Thermometric Enthalpy Titrations (TET)

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Outline

1. *Concept of TET*
2. *Instrumentation & Methodology of TET*
3. *Interpretation of TET Curve*
4. *Factors Affecting to TET*
5. *Advantages*
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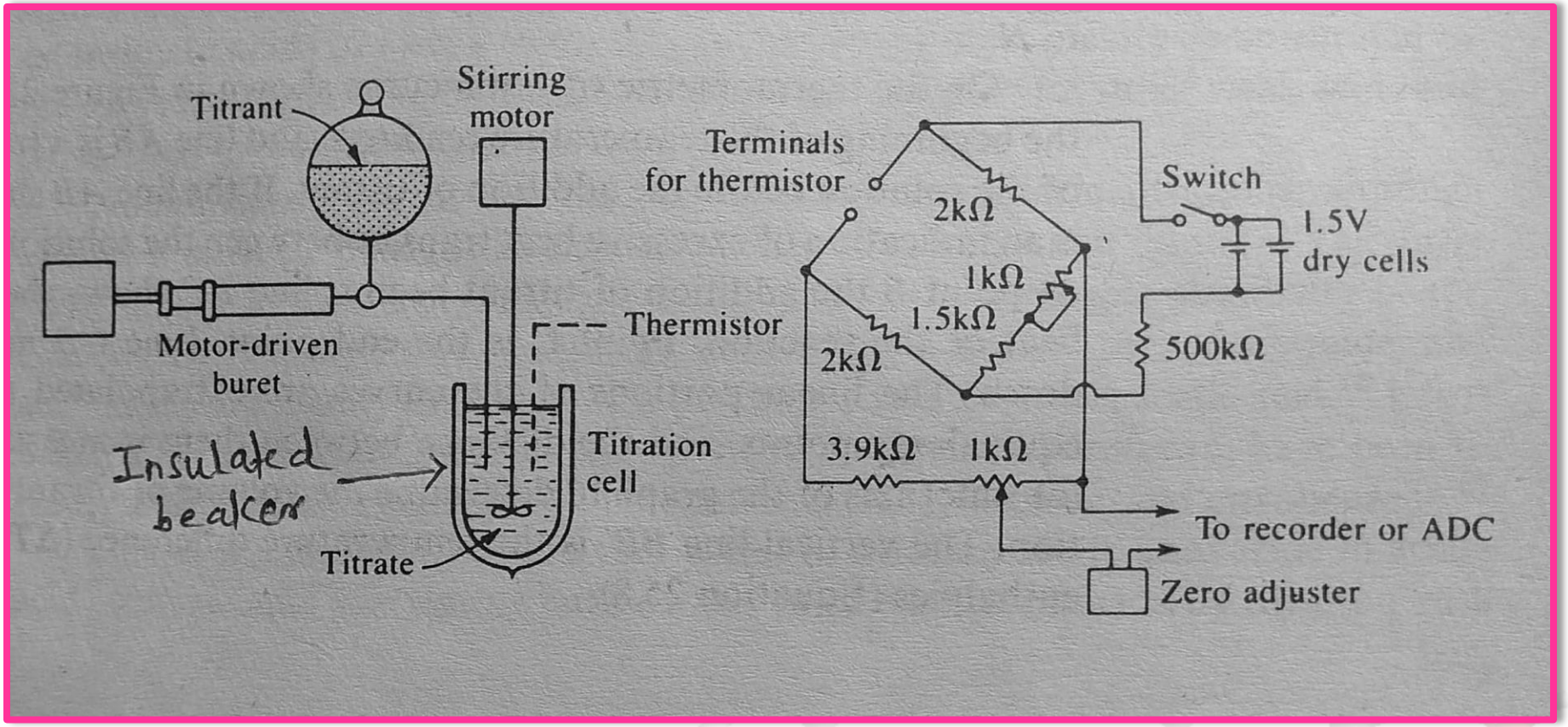
1. Concept of Thermometric Enthalpy Titrations (TET)

- ***Type of Enthalpimetric Analysis:*** *Use of enthalpy change of react^{n} to locate end point.*
- *Proposed by Bell & Cowell (1913)*
- *titrant is added at a known constant rate into analyte until the completion of the reaction is indicated by a change in temperature.*
- *Tempt changes during titration are due to the heat evolved or absorbed by the reaction bet^{n} titrant & analyte*
- *Also defined as titration in an adiabatic system gives a plot of tempt. Vs vol. of titrant*
- *The graph is similar to the graph of conductometric, potentiometric, amperometric titrations etc.*

2. Instrumentation of TET

- ***Precision fluid dispensing devices:*** *Burette for adding titrant and other reagent.*
- ***Thermistor*** *based thermometric sensor*
- ***Titration vessel*** *(100-250 ml): Adiabatic & closed*
- ***Stirring device:*** *efficient stirring without splashing.*
- ***Wheatstone Bridge:*** *Measure unknown resistance in the form of tempt*
- ***Computer*** *with thermometric Operating system.*
- ***Thermometric titration interface module:*** *Regulates the flow (0.1-1.0 mL/min) bet^{n} burette, sensor & computer.*

Schematic of TET

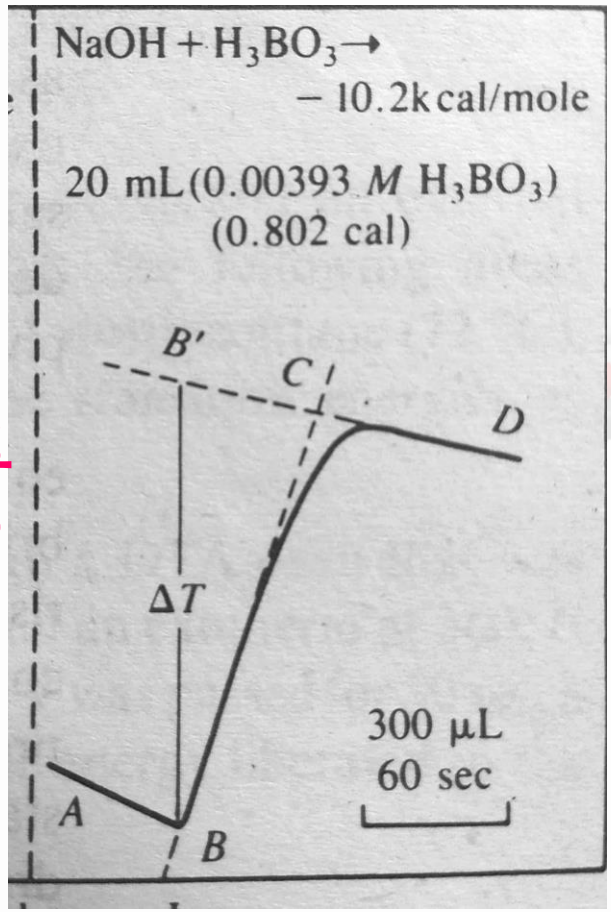


Once switch is turn on , 1.5 V voltage applied across the bridge, then bridge measure unknown resistance in the form of tempt

Methodology of TET

- *Take analyte into flask:* **Amt. of analyte selected such that a required vol. of titrant not exceeding 1-3 ml.**
- *Tempt of Sample & Titrant should be within 0.2^{O}C before titration is begun.* **(Use of heating element in the flask)**
- **The titrant is delivered at flow rate of 0.1 to 1ml/min untill completion of react^{n} is indicated by change in tempt**
- *Keep conc^{n} of titrant usually 100 times greater than reactant: To avoid volume corrections & to minimize tempt variations between Sample & titrant.*
- **Range of tempt change is 0.1-0.2^{O}C,**
- **Accuracy of thermistor to measure tempt Should be 10^{-4} ^{O}C.**

Interpretation of curve obtained n TET



- Point **A** observed at beginning of tempt reading.
- **Line AB** is trace tempt of sol^n before addition of titrant.
- If **line AB** shows marked slope, indicates excess transfer of heat bet^n Sol^n and Surrounding.
- At **B** add^n of titrant begins.
- **Line BC** shows gradual evolution of heat of the reaction
- **Point C** is the End point of titration.
- **Line CD** may slope up or down.
- Linear extrapolated portion of curve gives initial and equiv. point & its distance gives vol. of titrant consumed
- The vertical **line BB'** is the tempt. (ΔT)used to evaluate enthalpies

Factors affecting to TET

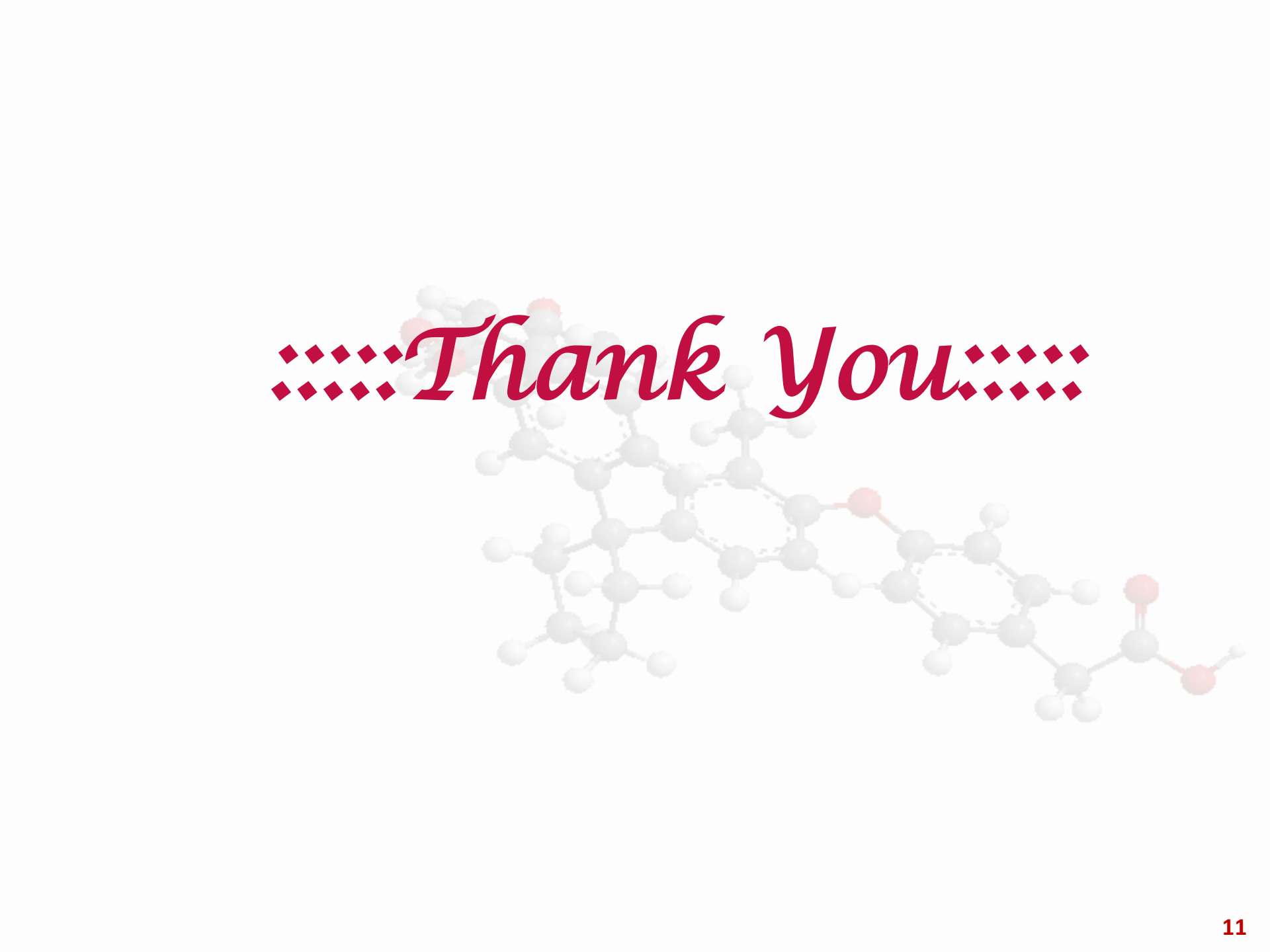
- Heat Losses or gains from outside the system via vessel
- Diff in tempt bet titrant and titrand
- Evaporative losses from surface of rapidly mixed fluid
- Heat of solution when titrant mixed with analyte
- Heat introduced by the mechanical action of stirring
- Heat produced by thermistor itself.

Advantages of TET

- ***Thermometric titration not depend on free energy***
- ***It has a well defined end point for weak acid***
- ***The change in tempt depends on enthalpy of reaction***
- ***The lowest limit of conc^{n} that can be successfully titrated is 0.0001M.***
- ***All acids with Ka ≥ 10^{-10} can be titrated in 0.01 M Sol^{n} with precision of 1 %.***

6. Applications

Sr. No.	Type of titration	Applications
1.	*Acid-base titrations*	*Titration of weak acids , Titration of complex alkaline solutions, Titration of acid mixtures, Non-aqueous acid-base titrations, etc.*
2	*Redox titrations*	*Titrations with permanganate and dichromate, titration with thiosulfate, etc.*
3	*Complexometric titrations*	*EDTA Titrations with various metal ion*
4	*Precipitation titrations*	*Titration of sulfate, Titration of nickel , Titration of anionic and cationic surfactants, Titration of non-ionic surfactants*
5	*Miscellaneous methods*	*Titration of fluoride with boric acid , Determination of formaldehyde , Thermometric titration of water, etc.*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