THERMOMETRIC AND ENTHALPIMETRIC ANALYSIS*

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It is essential to define the position of Thermometric and Enthalpimetric Analysis (T.E.A.) with relation to the broad field of Thermal Analysis (T.A.). The latter has been defined [1] as "Thermal Analysis is a term covering a group of techniques in which a particular property of a substance and/or its reaction product(s) is measured as a function of temperature, whilst the substance is subjected to a controlled temperature programme"; putting this perhaps less precisely – in Thermal Analysis a temperature change is used to cause a reaction. One may thus regard the techniques of Thermometric and Enthalpimetric Analysis as the obverse, since in these techniques a reaction is used to bring about a temperature change, and this change is monitored for analytical purposes.

Another, empirical division and classification arises from the physical nature of the sample. Broadly speaking Thermal Analysis uses solid samples, whereas Thermometric and Enthalpimetric Analysis uses solutions; in Thermal Analysis the analyte is often the whole sample; in Thermometric and Enthalpimetric Analysis, the analyte is rarely the whole sample and is usually one of the solutes. There are similarities in the two areas, which account for the divisions within each area; for example, when we use a balance (in (TA)) to monitor a mass change, then we have Thermogravimetry (TG); if we use a burette to monitor the volume change in a solution (as a result of addition of a titrant), then we have Thermometric Titrimetry.

Similarly, if we use a calorimeter or its equivalent to monitor a heat change, we use the techniques of Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), and Direct Injection Enthalpimetry (DIE).

It is necessary to distinguish the two techniques of Thermometric and Enthalpimetric Analysis more clearly than in the above classification and a preferred distinction is [2] that in Thermometric Titrimetry, the temperature change is used to *indicate* the cessation of a particular reaction between the analyte and the added reagent; and in Enthalpimetry the temperature change is used to *measure* the amount of product formed in the reaction of the analyte and the added reagent.

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Such a division will be used to define, and delineate the two techniques in this present work.

When one considers the basic equation

$$\Delta H^0 = \Delta G^0 + T\Delta S^0$$

it can be seen that if one uses a measure of the enthalpy change for monitoring an analytical process, then this method will be in contradistinction to the more classical methods of say colorimetric analysis, potentiometric titrimetry, visual coloured indicators, which utilise ΔG only or some function of ΔG in the measurement and comparison of equilibrium systems.

Since the entropy change is often very significant and often enhances the free energy change in a system, it is thus feasible to monitor changes, by using or observing some measure of the enthalpy change in reactions which cannot be monitored by only measuring the relatively small free energy changes.

If one considers the titration of hydrochloric and boric acids with sodium hydroxide solution we find that a plot of the volume of sodium hydroxide solution added against the change in the pH of the sample, or in the change of the junction potentials of an electrode system placed in the sample (both of which are essentially a measure of the free energy changes), gives for hydrochloric acid a usable curve, but for boric acid a smooth sigmoid curve (see Fig. 1A) from which it is impossible to obtain an equivalence point; yet when the change in the temperature of an adiabatic system containing the reaction is plotted against the volume of sodium hydroxide added the curves shown in Fig. 1B are obtained. Since the molar heats of reaction of the two acids are approximately of the same order (HCl/NaOH – 56.7 kJ mol^{-1}; HBO_2/NaOH – 53.8 kJ mol^{-1}) the two heats evolved for equivalent amounts of the acids are approximately of the same order. In a mixture of the two acids a serial titration (Fig. 1C) may be accomplished, since the ionisation of the hydrochloric acid (pKa = ∞) effectively suppresses the ionisation of the boric acid (pKa = 4) and not until practically all the protons from the stronger acid are used in the neutralisation reaction, are the protons liberated from the weaker acid.

The phenomenon of serial titration is excellently illustrated by the work of Jordan and Jespersen [3] who compared the potentiometric and thermometric titration curves of egg albumin titrated with dilute sodium hydroxide solution. The sample, an extremely dilute solution of a purified protein fraction with a primary structure of 277 polypeptide links, and 46 side chains containing carboxylic acid groupings (pKa = 4.3 $\pm$ 0.3), 7 imidazole units (pKa = 7.5 $\pm$ 0.3) and 19 primary amino groups (pKa = 10.4 $\pm$ 0.3) has a molecular weight of approximately 43,800. Conventional pH titrations give only a smooth sigmoid curve, with no indication of any difference in the types of protons being titrated; on the other hand a thermometric titration gives 3 distinct breaks, corresponding to the 3 sets of protons. Such a titration gives some indication of the potential of the technique and its advantages over the more usual electroanalytical techniques.

If one considers the basic equation $\Delta H^0 = \Delta G^0 + T\Delta S^0$ in some detail, it is obvious that to have complete or even practically acceptable thermodynamic validity, there must be some restrictions placed on the system. First, the system should be a closed system; however, in any titrimetric system this is practically

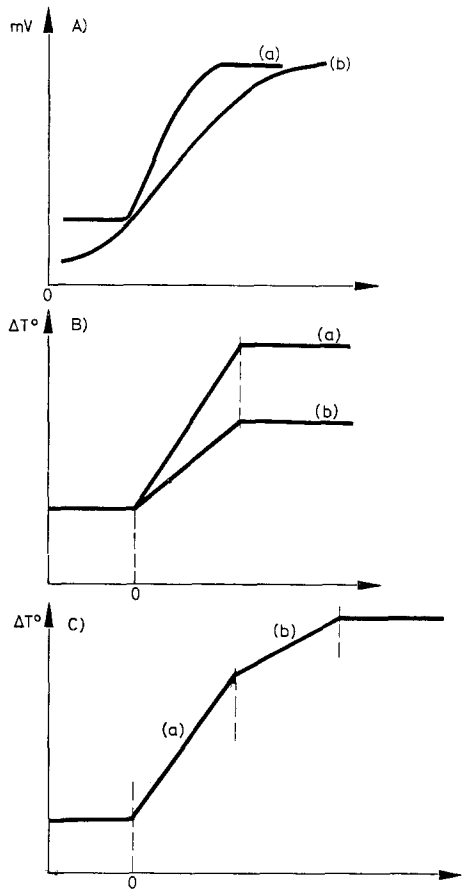

Fig. 1. a) Titration of HCl *vs.* NaOH; b) titration of H_3BO_3 *vs.* NaOH

impossible since the addition of a titrant is necessary. In practice therefore there must be the minimum practicable increase in volume. This means that the titrant must be added in a relatively highly concentrated form.

Secondly if there is to be a measure of the amount of enthalpy change or some directly related parameter then the system must be adiabatic or quasi-adiabatic so that any temperature change is from within the system. Such changes must also be relatively small so that the actual change in temperature is such that it represents only 1% or so of the total temperature, i.e. a maximum change of the

order of 2–3°. These practical restrictions have played an important part in the development of the techniques and the apparatus associated with them.

The development of these techniques has to a large extent been determined by the development of the apparatus associated with them. If we consider the two techniques separately we find that Thermometric Titrimetry has been used since 1913 [4] and Enthalpimetric Titrimetry since 1917 [5] although it was not named as such until 1964 [6].

The earlier workers in Thermometric Titrimetry used fairly simple apparatus; the reaction system was contained in a Dewar flask, the temperature sensor was usually a Beckmann thermometer, and the titrant was added discontinuously from a thermostated burette. After each addition of titrant the system was stirred until temperature equilibrium was attained; the change in temperature of the system was then plotted against the change in volume of the system; for a single stage reaction a single step was indicated, the equivalence point of the system being revealed by the break point in the curve. For a multistage reaction, several break points are indicated, each corresponding to the cessation of the reaction and the onset of a further reaction. A relatively large amount of significant work was reported including the determination of weak organic acids such as phenols, the determination of analytes using precipitation reactions, the determination of the stoichiometry of complexes, both stable and labile. Such reactions and studies have been previously reviewed in detail [7].

It is unfortunately the case that the relatively large thermal capacity of the temperature sensor and its relatively slow response to temperature change prevented progress in this area. The use of the small thermistors [8] glass clad, with a high electrical resistance, negligible heat capacity and practically immediate thermal response was probably the most significant step in the progression of these techniques. The immediate thermal response obviates the need for elaborate adiabatic calorimeters; it is therefore practicable to replace the Dewar flask with a polyethylene beaker. Using the thermistor as one arm of a relatively simple D. C. Wheatstone bridge allows the use of a simple potentiometric chart recorder to indicate and record the changes in the voltage imbalance of the bridge, brought about as a result of the change in resistance of the thermistor. This change, usually about 4% for 1° change in temperature, is sufficient to give a suitable signal. The normal procedure is to deliver the titrant from a piston burette [8], or a multi-roller peristaltic pump, whose delivery rates are synchronised with the chart movement of the potentiometric recorder; such synchronisation enables the volume of titrant delivered (per sec) to be related to the distance travelled (per sec) by the chart.

Using a Wheatstone bridge with a 10 Kω thermistor, then the accuracy for a reaction with a molar heat change of approx. 20 kJ mol^{-1} is 0.5–1.0%, providing the reaction is sufficiently fast to be completed within the time of delivery of the titrant. Some typical heats of reactions which can be used in direct assays, since both the molar heat change and the kinetics are favourable. are illustrated in Table 1.

Table 1

Heats of reaction

Reaction	Molar heat, kJ Mol^{-1}
$NaOH + HCl$	—58
$NaOH + H_3BO_3$	—52
$NaOH + C_6H_5OH$	—33
$C_5H_5N + HClO_4$ in glacial acetic acid	—34
$Ag^+ + Cl^-$	—45
$MnO_4^- + SO_3^{2-}$	—252
$Ce^{4+} + Fe^{2+}$	—100
$BrO_3^- + N_2H_4$	—820
$IO_4^- + N_2H_4$	—336
$Ag^+ + CN^-$	—116
$EDTA + Ca^{2+}$	—24
$EDTA + Mg^{2+}$	+22

The precision and the sensitivity of the overall system are dependent upon 3 main factors: a) the molar heat of the reaction; b) the sensitivity of the sensing and recording system; c) the thermal capacity of the titration system.

For example, in a particular reaction the molar heat change is constant, thus if we alter the sensitivity of the bridge by say replacing a thermistor of a low resistance (say 6–8,000 ohms) with one of the higher resistance (say 60–70,000 ohms) and modify the other arms of the bridge accordingly, then for the same heat change in the titrimetric system we can obtain a much larger voltage imbalance and hence a larger recorder signal; and the sensitivity is also increased. We may at the same time also increase the rate of delivery of the chart, and hence assuming that the break points are still discernible, we obtain a greater chart distance per unit volume of titrant delivered. Thus the precision of the system is increased.

If a particular reaction is done in a media of different thermal capacity, then the temperature changes brought about by the same amounts of reaction will be different. If we consider the acid–base neutralisation of pyridine and perchloric acid, then if this is done in acetic acid medium of specific heat of approximately 0.45 (compared to that of water), then the temperature change will be of the order of twice that obtained for a similar reaction in water. Since many hydrocarbon and similar solvents have low specific heats, it is obviously advantageous to use them. In contrast to their use in potentiometric or conductometric titrimetry, it is not necessary to add materials to give electrical conductance and the system is thus not diluted. In an analogous fashion the titrants need not be of the conventional type.

Table 2

Titrant	Application
$AgNO_3$ in $LiNO_3/KNO_3$ eutectic at 158°	Chloride in potassium chloride
Dipyridyl	Zinc alkyls and aluminium alkyls
Thallium(I) ethoxide	Weak organic acids in hydrocarbons
Diphenyl guanidine in acetonitrile	Weak organic acids
Dioxane in benzene	Lewis acids
H_2S as gaseous titrant	Copper and zinc in brass

Table 2 indicates some of the more unusual titrants which have been used. Jordan and coworkers [9] used the molten lithium nitrate/potassium nitrate eutectic as a solvent; the use of chelating agents such as dipyridyl and 8-hydroxyquinoline [10] for the assay of organo-metallic compounds, and of hydrogen sulphide gas as titrant for components of brass [11], are examples of the varied types of titrants which are available in this technique.

Not only are titrants unusual but many of the samples used are also different from those used in more conventional assay methods. This is a direct consequence of the use of the thermistor; it is not necessary to have a clear solution as in titrations using visual indicators, either conventionally or in a spectrophotometric of fluorimetric titration; neither is it necessary to remove surface active materials as in many electrometric methods where these materials often give rise to spurious junction potentials. In many instances it is unnecessary to have a preliminary extraction of the active ingredient prior to the assay reaction. The determination of sorbitol in some dietary foodstuffs [12] (see Table 3) is a typical example of all these points, the seeds and rinds of the fruit, the food dyestuffs used in the colouring of the samples, the fats and solid cocoa of the chocolate, need not be removed directly titrating the sorbitol with potassium periodate.

A comparison of the results obtained by direct assay and those obtained using the B.P. method [13] reveals that the thermometric method gives results which are analytically acceptable. The time taken to obtain the results thermometrically is about one third of the time taken using the B.P. method.

Table 3

Sorbitol assays

Sample	Sorbitol, g per 100 g of sample		
	thermometric	polarimetric	nominal
Blackcurrant jelly	59.21	58.35	60
Orange conserve	60.25	59.5	58
Strawberry conserve	60.25	60.1	60
Raspberry jam	61.29	58.0	60
Chocolate (dietetic)	34.20	Not possible	33

It has already been stated that for a direct titration it is necessary to have suitably fast kinetics, especially near the equivalence point; when determining organic functional groups as in many pharmaceutical analyses, it is not possible to obtain a direct assay, and it is usual to react the sample with an excess of the required functional group reagent, and then after establishing thermal equilibrium, to determine the excess of the reagent by a direct titration using an appropriate reagent for a fast reaction. In most cases it is possible to choose the reaction sys-

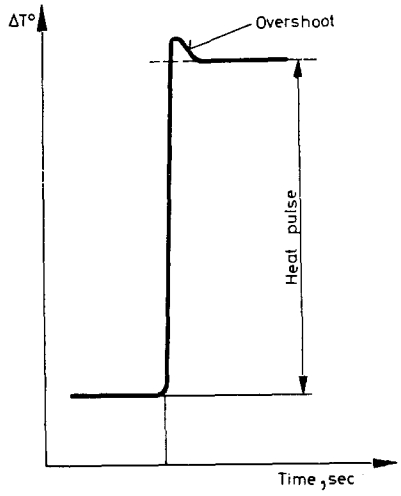

Fig. 2

tems such that the excipients contained in the pharmaceutical product are inactive towards the reagents, and are thus thermally neutral; they only 'dilute' the temperature change by increasing the overall thermal capacity of the titration system, but do not significantly decrease the precision of the method. It is therefore generally possible to assay pharmaceutical products without prior removal of the excipients.

In enthalpimetry an excess of the reagent is injected rapidly into a fixed volume of the sample, and the heat pulse obtained as a result of the reaction is then measured as a voltage signal. The reagent is generally contained in a submersible pipette beneath the surface of the sample [14] in order to obtain rapid thermal equilibrium and to ensure that the heat changes come only from the reaction and not from any external source. The shape and size of the pipette depend upon the reaction system [15] and in the case of transfer of the heat of reaction throughout the solution. The type of reaction pulse obtained is shown in Fig. 2. The small amount of overshoot is the result of local overheating and the inertia of the pen of the recorder; it is generally possible by suitable arrangement of the geometry of the stirring point of injection and the thermistor tip to eliminate this effect.

One feature on enthalpimetric analysis which must be emphasised is the fact that most reagents have a heat of dilution and/or a heat of mixing and that this must be accounted for in some manner. It is possible to do this by at least 3 methods: 1. Measure the heat pulse obtained on injecting the reagent into a blank, and add or subtract this pulse from that obtained in injection of the reagent into a sample containing the analyte in a known concentration. For each point of the calibration curve it is necessary to adjust the pulse obtained. Theoretically the amount of dilution may vary significantly depending on the amount of analyte present, but in practice it is usual to use such a large excess of a reagent, with a low heat of dilution, that the effect is practically constant over the analyte concentration range used for calibration. 2. Where a heat of dilution of the reagent is significantly exothermic, it is possible to compensate for this by the simultaneous addition of a substance, which does not react with the analyte, but has an endothermic heat of dilution. For example if sulphuric acid is to be used for the precipitation of barium ions as barium sulphate, then the relatively large exothermic effect caused by the use of a relatively concentrated solution of sulphuric acid may be compensated with simultaneous addition of ammonium sulphate, which has an endothermic heat of dilution. Significant work has been done in this area by Sajó and co-workers [14] who have prepared several thermally neutral injection solutions for use in steel and silicate analysis. It is possible to have simultaneous injection of the reagent into the analyte and a blank, and by the use of suitably matched thermistors in a modified Wheatstone bridge [17] the heats of dilution can be compensated, and the bridge imbalance is due solely to the analyte reaction. This system has been used for the determination of ascorbic acid in vitamin tablets [17] and for several related systems.

The use of direct injection enthalpimetry is fairly widespread and two commercial instruments, the Directhermom and the Silicotherm, based on the designs of Sajó and co-workers, are available. Its use in glass analysis and associated materials analysis has been established by the work of Doering [18], who has used the method for the rapid assay of silicates and other materials used in glass manufacture. It is a rapidly expanding area of assay techniques. The main disadvantage is that it is impossible to perform sequential titration, the basic concept, i.e., the addition of a large and excess amount of reagent, prevents reactions taking place in sequence. The advantages of the techniques have been previously reviewed [19]; the main advantages are the speed, the relatively simple apparatus and the fact that since it is a comparative method, there is no need for precise preparations of reagent solutions. It is readily automated and for batch analysis of routine samples it has great potential.

Probably one of the major developments in Thermometric and Enthalpimetric techniques has been that of Catalysed Thermometric Titrations or Catalimetric Titrimetry. This technique, based on the continuous addition of titrant to the analyte, dissolved in an appropriate solvent, uses two contiguous reactions. The first is the 'Analyte Reaction' in which the analyte reacts with the reagent added; the heat change is very small; the second is the "Indicator Reaction" in which

the first excess of the reagent added *catalyses* a reaction of the *solvent matrix.* This catalysed reaction may have a small molar heat change but because of the high concentration of the reactant, the amount of heat change is relatively large; and the cessation of the analyte reaction is indicated by the onset of the catalysed solvent reaction with its attendant large heat change. It is perhaps appropriate to mention that such changes have been previously discussed under the heading "The use of the solvent as an indicator" [2].

One of the most well known of this type of reaction is that reported by Vaughan and Swithenbank [20] who used the base catalysed dimerisation of acetone (to give diacetone alcohol) to indicate the cessation of the neutralisation of weak tar acids, dissolved in acetone, by sodium hydroxide dissolved in isopropanol. The method proved to be very successful; even the acids on the surface of coal could be titrated directly; the finely powdered sample, suspended in acetone was titrated with the isopropanolic solution of alkali hydroxide; the heat change caused by the onset of the dimerisation reaction was sufficiently great to allow for the temperature sensor to be a simple laboratory thermometer.

Other catalysed reactions reported include the perchloric acid catalysed hydrolysis of acetic anhydride with water in glacial acetic acid [21]; the reaction was preceded by the acid–base neutralisation reaction of some organic bases dissolved in glacial acetic acid containing 20–30% v/v acetic anhydride and approximately 5% v/v of water. The titrant used was perchloric acid in glacial acetic acid. Vajgand and co-workers generated the protons used for the neutralisation by a coulometric method [22].

Other reactions used include the Ce(IV)/As(III) catalysed reaction and numerous applications involving these ions [23], the catalysed polymerisation of methyl cyanide [24] and some excellent work by Greenhow and co-workers [25, 26] on the catalysed polymerisation of compounds such as α-methyl styrene. Using an acid catalysed reaction, Greenhow was able to determine some alkaloids in the parts per million concentration range.

Non-selective reactions

In the previously reported assay of mixtures, all the reactions discussed have been selected so that only one functional group reacted at any one time. Although one may have a serial titration system as in the titration of egg albumin, where different types of protons react [3], or in a series of bases reacted with hydrochloric acid [27], on the titration of sulphuric acid in copper plating solution [28] only one functional group is titrated at any one time and this is only in a thermometric mode. In an enthalpimetric mode, the reactions have been selected so that sequential titrations can be done but at any one injection only one functional group reacted. There have been recently reports of the use of non-selective reaction in enthalpimetry, for the determination of mixtures of analytes [29, 30]. Bark and co-workers [31] have suggested several features concerning the assay of mixtures; these include the postulation of the concept of Partial System Molar Heats, in

which the partial system molar heat change of an analyte and a particular reagent is defined as that heat change which would be generated if the particular analyte alone occupied the system; they postulate additivities of partial system molar heats; they further suggest that the reactions should be practically instantaneous, have similar molar heats of reactions and that for 'X' analytes there must be 'X' conditions of injection. For the assay of mixtures containing chloride, bromide and iodide [30], they report that injection of Ag^+, *N*-bromosuccinimide in acidic and neutral conditions, is sufficient to give, with a programmed calculation, an answer of within 1.0% in 1–2 minutes. Similarly mixtures of sulphur and sulphur containing anions have been assayed in mixtures [31]. This is considered to be a growth area in enthalpimetric analysis.

There are several important areas which cannot be covered in a brief review; nontheless they must be mentioned since they are of importance and potential. The use of thermometric titrimetry for the determination of the stoichiometry of complexes, both stable and transient, is an old established technique, and work on unstable complexes of transitional metals [32] in the earlier period of thermometric work has progressed as far as the determination of the stoichiometry of complexes of molybdates and tungstates, using sophisticated computer analysis of the titration curves [33].

The use of high precision thermometric and enthalpimetric techniques has occupied and continues to occupy the attention of many workers, notably Barthel, Christensen and Izaak, Jordan and co-workers; these works have been extensively reviewed [34]. Whilst this work is essentially calorimetry, it is correct to regard it as an adjunct of the present techniques. Similarly the use of continuous thermal assay of the reactions of enzymes, antibodies, etc. with selected substrates [35, 36] is an area of thermal analysis which must be accepted to be a growth area of thermometric analysis. One definite spin-off the enthalpimetric technique is that of on-line or continuous analysis. Probably the major initiative in this field is the work of Priestley et al. [37] for the design of an on-line analyser. Development of this includes the design of analysers for various specific purposes [38]. These areas are developing areas, and as with most of thermometric and enthalpimetric techniques, progress is dependent mainly on developments in instrumentation.

In conclusion, it must be noted that the almost universal applicability of Thermometric and Enthalpimetric Analysis is due to the fact that the phenomenon basic to these techniques is the most general property of chemical reactions. The potential applicability of these techniques is thus widespread, the progress of instrumentation, especially in the calorimetric field, will undubitably extend its uses. For the present reviewer, a personal restriction is inherent in the remarks of earlier workers in the field [5]. In 1917, reporting the assay by enthalpimetry, of free anhydride in glacial acetic acid, by the injection of an aniline, when discussing the relative ease of the technique – the authors stated "They (the determinations) are moreover carried out easily by an ordinary intelligent worker. The time required for the determination should not exceed 3–4 minutes from the start."

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