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A COMBINED TITRATION CALORIMETER AND FIXED WAVELENGTH COLORIMETER

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ABSTRACT

A combined titration calorimeter and fixed wavelength LED colorimeter is described. The apparatus consists of a conventional thermistor–Dewar calorimeter and includes a LED light source—light pipe-phototransistor colorimeter. Not only can the temperature change of the reacting system be recorded but the color change of the solution as well. The use of the apparatus is illustrated with the acid–base (indicator) reaction, iodine and formaldehyde clock reactions, and an oscillating iodine clock reaction.

INTRODUCTION

There have been numerous titration calorimeters described in the literature since the use of a thermistor temperature detector was advocated by Linde et al.[1] in 1953. Most of these instruments consist of a Dewar or other insulated container, a thermistor detector, a Wheatstone bridge and recording system, and a constant delivery buret[2]. The applications of these calorimeters to the study of various chemical systems has been well documented[3] and includes not only classical acid–base reactions of all types, but precipitation, complexation, redox, enzyme, and many other types of reactions.

There are some chemical systems in which it would be desirable to be able to detect the color changes of the reactants or products as the titration reactions progesses. The simple apparatus described here is capable of detecting the color change of the reaction solution as well as providing calorimetric data. Application of this apparatus is illustrated by an acid–base reaction with indicator, several "clock" reactions, and an "oscillating" chemical reaction.

EXPERIMENTAL PART

Apparatus

The combined calorimeter–colorimeter apparatus is illustrated in Fig. 1.

The apparatus consiste of a conventional Dewar Type thermistor temperature de-

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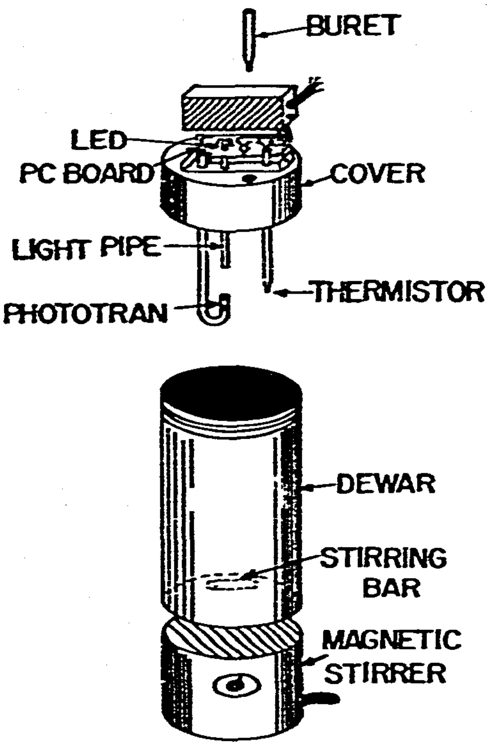

Fig. 1. Calorimeter–colorimeter apparatus.

tection titration calorimeter containing a LED-light pipe-phototransistor colorimeter. The Dewar is an insulated PVC plastic container, 8.0 cm in diameter by 14.0 cm in height. All electrical connections to the Dewar are made on a small printed circuit board, 2.5 × 5.0 cm, attached to the cover. A green-colored LED (light emitting diode) is soldered to the PC board and is positioned directly above a quartz light pipe. Other color LED's could be used such as red, yellow or orange, with the choice depending upon the color of the solutions to be investigated. Unfortunately, a potentially very useful blue colored LED is not presently commercially available. The transmitted light from the LED is detected by a phototransistor, which is enclosed in a sealed U-shaped glass tube. Normally, the light path through the solution is 10 mm but this distance can be varied by adjustment of the light pipe and U-tube positions. The voltage output from the phototransistor is amplified by a one-transistor amplifier (also on the PC board)[4] and is recorded on one channel of a two-pen strip-chart recorder, full scale response of which is 0–100% transmission.

The thermistor temperature detector and Wheatstone bridge circuit are conventional; the thermistor has a nominal room temperature resistance of about 2.5 kΩ. Voltage unbalance of the bridge is recorded on the second channel of the recorder. full scale response of which is either 0.1 or 1.0°C. Stirring of the solution is effected by means of a Teflon-covered stirring bar and magnetic stirrer. Titrant is added to the apparatus by means of a Sargent constant delivery buret which has a delivery rate of 2.50 ml min^{-1}.

Titration procedures

Acid-base. Five ml of 0.1 N NaOH were diluted to a total volume of 50 ml, several drops of an indicator were added, and titrated with 0.1 N HCl.

Clock reactions. Two clock reactions were investigated: an IO_3^-–SO_3^{2-} system[5] and a HCHO–SO_3^{2-} system[6]. The IO_3^-–SO_3^{2-} (iodine clock) system consisted of two solutions: (A) 1.26 g of Na_2SO_3 and 5 g starch in 1 l of solution with sufficient H_2SO_4 to make solution 0.04M; and (B) 0.02M KIO_3. To initiate the reaction, 20 ml of (B) were added to a mixture of 30 ml of (A) in 150 ml of water. The HCHO–SO_3^{2-} (formaldehyde clock) system consisted of three solutions[1,2]: (A) 0.354 g of Na_2SO_3 in 1 l of H_2O; (B) 1.47 g $Na_2S_2O_5$ in 1 l of H_2O; and (C) 10.7 ml of 37% formaldehyde in 1 l of H_2O. The reaction was initiated by addition 50 ml of (C) to a mixture of 50 ml of (A) and 50 ml of (B) plus 100 ml H_2O to which 10 drops of a phenolphthalein indicator was added.

Oscillating iodine clock. The reaction proposed by Briggs and Rauscher[7] was used to demonstrate this type of system. It consisted of three solutions: (A) 0.067 M KIO_3 in 0.053 M $HClO_4$; (B) 1.2M H_2O_2; and (C) 0.050 M malonic acid, 0.0067 M $MnSO_4$, and 0.01% starch. The reaction mixture contained 80 ml of each of the above solutions.

RESULTS AND DISCUSSION

Typical acid-base titration curves are illustrated in Fig. 2. Curves B and C show the changes of temperature of the solutions while curves A and D indicate the

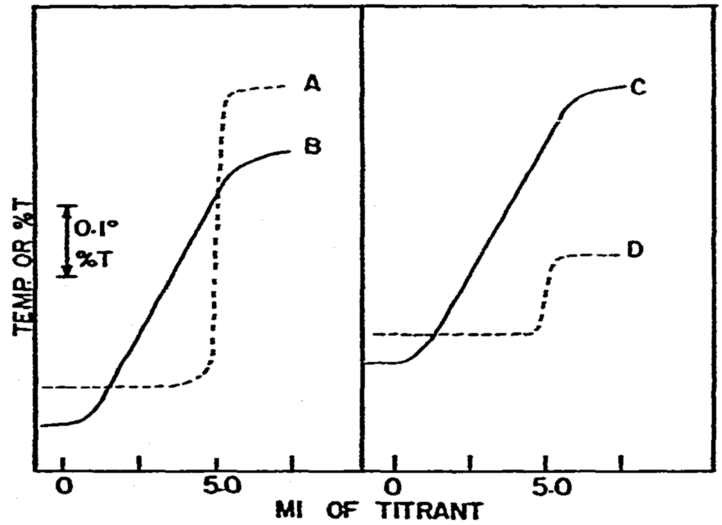

Fig. 2. Typical acid-base titration curves. Curves B and C are for temperature while curves A and D indicate the color changes of the solutions.

relative changes in light transmittance due to the color change of the two indicators employed, phenolphthalein (curve A) and bromocresol green (curve D). Both of the latter curves clearly indicate the regions of the titration where color changes occur.

The well-known IO_3^-–SO_3^{2-} clock reaction is illustrated in Fig. 3. When all of the components of this system are mixed together, the resulting solution is colorless. After a specific time interval, depending upon the relative concentration of IO_3^-, SO_3^{2-} and temperature, the solution becomes a deep blue color due to the starch–iodine complex. The curves given here show the temperature and the light transmission changes at a temperature of 21.6°C. After mixing the solution, the temperature decreased due perhaps to a dilution effect, and then increased as a result of the exothermicity of the reaction. At a time interval of 0.75 min, the color of the solution changed from colorless to a deep blue color. This reaction time could be changed by altering the relative amounts of the KIO_3 and Na_2SO_3 solutions.

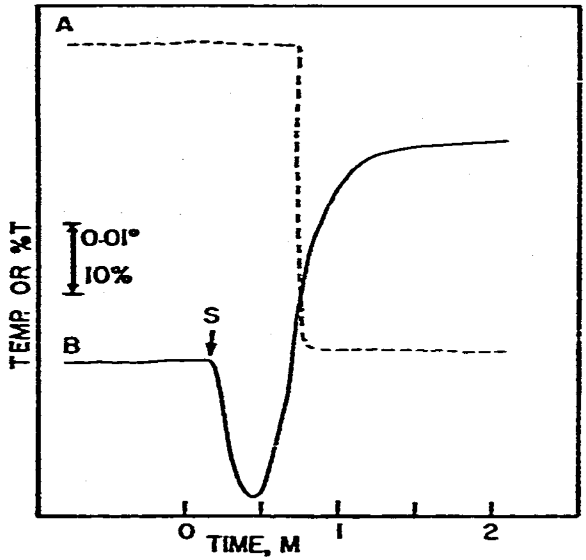

Fig. 3. The IO_3^-–SO_3^{2-} clock reaction. Curve A, % *T* curve; curve B, temperature curve. Point S indicates where the timing interval began.

The other clock reaction investigated is that containing formaldehyde, Na_2SO_3, and $K_2S_2O_5$, as shown in Fig. 4. This rather interesting reaction has a color change of from colorless to red, the latter being due to the color of phenolphthalein in basic solution. The reaction is thought to consist of the following steps[6]:

$$HCHO + HSO_4^- \rightarrow CH_2OHSO_3^- \quad (1)$$

$$H_2O + HCHO + SO_3^{2-} \rightarrow CH_2OHSO_3^- + OH^- \quad (2)$$

$$OH^- + HSO_3^- \rightarrow SO_3^{2-} + H_2O \quad (3)$$

Reactions (1) and (2) are fairly slow rate determining steps while (3) is practically instantaneous. As can be seen from the temperature curve, the reaction is exo-

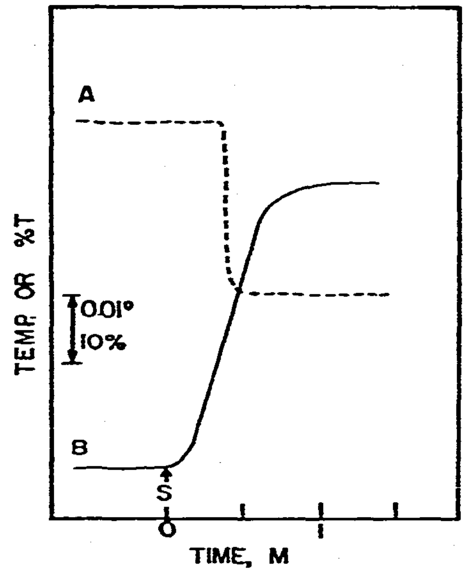

Fig. 4. Formaldehyde clock reaction. Curve A, % *T* curve; curve B, temperature curve. Point S indicates where timing interval began.

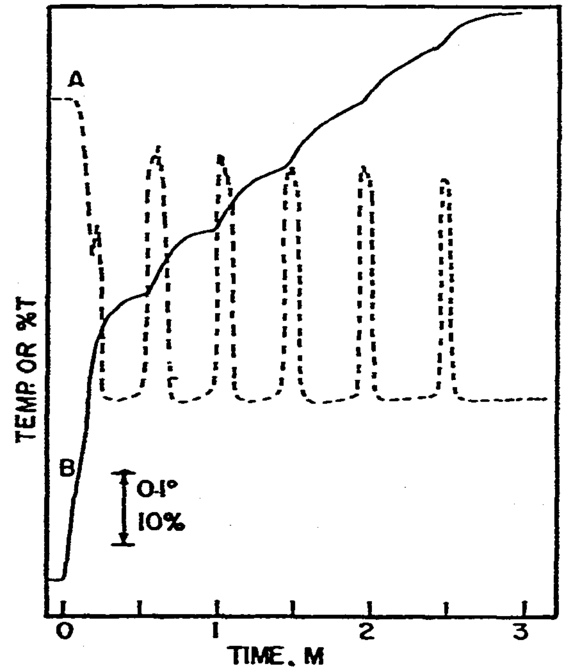

Fig. 5. Oscillating clock reaction. Curve A, % *T* curve; curve B, temperature curve.

thermic. Also, due to the color change, the % *T* decreases at the completion of the reaction.

Perhaps the most interesting reaction investigated here was the IO_3^-–malonic acid–H_2O_2 oscillating clock reaction, as shown in Fig. 5. This reaction, proposed by Briggs and Rauscher[7], resembles the iodide–H_2O_2 peroxide oscillating reaction of Bray[8] but it operates at room temperature with greater intensity. The former measured the iodide oscillations in the reaction by means of a silver–silver iodide electrode. Since little is known about oscillating reactions in general[9,10] no simple mechanism can be given for this reaction. If malonic acid is not present, manganese ion catalyses a rapid initial formation of iodine so the former is both an iodine consumer and iodide producer. Much the same type of behavior occurs with the bromate ion in the Belousov reaction[11].

The temperature curve indicates that the reaction is exothermic and that it occurs stepwise, with the periodicity of the steps increasing with time. Colorimetrically the initial solution is colorless but turns a deep blue (starch–iodine) color at periodic intervals, as shown in curve A. The periodicity frequency increases with time also.

The above examples indicate some of the uses of the combined calorimeter–colorimeter apparatus. There are no doubt many other reactions in which the apparatus may prove useful.

ACKNOWLEDGMENT

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