A thermometric titration experiment for analytical and physical chemistry

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · NOVEMBER 1971

Impact Factor: 1.11 · DOI: 10.1021/ed048p851

Lee D. Hansen,
David Kenney,
William M. Litchman,
and **Edwin A. Lewis**
University of New Mexico
Albuquerque, New Mexico 87106

A Thermometric Titration Experiment for Analytical and Physical Chemistry

Thermometric titration has become a commonly used method for analytical (*1*) and enthalpy change determinations (*2*). The unique advantages of the thermometric titration method in both of these applications can be illustrated by the titration, with strong acid, of mixtures of pyridine and TRIS (*tris*-(hydroxymethyl)aminomethane).

The analytical sensitivity of the thermometric titration method is linearly related to concentration, in contrast to the logarithmic relation to concentration which exists for many other analytical methods, e.g., potentiometric methods. A linear relation is an advantage when very dilute solutions or solutions with high concentrations of interfering ions are being analyzed. For example, a *p*H titration of a solution containing pyridine at a concentration below 0.05 *M* will give a poorly defined end point, while the end point of a thermometric titration is well defined.

One of the advantages of the thermometric titration method in making calorimetric measurements is that an analysis of the reactant mixture is made during the course of the reaction. For example, CO_2 contamination of NaOH solutions becomes obvious during the course of the titration, loss of volatile reactants such as ammonia can be accounted for, and the effects of impurities present in the system can often be eliminated. In addition, a visual representation of all the heats of reaction are presented for each stage as the reactions proceed. It is also possible to make a chemical calibration of the heat capacity during each titration if one of the successive reactions has a known heat of reaction.

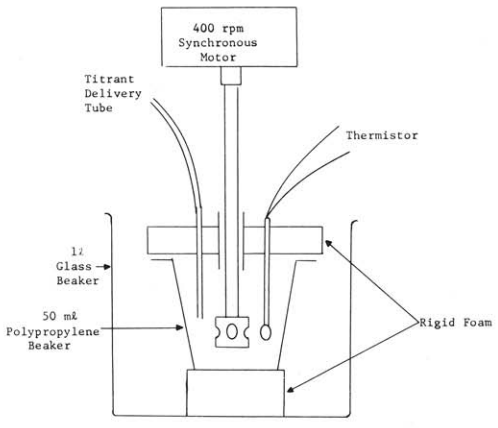

Figure 1. Schematic diagram of titration vessel. The stirrer is a perforated cylinder (~1 × 1 cm), the thermistor is a 10K, General Electric No. 81G-103, and the titrant delivery tube is ~0.030 inch i.d. Teflon.

Equipment

A constant-rate buret, an insulated titration vessel, a stirrer, and a recording Wheatstone bridge are needed for this experiment. An advantage is that there are no expensive pieces of equipment involved other than the recorder. A schematic diagram of a suitable titration vessel is shown in Figure 1. All electrical and mechanical parts entered the vessel through the lid and were cemented in place with silicone rubber. A 400 rpm synchronous motor was used to drive the stirrer. The circuit diagram for the recording Wheatstone bridge is given in Figure 2. The constant rate buret used has previously been described (*3*).

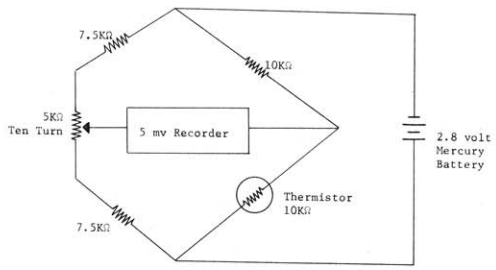

Figure 2. Recording wheatstone bridge. All resistors are wire wound or metal film.

Experiments

Analytical Experiment

A good exercise for an advanced undergraduate analytical laboratory is the analysis of mixtures of TRIS and pyridine. A typical titration curve obtained for the thermometric titration of such a mixture with strong acid is shown in Figure 3.

After the start of the titration at *S*, the upward line, *SA*, indicates the reaction of TRIS with acid with the end point occurring at *A*. Following this, the reaction of acid with pyridine occurs as indicated by the different slope between *A* and *B* with the end point for this reaction occurring at *B*. Between *B* and *C*, additional titrant is added with no further chemical reaction occurring. At point *C*, the buret is turned off.

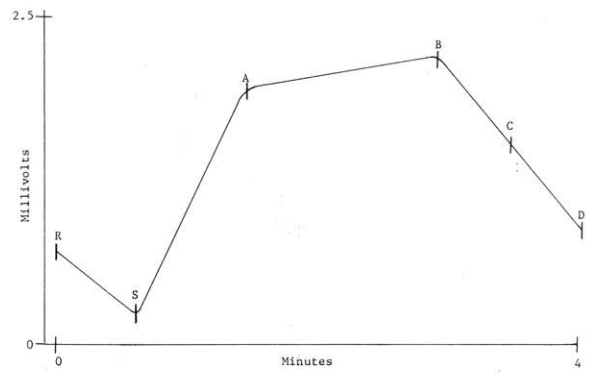

Figure 3. A typical thermogram for titration of a mixture of TRIS and pyridine with HCl.

Table 1. Results of Tris-Pyridine Determinations

Exp.	TRIS found mmoles	Pyridine found mmoles
1	0.494	0.557
2	0.500	0.539
3	0.497	0.536
4	0.494	0.539
5	0.500	0.545
6	0.497	0.545
7	0.500	0.536
8	0.476[a]	0.551
9	0.497	0.545
10	0.494	0.551
Average	0.497	0.554
Standard deviation	±0.003	±0.012
Error	±0.005	...

[a] Not included in average.

Table 2. Results of Determinations of the Enthalpy Change for Protonation of Pyridine (aq)

Run Number	$-\Delta H$ cal/mmole	Run Number		$-\Delta H$ cal/mmole
1	5.5	7		3.1
2	4.5	8		4.5
3	5.2	9		4.1
4	4.9	10		4.0
5	4.8		Average	4.5[a]
6	4.7		Standard deviation	±0.7

[a] Literature value at 25°C is 4.8 cal/mmole, Sacconi, *et al.*, *J. Amer. Chem. Soc.* **82,** 3831 (1960).

The results obtained by an undergraduate student for the titration of 40 ml of a solution containing TRIS and pyridine are presented in Table 1. The titrant was 1.53 *M* HCl delivered at the rate of 0.198 ml/min and recorded at a rate of 5 in./min on a 5 mV recorder.

The deviation given in Table 1 is the standard deviation while the error is the absolute difference between the average and the amount of TRIS actually taken, 0.492 mmoles by weight. No error is given for pyridine because to the student's consternation (and education) he found that the stock pyridine solution could not be standardized by the usual analytical methods. Considering the ±0.5% uncertainty introduced by the buret (*3*), the deviations found are reasonable.

Physical Experiment

The rate of rise of the temperature, as indicated by the slopes of the lines in Figure 3, is proportional to the heat of the reaction involved if it is corrected for the rate of heat gain or loss caused by the surroundings, the stirrer, the "heater" effect of the thermistor, and the heat of dilution of the titrant. All of these corrections can be made using the data obtained from the same curve used for the analytical experiment.

The equipment is calibrated for heat capacity using the slope, $\overline{SA}$, for the reaction of strong acid with TRIS, for which the heat is accurately known (11.35 cal/mmole) (*4*). The correction for heat loss or gain to the surroundings, the stirrer, and the "heater" effect of the thermistor is made for all regions of the titration by using Newton's Law of cooling and slopes $\overline{RS}$ and $\overline{CD}$ (*5*). The first step in this correction is to determine the slope of the titration curve subsequent to point *A* or *B* if the reaction were to have been stopped at either of those points. Such a calculated slope is then used to find the actual temperature change caused by the reaction by extrapolating both the fore- and after-period (calculated) slopes to the midpoint of the reaction region to find the temperature change by difference (*6*).

The slope of the calculated line beyond the finish of the TRIS reaction (point *A*) and the pyridine reaction (point *B*) is given by statements 5 and 6 of the program given in the Appendix. Temperature changes for regions *SA* and *AB* are given by statements 9 and 12 respectively. Heat capacities in calories per millivolt for points *A*, *B*, and *C* are given by statements 17, 18, and 19 respectively. The heat of reaction for pyridine is given by statement 23. Finally, the measured amounts of TRIS and pyridine are given by statements 24 and 22 respectively. Statement 18 contains the bridge sensitivity in deg/mV which is obtained from an analysis of the circuit (Kirchoff's Laws).

The program will calculate the heat of reaction of pyridine in kcal/mole, the amount of TRIS and pyridine found, and the actual amount of heat in calories produced by the TRIS and pyridine reactions with titrant. The input data required are time (minutes) and temperature (millivolts) coordinates for all points labeled in Figure 3, millimoles of TRIS, concentration of titrant (*M*), and titrant delivery rate in ml/min. Examples of input and output data are supplied with the program in the Appendix.

A typical set of data obtained by an undergraduate student is given in Table 2.

Summary

The experiment described here has great usefulness both as an analytical tool and as a physical chemistry experiment because it allows the student to use techniques not generally offered in a regular analytical or physical laboratory. As an advanced experiment, it allows the student to use the computer, to study the thermodynamics of a complex system, and to analyze a difficult mixture accurately. Finally, the student has the opportunity to perform a circuit analysis on his individual set-up to obtain the bridge sensitivity (deg/mV).

Literature Cited

(1) Bark, L. S. and Bark, S. M., "Thermometric Titrimetry," Pergamon Press, Elmsford, N. Y., **1969.**
(2) Christensen, J. J., and Izatt, R. M., "Thermochemistry in Inorganic Chemistry," Chapter 11 (*Editors:* Hill, H. A. O., and Day, P.), *in* "Physical Methods in Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., **1968.**
(3) Hansen, L. D., Litchman, W. M., Lewis, E. A., and Allred, R. E., J. Chem. Educ., **46,** 876 (1969).
(4) Hansen, L. D., and Lewis, E. A., *J. Chem. Thermodynamics*, in press.
(5) Rossini, F. D., *Editor*, "Experimental Thermochemistry," Interscience, New York, N. Y., **1956,** p. 30.
(6) Christensen, J. J., Izatt, R. M., Hansen, L. D., and Partridge, J. A., *J. Phys. Chem.*, **70,** 2003 (1966).

Appendix

```
/FTC LIST
C       TIME=MINUTES, TEMP=MILLIVOLTS
    1   READ, TIMER, TIMES, TIMEA, TIMEB, TIMEC, TIMED
          IF(TIMES.EQ.0.)GO TO 26
        PRINT,TIMER,TIMES,TIMEA,TIMEB,TIMEC,TIMED
        READ,TEMPR,TEMPS,TEMPA,TEMPB,TEMPC,TEMPD
        PRINT,TEMPR,TEMPS,TEMPA,TEMPB,TEMPC,TEMPD
C       TRIS=MMOLES OF TRIS,CTIT=CONC. /F TITRANT IN
          MOL/L.
C       DRTIT=BURET
C       DELIVERY RATE IN MLS/MIN.
    2   READ,TRIS,CTIT,DRTIT
        PRINT,TRIS,CTIT,DRTIT
    3   RS=(TEMPS-TEMPR)/(TIMES-TIMER)
    4   CD=(TEMPD-TEMPC)/(TIMED-TIMEC)
    5   SLOPA=RS+(CD-RS)*(TEMPA-TEMPS)/(TEMPC-TEMPS)
    6   SLOPB=RS+(CD-RS)*(TEMPB-TEMPS)/(TEMPC-TEMPS)
    7   TEMP1=TEMPS+RS*(TIMEA-TIMES)*0.5
    8   TEMP2=TEMPA-SLOPA*(TIMEA-TIMES)*0.5
    9   CHANG1=TEMP2-TEMP1
C       CHANG1 IS THE TEMP CHANGE PRODUCED BY REAC-
          TION OF TRIS
   10   TEMP3=TEMPA+SLOPA*(TIMEB-TIMEA)*0.5
   11   TEMP4=TEMPB-SLOPB*(TIMEB-TIMEA)*0.5
   12   CHANG2=TEMP4-TEMP3
C       CHANG2 IS THE TEMP CHANGE PRODUCED BY REAC-
          TION OF PYRIDINE
   16   QTRIS=TRIS*11.35
C       11.35=HEAT OF PROTONATION OF TRIS
   17   HTCAPA=QTRIS/CHANG1
   18   HTCAPB=HTCAPA+(TIMEB-TIMEA)*DRTIT*1.0*(1/30)
C       1.0 IS THE HEAT CAPACITY OF THE REACTION MIXTURE
          IN
C       CALS/ML/DEGREE
C       1/30 IS THE CALCULATED BRIDGE SENSITIVITY IN DEG/
          MV.
   19   HTCAPC=HTCAPB+(TIMEC-TIMEB)*DRTIT*1.0*(1/30)
   20   QPYR=CHANG2*HTCAPS
   22   PYR=CTIT*DRTIT*(TIMEB-TIMEA)
   23   HPYR=QPYR/PYR
   24   TRISC=CTIT*DRTIT*(TIMEA-TIMES)
   25   WRITE(6,99)HPYR,PYR,TRIS,TRISC,QTRIS,QPYR
   99   FORMAT(6E12.5)
        GO TO 1
   26   STOP
        END
```

```
INPUT-OUTPUT

        0.00, 0.56, 2.21, 4.01, 5.00, 6.00
        0.50, 0.03, 2.96, 3.70, 3.10, 2.40
        0.491, 1.53, 0.198
        4.82, 0.545. 0.492, 0.500, 5.58, 2.63
```