Thermal Analysis

By

Dr. Firasat Hussain

http://people.du.ac.in/~firasat

- Thermal Analysis (TA) is a group of analysis that study the properties of materials as they change with temperature.
- The term thermal analysis is associated to the techniques which involves the measurement of a physical parameters as listed while the temperature is changed or maintained in a controlled and measured manner.
- The rate of degradation of the material if measured accurately can help in predicting the properties of the material.
- It provides information on the thermally induced processes like decomposition, thermal transitions etc.
- TA is extensively employed in both industrial and scientific domains.
- TA can be used to characterized a variety of materials both quantitatively and qualitatively over a considerable temperature range.
- The ability of these techniques to characterize, quantitatively and qualitatively, a huge variety of materials over a considerable temperature range has been pivotal in their acceptance as analytical techniques.

Property	TA method	Abbreviation
Mass	Thermogravimetry	TGA
	Isobaric mass change determination	EGD
	Evolved Gas Detection	EGA
	Evolved Gas Analysis	ETA
	Emanation Thermal Analysis	
Difference temperature	Differential thermal analysis	DTA
	Heating or cooling curve determination	
Enthalpy	Differential scanning calorimetry	DSC
Dimensions	Thermodiliatometry	
Mechanical characteristics	Thermochemical measurements	
	Dynamic thermomechanical measurement	

Acoustic characteristic	**Thermosonimetry** **Thermoacoustimetry**	
Optical characteristic	Thermoptometry	
Electrical characteristic	Thermoelectrometry	
Magnetic characteristic	Thermomagnetometry	

Course Content

1. **Thermogravimetry Analysis**
2. **Differential Scanning Calorimetry and differential analysis**
3. **Thermometric titrations**
4. **Thermomechanical analysis**

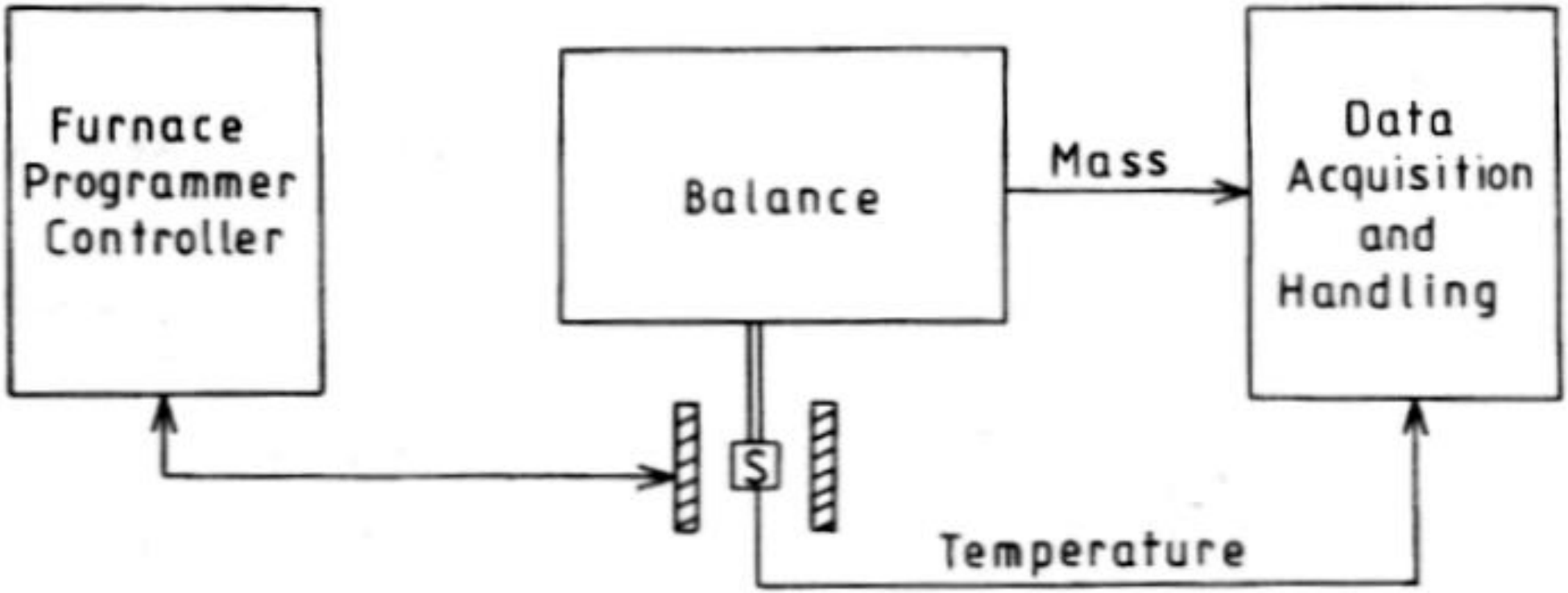
The key components of a thermal analysis system can be distinguished as:

1. Sample holder comprising thermocouples, sample containers and a ceramic or metallic block.
2. Furnace
3. Temperature programmer
4. Recording system

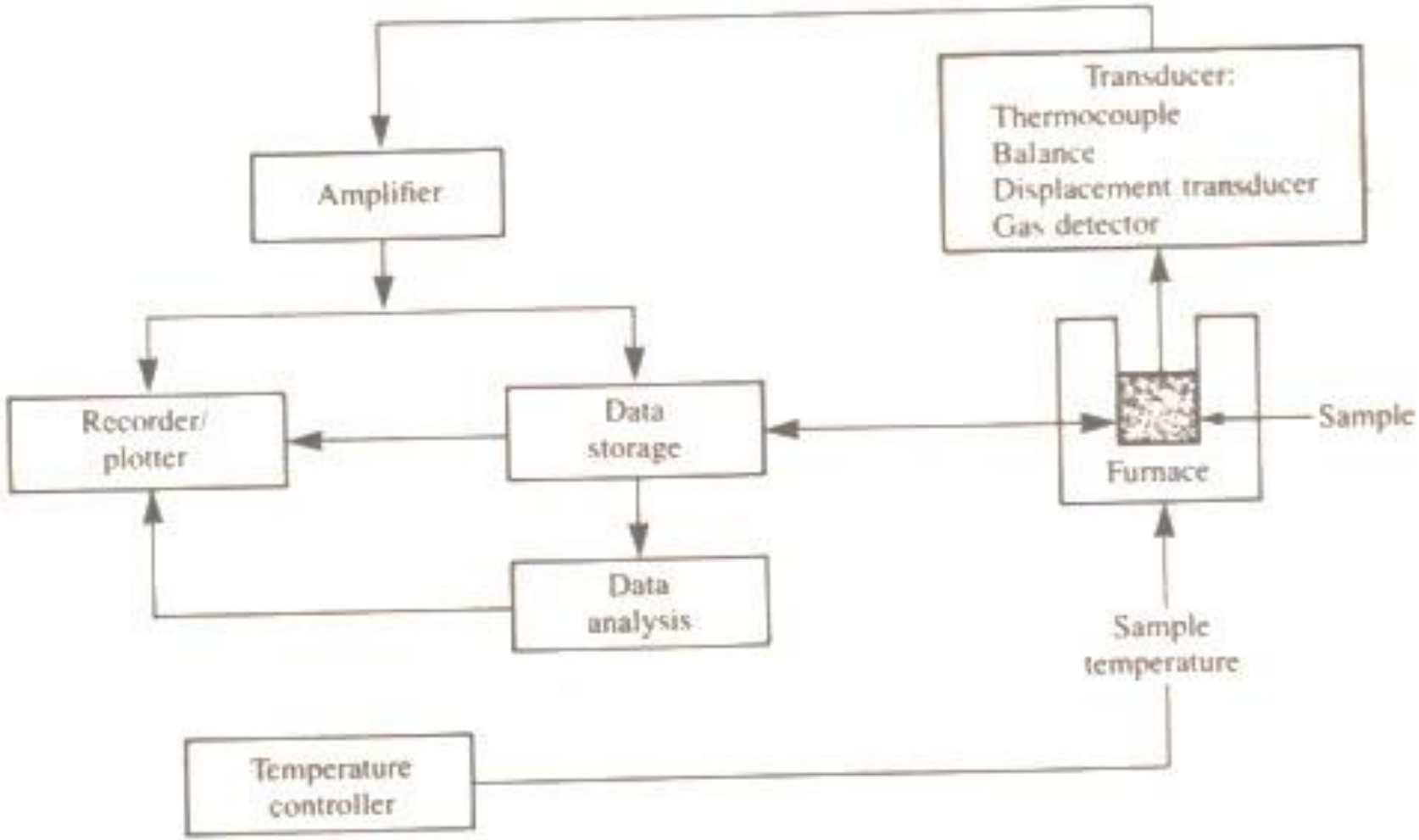
Thermogravimetry Analysis:

Principle

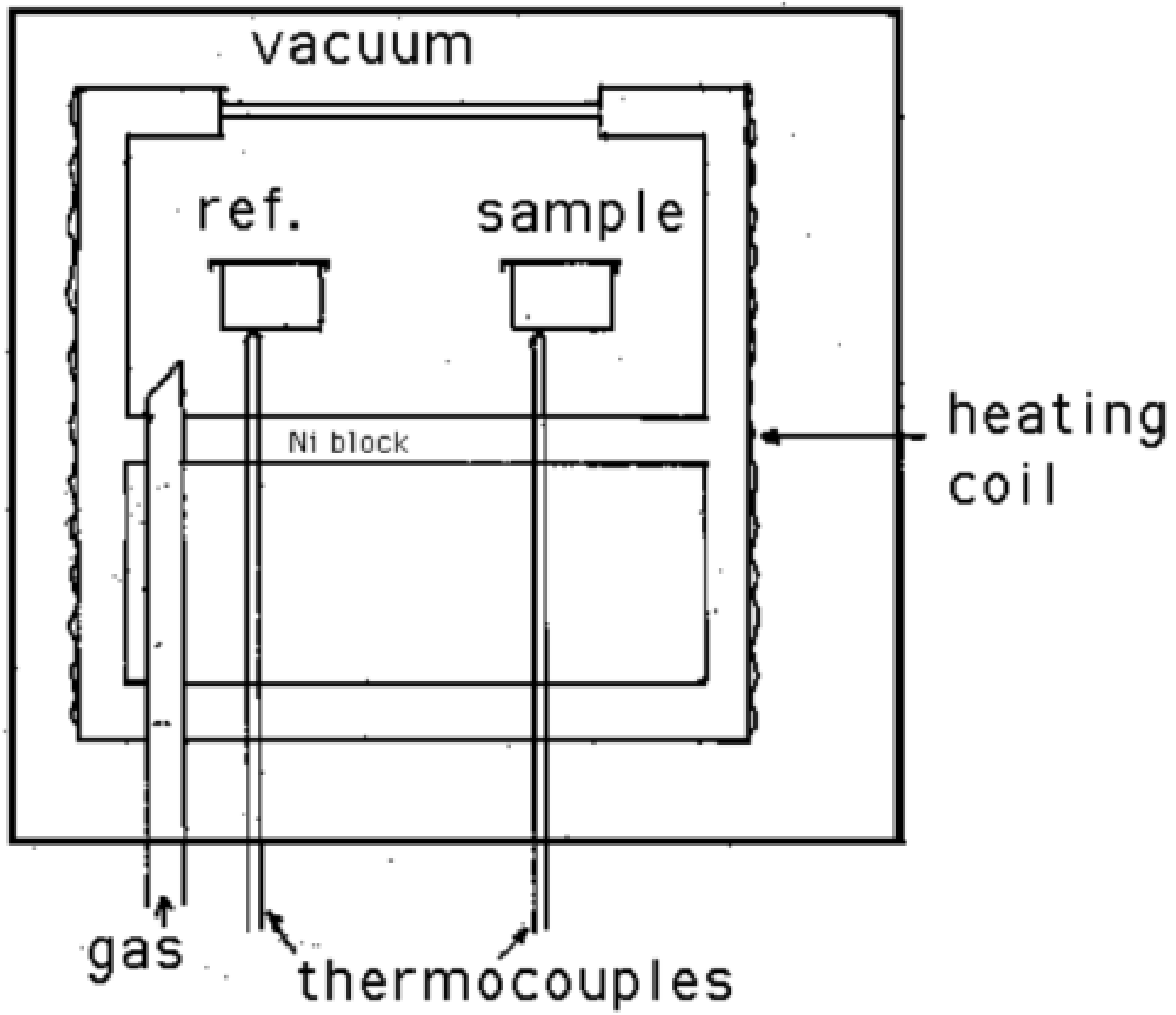
In this technique mass of a substance is measured as a function of temperature while it is subjected to a controlled temperature programme. The record is the *thermogravimetric or TG curve*; the mass is plotted on the ordinate decreasing downwards and temperature (T) or time (t) on the abscissa increasing from left to right.

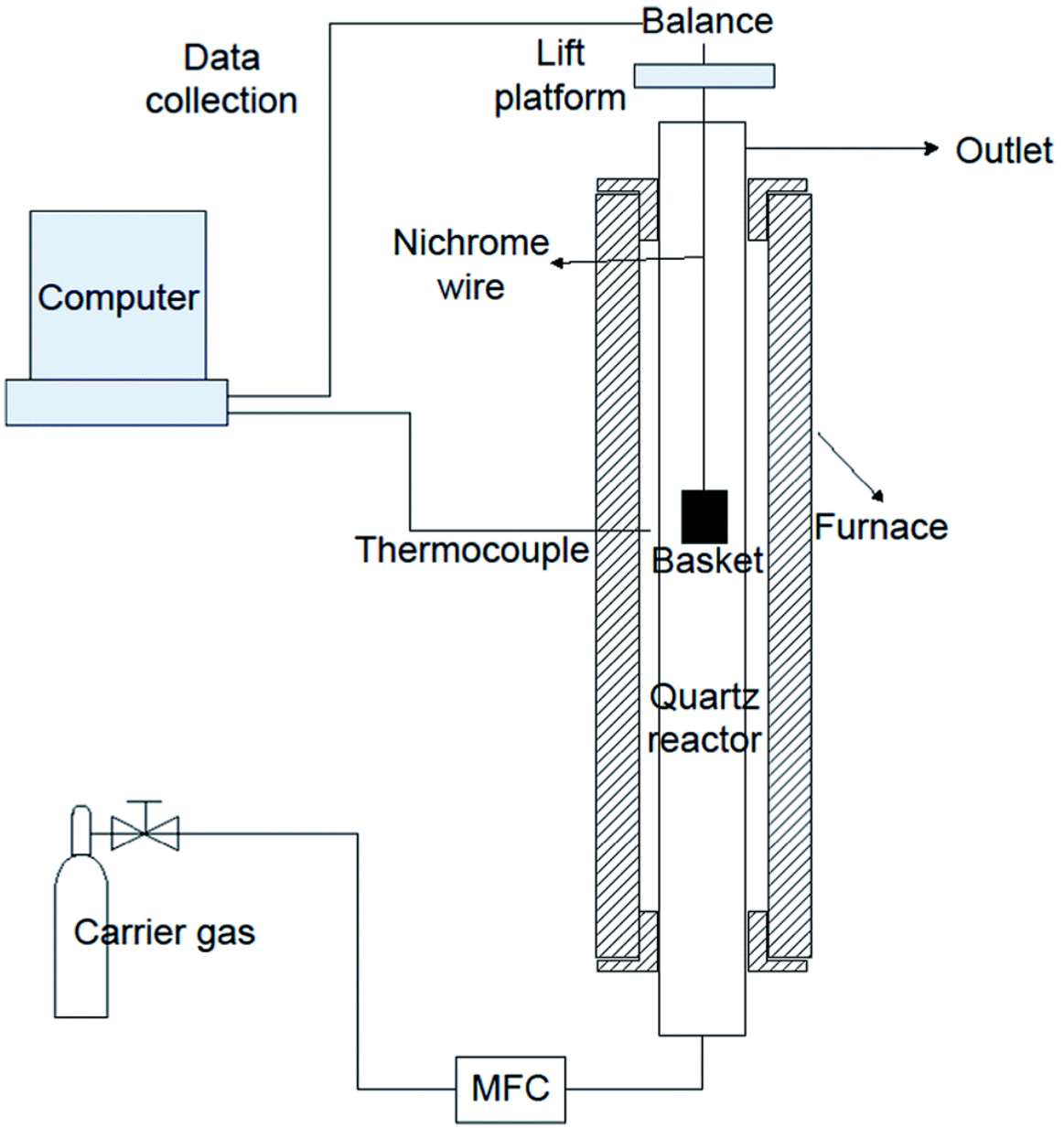


Basic model of TGA



Block Diagram of thermal analysis system


vacuum
ref.
sample
Ni block
heating
coil
gas
thermocouples



INSTRUMENTATION OF TGA

The samples are placed in a crucible or shallow dish or basket which is positioned in a furnace on a quartz beam attached to a recoding balance.

The quartz beam is maintained at null position by the current flowing through the transducer of electromagnetic balance.

The movement of the beam is maintained through the photosensitive diodes which are position sensitive.

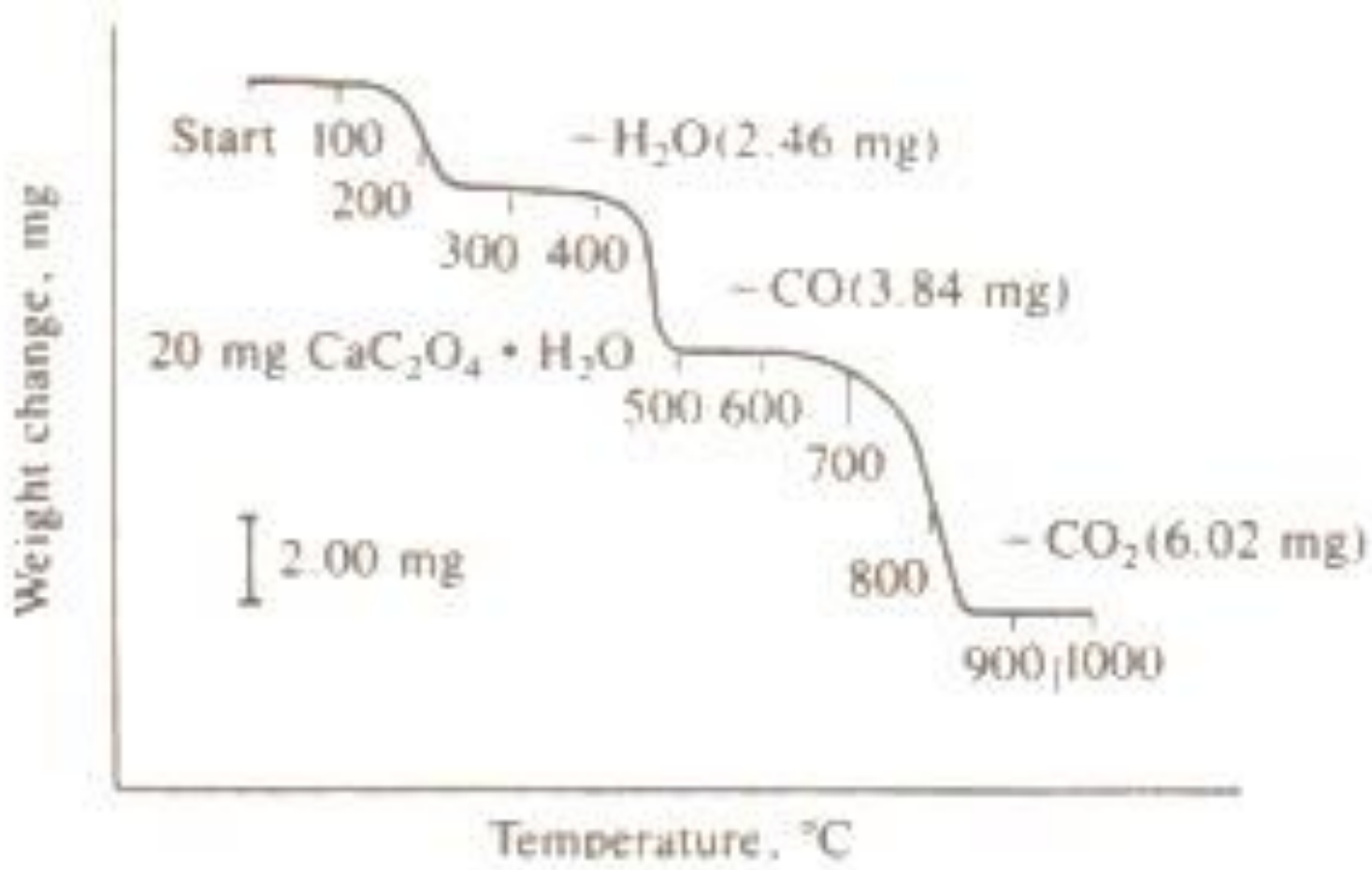
Any change in the weight of the sample is detected through the deflection in beam which is sensed by the photodiodes.

The current is proportional to the change in the weight of the sample.

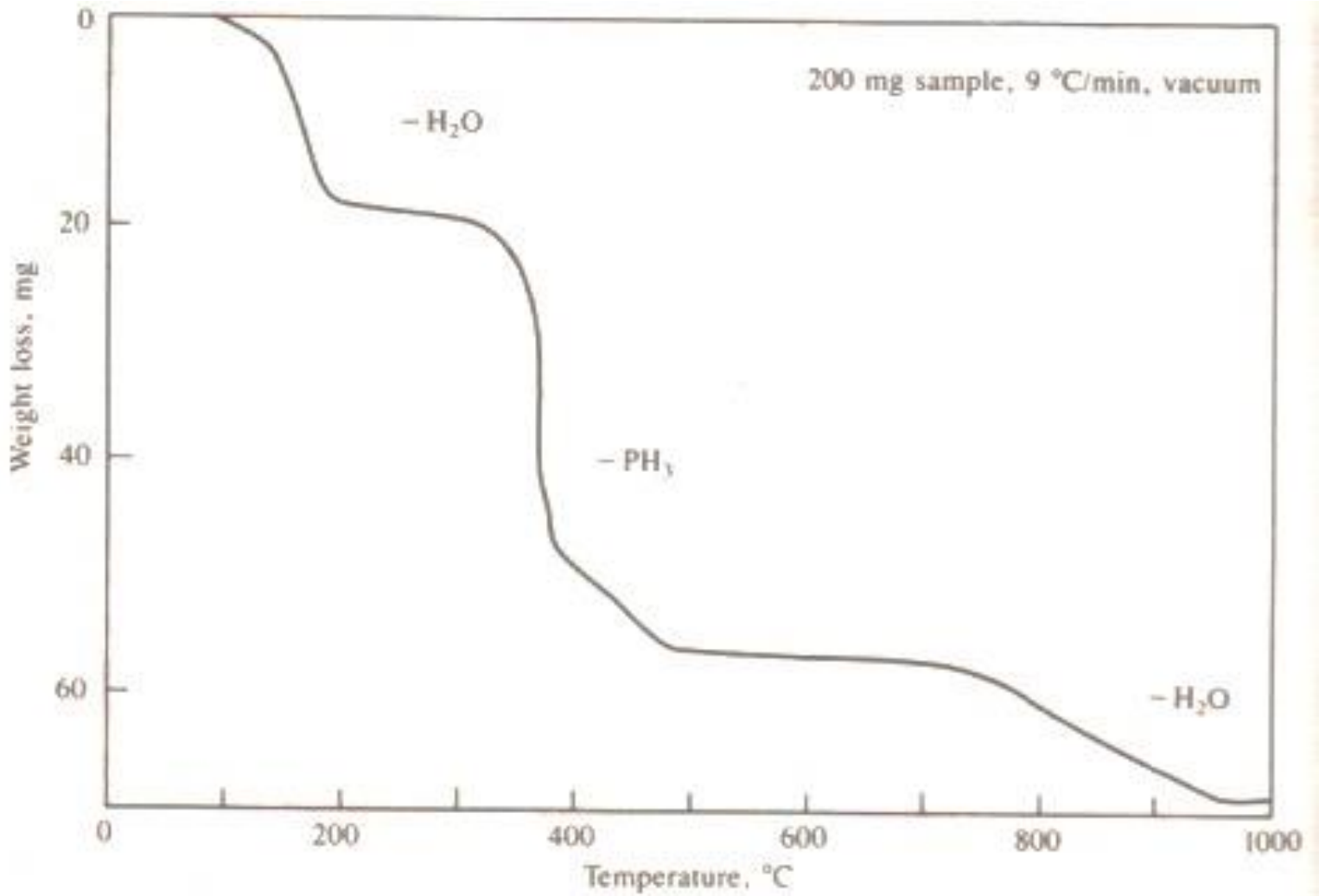
Heating rates are usually 5 to 10°C /min.

Amount the sample ranges from 1 to 300 mg.

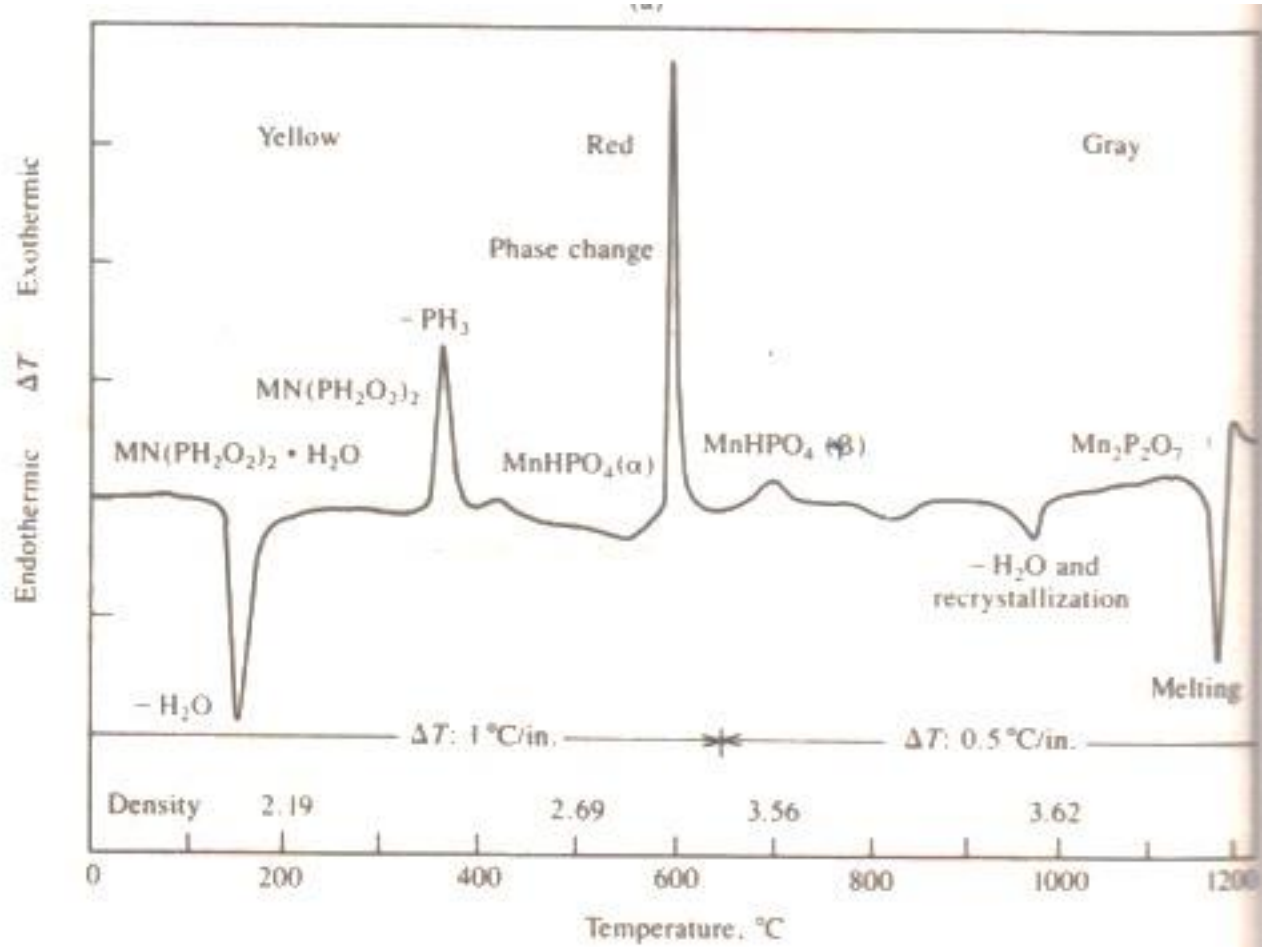
The computer software allows computation of $\Delta w/\Delta t$.



Thermogravimetric evaluation of calcium oxalate monohydrate



TG – Curve for manganese phosphinate monohydrate



DTA – Curve for manganese phosphinate monohydrate

$$Mn(PH_2O_2)_2 \cdot H_2O(s) \rightarrow Mn(PH_2O_2)_2(s) + H_2O(g)$$

$$Mn(PH_2O_2)_2(s) \rightarrow MnHPO_4(s) + PH_3(g)$$

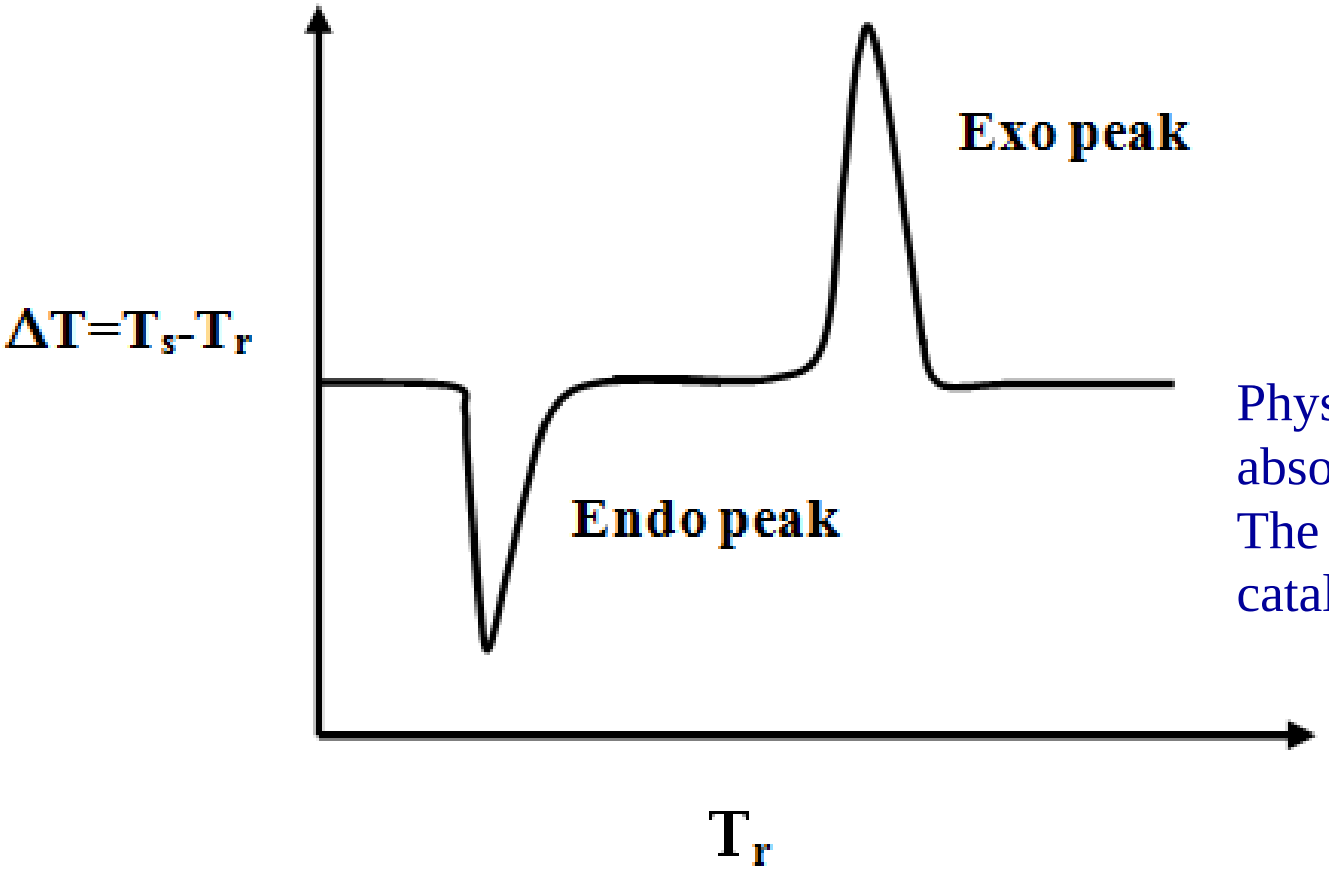
$$\alpha\text{-}MnHPO_4(s) \rightarrow \beta\text{-}MnHPO_4(s)$$

$$2MnHPO_4(s) \rightarrow Mn_2P_2O_7(s) + H_2O(g) \text{ (and recrystallization)}$$

$$Mn_2P_2O_7(s) \rightarrow Mn_2P_2O_7(l)$$

DTA - Principle

A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to the same controlled temperature programme.



Physical changes like vaporisation, sublimation and absorption are endothermic in nature.
The chemical changes like oxidation, polymerization and catalytic reactions are usually exothermic.

Thermal Techniques TGA

I. Isothermal TG – Sample mass recorded with time at constant temperature

II. Quasi TG – Sample heated to a constant mass at a particular temperature

III. Dynamic TG – Sample is heated in an atmosphere where temperature changes at a linear rate

Sensitivity of Thermobalance

- Good recorder to record the mass loss or gain as a function of temperature and time
- Furnace should sustain high temperature
- Accuracy of mass loss (+_0.001%),temperature accuracy (+_ 1 to +_ 0.1 %)
- Physical effects like convection, radiation, magnetic effects due to heating should not effect the balance
- Position of crucible (for uniform heating)
- Scan rate
- Calibration

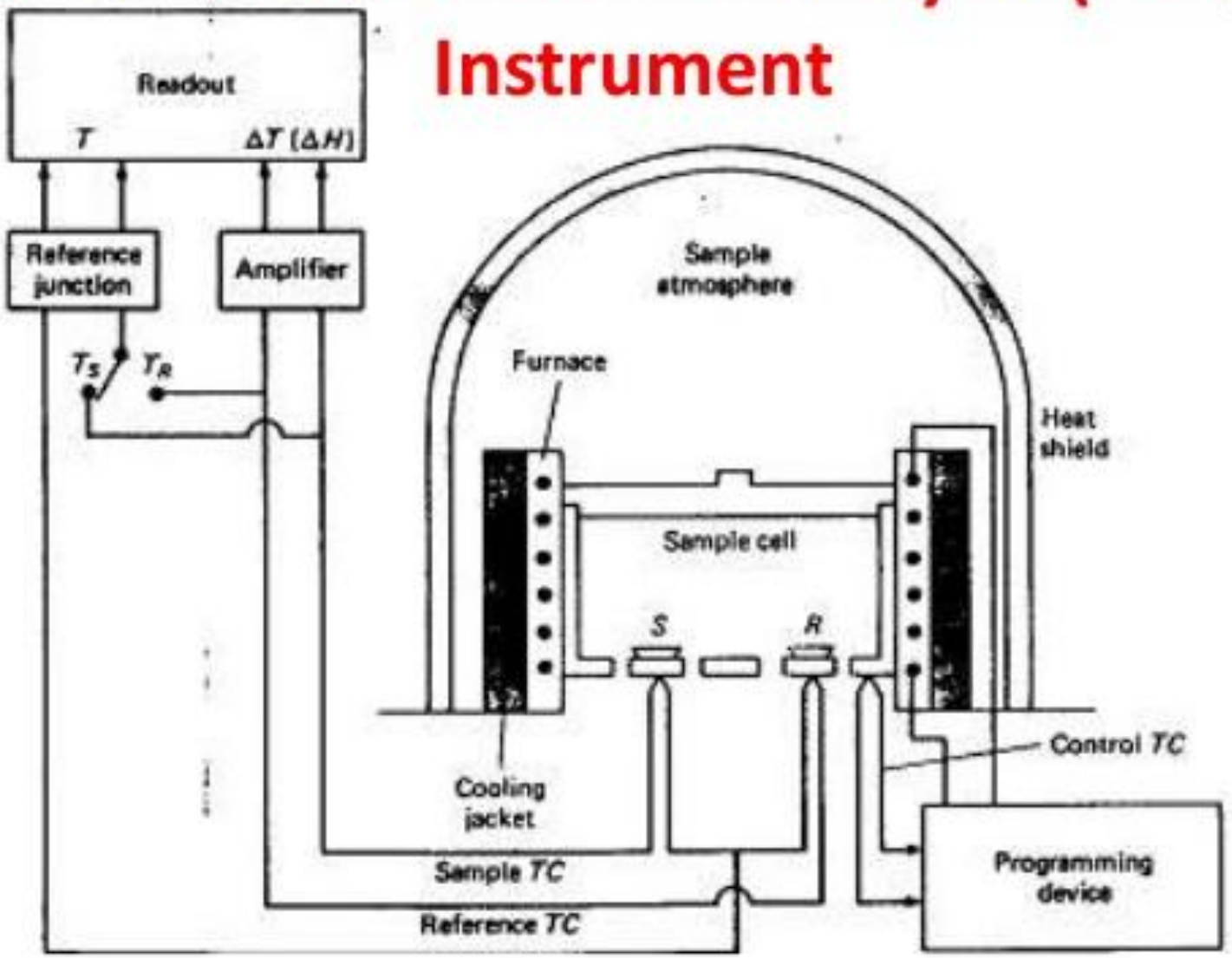
DTA

Thermal technique in which temperature of the sample compared with the temperature of a thermally inert material (reference) is recorded as a function of the sample or inert material or furnace temperature as the sample is heated or cooled at uniform rate

- ✓ Temperature changes are due to endothermic or exothermic enthalpies transition or reaction like phase changes
- ✓ Fusion
- ✓ Crystalline structure inversion or destruction of crystalline lattice
- ✓ Dehydration, reduction and decomposition
- ✓ Physical changes like vaporisation, sublimation and absorption are endothermic in nature
- ✓ The chemical changes like oxidation, polymerization and catalytic reactions are usually exothermic.

Differential Thermal Analysis (DTA)

Instrument



Reference material ($\alpha - Al_2O_3$).

Furnace contains a block and identically and symmetrical located chambers.

The difference in temperature between sample and reference (S,R) thermocouples couples connected in series is continuously measured. With amplification of high Signal and low noise the data is collected.

Because the thermocouples are placed in direct with the sample, DTA provides the highest thermometric accuracy of all thermal methods.

The area of DTA peaks are proportional to the **heat of the reaction and the mass of the sample,** it is inversely proportional to the sample thermal diffusivity.

Factors affecting the DTA curve

Instrumental Factors:

- Size of furnace
- Material of sample holder
- Rate of heating
- Characteristics of thermocouple
- Scan rate

Sample Characteristics:

- Size of sample, amount, nature, hygroscopic
- Thermal Conductivity
- Heating capacity of material
- Packing density
- Degree of crystallinity

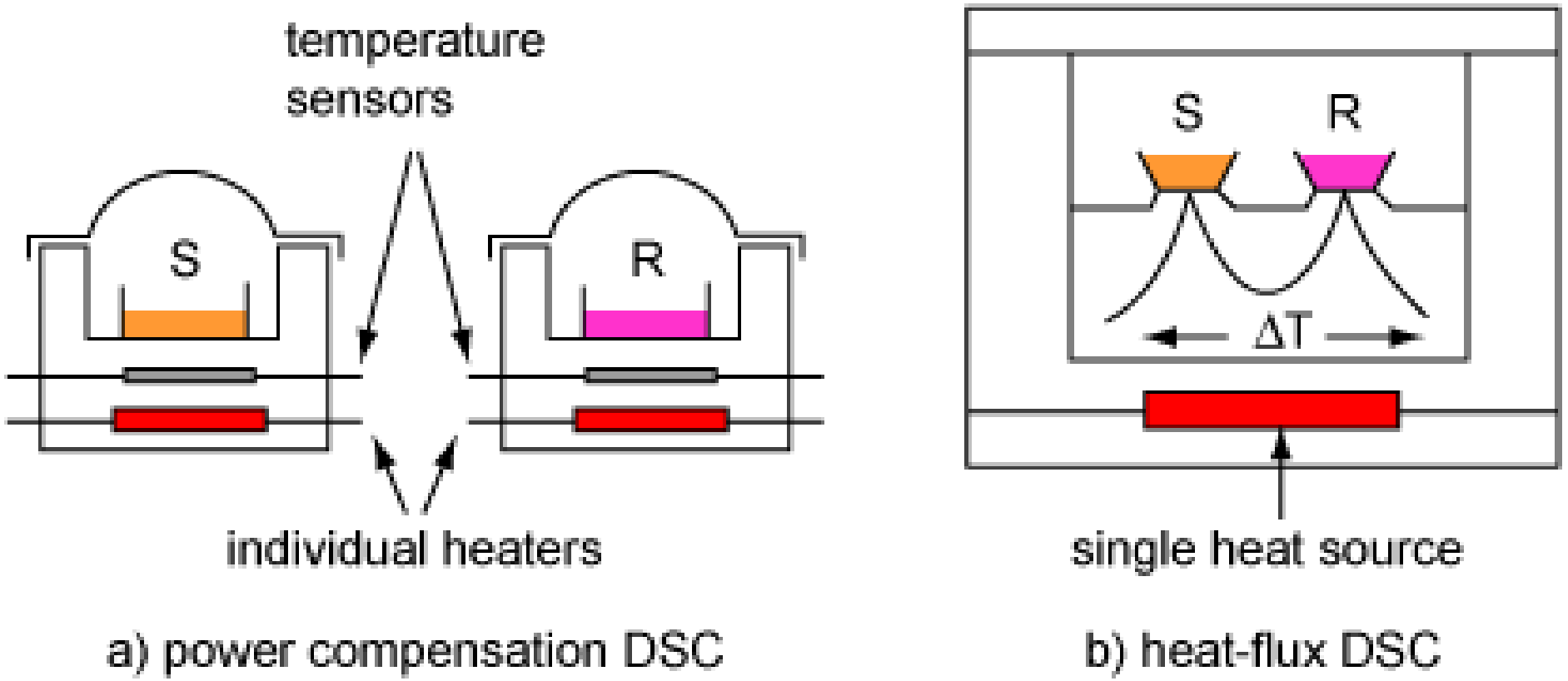
Principle of DSC

- Differential scanning calorimetry (DSC) is a technique of thermal analysis which looks into the heat effects associated with phase transitions and chemical reactions as a function of temperature.
- In DSC, the difference in heat flow to the sample and a reference at the same temperature is recorded as a function of temperature.
- The temperature of both the sample and reference are increased at a constant rate. Differential Scanning Calorimeter is at constant pressure, heat flow is equivalent to enthalpy changes:

  $(dq/dt)_p = dH/dt$, Here dH/dt is the heat flow measured in mcal/sec.
- The heat flow difference between the sample and the reference:

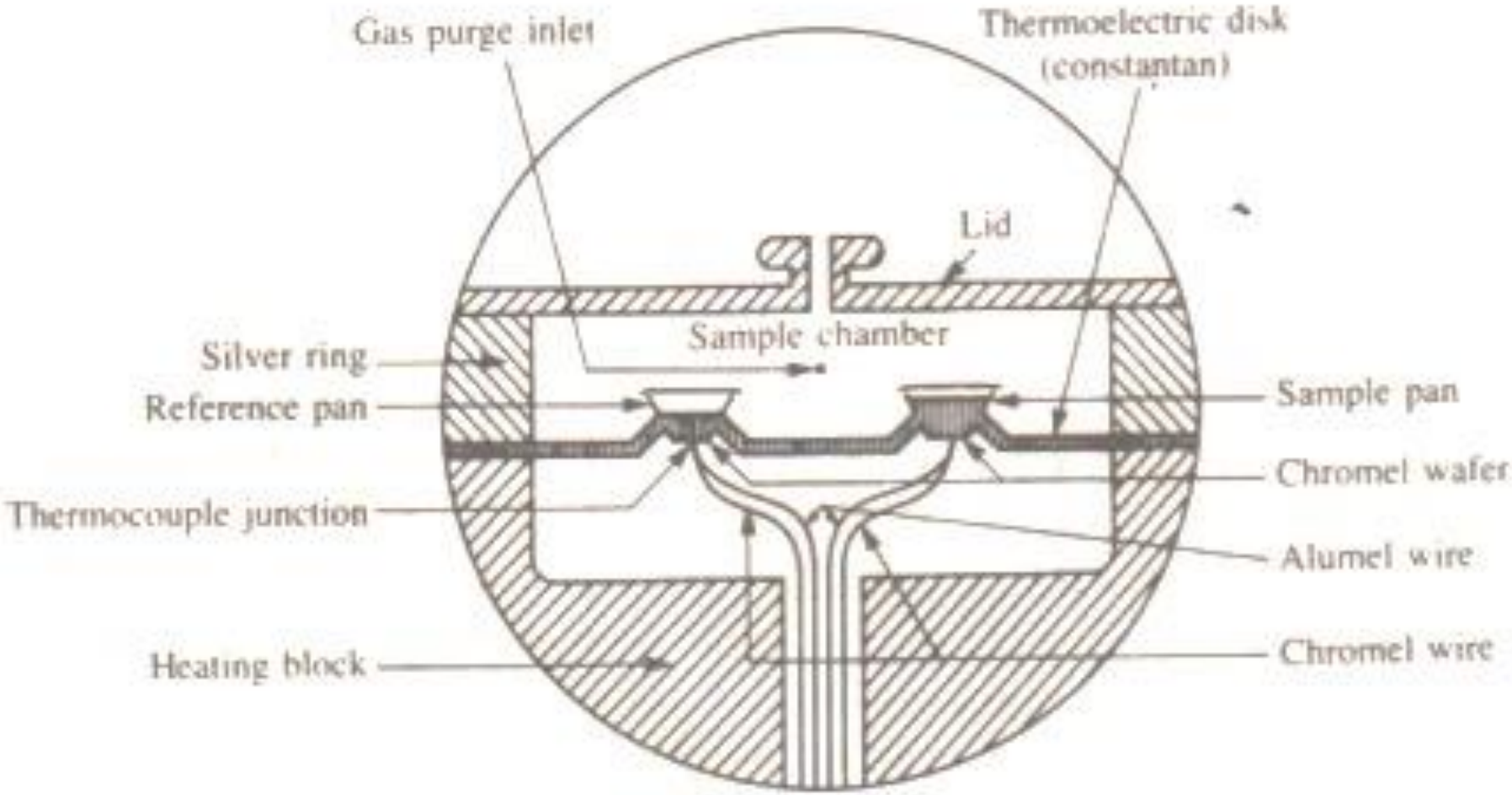
  $\Delta dH/dt = (dH/dt)_{sample} - (dH/dt)_{reference}$
- It can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence ΔdH/dt is positive.

Instrumentation



1. **Power-compensation DSC**: Temperature difference between the sample and reference is maintained constant as the sample is scanned. The resulting power difference is proportional to heat flow.

2. **Heat-flux DSC:** Temperature difference is allowed to vary, and the signal is converted to heat flow through the equation q = dT/R where R= the well defined thermal resistance of the transducer.



Chromel/alumel thermocouple is used to directly monitor sample temp.

Change in enthalpy $\Delta H = Q_s - Q_r$

Q_s : Heat flow to or from the Sample

Q_r : Heat flow to or from the reference Material

$$\Delta H = Q_s - Q_r \quad \text{-- eq}^n \text{(1)}$$

Thermal analog of Ohm's Law

$$Q = \frac{T_2 - T_1}{R_{th}} \quad \text{-- eq}^n \text{(2)}.$$

Combining eq^n (1) and (2)

$$\Delta H = Q_s - Q_r = \frac{T_c - T_s}{R_{th}} - \frac{T_c - T_r}{R_{th}}$$

$$\Delta H = -\left(\frac{T_s - T_r}{R_{th}}\right)$$

T_c : const. Temp

T_s : Sample Temp^r

T_r : Reference Temp^r

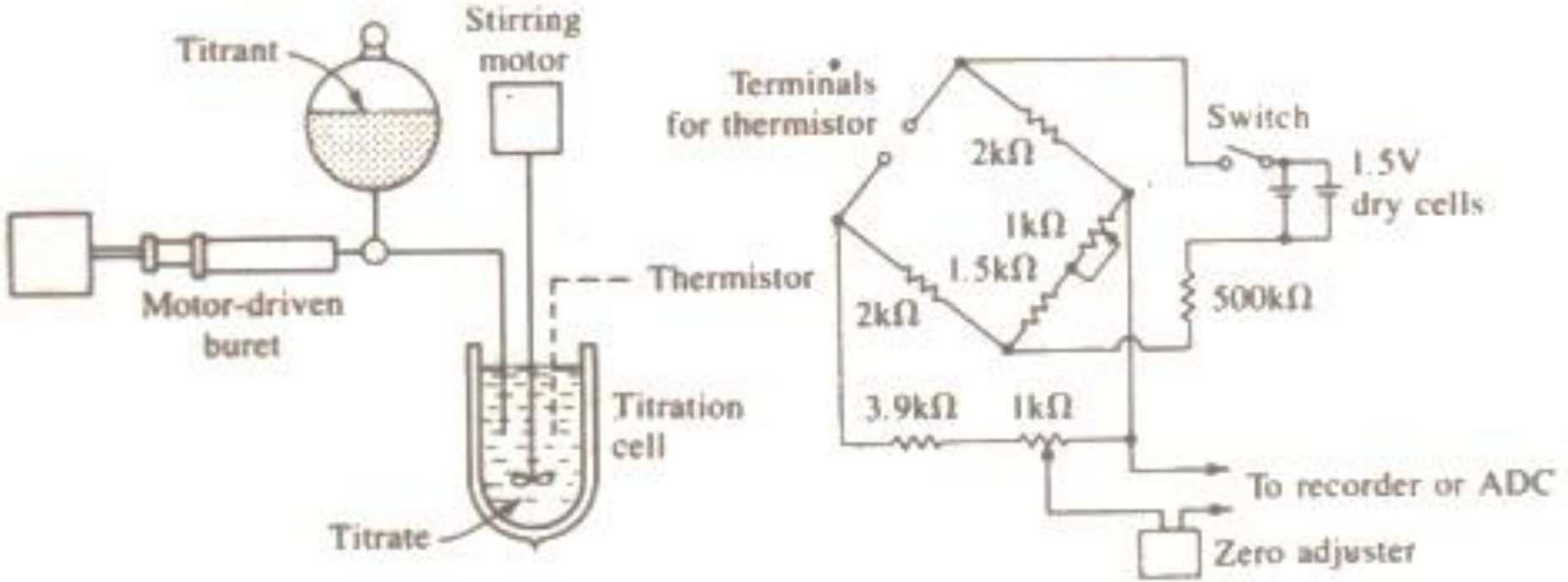
$$A = -k' m \Delta H$$

A = Area.

m = mass

k' = Instrument constant

Thermometric titrations of Enthalpimetric analysis



Titrant delivered @ flowrates of 0.1 – 1.0 ml/min

Titrant concentration is usually 100 times greater than reactant - Why?

To obviate volume corrections and to minimize temperature variations between the titrant and sample.

Methodology

Potentiometric titrations depend solely on equilibrium constant K.

Free Energy $\Delta G = -RT \ln K$

Thermometric titration depends only on the enthalpy of the reaction

$$\Delta H = \Delta G - T\Delta S$$

Thermometric titration curve has a well defined end point for the weak acid.

The change in temp. of the titration curve is dependent on the heat of reaction of the system

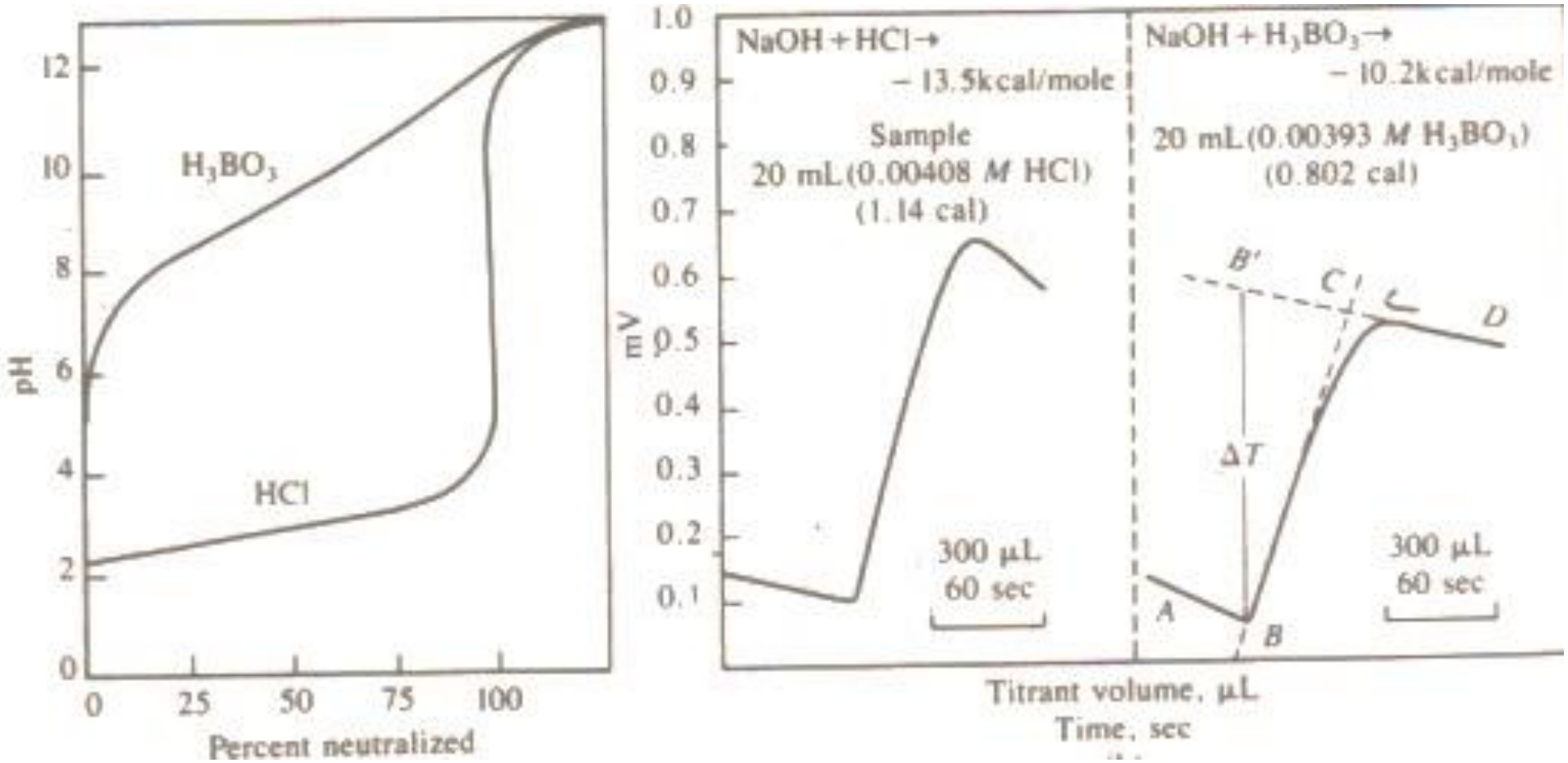
$$\Delta T = \frac{N \Delta H}{Q}$$

N: No: of moles of H_2O formed in the neutralization

ΔH: Molar enthalpy of neutralization

Q: Heat capacity of system.

$\Delta T \propto N$


pH
12
10
8
6
4
2
0
H_3BO_3
HCl
0
25
50
75
100
Percent neutralized
mV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
NaOH + HCl →
− 13.5kcal/mole
Sample
20 mL(0.00408 M HCl)
(1.14 cal)
300 μL
60 sec
NaOH + H_3BO_3 →
− 10.2kcal/mole
20 mL(0.00393 M H_3BO_3)
(0.802 cal)
B'
C
D
ΔT
A
B
300 μL
60 sec
Titrant volume, μL
Time, sec

Applications of enthalpimetry

- ✓ Determination of concentration of unknown substance, thermodynamic quantities
- ✓ Titrating acetic anhydride in acetic acid – sulphuric acid acetylating baths
- ✓ Used in enzyme assay and immunological determinations
- ✓ Analysis of alkaloid drugs such as codeine phosphate or morphine sulphate
- ✓ Benzene in presence of cyclohexane by measuring heat of nitration