The History and Development of Thermometric Titrimetry

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Introduction

Heat or enthalpy is a thermodynamic, and often easily measured, characteristic of all chemical reactions and has been used for many years for the estimation of such things as bond strengths, equilibrium constants and Born-Haber calculations. Only recently has significant advance been made in the precise measurement of minute temperature differences occurring in small volumes of solution, thus allowing for the measurement of enthalpies of reaction using micro-quantities of chemicals. This development was vitally important for the field of thermometric titrimetry because, almost immediately after the introduction of the thermistor as the temperature-sensing element, further new technology was developed and available to the scientific market, for example the transistor, which accelerated the evolution of the area to the precise, versatile and sophisticated field that it is today.

Initial Stages

A little less than a century ago, in 1886, C. B. Howard presented a paper before a meeting of the Finsbury Technical College Chemical Society in London concerning a simple method for the quality control of certain industrial chemicals, for example acetic anhydride. Unfortunately, apart from one reference to this (17), the society and its records seem to have been lost to posterity, although a number of attempts have been made to locate them. However, it is reasonable to assume that the apparatus used consisted of a thermometer and a Dewar flask. The method itself was likely to have been more akin to direct injection enthalpimetry (DIE) in its application *ie*: a known volume of acetic anhydride being placed into a Dewar flask and having a metered volume of water injected into it. If the temperature rise was over a certain predetermined value, the industrial product was considered to be of appropriate quality. It appears that the method was little used.

Twenty-five years later in 1909 an American, Henry Howard, published the results of his work on fuming sulfuric acid (13). He used the method for rapid assaying of industrial fuming sulfuric acid and had a somewhat more quantitative approach than did C. B. Howard. He used concentrated sulfuric acid as the reagent and made a few measurements of enthalpy of dilution which could, at best, be regarded as crude. Generally speaking, the method could still not be referred to as a genuine titration.

November of 1912 brought the submission of a paper to the Journal of the American Chemical Society (2), and it is regarded as the classic one on the topic. It was by James Bell and Charles Cowell and described what they referred to as 'the temperature method' for preparing neutral solutions of ammonium citrate. In this case a Dewar flask and buret were used, the former incorporated a mechanical stirrer, and the temperature differences after each addition of titrant were measured using a Beckmann thermometer. Quite clearly, with the publication of this paper, the method of thermometric titrimetry was born.

Instrumental Developments

a. *Vessel Design*

Various vessels have been used in which to conduct this type of analysis; for

example, Dewar flasks (3), metal cans (6), custom design flasks (12), and expanded polystyrene cups (8). In most cases, depending on how precise the determination is to be and whether or not the data are to be used thermodynamically, the vessel is surrounded by a thermostatted water jacket in order to decrease heat flow from the vessel. This heat flow has been eliminated in other ways, largely by careful design of the vessel (5). The solution of Christensen et al. was a specially designed and constructed thin-walled Dewar vessel, of perhaps 100 ml. capacity, which had a sconce machined from Teflon to eliminate further heat loss.

b. *Reagent Delivery Systems*

A number of devices have been used to deliver reagent into an analyte solution. Initially, a simple buret was used for the stepwise addition of reagent (7). This has been one of the preferred methods for many years, particularly for titrations on a fairly large scale; however, other methods have been used. For example, a simple pipet which was used for non-continuous delivery of titrant (10). This device, although simple to use, had the disadvantage of severely limiting the total volume of titrant deliverable, and so other more flexible devices had to be developed.

Ideally, continuous addition of titrant to analyte is the technique to consider and although Schlyter (19) partially solved this problem, there were inherent difficulties, again with reagent volumes. More sophisticated devices were constructed, in particular, ones in which the titrant could be kept at the same initial temperature as the sample solution (9). A far simpler arrangement using a syringe and a synchronous motor was devised by Linde et al. (15), and this allowed for simple temperature matching between titrant and analyte, rapid change of titrant and rapid filling of the titrant syringe. For most purposes, however, a slow delivery motor syringe is to be preferred (11, 14).

c. *Temperature Monitoring Systems*

Naturally enough, the first device for monitoring solution temperature was the mercury-in-glass thermometer (3, 17), but this was quickly exchanged for one of greater precision, the Beckmann thermometer (2). The latter, although capable of giving quite reproducible data, proved to be cumbersome and slow to use thus marking the way for a more sensitive device. The problem was solved, apparently fortuitously, by Linde, Rogers and Hume (15) when they became the first people to use an electronic temperature measuring device, the thermistor (4). Prior to this a number of other resistance devices had been used these being largely thermocouples and thermopiles (16). These devices had somewhat of a disadvantage in that they were slightly slow in response, and also their response was quite small. Most commonly thermistors are used in modern apparatus, having the advantages that they are very rapid in response and several orders of magnitude more sensitive than thermopiles (4).

d. *Recording and Measuring Systems*

Initially, the record of a thermometric titration was merely the transfer of a thermometer reading to a piece of graph paper (2, 7), but a number of quite ingenious devices have been used since then. For example, in 1941, Muller (16) replaced the Beckmann thermometer with a multijunction thermopile and used a differential thermoelectric experimental arrangement. The output, in this case, was on a mirror galvanometer, although a later modification was a recording millivoltmeter.

When Linde, Rogers and Hume introduced the termistor as a measuring device (15) they also incorporated a suitable measuring and recording circuit: this was the Wheatstone bridge. This apparatus is to be found in most modern equipment, and is the central component for many resistance-measuring devices. It may be powered

by both alternating and direct current sources but the latter is usually the case, and has a recording millivoltmeter attachment to measure the extent of bridge imbalance. For particularly small temperature changes, perhaps less than 0.001 °C, an amplifier may be inserted between the bridge and the recorder, provided that appropriate electronic filtering devices are used.

In some of the modern systems a deal of flexibility is made available by introducing a computer in place of the chart recorder (14). This has the advantage that it may be programmed to process the experimental information as it becomes available, so that the final hard-copy output has had all the necessary corrections applied to it and any detailed calculations performed for the determination of enthalpy, Gibbs free energy, entropy and so on.

e. *Commercial Apparatus*

Several pieces of apparatus are currently available but the first instrument marketed commercially was the "Titra-Thermo-Mat" (1) by the American Instrument Company. This device incorporated most of the modifications mentioned in previous sections: the titration vessel was a beaker embedded in styrofoam; the sensor was a thermistor with the associated Wheatstone bridge circuitry; recording was accomplished with a strip chart recorder. Also provision was made for stirring and variable volume titrant delivery. Many of these instruments were in use at universities and in industry, but there appears to be a dearth of accurate information as to precisely how many had been sold or were in use just before the apparatus was discontinued.

A more recent development, although designed for the specific task of determining silica, is the SILICOTHERM, appropriately named. It is an up-to-date modification of its predecessor the DIRECTHERMOM-"D" and contains a plastic reaction vessel fitted with a magnetic stirrer; otherwise the apparatus follows the design features of similar instruments with regard to titrant delivery, temperature sensing and recording. This device is manufactured in Hungary by Hungarian Scientific Instruments (20).

One final example of a commercial device is the Thermo-Titrator manufactured by Sanda Inc. of Philadelphia. This apparatus represents a slight departure from conventional apparatus in that it incorporates circuitry to provide a first derivative of the normal thermometric curve (18). The device is able to record conventional curves, "instant cut-off" curves and derivative curves with ease. The example shown in the paper quoted is the titration of phosphoric acid where all three protons are titrated.

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