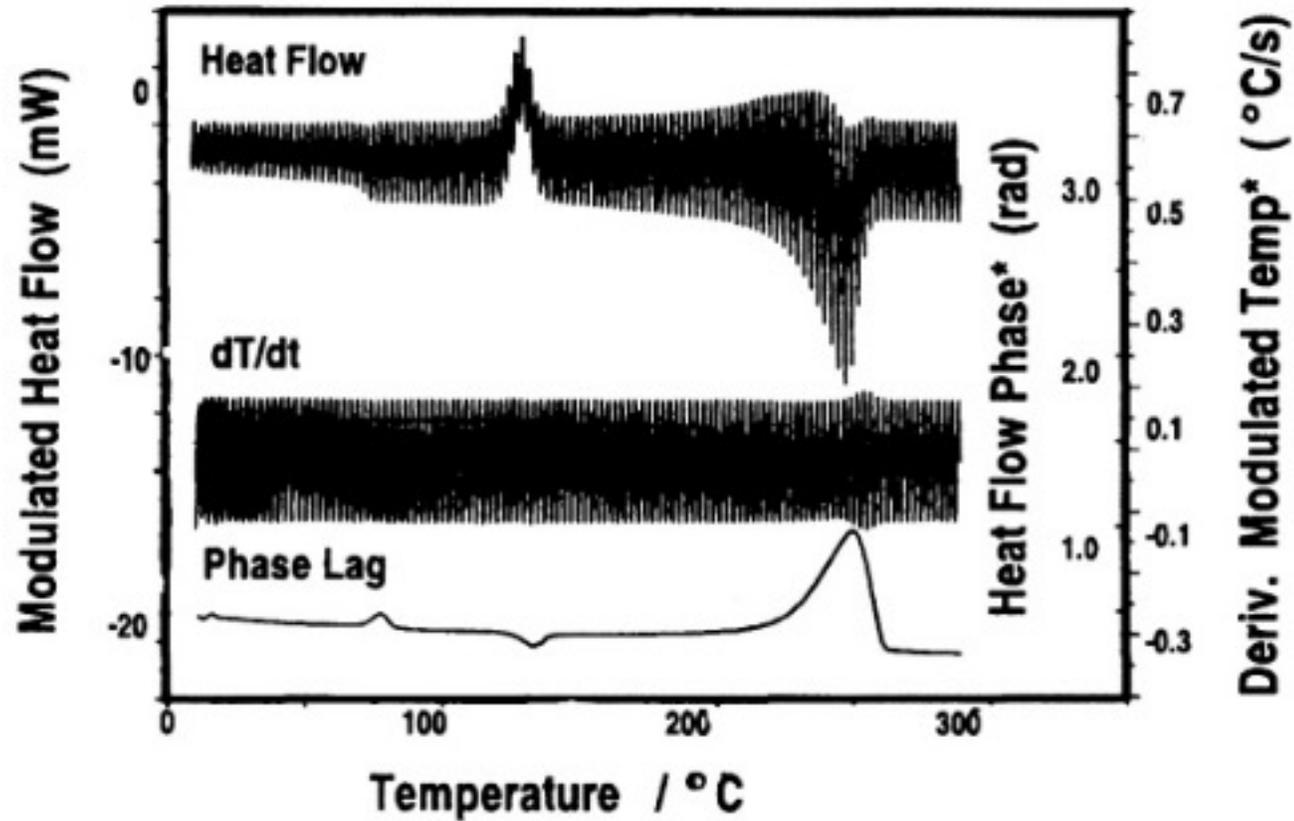
$$\frac{dq_S}{dt} \neq 0$$

$$\text{From } \frac{dq}{dt} = C \frac{dT}{dt}$$

$$\Delta \frac{dq}{dt} = \frac{dT}{dt} (C_S - C_R)$$



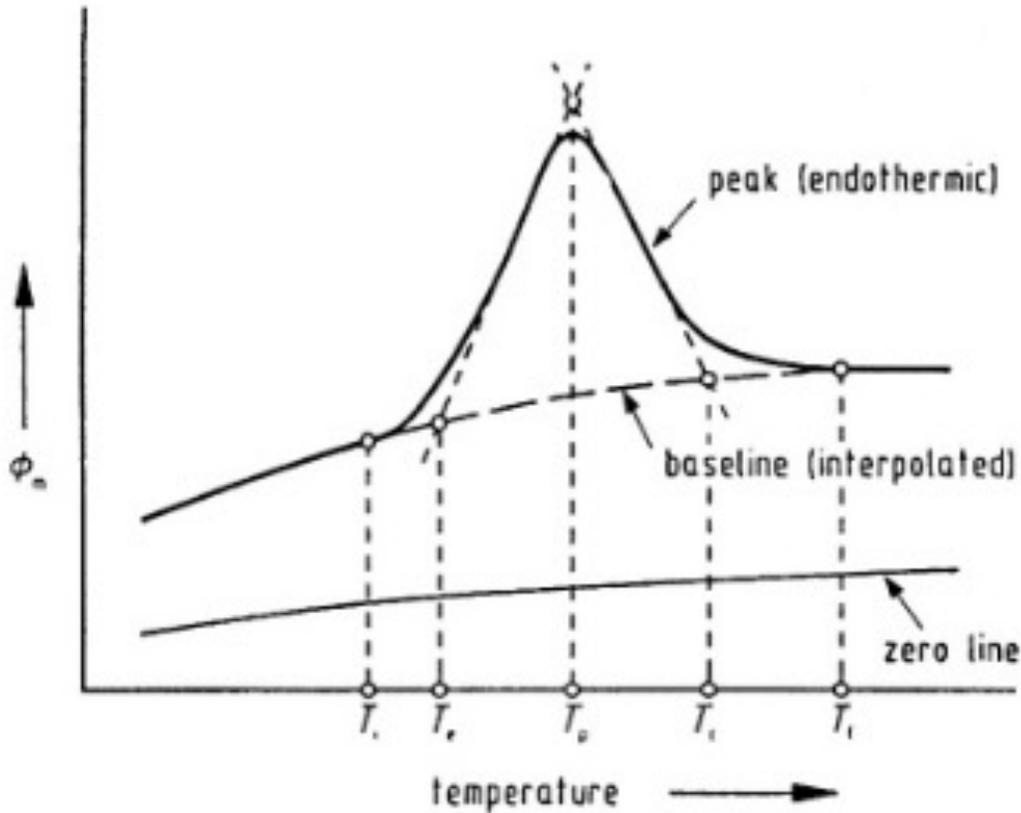
Modulated Temperature DSC



$$T = T_0 + \beta T + \gamma \sin \omega t$$

The heat flow $\frac{dq}{dt}$ is monitored for both the amplitude and phase difference with the temperature change!

Characteristics of DSC Curves



Y-axis – heat flux

Zero-line – is the curve obtained when the sample crucible is empty

Once the measurement is made,

A interpolated baseline is obtained when a peak is observed.

The line is drawn to match regions before and after a peak such that the peak was non-existent.

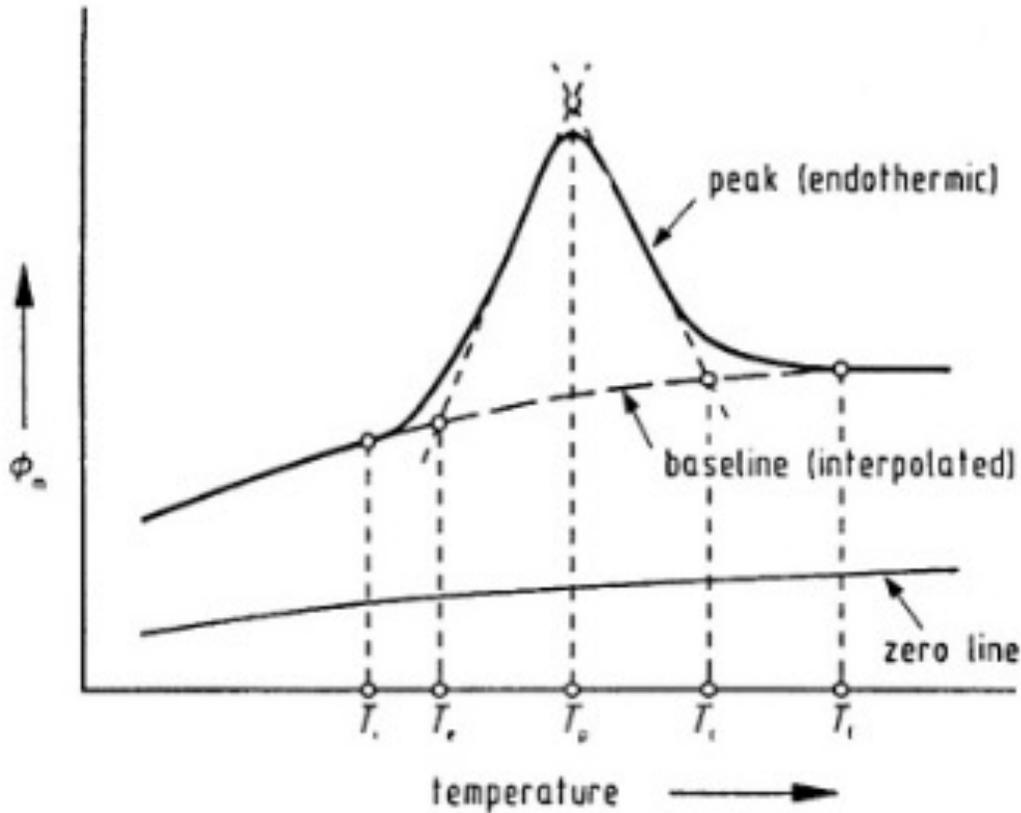
T_i – Initial temperature where the measured line deviates from baseline.

T_e - Actual onset is observed at intersection of baseline with the tangent to half-peak

T_c – extrapolated completion temperature

T_f – final peak temperature

Characteristics of DSC Curves



Zero-line – is the curve obtained when the sample crucible is empty

Once the measurement is made,

A interpolated baseline is obtained when a peak is observed.

Remember certain transitions such as glass transitions, just gives a change in the shape of the baseline

Ti – Initial temperature where the measured line deviates from baseline.

Te - Actual onset is observed at intersection of baseline with the tangent to half-peak

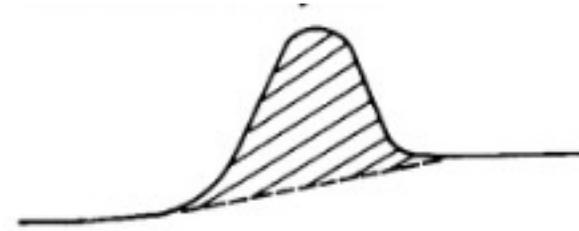
Tc – extrapolated completion temperature

Tf – final peak temperature

Measured Enthalpy: If A is the area of the peak

$$\Delta H = A \times \frac{k}{M}$$

M – mass of the sample, k – calibration factor



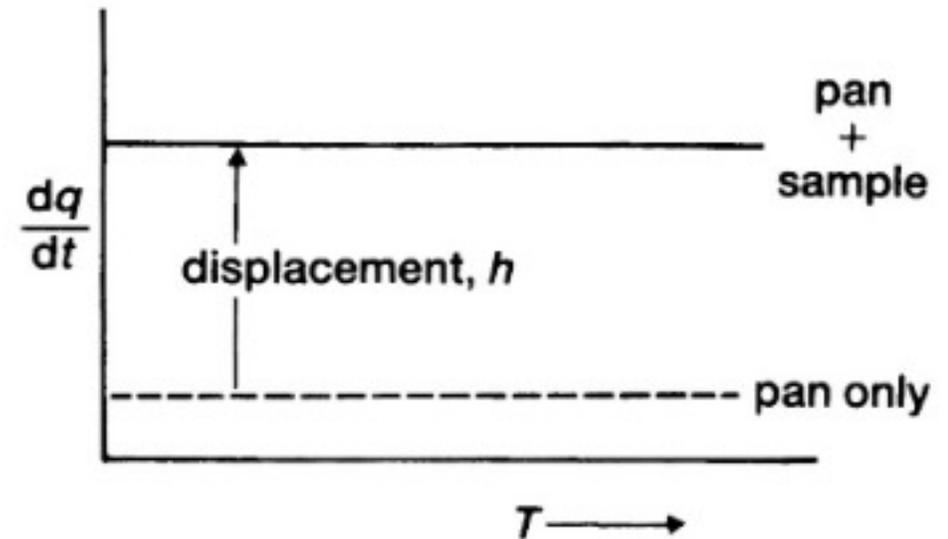
Measurement of heat Capacity

If h is the displacement after placing the sample,

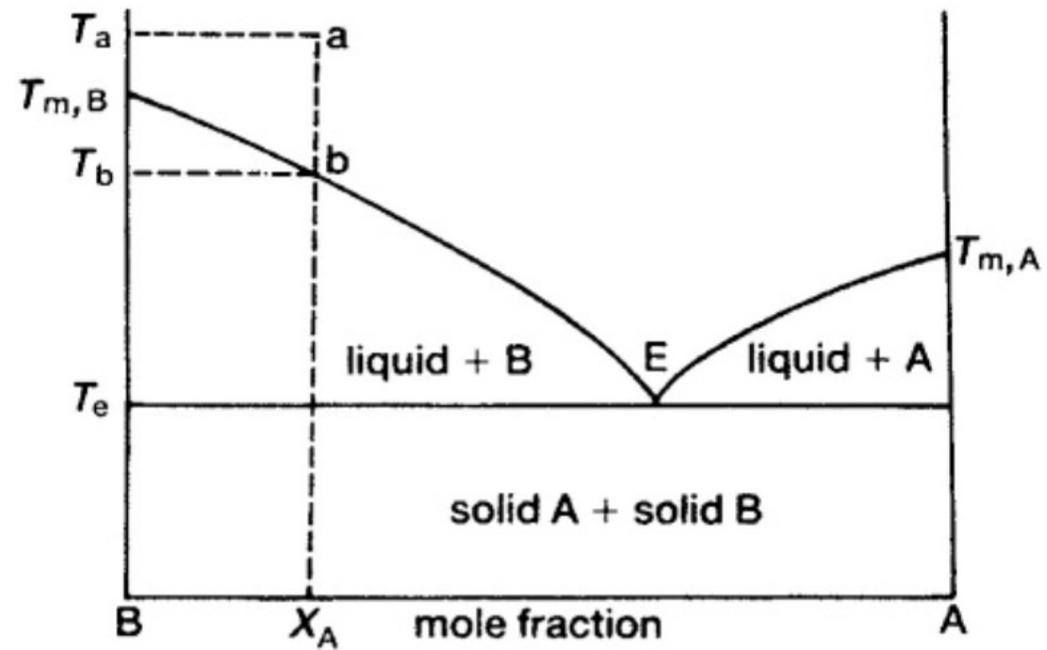
$$h \propto C_p$$

$$h = B\beta C_p$$

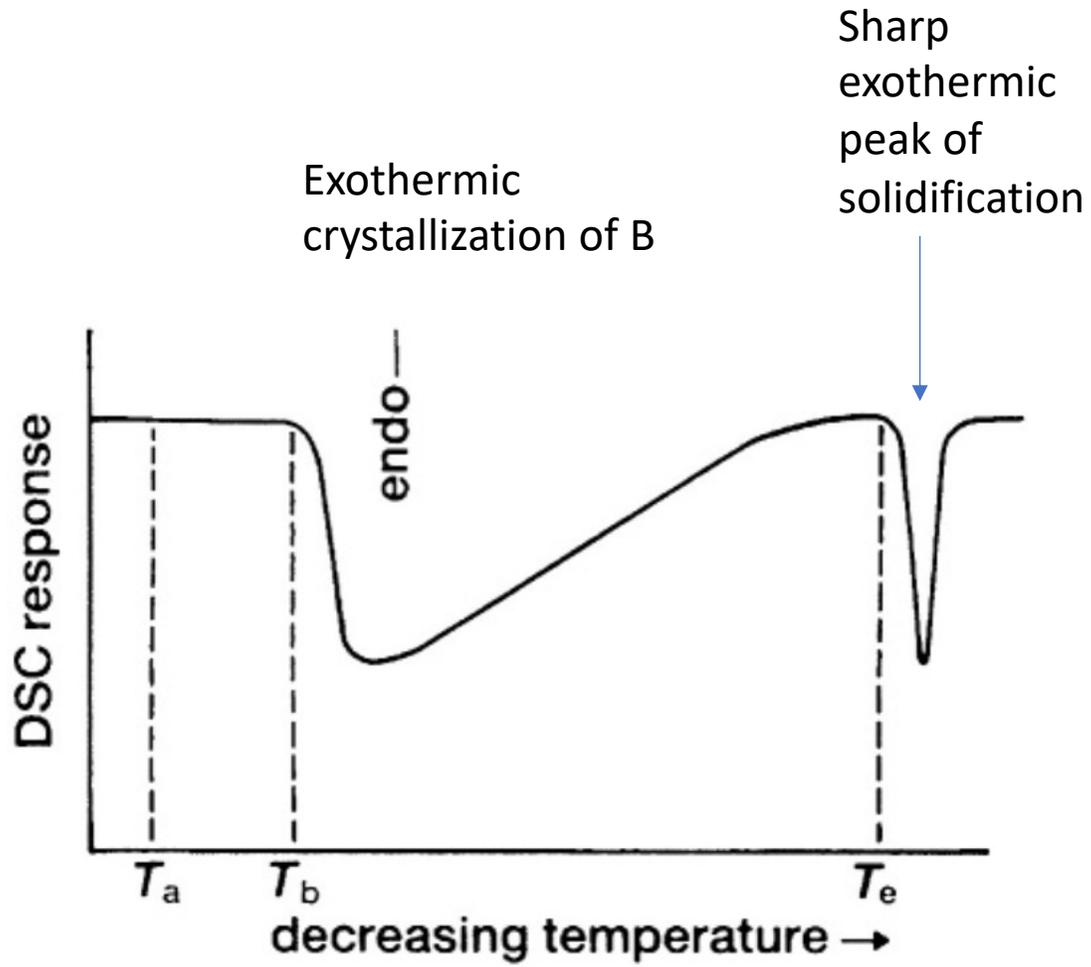
Where β is the heating rate, and B is the calibration factor.



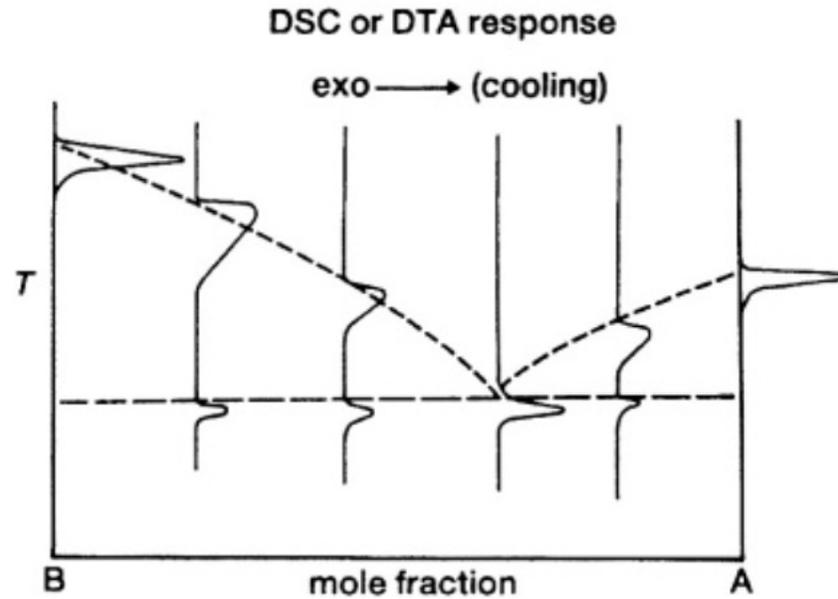
A case study:



If a composition X_A is taken, and cooled from $T_a \rightarrow T < T_e$, how will the DSc measurement look like ?

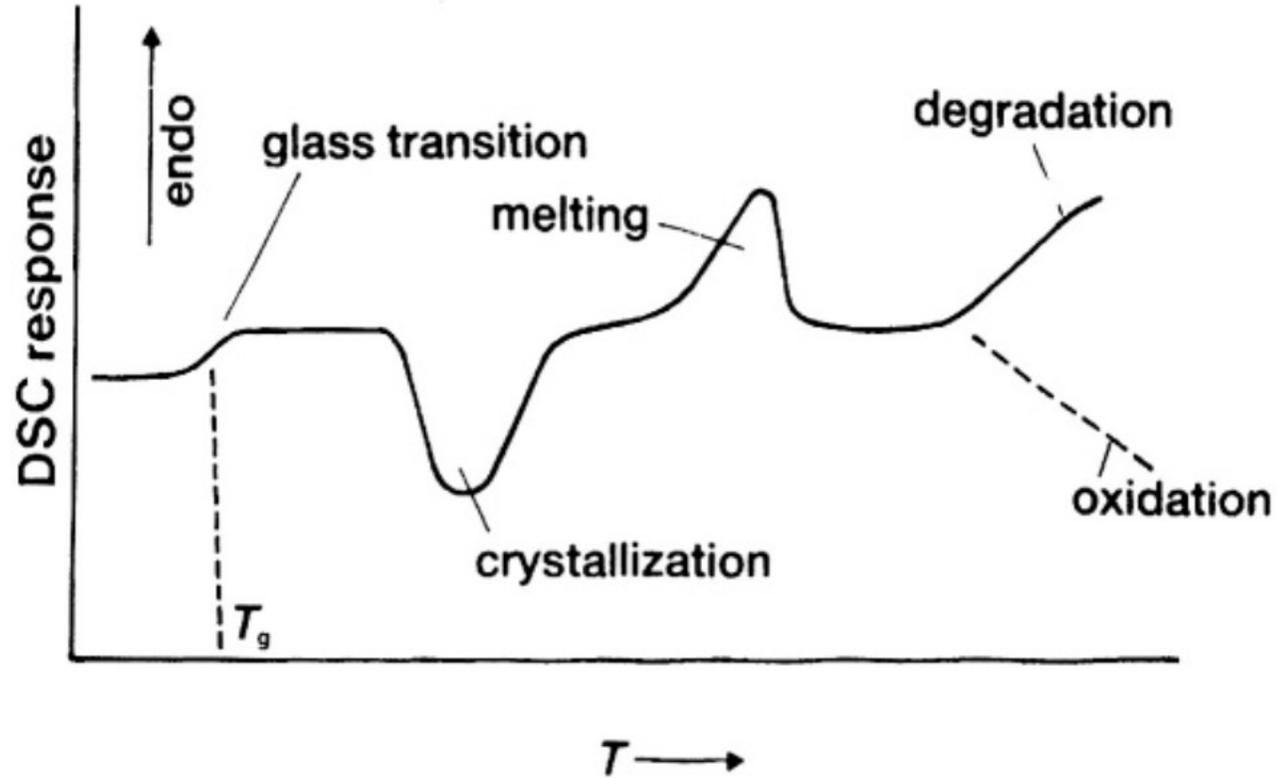


DSC – phase diagram relation



The ΔH enthalpy change – area under the peak gives a lot of information about the mixture

DSC of polymeric samples



Typical polymer is supercooled, hence at room temperature remain in a glassy state.

When heated, may undergo a glass transition to a rubbery state – associated with heat capacity change, but no enthalpy change