A THERMOMETRIC TITRATOR

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Abstract. — The construction of an inexpensive thermometric titrator is described whose linearity over a temperature range of 12° makes calibration easy.

The change in reaction temperature as a means of titrametric endpoint determination was first reported by Bell and Cowell in 1913. Further work on thermometric titrations followed using thermometers and ordinary burets (a review can be found in Linde, Rogers, and Hume, 1953). Because of thermometer response time lag, these titrations were long and tedious to perform making thermometric titrations unpopular. In 1953, a breakthrough occurred when Linde, Rogers, and Hume employed modern thermistor technology and continuous titrant addition to make thermometric titrations a fast, easy and now popular procedure. A unique and very useful feature is that the temperature change is not dependent upon free energy or equilibrium constants but on enthalpy (Jordan, 1958). For example, boric acid upon titration with sodium hydroxide gives as sharp a break at its equivalence point as hydrochloric acid.

In a thermistor bridge the thermistor is one arm of an equal-arm Wheatstone bridge with the unbalance voltage displayed on a recorder. Disadvantages of published thermistor bridges are nonlinearity over more than about 1°C and/or cost. A thermistor bridge based on a design by Averson (1967) is described here (see Figure 1) which is well suited for student use at a cost of less than $20 (since many of the components are on hand in

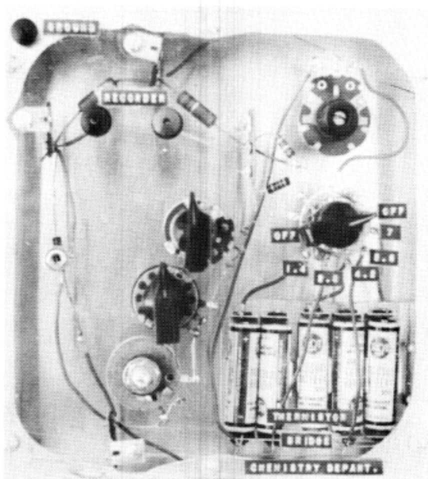

Figure 1. A student thermometric titrator.

most science departments, the actual cost is much less). Full scale readings on a 10 mv recorder vary from 1.4°C to at least 13°C and are linear with temperature as shown in Figure 2 thus making calibration easy.

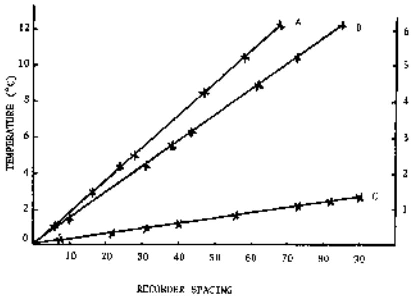

FIGURE 2. A, 12° range, 1.4 volts; B, 6° range, 1.4 volts; C, 1.4° range, 7 volts.

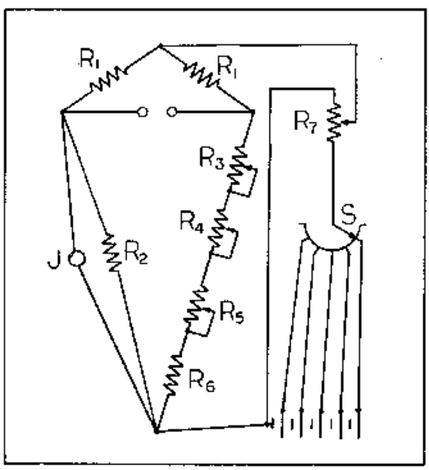

FIGURE 3. Circuit diagram of thermometric titrator.

The circuit is shown in Figure 3 as it is actually laid out with component values given in Table 1. Mercury cells of 1.4 volts, ½ watt 10% carbon resistors and ordinary variable resistors are used. The apparatus

TABLE 1. Components

R_1 82K	R_5 20 ohm
R_2 10K	R_6 4.7K
R_3 5K	R_7 25M
R_4 100 ohm	
S — Rotary switch, 12 positions	
J — Phone plug	

is housed in a 7-x 7½-x 2- inch aluminum box with its top cut out and replaced with ⅛ inch plexiglass so that students can see the various components. The two arms of the bridge and the voltage circuit are each of a different color wire for easy circuit tracing.

Thermistor resistance on the usual Wheatstone bridge is effectively linear over temperature ranges of about 1°C, but beyond that nonlinearity results. To extend the linear range, the current is made more constant by placing much larger resistances in the upper arms of the Wheatstone bridge than in the lower arms. Also, the thermistor is shunted by R_2.

A Fenwall 15K glass probe thermistor is cemented with epoxy into a glass tube, and the leads are lengthened to extend from the tubing and connected with alligator clips to a jack. A 10 mv recorder gives a full scale reading of 1.4°C using 7 volts across the bridge. Temperature span can be adjusted to any value greater than 1.4°C by varying R_7.

Several 10% carbon resistors are placed in series so that their resistances are equal to that of the thermistor at several temperatures around 25°C. The resistors are then calibrated in terms of temperature against a thermometer which reads to 0.02°C. These resistors are hereafter used for calibration instead of a thermometer.

To use the thermistor bridge, the bridge is balanced with the thermistor in place at the beginning of the temperature range to be used. The alligator clips are detached from the thermistor and attached first to one calibration resistor of known temperature equivalent and then another meanwhile changing the value of R_7 until a suitable temperature span is obtained. The clips are reattached to the thermistor and the bridge is set to work.

The titrant is delivered from a Mariotte bottle with a 220 mm piece of broken thermometer tubing used as capillary to give a constant delivery rate of 0.45± 0.02 ml/min. The adiabatic titration cell consists of a drinking glass with a polystyrene insulator (as used for keeping drinks cold) inside a one liter beaker with vermiculite as additional insulating material. A cork stopper has three holes to admit the buret tip, thermistor and thermometer when used for calibration; all three are positioned just below the surface of the liquid. A magnetic stirrer operating about 360 r.p.m. is used to agitate the solution.

An example of the results which have been obtained is the titration of 100 ml of 0.050M hydrochloric acid with 1.00M sodium hydroxide. Five determinations gave a value of 0.0050± 0.0003 mole of base.

The sensitivity of this bridge could be increased in several ways: a more sensitive recorder, a thermistor of higher resistance and a higher voltage across the bridge.

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