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CONSTRUCTION OF A THERMOMETRIC TITRATOR

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SUMMARY

"Thermometric titrimetry," a versatile and effective technique for the analytical chemist, utilizes heats of reaction to obtain titration curves. In conventional types of titrations (e.g., potentiometric, conductometric, colorimetric, etc.), determination of end points depends on free energy effects. Thermometric titration curves, however, represent a measure of the entire enthalpy change which includes the entropy as well as the free energy involved.

The method permits analysts to carry out, accurately and rapidly, many quantitative determinations not previously possible.

It was believed that a thermometric titrator would permit this laboratory to study certain reactions, i.e. EDTA determination of calcium, which could not be studied by conventional means.

This paper describes the construction of a thermometric titrator and certain improvements made upon the only existant commercial model.

On March 31, Mr. Pyzel and Mr. Bretthauer attended the Chemical Instrument Show in Los Angeles. On demonstration was a thermochemical titrator, made by the American Instrument Company.

"Thermometric titrimetry," a versatile and effective technique for the analytical chemist, utilizes heats of reaction to obtain titration curves. In conventional types of titrations (e.g., potentiometric, conductometric, colorimetric, etc.), determination of end points depends on free energy effects. They depend solely on equilibrium constants, which are correlated with free energies by the equation

$$-\Delta F^\circ = RT \ln K$$

where ΔF° denotes the standard free energy and K the equilibrium constant.

The reaction enthalpy is one of the most general properties of a chemical reaction

$$\Delta H = \Delta F + T\Delta S$$

Inspection of this equation reveals that analytical procedures based on heats of reactions may be workable when all free energies methods fail. Thermometric titration curves, therefore, represent a measure of the entire enthalpy change which includes the entropy as well as the free energy involved.

The method permits analysts to carry out, accurately and rapidly, many quantitative determinations not previously possible.

The thermometric titrator made by the American Instrument Company makes use of a thermistor for measuring temperature. The resistance of thermistors decreases drastically with temperature because these semiconductors possess a conduction band, separated from the valence band by an energy gap. As the temperature increases, electrons are transferred to the conduction band and resistance decreases accordingly. This thermistor is then incorporated into one arm of a Wheatstone bridge, thereby giving direct calorimetric data.

The thermotitrator marketed by the American Instrument Company has been available since January of 1963. This commercial model retails for about $1600 and consists of a thermistor Wheatstone bridge circuit, adiabatic tower with polyurethane insulated titration cell, teflon stirring bar attached directly to a synchronous motor, glass encapsulated heater, and a constant flow semi-micro buret.[1] It was felt that a thermochemical titrator would offer this laboratory the ability to evaluate pertinent reaction parameters heretofore unavailable and that such a titrator could be constructed with a sensitivity at least as great as the commercial instrument for a fraction of the cost.

On June 12, 1963, construction was begun on a model to be quite similar to that marketed commercially. As will be shown below, however, due to certain necessary modifications the finished model was remarkably different than envisaged.

A schematic of the Wheatstone bridge circuit is shown in Fig. 1. It was found that the circuit did not have the requisite stability in air. A much greater degree of stability was attained when the circuit was suspended in an oil bath, thereby minimizing any changes in resistance due to rapid changes in room temperature.

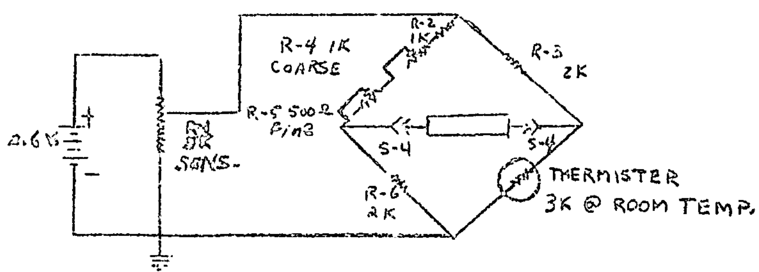

Figure 1

The titration cell was initially constructed of glass completely insulated in one inch of polyurethane. This cell was therefore quite similar to that found in the thermal titrator made by the American Instrument Company. However, due to the rapid temperature changing environment found in this laboratory, the cell did not provide adequate adiabatic character. The rapid changing temperature environment also provided great difficulty in keeping the titrant and titration solution initially at the same temperature. These difficulties were largely overcome by designing a titration cell with an attached titrant reservoir (Fig. 2), which was suspended in a large volume of oil. Figure 3 displays the thermistor-stirrer-heater assembly included in the titration cell.

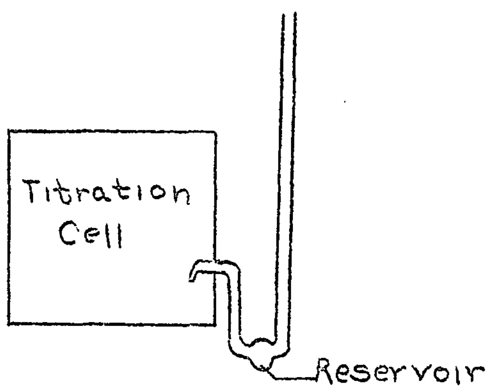

Figure 2

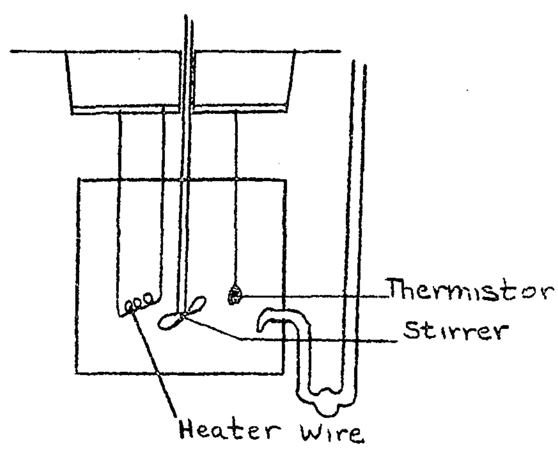

Figure 3

The stirrer was initially constructed with a teflon stirring bar attached to a synchronous motor. This also was identical to the stirring mechanism of American Instrument Company's Thermal Titrator. It was found, however, that a considerable amount of heat was conducted from the motor down the teflon bar into the reaction solution. This extraneous heat was eliminated by a belt driven stirrer.

It was also found that the sharpness of a thermogram during calibration tests was improved slightly by not encapsulating the heater wire. Of course, if corrosive solutions are used; encapsulation is necessary.

The thermal titrator, complete with an automatic semi-micro buret purchased from American Instrument,[2] is shown in Fig. 4.

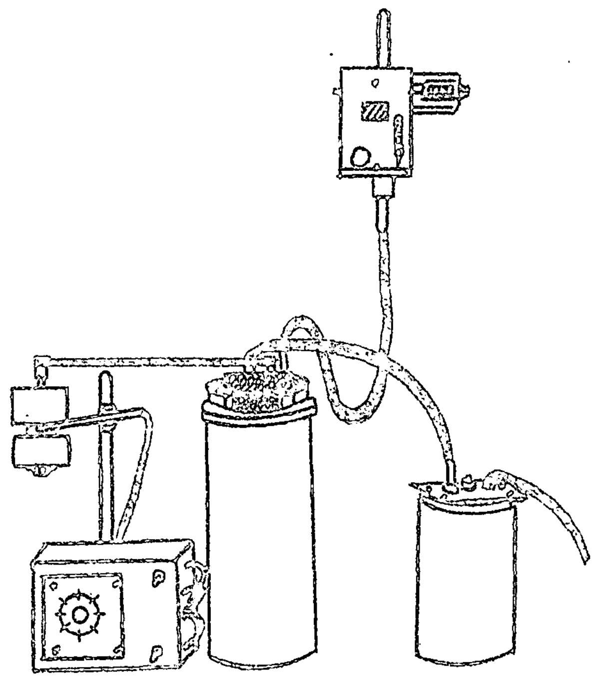

Figure 4

The sensitivity of the instrument is about the same as the commercial model. However, due to elimination of certain disadvantages discussed above, it is felt that this instrument has greater accuracy and versatility. No degree of improvement is certified for this instrument as comparison is difficult without availability of the commercial instrument.

BIBLIOGRAPHY

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2. American Instrument Co., Inc., (8030 Georgia Ave., Silver Spring, Md.), "Menisco-matic Buret," Instruction No. 774 B, 1963.

ACKNOWLEDGEMENT

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