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THERMOMETRIC TITRIMETRY - A SUITABLE WAY INTO THERMOCHEMISTRY

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ABSTRACT

A simple apparatus is described for the thermometric determination of the endpoint of reactions with analytical interest. Examples are the redox reaction Fe^{2+}/MnO_4^-, the neutralisation of H_3PO_4 and the determination of K^+, NH_4^+ (Rb^+,Cs^+) with $B\emptyset_4^-$ with an accuracy of about 2%.

INTRODUCTION

Many chemical processes are not only accompanied by a change of color or other visible phenomena but rather by a change of energy. Unfortunately only large changes in energy are directly detected by the chemists fingers (forinstance the heat of dilution of sulfuric acid with water) and therefore enthalpy changes are not commonly used as methods to determine the endpoint of an analytical process or the grade of a reagent. Although there are a lot of commercial instruments in the field of calorimetry we decided to build a simple and not too expensive apparatus for use in the beginners analytical courses at universities as well as in schools.

Theory

Unfortunately the amount of heat evolved or adsorbed within a reaction cannot be measured directely with any kind of an "energy-meter" but only the effect is measurable. If you look at a reaction

$$A + B \xrightarrow{\Delta H} AB$$

you have two ways to use the heat of reaction for analytical applications.

1) The two Substances A and B are mixed in one step and the measured temperature difference ΔT, multiplied with the

heat canacity of the whole system, gives us the molarity n.

$$-n \cdot \Delta H = \Delta T \cdot C_p$$

The analytical method employing this relation (where the molar heat of reaction must be known) is called enthalpimetric titrimetry.

2) In usual titrimetry the molarity of an unknown substance is determined white the ammount and the concentration of the reagent are known. Sometimes it is difficult to find a suitable method for the endpoint determination but the heat of reaction may be used to determine the endpoint of many kinds of reactions. Unfortunately in this technique the heat capacity of the system is changing during the experiment and therefore ΔH cannot be determined very easily; the method is called thermometric titrimetry.

To get curves as shown in fig 4 it is necessary to have a quick response of the temperature measuring system, a constant flow of the relative by concentrated reagent (to avoid large changes in heat capacity), good insolation, short reaction periodes and a quick and reproucibly working stirring system.

APPARATUS

The temperature measuring element is a thermistor (1o KΩ, 25°C, time constant o,2 sec, dissipation constant o,8 mW $^{o}C^{-1}$ from Siemens) in a constant voltage driven Wheatstone bridge. For small temperature changes the output of the bridge, which is recorded with a strip chart recorder, is proportional the temperature difference ΔT.

Fig 1 shows a simple home made system for the continuous reagent supply which is driven by a "grill motor". This system is usable for schools, the error is not bigger than 5%. In our experiments we used a n electronically controlled piston burette, which was build in our laboratories from a hand driven "Dosimat" from Metrohm". Good hose pumps are suitable too, but rather expensive and one must make sure, that they work pulse free.

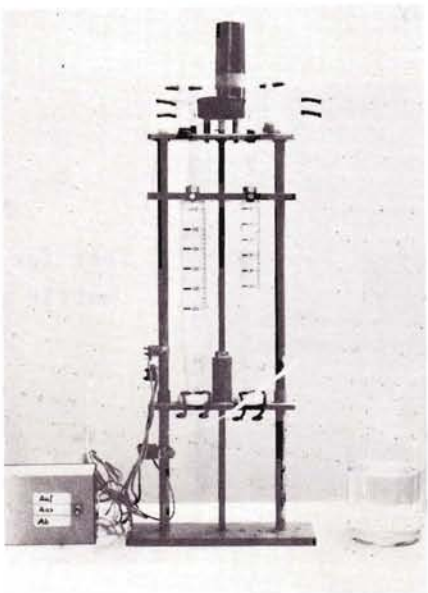

fig 1
piston burette

Careful design of the reaction vessel is very important. We use thin walled test tubes (Ø 3cm) with a magnetic stirrer in a foam isolated box as shown in fig 2

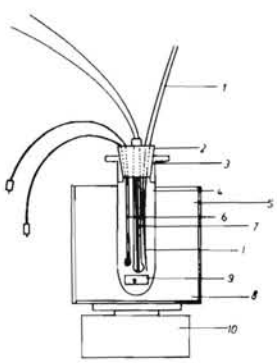

fig 2
Reaction vessel

1 PE capillary for the reagent
2 cork stopper
3 PE stopper
4 test tube
5 box
6 thermistor
7 conductivity elektrodes
8 foam isolation
9 spin ball
1o magnetic stirrer

Fig 3 shows the whole assembly.

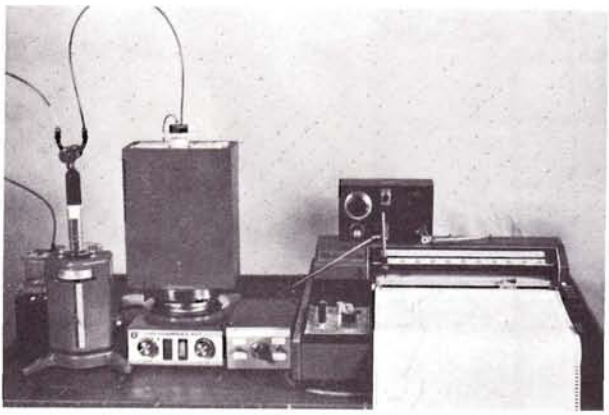

fig 3

set for thermo-metric titration

EXAMPLES

A variety of reactions have been studied by other authors[1] and ourselves[2]. We show here only three different types of reaction.

1) Redox titration of Fe^{2+}/MnO_4^-.
   We used 15 ml o,oo5 m Fe^{2+} and added 1,5 ml o,o2 m MnO_4^- within a time of ca 2o sec (fig 4)
2) Neutralisation of H_3PO_4 with NaOH.
   We used 15 ml o,o52 m H_3PO_4 and added 2,35 ml 1 m NaOH within a time of ca 45 sec. Fig 5 shows the result, the dotted line shows the change of conductivity which was simultaneously measured with the electrodes 7.
   This example shows that the change of conductivity, which is often used as endpoint determination for neutralisation reactions yields the first and second step only.
3) Determination of K^+ and NH_4^+ simultaneously.
   By adding $B\emptyset_4^-$ to a solution of K^+ and NH_4^+ both ions form unsoluable precipitations (pH =6).
   With formaldehyde which forms Hexamethylentetramin with the NH_3 in alkaline solution.

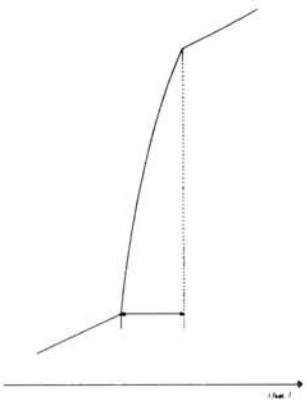

fig 4

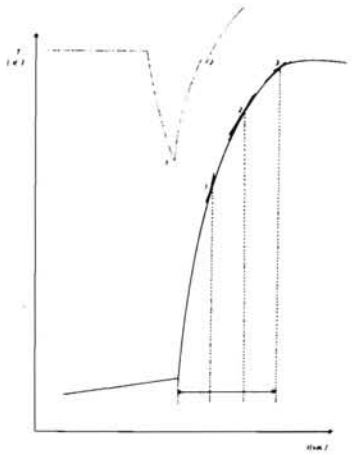

fig 5

We used 15 ml o,o1 to o,1 m (K^++NH_4^+) and titrated with o,1 m $B\emptyset_4^-$. In the second run only K^+ is determined, an exess of formaldehyd is used. This method is of great use in a quick determination of K^+ and NH_4^+ especially in fertilizers. An accuracy of about 2% can be reached[3].

These few examples may demonstrate how thermometric titrimetry can be used in analytic chemistry. Very good results are obtained by using solvents and reagents with low heat capacity.

Enthalpimetric titrimetry can be used not only for analytical purpose, but also for a quick determination of ΔH by using a submerged burette with a known ammount of reagent and an excess of solution in the reaction vessel. The result is a jump of temperature. For simple calibration the stored energy of a capacitor should be used which generates a known amount of heat in a little heating element within the vessel leading to a second temperature jump. In this way to exotherm heats can be directy compared. Without used of knowing amy cali-

bration of the temperature measuring unit and the heat capacity of the whole system the unkown heat is measurable.

LITERATURE REFERENCE

(1) G.A. Vaughan, Thermometric and Enthalpimetric Titrimetry, Van Nostrand Reinhold Company, London 1973

(2) H.J. Morgret, G. Thiel u. H. Wöhrmann, Thermometrische Titrationen, MNU 32 (1979), S. 478

(3) L. Stäudel, A. Stille u. H. Wöhrmann, Thermometrische Titrationen von Alkalimetall- und Ammoniumionen mit Natriumtetraphenylborat, GIT Fachz.Lab., 23 (1979), S.291