

THERMOMETRIC TITRATION AND SOME OF ITS CHEMICAL APPLICATIONS

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الخلاصة

طريقة المعايرة الحرارية هي إحدى طرق التحليل الحرارية وتعتمد هذه الطريقة على قياس الفرق بين المحتوى الحراري في وحدة كتلة المتفاعل (Enthalpy) وبين المحتوى الحراري في وحدة كتلة الناتج ورسم هذا الفرق بياناً ضد كمية المحلول المعاير المضاف (Titrant) أو ضد وقت الإضافة إذا كان المحلول مضافاً بنسبة ثابتة . . . وقد كانت نقطة التحول في هذا الأسلوب التقني هي استخدام قنطرة الترمومتر وكذلك السحاحة الكهروكيميائية ذات نسبة الصب الثابتة مما جعل من الممكن معايرة محاليل مخففة لدرجة ١٠-٤ ووزن جزئي لكل لتر ويتغير بسيطاً في الحرارة (٠,٠٥ درجة مئوية) بوقت يقل عن عشرة دقائق . . .

بواسطة هذه الطريقة يمكن تحليل جميع أنواع التفاعلات من عضوية وغير عضوية وبيوكيميائية لأن جهاز القياس (الترمومتر) لا يتطلب وجود نوعاً معيناً من المتفاعل . . . ومن أهم مميزات هذه الطريقة هي أن التغير في المحتوى الحراري بين المتفاعلات والنواتج لا يعتمد على التغير في الطاقة الحرة (Free Energy) فحسب بل أيضاً على قياس الطاقة اللامتاحة (Entropy) .

ABSTRACT

Thermometric titration technique is one of the thermal methods of analysis. It is based upon measuring the change in enthalpy of a chemical system and plotting this change against volume of titrant added or against time if the titrant is added at a constant rate. The introduction of a thermistor bridge coupled with an electrical constant rate burette made the major breakthrough in the automation of this method. Now it is capable of titrating very dilute solutions of the order of 10^{-4} M with a temperature change of 0.05°C in about ten minutes. It can analyse inorganic, organic and biochemical reactions.

This technique has many advantages over other methods of analysis due to the fact that its sensor, the thermistor, is a universal one as compared to other methods that require special conditions for each type of a reaction. Another main advantage is that the change in enthalpy is dependent on both ΔG and ΔS .

Thermometric titration technique is one of the many thermal methods of analysis, which are based on measuring the change in a specific property of a substance as a function of temperature or heat. A list of some of these techniques is shown in Figure 1. The first three techniques in the figure, thermogravimetry [1], dilatometry [2], and evolved gas analysis [3], are of less importance and fewer applications than the last techniques that are dependent on enthalpy change of chemical systems. These techniques are divided into two main methods:

1. Differential Thermal Analysis (DTA)

In DTA the change in enthalpy is detected in the form of a temperature difference between a sample and an inert reference substance, such as aluminum oxide, that does not change in any manner through

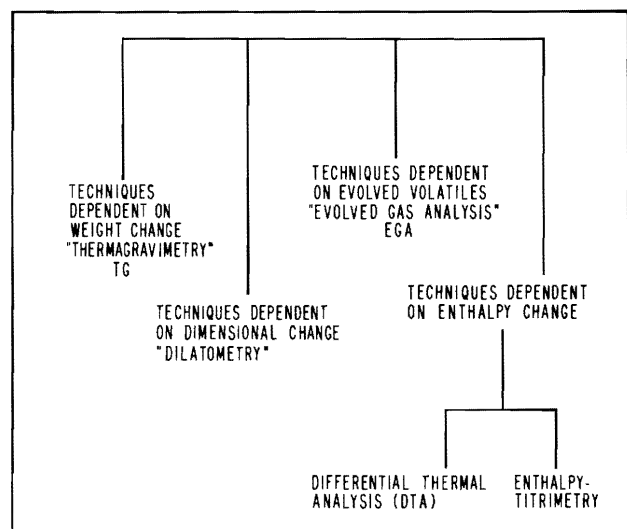


Figure 1. Thermal Analysis Methods

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the temperature range to be studied. This technique is suited to studies of structural changes within a solid at elevated temperatures. A recent modification of this technique for quantitative studies was introduced by Perkin-Elmer manufacturers in an apparatus called Differential Scanning Calorimeter, in which the temperature of both the sample and reference is kept constant by an automatic control loop that sends just enough power into whichever of the two samples is the coldest [5]. The thermogram obtained resembles that of a conventional DTA but the area beneath a peak is an exact measure of energy supplied.

2. Thermometric Titration Analysis (TTA)

Thermometric titration analysis is also based upon the change in enthalpy of a chemical system. It measures the enthalpy difference between liquid reactants and products. The difference in the form of a temperature change, is plotted versus the amount of titrant added or versus time if the titrant is added at a constant rate.

This technique, is also called Calorimetric Titration, Enthalpimetric Titration, and Entropy Titration according to the preference of the scientist.

Historical Development

One of the early thermometric titration experiments was that reported by Bell and Cowell [6] which involved a discontinuous addition of small increments of a base to an acid from a regular buret. After each addition of titrant, the corresponding reading of temperature was taken from a thermometer immersed in the titration cell. The shape of the curves of change in temperature versus volume added was not reproducible for the following reasons:

1. The temperature change had to be high to be detected by the thermometer, thus the heat exchange with the environment was large.
2. The thermometer response was slow which allowed for more dissipation of heat between addition time and temperature reading time.
3. The thermometer heat capacity was large resulting in the consumption of some of the heat released.

The first cause of irreproducibility was corrected by placing the titration cell in an insulated constant temperature bath. The last two problems were solved

in the fifties when Hume and Coworkers at M.I.T.[7] introduced to this technique a rapid response temperature sensing device of negligible heat capacity known as a thermistor. This, coupled with the development of electronic recorders and constant rate burets, made the major breakthrough in the automation of this method of analysis.

The combination of a thermistor connected to a wheatstone bridge, an electronic recorder, an automatic constant rate buret, and a well controlled constant temperature bath made this method a very rapid, effective, and accurate analytical procedure. It is capable of titrating, continuously or incrementally, very dilute solutions of the order of 10^{-4} M with a temperature change of about 0.05°C in less than ten minutes. The general arrangement used in this technique is shown in Figure 2 and a typical thermogram, for an exothermic reaction involving only one step reaction, is shown in Figure 3.

Potentiality of This Method

Thermometric titration technique possesses a great potentiality as an analytical method. Its main advantages are:

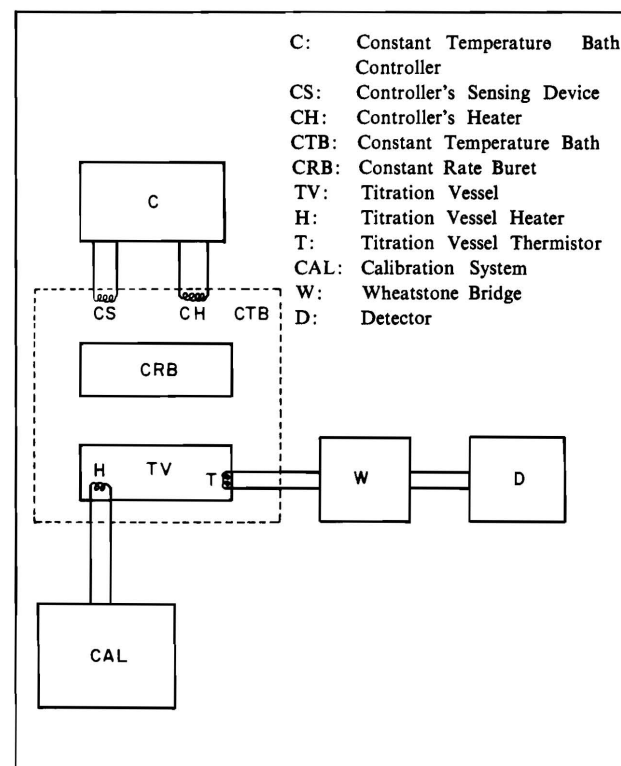


Figure 2. Block Diagram Showing the General Arrangement of a Thermometric Titration Apparatus.

1. The analysis is fast and easy.
2. The instrumentation is cheap and simple.
3. The nature of reaction in solution is not critical (Table 1)
4. The media in which the reaction takes place is irrelevant (i.e. titration can be carried out in water, alcohol, benzene, acetone, etc.)
5. Colloids as well as true solutions could be easily titrated.
6. The thermogram obtained will depend on both ΔG and ΔS because $\Delta H = \Delta G + T\Delta S$ and thus weak acids may give just as good titration curves as those obtained from strong acids titrated with a strong base [8,9] as seen in Figure 4.
7. One thermogram usually provides a great variety of information. It may include a measurement of ΔH , quantity of solute, number of steps taking place (as in the analysis of mixtures and polyprotic acids) (Figures 5-7) and calculation of equilibrium constants for incomplete reactions[9].

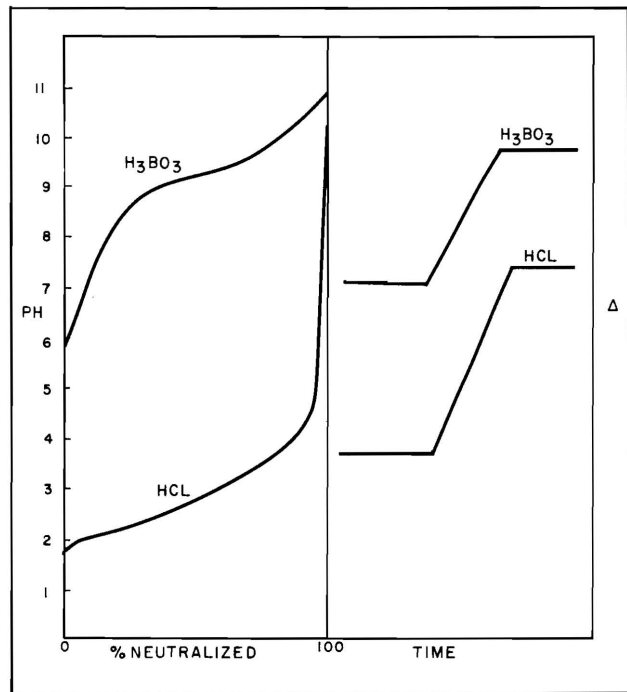


Figure 4. Comparison Between Potentiometric and Enthalpimetric Titrations of HCl and H_3BO_3 .

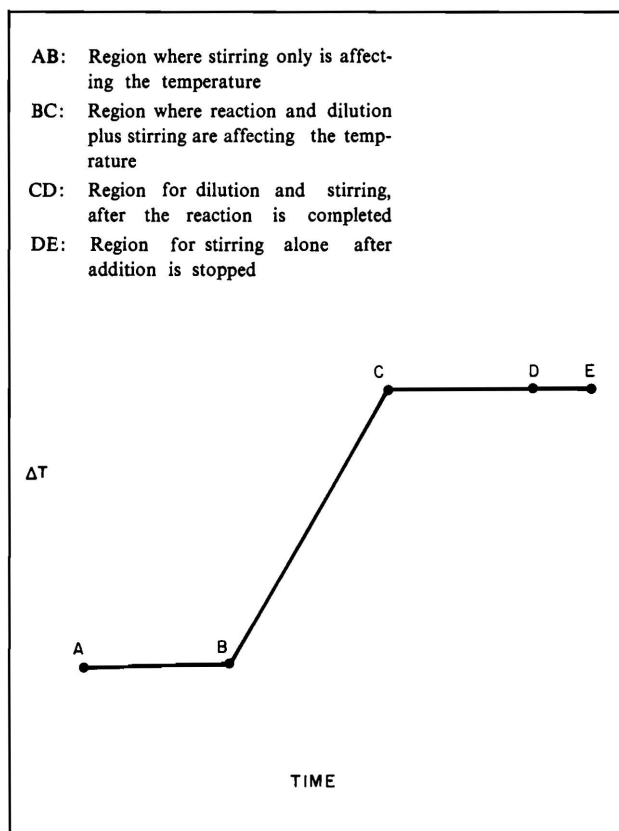


Figure 3. Typical Thermogram for an exothermic reaction

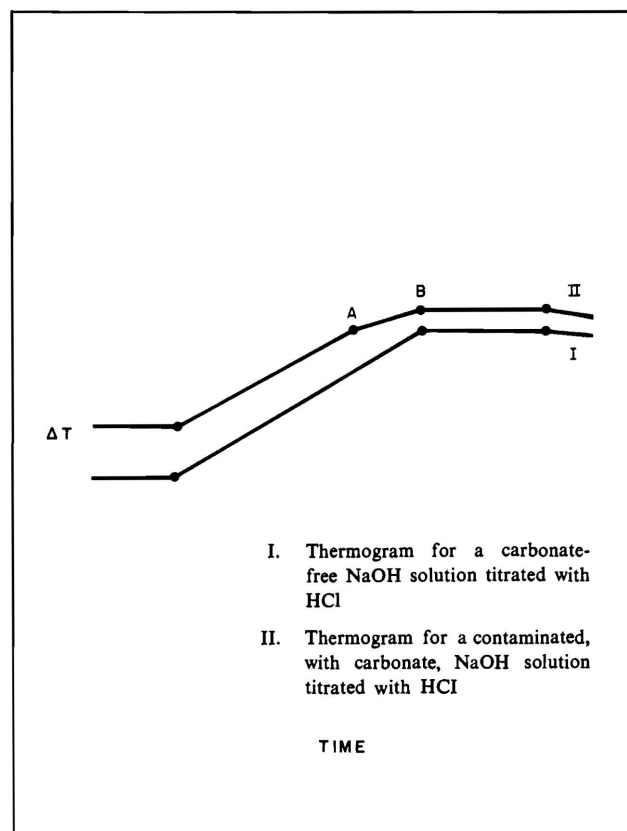


Figure 5. Simultaneous quantitative determination of a solution containing NaOH and carbonates at $25^\circ C$.

The use of this method for accurate quantitative results is limited by the fact that the reaction under study must be rapid, complete, and gives a measurable heat effect. Despite this handicap regarding quantitative measurements, the titration curves in general depend on a fairly nonspecific property of the system, that is heat evolved or absorbed. The sensor used, a thermistor, is a universal one as compared to

the sensors used in other titration systems that require a specific indicator for different reactions. The universality of the sensor, nonspecificity of the property monitored, plus the fact that the change in entropy of the reactions under study contributes a great deal to the shape of the titration curve, are the unique features of this method.

TABLE I

Some of the Reaction Types Studied by Enthalpy Titration ^a	
Reaction Type	Typical Reaction System
1. Inorganic	
Acid-Base	HClO ₄ and NaOH H ₃ BO ₃ and NaOH
Precipitation	Silver and Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , etc Oxalate and Ca ²⁺ , Sn ²⁺ , Ba ²⁺ , Hg ²⁺ , etc.
Complexation	Carbonates and Pb ²⁺ , Ag ⁺ , Zn ²⁺ , Cu ²⁺ , Al ³⁺ , etc. Tetraphenylborates and K ⁺ , Tl ⁺ , NH ₄ ⁺ , etc. EDTA and Ca ²⁺ , Ni ²⁺ , Cu ²⁺ , Cd ²⁺ , Zn ²⁺ Ag ⁺ , Al ³⁺ , Co ³⁺ , Ce ⁴⁺ , Sn ⁴⁺ , etc.
Redox	Fe ²⁺ —MnO ₄ ⁻ , UO ²⁺ —Cr ₂ O ₇ ²⁻ Ce ⁴⁺ —I ⁻ , Ce ⁴⁺ —Fe ²⁺ , etc.
2. Organic	
Nonaqueous Acid-base	
Oxination	
Phenol coupling	Weak acids and bases in appropriate solvents Aliphatic Carbonyl compounds Mono - and disubstituted phenols and naphthols.
3. Biochemical	
Acid - base	
Precipitation	
Bacterial growth	Proteins Antigens-antibody reactions Actively growing bacterial culture added to growth media (streptococcus Fecalis in 1.0% Glucose, 0.5% Amino acids, 0.5%K ₂ HPO ₄ and 0.5% yeast extract)

^aCarr, P., *CRC Critical Reviews in Anal. Chem.*, Jan. 1972, p. 495.

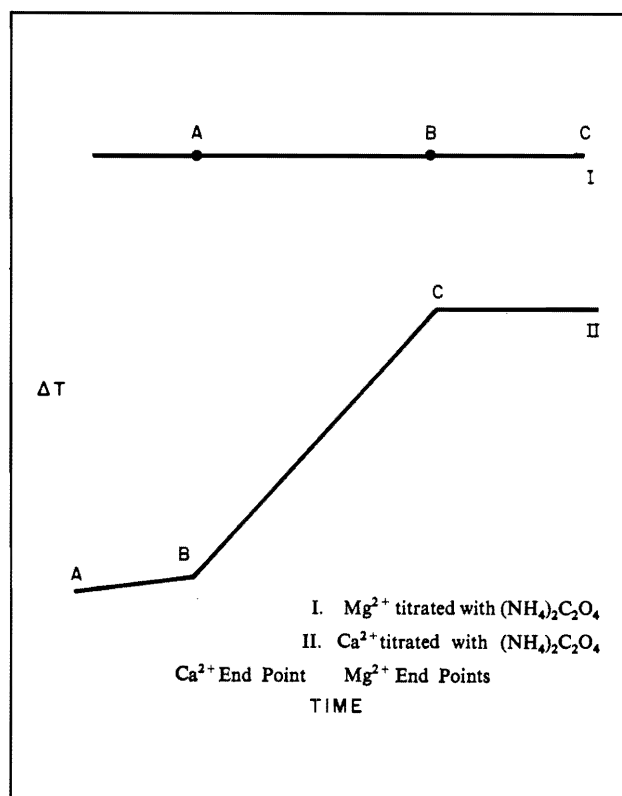


Figure 6. Enthalpy Titration Curves of Mg^{2+} and Ca^{2+} At $25^\circ C$

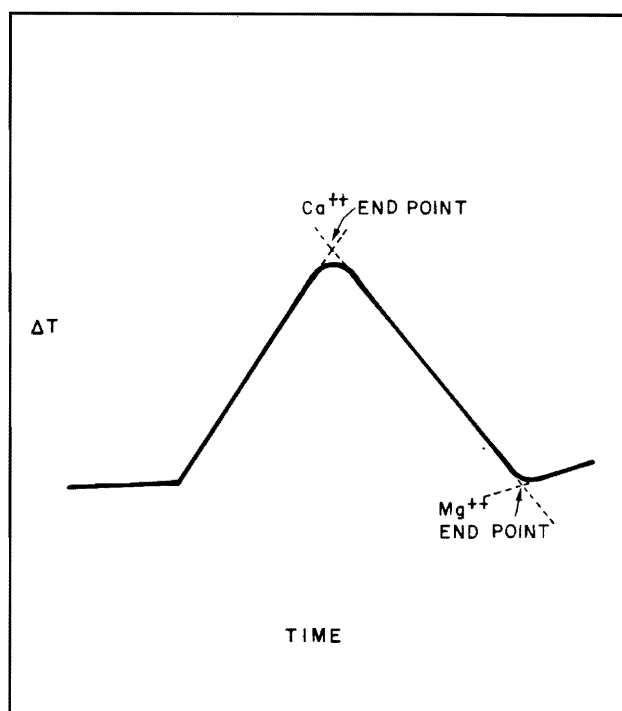


Figure 7. Enthalpy Titration Curve of Ca^{2+} and Mg^{2+} with EDTA At $25^\circ C$

REFERENCES

- [1] C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd Ed. Amsterdam: Elsevier, 1963.
- [2] J. P. Redfern, *Complementary Methods in Differential Thermal Analysis*, Vol. 1, Chapter 5, R.C. Mackenzie, Ed. London: Academic Press, 1970.
- [3] F.E. Austin, et al, "Evolved Gas Analysis" in *Thermal Analysis, Vol.2*, Schwender and Garn, Eds. London: Academic Press, 1969.
- [4] W. W. Wendlandt, *Thermal methods of Analysis* New York: Interscience Publishers, 1964.
- [5] R. C. Wilhoit, *J. Chem. Education*, **44** (1967). A571, A629.
- [6] J. M. Bell and C.F. Cowell, *J. Am. Chem. Soc.*, **35** (1913), 49.
- [7] H. W. Linde and D.N. Hume et al, *Anal. Chem.*, **25** (1953), 404.
- [8] L. Hansen, et al, *Modern Methods in Analytical Chemistry*, J. Jordan, Ed. New York: Marcel Dekker, 1974.
- [9] K. Khalaf, *Thesis*, University of Cincinnati, Ohio, U.S.A. (1974).

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