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Neuere analytische Verfahren

Thermochemical Titrations[1]

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Summary

"Enthalpy titrations" represent one of the newest methodological tools in the arsenal of modern instrumental analysis. In principle, they depend on differential plots of temperature *versus* volume of titrant, recorded in an adiabatic titration cell. The use of temperature sensitive semiconductors (called "thermistors"), wired in a Wheatstone bridge circuit as resistance thermometers, has made it possible to record automatically "enthalpograms" (= thermometric titration curves) in extremely dilute solutions (10^{-4} to 10^{-2} molar). The response of a thermistor bridge corresponds typically to that of a one thousand junction conventional thermocouple, permitting the measurement of temperature changes as small as 0.01 °C with a precision and accuracy of ± 0.0001 °. Applications to quantitative analysis are described, including proton transfer (acid—base), electron transfer (oxidation—reduction), precipitation and chelation reactions. The significance of enthalpy titrations is discussed as rapid and convenient means for determining heats of reaction within extremely narrow temperature intervals. Examples are presented illustrating the types of thermodynamic information which have been obtained by judicious interpretation of enthalpograms, in a wide range of temperatures (25 to 500 °C) and media (water, conventional organic solvents and molten salts): The nature of solvated species and of associated ion aggregates, which are the chemical entities actually present in solution, have been elucidated. Unique potentialities of thermochemical titrations are inherent in the fact that they depend *in toto* on the enthalpy term in the equation:

$$\Delta H^0 = \Delta F^0 + T\Delta S^0.$$

In contradistinction, most of the common procedures used in analytical chemistry are solely a function of the free energy parameter:

$$\Delta F^0 = -RT \ln K.$$

[1] Lecture presented at the Technical Congress of the 2nd International Exhibition of Laboratory Measurement and Automation Techniques in Chemistry (ILMAC), October 15th to 20th 1962, in Basle (Switzerland).

In contradistinction to Western Europe, in America analytical chemistry is an independent research subject at most major universities. A doctoral candidate may obtain his degree by majoring—in accordance with his preference—in one of the following four fields in chemistry: Analytical Chemistry, Organic Chemistry, Inorganic Chemistry, and Physical Chemistry. As a result of this situation a basic approach has characterized developments in analytical chemistry which is considered in the United States of America a science in its own right, comparable in status to the other three areas of chemistry. We feel that in order to develop new analytical methods, it is necessary to understand thoroughly the quantitative correlations which govern the processes involved. However, it is impossible to study novel reactions without having available appropriate analytical tools for their quantitative characterization. As a result, the fundamental and the analytical aspects of such investigations represent really the two sides of the same coin: Progress in one is contingent on advances in the other. Our interest at The Pennsylvania State University in thermochemical titrations was engendered by this very philosophy of a fundamental approach to analytical chemistry. In reviewing the multitude of available methods of chemical analysis, one finds that their vast majority depends ultimately on some property of the reaction related to free energy parameters. A typical example of a "free energy method" is a potentiometric titration. Corresponding titration curves are shown in Figure 1 obtained in the conventional alkalimetric titration of 0.01 M hydrochloric and boric acids with standard sodium hydroxide. The hydrogen ion concentration [which determines the *p*H and the potential of the

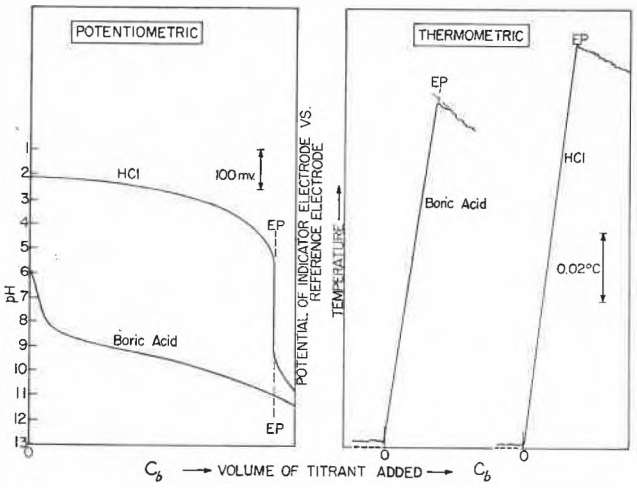

Figure 1. Comparison of Potentiometric and Thermometric Titration Curves: 0.01 M Acids Titrated with Standard Sodium Hydroxide in Aqueous Solution at 25 °C. EP: Equivalence Point

indicator electrode] is governed by the well-known equation

(c) $$H^+ - \frac{K_w}{[H^+]} = \frac{C_a K_a}{[H^+] + K_a} - C_b \qquad (1)$$

where K_w and K_a denote, respectively, the ionization product of water and the ionization constant of the acid C_a is the initial stoichiometric concentration of the acid, and C_b is the concentration of the added sodium hydroxide titrant. Evidently, for a given value of C_b [which is the abscissa in the figure and proportional to the volume of the titrant added], Equation (1) yields a corresponding *p*H value. *Ceteris paribus,* the *p*H depends on the value of the ionization constant K_a which is correlated with the standard free energy of ionization by equation (2).

(e) $$\Delta F_a^0 = -RT \ln K_a \qquad (2)$$

The fundamental reason that in Figure 1a hydrochloric acid yielded an excellent inflection at the end point, while in the case of boric acid the equivalence point was ill-defined, is inherent in the difference between the ionization constant of the strong acid [$K_{HCl} \to \infty$] and the very small ionization constant [$K_{H_3BO_3} = 5 \times 10^{-10}$] of boric acid. Quite generally, no acid of comparable weakness can be titrated by any direct free energy dependent end-point determinative procedure. In principle, all visual color indicators represent such free energy methods. There exists, however, one universal property of chemical reactions which is not solely dependent on the free energy, viz. the heat of reaction. Because

$$\Delta H = \Delta F + T\Delta S, \qquad (3)$$

it is conceivable that a titration curve based on the measurement of ΔH may yield a well-defined end point when all free energy methods fail. That this is actually possible, is strikingly illustrated in Figure 1b which shows thermometric titration curves of boric acid and of hydrochloric acid, obtained under exactly the same conditions as the juxtaposed potentiometric curves. The shape of these thermometric curves depends on the heat evolved in the neutralization of the two acids: They have been obtained by recording the change in temperature in an adiabatic titration cell. As can be seen in Figure 1b, the experimental end points in the two thermometric titration curves are comparably well-defined for the weak and for the strong acid. This is a performance unmatched by any free energy method. The immediately apparent reason for the similarity of the two "enthalpy titration curves" in Figure 1b, as compared to the difference in the two potentiometric curves in Figure 1a, is that the heats of neutralization of the two acids differ much less than their ionization constants. The pertinent numerical data are summarized in Table 1.

Table 1: Ionization Constants and Heats of Neutralization in Aqueous Solution at 25 °C

Acid	K_a	Heat of Neutralization (kcal/mole)
HCl	∞	−13.5
H_3BO_3 [a]	5.8×10^{-10}	−10.2

[a] Exhibits behavior of a monoprotic acid; $K_a = \frac{[H^+]\,[HBO_2^-]}{[H_3BO_3]}$

It is illuminating to consider why the heats of neutralization of hydrochloric and boric acids differ by as little as 30 %. This remarkably small variance is due to a compensatory effect between the free energy of ionization of boric acid and the corresponding entropy of ionization yielding altogether a relatively small heat of ionization. Evidently the thermodynamic functions for the neutralization reaction

$$H_3BO_3 + OH^- \rightleftharpoons H_2O + H_2BO_2^- \qquad (4)$$

can be calculated from the appropriate additive functions of discrete ionization and neutralization steps, viz.:

$$H_3BO_3 \rightleftharpoons H^+ + HBO_2^- \qquad (5)$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad (6)$$

The heat corresponding to equation (6) is the same as the heat of neutralization of HCl [or of any other strong acid], i. e.

$$\Delta H_6^0 = -13.5 \text{ kcal/mole at } 25\,^\circ\text{C}. \qquad (7)$$

The heat of ionization of boric acid [equation (5)] is:

$$\Delta H_5^0 = \Delta H_4^0 - 13.5 = \Delta F_5^0 + T\Delta S_5^0 = RT \ln K_5^0 + T\Delta S_5^0. \qquad (8)$$

The relevant numerical values of the parameters in equation (7) are listed in Table 2.

Table 2: Parameters of Equation (8) for Boric Acid

T (°K)	K_a	ΔF_5^0 (kcal/mole)	ΔS_5^0 cal/mole-degree	$T\Delta S_5^0$ kcal/mole	ΔH_5^0 kcal/mole
298	5.8×10^{-10}	+12.6	−31.1	−9.3	+3.3

Comparison of equations (6), (7) and (8), in conjunction with Table 2, makes it apparent that the well-defined shape of the thermometric titration curve of boric acid [Fig. 1b] is accounted for by the fact that the ionization of boric acid is endoenergetic but exentropic, yielding altogether a heat of ionization which is small compared to ΔH^0_6. In other words, in the ionization step for boric acid, a large positive free energy of ionization is compensated by a comparable $T\Delta S$ term which has an opposite sign. In our studies, this type of inter-energetic compensation, between free energy and entropy terms, turned out to be a quite general phenomenon occurring in important categories of analytical reactions, including proton transfer [acid—base], electron transfer, precipitation, and complexation processes. Consequently, thermochemical titrations, carried out under judiciously controlled experimental conditions, represent an analytical tool of wide applicability in instances where conventional "free energy" methods of analysis are bound to fail. Furthermore, the rise in the temperature, recorded on the ordinate in Figure 1b, can be used [if appropriately calibrated] as a rapid and convenient method for the determination of heats of reaction in extremely dilute solutions. In this sense, the thermometric titration curves of the type illustrated in Figure 1, represent genuine enthalpy titration curves (or "enthalpograms"), from which both the stoichiometry and the heat of reaction can be determined. In instances [which will be discussed later in this paper] when the "titration reaction" is appreciably incomplete in the vicinity of the equivalence point, it is also possible to calculate from enthalpograms the equilibrium constant (and the free energy) of the process. Thus, thermochemical titrations may make it possible to elucidate all the thermodynamic parameters (enthalpy change, free energy and entropy) of a reaction from a single experiment. Thermochemical information on analytically important reactions occurring in dilute solutions is conspicuous by its absence in the literature, due to the extreme laboriousness of classical calorimetric methods. As will be illustrated later on in this article, thermochemical "enthalpy titrations" have made it possible to accumulate information on the entropies of many important processes, yielding illuminating insights into the detailed nature of the chemical species actually prevailing in various solvents. Knowledge of entropies has made it possible, in particular, to elucidate association phenomena, such as solvation and ion pair formation, which involve relatively small free energy effects but appreciable entropy changes, because they are accompanied by drastic order-disorder transitions.

For a future historian of science, the development of analytical chemistry during the past few decades will appear in retrospect as a period of spectacular development of electroanalytical chemistry characterized concomitantly by significant advances in the understanding of the kinetics and mechanism of electrode processes. Similarly, I anticipate that the coming few years will witness extensive analytical applications of thermochemical titrations, as well as the development of "enthalpography", the maturing of thermochemical titrations into a major analytical tool, accompanied by an enhanced understanding of reaction entropies.

History and Nomenclature

The basic idea to monitor, in an adiabatic system, the change in temperature occuring during a titration, is quite old. The first "thermometric titration" has been reported in 1913 in the *Journal of the American Chemical Society*.[2] It was followed by systematic studies in the 20's and 30's performed by French and Swiss scientists.[3] All this "early work" however, is mainly of historic interest, and has no exact significance as far as fundamental thermochemistry is concerned. These pioneering studies were performed by discontinous manual procedures, adding increments of a titrant from a conventional volumetric buret to a sample ("the titrate") in a Dewar Flask. After each addition of titrant, a temperature reading was taken from a Beckman thermometer. The shape of such manual enthalpograms was poorly reproducible. Temperature changes amounted to several degrees and it was necessary to wait several minutes before taking each reading, due to the slow response and appreciable heat capacity of the mercury thermometer. Each titration required about an hour. Heat exchange with the laboratory environment was inevitable, with the result that the titration curve obtained depended somewhat on the patience of the experimenter. These drawbacks were eliminated in 1953 with the introduction (by LINDE, ROGERS and HUME) of temperature sensitive semiconductors as temperature detecting devices used in conjunction with a constant flow gravity buret.[4] With these improvements, it has become possible to titrate extremely dilute solutions (0.0001 to 0.01 molar), to minimize temperature changes to one tenth of a degree or less, to reduce the time required for a titration to a few minutes and to eliminate human error entirely. With the availability of automatic instrumentation, thermochemical titrations have been transformed from an art into a science. In this field, automatic instrumentation represents not merely a convenience but a methodological necessity. Use of an instantaneous electric signal for monitoring temperature is an absolute requirement for eliminating the irreproducibility which has haunted the manual thermometric titration techniques of yesteryear.

The first "enthalpy titrator" equipped with a motor driven buret was put in operation at The Pennsylvania State University in 1956.[5] Six years later, in February 1962, the first commercially manufactured automatic

[2] J.M. BELL und C.F. COWELL, *J. Amer. Chem .Soc. 35* (1913) 49.
[3] For a review see S.T. ZENCHELSKY, *Anal. Chem. 32* (1960) 289.
[4] H.W. LINDE, L.B. ROGERS and D.N. HUME, *Anal. Chem. 25* (1953) 404.
[5] J. JORDAN and T.G. ALLEMAN, *Anal. Chem. 29* (1957) 9.

thermochemical titration instrument, tradenamed the Titra-Thermo-Mat, was made available by the American Instrument Company of Silver Spring (Maryland, U.S.A.).[6]

Growing interest in "thermoanalytical titrimetry" in the U.S. was reflected in a symposium scheduled under the auspices of the Analytical Division of the American Chemical Society in September 1957 in New York City.[7] In a round table discussion on pertinent nomenclature the designations "thermometric titration," "thermal titration," "calorimetric titration" and "enthalpy titration" (used by various authors to describe essentially the same method) were reviewed. The consensus of opinion appeared to be that the term "thermometric titration" should be adhered for procedures yielding plots of temperature *versus* volume of titrant.[8] Recently, Dr. JAMES PENDERGRAST coined the designation "enthalpogram" for thermometric titration curves.[9] The corresponding generic term "enthalpography," for describing the method, is analogous to accepted terminological usage exemplified by "polarogram" and "polarography."

Several recent comprehensive and selective reviews on thermochemical titrimetry are available in the literature.[10] In America, a special chapter has been devoted to enthalpy titrations in a widely used textbook of instrument analysis.[11] A renaissance of West European interest in thermochemical titrations is reflected in recent publications.[12]

Experimental Methodology

The titration curves shown in Figure 1b represent "normal enthalpograms," i.e. plots of volume of titrant, v, *versus* temperature, T. Derivative and differential enthalpograms will be discussed later. The shape of normal enthalpograms may vary, depending on the relative initial temperatures of the titrant and titrate solutions and on whether the titration reaction is exothermic or endothermic. Typical normal enthalpograms are shown in Figure 2. In these titration curves, $\overline{AB}$ represents temperature-time plots obtained prior to the start of the titration; $\overline{BC}$ is the "titration branch" proper, point B denoting the time when addition of titrant was started; C is the end-point in situations

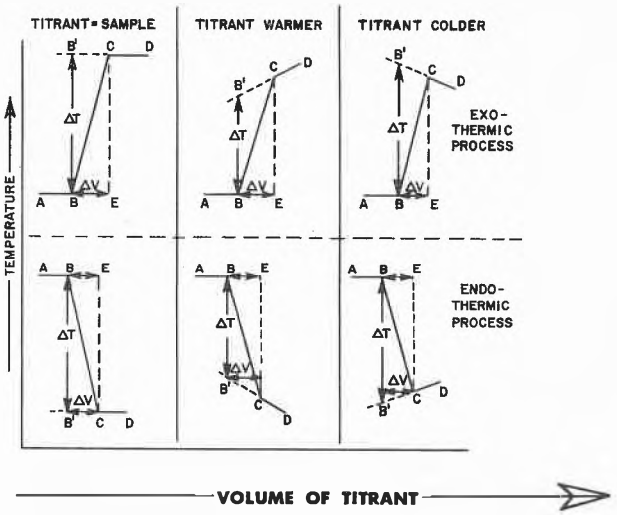

Figure 2. Shapes of "Normal Enthalpograms" as Function of Relative Temperature of Titrant and Sample: AB Temperature-time blank ("base line") obtained prior to start of titration. B Start of titration. C End Point. $\overline{CD}$ Excess Reagent Line. $\overline{CB}$ Back Extrapolation correcting for extraneous Heat Effects. ΔT Temperature change due to titration reaction (Courtesy of American Instrument Co.)

when the titration reaction is virtually complete at the theoretical equivalence point; $\overline{CD}$ is the excess reagent line. The back extrapolation $\overline{CB'}$ corrects for extraneous effects, including heats of dilution, differences of temperature between titrant and titrate, etc.—ΔV, the volume of titrant corresponding to the end-point, can be employed for quantitative analysis, whenever the stoichiometry of the titration reaction is known and an accurately standardized titrant is used. This procedure represents an "end-point determinative technique." Naturally, it is also applicable to the determination of unknown reactions stoichiometries, if both titrate and titrant solutions are standardized by independent methods. Quantitative analysis can also be performed by a direct enthalpimetric procedure which does not require a standardized titrant. However, the heat of the titration reaction must be known. It is then evidently possible to correlate the experimentally accessible "corrected temperature change"

$$\Delta T = \overline{BB'}$$

with the number of moles, x, of an unknown, P, which reacts with a reagent, R, in accordance with the stoichiometry:

$$P + rR = \text{Product}. \qquad (10)$$

The relevant equation has the simple form

$$\Delta T = \frac{Q}{k} = -\frac{x\Delta H}{k} \qquad (11)$$

where Q (expressed in kcal) denotes the integral heat, evolved or absorbed by the titration process, ΔH is the corresponding heat of reaction expressed in kcal per mole of P, and k is the effective heat capacity (expressed in kcal per degree) of the system. In order to minimize

[6] Bulletin 2375, American Instrument Co., Inc., Silver Spring (Maryland, U.S.A., 1962).

[7] *Abstracts of Papers, 132nd National Meeting*, American Chemical Society, New York (N.Y.) 1957, p. 5–13B.

[8] D.N. HUME and J. JORDAN, *Anal. Chem. 30* (1958) 2064.

[9] J. PENDERGRAST, Ph.D. Thesis, Pennsylvania State University, 1962.

[10] J. JORDAN, *Record Chem. Progr. 19* (1958) 193; S.T. ZENCHELSKY, *l.c.*, reference 3; J. JORDAN and G.J. EWING, "Thermometric Titrations" in *Handbook of Analytical Chemistry*, L. MEITES, Editor-in-Chief, McGraw-Hill, New York 1963, in print.

[11] H.H. WILLARD, L.L. MEERITT and J.J. DEAN, *Instrumental Methods of Analysis*, 3rd ed., Van Nostrand, Princeton (N.J.) 1958, p. 594–8.

[12] K. SCHLYTER *et al.*, *Trans. Roy. Inst. Techn. Stockholm, Pure & Applied Chem. 2* (1959) No. 132; *11* (1961) No. 175; *15* (1961) No. 182. – J. BARTHEL, F. BECKER and N.G. SCHMAHL, *Z. physik. Chem.* (Frankfurt), *N.F. 29* (1961) 58.

variations in k, titrants used in enthalpography are usually 50 to 100 times more concentrated than the "unknown" titrates. Thus the volume of the titrate solutions (and k) are maintained virtually constant.

The applicability of enthalpograms to the determination of heats of reaction is also inherent in Equation (11). If a known amount of titrant ($=x$) is used, ΔH can be readily computed from the measured ΔT value. For this purpose it is convenient to calibrate the ordinate charts of enthalpograms directly in calorie units, since:

$$k \approx \text{const}; \quad \Delta T \; prop \; Q. \tag{12}$$

This particular procedure has unique advantages as compared to conventional reaction calorimetry, viz.:

(a) Heat outputs as small as 2 to 5 calories can be measured within $\pm 1\%$ in volumes of solution of 100 ml.

(b) ΔH values can be determined in solutions in the millimolar and centimolar concentration range, where

$$\Delta H \approx \Delta H^0, \tag{13}$$

heats of dilution being negligible. Thus ideal thermochemical parameters are obtained, corresponding to virtually infinite dilution.

(c) The changes in temperature during a titration are of the order of 0.05 °C which is negligible relative to the temperature variability of thermodynamic parameters. Consequently, although enthalpography is an adiabatic method, it is capable of yielding data corresponding to virtually isothermal conditions.

When the titration reaction is appreciably incomplete in the vicinity of the equivalence point, "normal enthalpograms" exhibit curvatures from which equilibrium constants (and corresponding free energies) can be calculated. Such an enthalpogram is shown in Figure 3,

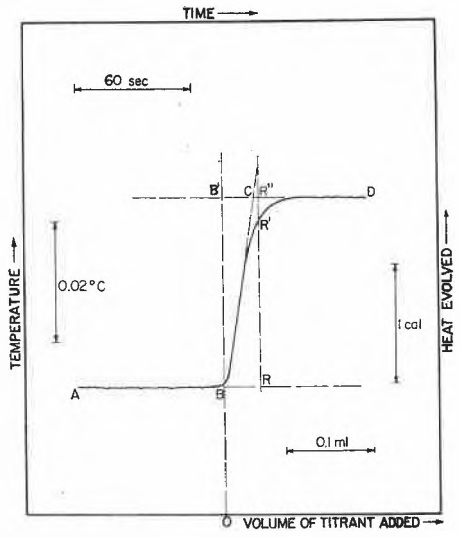

Figure 3. Thermometric Titration Curve of 8.6×10^{-4} molal potassium chloride with 1.4 molal silver nitrate in a molten $LiNO_3-KNO_3$ eutectic solvent at 158 °C. *B* Start of Titration, *C* Equivalence Point

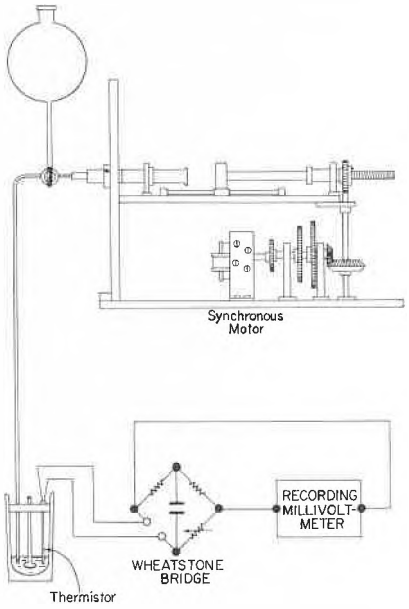

Figure 4. Sketch of an Automatic Thermometric Titrator, assembled at The Pennsylvania State University

which was obtained by titrating, at 158 °C, potassium chloride with silver nitrate, both being dissolved in a molten nitrate solvent. The titration reaction is the precipitation process:

$$Ag^+ + Cl^- \rightleftharpoons AgCl\,(s) \tag{14}$$

The curvature in the enthalpogram in the vicinity of R' is due to the fact that at the equivalence point silver chloride was soluble to the extent of approximately 20 % under the prevailing experimental conditions. Comparison of the "ordinate projections" $\overline{RR''}$ and $\overline{RR'}$ permits calculation of the solubility product, $K_{sp} = 3 \times 10^{-8}$ (moles/1000 g solvent)^2, and of the corresponding free energy and entropy of solution [via equations (2) and (3)]. In this manner all three thermodynamic functions ΔH, ΔF and ΔS have been determined from one single enthalpogram.

Instrumentation. The temperature detector used in all modern automatic thermochemical titration instruments is a solid state device known in the U.S.A. as a thermistor and in Western Europe as an NTC (*N*egative *T*emperature Coefficient). It has been developed for electronic applications in the communication industry. In thermometric titrators, thermistors (which are made of sintered metallic oxides) are used in the shape of small beads (1 mm in diameter) covered by a thin glass envelope. They are wired as one arm of a DC Wheatstone bridge. A sketch of a thermistor-titrator, which can be readily assembled from components available in any normal analytical laboratory, is shown in Figure 4. Thermistors function as sensitive resistance thermometers. Their large and negative temperature coefficient of resistance, is at variance with the small and positive coefficient which is typical of metallic conductors, as shown in

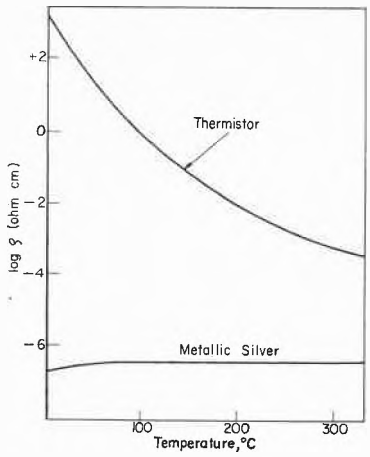

Figure 5. Variation of Resistance with Temperature

Figure 5. In metals, the number of electrons available for conduction is the same irrespective of temperature, but their mobility is decreased by enhanced thermal fluctuations of the atomic nuclei. In contradistinction, the resistance of thermistors decreases rapidly with increasing temperature, because they possess a conduction band, separated from the valence band by an energy gap of the order of $\varkappa T$: As the temperature increases electrons are transferred to the conduction band and resistance decreases.

Within small temperature intervals the unbalance potential of a thermistor bridge varies linearly with temperature. Performance characteristics of thermistors include: Negligible heat capacity, power dissipation and response lag; temperature coefficient −0.04 ohm/ohm/degree. A thermistor of 2000 ohm at 25 °C wired as illustrated in Figure 4, produces an unbalance potential on the order of 40 millivolt per degree C, which is equivalent to the response of a two-thousand junction thermocouple.

Most thermometric titrators record automatically normal enthalpograms. As an example, the operation of the Titra-Thermo-Mat is described below. A photograph of this instrument is shown in Figure 6. It consists essentially of:

1. a constant speed motor driven buret,
2. an "adiabatic titration tower,"
3. a thermistor bridge,
4. a recording potentiometer.

Components 1 to 3 are arranged in one vertical unit. The recorder (4) shown in the figure displays two titration curves of hydrochloric acid with standard sodium hydroxide.

The buret is equipped with a precision machined glass plunger which is driven by a synchronous motor. The plunger displaces a volume of titrant at a constant rate of 600 microliters/min. Embedded in the titrant reservoir is a thermistor which can be connected to the Wheatstone bridge for measuring the temperature of the titrant. A digital counter provides direct readout of the volume of titrant dispensed.

The "adiabatic titration tower" is shown in a loading position in Figure 6, and in its "titration position" in the cross-sectional drawing in Figure 7. The tower is made of styrofoam plastic which is a thermal insulator. It contains a beaker into which the titrate solution is placed. In the "titration position" the beaker is raised to immerse into it the buret tip, a small heater, a stirrer

Figure 6. The First Commercial Automatic Thermometric Titrator: The Titra-Thermo-Mat (Courtesy of American Instrument Co.)

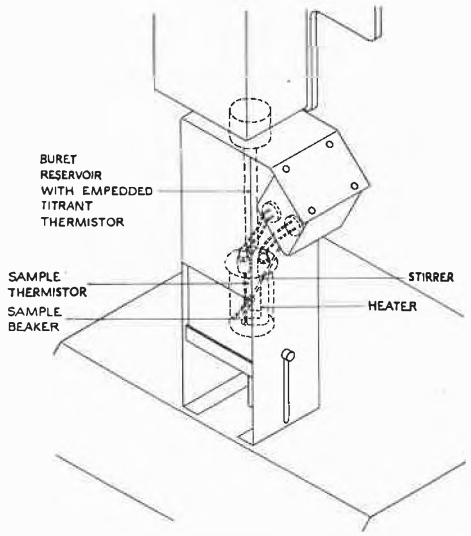

Figure 7. Adiabatic Tower of Titra-Thermo-Mat (Courtesy of American Instrument Co.)

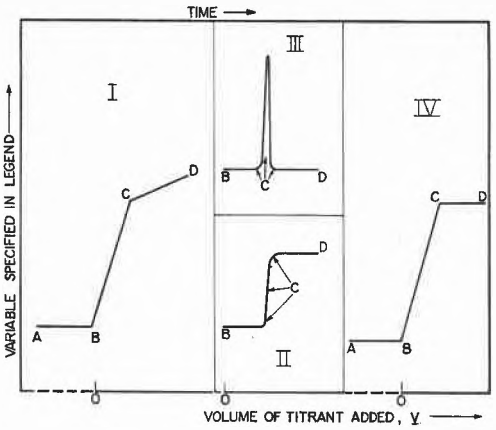

Figure 8. Comparison of Various Types of Enthalpograms: I. "Normal": Plot of T *versus* v. II. "First Derivative": Plot of $\frac{dT}{dv}$ *versus* v. III. "Second Derivative": Plot $\frac{d^2T}{dv^2}$ *versus* v. IV. "Differential": Plot of $(T - T_{blank})$ *versus* v. AB Temperature-time "base line"; B Start of Titration; C Equivalence Point Region; $\overline{CD}$ Excess Reagent Line

and a "sample" thermistor. The heater serves two purposes: It can be used as a calibrating device for determining heats of reaction; and if the sample solution is colder than the titrant, it may be warmed up with the aid of the heater. When performing a titration, a "base line" is first obtained on the recorder chart. Subsequently, the titration proper is carried out with the sample thermistor connected to the Wheatstone bridge. On the recorder chart, the ordinate deflection is proportional to change in temperature. The abscissa is proportional to volume of titrant, because the chart is driven by a synchronous motor at a constant rate, as is the buret.

Special techniques. In addition to normal enthalpograms, various derivative, differential and "genuinely isothermal" thermometric titration curves have been obtained by various authors.[13] "Differential enthalpograms" are obtained with the aid of a twin-thermistor bridge which records the temperature difference between an actual titration (titrate solution plus titrant) and a blank titration (pure solvent plus titrant): This corrects automatically for extraneous effects (as exhibited by the slope of the excess reagent line of the normal enthalpogram in Figure 8, Curve I), yielding the ideally shaped titration curves illustrated in Figure 8, Curve IV. Derivative enthalpograms can be recorded with the aid of electronic differentiation, yielding plots of $\frac{dT}{dv}$ *versus* v (first derivative), or of $\frac{d^2T}{dv^2}$ (second derivative), as illustrated in Figure 8, Curves II and III. Isothermal enthalpograms involve a laborious point by point recording of thermometric titration curves, the "titrate system" being reequilibrated to its initial temperature after every addition of titrant.

[13] S.T. Zencheisky and P.R. Segatto, *Anal. Chem. 29* (1957) 1856; B.C. Tyson jr., W.M. McCurdy jr. and C.E. Bricker, *ibid. 33* (1961) 1640; K. Schlyter, *l. c.*, reference 11.

Each of these special methods has advantages and limitations. However, the bulk of thermotitrimetric research and analysis has relied on the use of normal enthalpograms.

Scope and Significance of Thermochemical Titrations

A summary of the types of information obtainable from enthalpograms is presented in Table 3.

Table 3: Applications of Thermochemical Titration Curves

Application	Procedure for obtaining data
Quantitative Analysis	Enthalpimetric [Eq. (11)] End-point determinative
Determination of Reaction Stoichiometry	From Δv corresponding to end-point
Determination of ΔH	From ΔT
Determination of ΔF	From curvature of enthalpogram
Determination of ΔS	From Equation (3)

Regarding applications of enthalpography to quantitative analysis in 0.01 M solutions, the end-point determinative procedure is generally more precise and accurate than the enthalpimetric approach. However, in very dilute solutions (< 0.001 M) the latter method may be preferable, particularly when the heat of the "titration process" is large: For instance, divalent iron can be determined enthalpimetrically with an accuracy of 2 % at concentrations as low as 4×10^{-4} M, by oxidimetric titration with standard sulfatocerate (IV) solution, the heat of the reaction

$$Fe(II) + Ce(IV) \rightleftharpoons Fe(III) + Ce(III) \qquad (14)$$

being (-24.2 ± 0.5) kcal/mole. In Table 4 are summarized selected instances of volumetric determinations for which the use of thermochemical titrimetry in aqueous solutions appears to be particularly well suited.

Table 4: Volumetric Analysis by Thermochemical Titrations in Aqueous Solution (Concentration range: 0.0001 to 0.01 Molar)

Type of Process	Specific Examples	Range ΔH^0 kcal/mole	Precision and Accuracy %
Proton Transfer (Acid—base)	Alkalimetric determination of acids with $K_a \geqslant 10^{-10}$. Acidimetric determination of bases including pyridine, carbonate ion and ammonia	— 10 to — 14	0.2 to 1
Electron Transfer (Redox)	Fe(II) with Ce(IV), Dichromate and Permanganate; Ti(III) with Ce(IV)	— 9 to — 28	0.5 to 2
Complexation	Ca, Cd, Co, Cu, Mg, Ni, Pb, and Zn with Ethylenediaminetetraacetate	— 4 to — 13	0.1 to 1
Precipitation	Ag with HCl Ca with oxalate	— 6	0.3 to 1

Considerations affecting precision and accuracy include two interesting features.

1. For a given experimental set-up, it is possible to define an invariant "enthalpimetric sensitivity index," P_n (expressed in calories per liter) by the Equation:

$$P_n = C_n^{min}\, \Delta H \qquad (15)$$

where C_n^{min} denotes the minimum concentration (conveniently expressed in millimoles per liter) of any unknown which can be determined with a relative accuracy of n per cent. For the titrator used in the author's laboratories, $P_1 = 30$ cal/l: The minimum concentration of an unknown, which reacted with a heat of -10 kcal/mole and could be determined with an accuracy of 1%, was 3 millimolar; however, for titration reactions with $\Delta H = 5$ kcal/mole, a minimum concentration of 6 millimoles/l was needed, in order to attain the same accuracy.

2. ΔT in a given titration does not depend on sample size (because both Q and k in Equation [11] are proportional to sample volume), but only on the concentration of the unknown: Consequently, enthalpy titrations are ideally suited for micro-analysis.

Thermochemical titrations have also found widespread applications in non-aqueous solvents. For instance, Lewis bases such as dioxane, morpholine, pyridine and tetrahydrofuran have been titrated with the Lewis acid $SnCl_4$ in the solvents carbon tetrachloride, benzene and nitrobenzene.[14] Extensive applications of thermometric titrations have been reported in molten salts at elevated temperatures (up to 500 °C), including determination of halides, chromate, silver and cyanide.[15]

In the analysis of mixtures, thermochemical titrations may have unique advantages. For instance, calcium in limestone can be determined by a precipitation titration with oxalate without separating magnesium: Calcium yields an instantaneous exothermic titration curve, with a well defined end-point, corresponding to the process

$$Ca^{++}(aq.) + C_2O_4^{--}(aq.) \rightleftharpoons CaC_2O_4 \cdot H_2O\,(s);\quad \Delta H^0 = -6.1 \text{ kcal/mole:} \qquad (16)$$

Magnesium does not interfere, due to a "kinetic masking" effect: The reaction

$$Mg^{++}(aq.) + C_2O_4^{--}(aq.) \rightleftharpoons MgC_2O_4 \cdot 2H_2O\,(s) \qquad (17)$$

is so slow that the precipitation of calcium can be completed while magnesium still yields an isothermal line.[16] Using a complexometric titration with standard ethylenediaminetetraacetate (EDTA), calcium and magnesium can be determined simultaneously, because one reacts exothermically and the other endothermically, yielding the interesting enthalpogram plotted in Figure 9. This figure also illustrates the potentialities for fundamental research inherent in thermochemical titrations. The titration curve shown has resolved unambiguously and definitively the controversy whether the chelation of magnesium with EDTA was an exothermic process (as inferred erroneously from the Van t' Hoff Isochore applied to experimental values of the stability constant at several temperatures), or an endothermic reaction (as correctly concluded from classical calorimetry).[17]

Significant contributions to important theoretical studies have resulted from thermochemical titrations, by making accessible a wealth of hitherto unknown entropy data. Thus, it was found that the entropies of ionization of substituted halo-acetic acids in aqueous solution exhibited the remarkable trends shown in Table 5.

Table 5: Entropies of Ionization (ΔS_a, expressed in cal/mole-degree) of Haloacetic Acids[18] (Aqueous solutions at 25 °C)

No. of Halogen Substituents	Fluoroacetic Acids	Chloroacetic Acids	Bromoacetic Acids	Difference
0		−22		7
1	−15	−18	−15	7
2	− 6	− 6	− 8	6
3	− 1	+ 2	− 2	

The fact that ΔS_a in the halo-acetic acid series is quasi-quantized in steps of 6 to 7 cal/mole-degree (which is equal to the molar entropy of freezing of water) is accounted for by differences in solvation as exemplified in Equations (18) to (21).

$$CH_3{-}COOH \cdot \overbrace{w H_2O}^{3H_2O} + 4H_2O \rightleftharpoons CH_3{-}COO^-(w+3)\,H_2O + H_3O^+; \qquad (18)$$

$$CH_2Br{-}COOH \cdot \overbrace{x H_2O}^{2H_2O} + 3H_2O \rightleftharpoons CH_2Br{-}COO^-(x+2)\,H_2O + H_3O^+; \qquad (19)$$

$$CHBr_2{-}COOH \cdot \overbrace{y H_2O}^{1H_2O} + 2H_2O \rightleftharpoons CHBr_2{-}COO^-(y+1)\,H_2O + H_3O^+; \qquad (20)$$

$$CBr_3{-}COOH \cdot \overbrace{z H_2O}^{0H_2O} + H_2O \rightleftharpoons CBr_3{-}COO^- \cdot z H_2O + H_3O^+. \qquad (21)$$

It appears that the water of hydration is quasi-frozen around the solvated species, yielding an entropy effect similar to the analogous genuine freezing process.

In molten nitrates, an extensive study revealed the remarkable fact that the precipitation of silver chromate was anomalously anentropic ($\Delta S = 0$) at 160 °C, but became normally exentropic at higher temperatures.

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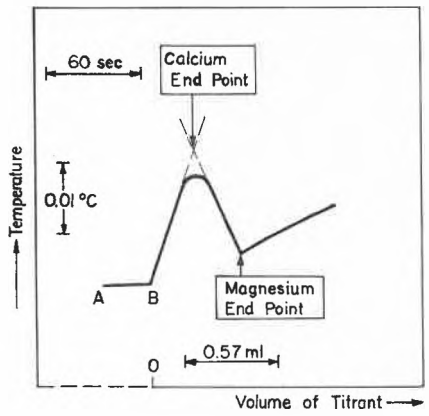

Figure 9. Enthalpogram obtained by titrating mixture of Calcium and Magnesium with Ethylenediaminetetraacetate in Aqueous Solution at 25 °C

This is accounted for by the prevalence of the associative equilibrium

$$(CrO_4^{--})_x = x \cdot CrO_4^{--} \qquad (22)$$

involving a "polychromate" species. Similar evidence has indicated the existence of the "ionic polymers"

$$\underset{\text{Polysulfate}}{(SO_4^{--})_x} \quad \text{and} \quad \underset{\text{Polycyanide}}{(CN^-)_x}$$

in molten salts. Quite generally, thermochemical titrations appear to be ideally suited for the study of "entropy compounds" of this type.

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