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THERMOMETRIC DETERMINATION OF REACTION ENTHALPIES USING A POLYPROPYLENE CELL IN AN ISOTHERMIC AIR BATH

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ABSTRACT

An isoperibolic system consisting in a polypropylene cell of thin walls surrounded by an isothermic air bath is proposed. Heat leaks are evaluated and corrected for each experiment. The system is calibrated making use of the NaOH–HCl reaction and tested by carrying out the determination of the enthalpies of neutralization of acetic, oxalic and citric acids.

INTRODUCTION

Accuracy and precision in thermometric methods of analysis depend on the sharp definition of the calorimetric system: cell, solution and the auxiliary elements, e.g., temperature sensor, stirrer and the tip of the burette or syringe.

The elements of a well-defined system must adhere instantaneously the new temperature of the solution when a thermal change occurs. Besides, in the adiabatic approach other adjacent elements, e.g., holders or electrical conductors and, in general, the surroundings, must not exchange any heat with the system, whereas in isoperibolic calorimeters small and reproducible amounts of heat may be exchanged between the system and the surroundings.

Actually, heat leaks are not completely eliminated, but are minimized to a negligible level in adiabatic calorimeters. On the other hand, in isoperibolic systems an isothermic bath surrounds the cell, making it possible to perform corrections by calculation, or to carry out differential measurements against a reference system [1–6].

In another approach based on the Peltier effect, experiments are carried out in isothermic conditions and the total heat generated or absorbed by the system is measured. In this way, accurate determinations in truly isothermic conditions can be performed, but complex and expensive equipment is required [7].

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Adiabatic systems make use of large volumes of solution, usually more than 100 ml, in order to decrease the surface/volume ratio and, thereby, the relative importance of heat leaks. However, the use of small volumes is very convenient, and frequently necessary (e.g., with biochemical compounds) making the isoperibolic approach more attractive [8].

In isoperibolic calorimeters experiments are usually carried out in a Dewar vessel, whose walls are in direct contact with the solution. Because of the inner vacuum of the vessel, the wall thickness must be at least ~ 0.6 mm [9], implying a large mass of glass, leading to a considerable thermal inertia. Besides, the heat flows up the walls over the solution surface, causing a loss of definition in the system. In this way, false initial peaks are obtained in direct injection enthalpimetry and systematic errors are produced when time is a significant variable, as in thermometric titrimetry and kinetics. These effects can be taken into account, but considering more than one single heat sink leads to a complex calculation [10,11].

In this work, a polypropylene cell of thin walls is used. The surroundings are practically limited to an isothermic air bath constituted by a mild air stream in a thermostated room. The cell has a small heat capacity and, therefore, its thermal inertia is negligible. Heat flow along the thin walls is also very small because of the very low thermal conductivity of the material. In this way, only a single heat sink, the isothermal air bath, may be considered in heat leak calculations.

The proposed system has been tested carrying out the determination of enthalpies of neutralization of acetic, oxalic and citric acids from thermometric titrations. The system has been calibrated making use of the NaOH–HCl reaction. Heat leakage is evaluated and corrected for each experiment.

CALIBRATION OF THE SYSTEM

Determination of the heat capacity, C_p, may be performed by titrating an initial volume V of HCl with NaOH, whose concentrations are C and C_v, respectively.

In Fig. 1 a typical enthalpigram is shown. The baseline may be approximated to a straight line with a small positive slope (AB section). At a time t_j when a volume of the titrant v_j has been added, the heat balance is given by:

$$\Delta T_j (C_p + v_j) = Q_{g,j} + Q_{d,j} - Q_{p,j} \tag{1}$$

where $Q_{g,j}$ is the total heat generated by the reaction, $Q_{d,j}$ the dilution heat of the titrant and $Q_{p,j}$ the total heat exchanged with the surroundings from the beginning of the titration. The product of the density of the titrant and its specific heat has been assumed to be unity.

The heat of dilution of the titrant at each point along the titration can approximately be calculated assuming the linear relation:

$$Q_{d,j} = v_j \Delta T_d (C_p + 1) \tag{2}$$

where $\Delta T_d(C_p + 1)$ is the integral dilution heat of 1 ml of the titrant. The value of ΔT_d can be experimentally determined by direct injection enthalpimetry.

The heat generated by the reaction is given by:

$$Q_{g,j} = -v_j C_v \Delta H_w \tag{3}$$

where ΔH_w is the molar enthalpy of the reaction. The amount of heat exchanged can be easily established for each titration by means of Newton's cooling law. If the addition of titrant is stopped at an arbitrary point R after the equivalence point has been reached, a cooling curve is obtained (RS section). Newton's law applied to the points (t_i, ΔT_i) on the curve gives:

$$\mathrm{d}Q_{p,i} = \frac{C_p + v_R}{\tau} \Delta T_i \quad \mathrm{d}t \tag{4}$$

that is:

$$\frac{\mathrm{d}\Delta T_{p,i}}{\mathrm{d}t} = \frac{\Delta T_i}{\tau} \tag{5}$$

where τ is the time constant of the system (ratio of heat capacity to overall heat transfer coefficient) [11]. If τ is constant, it is possible to integrate eqn. (5) in the form:

$$\tau = \frac{t_R - t_i}{\ln \Delta T_R - \ln \Delta T_i} \tag{6}$$

We have found constant values of τ along the cooling curves of all the titrations performed.

As illustrated in Fig. 2, if a linear change of ΔT within each small interval of time, Δt, is assumed, the value of $Q_{p,j}$ can be obtained by integration of

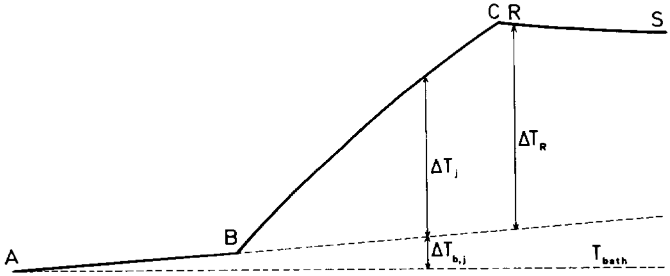

Fig. 1. Enthalpimetric titration curve.

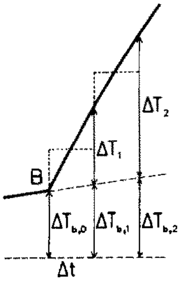

Fig. 2. Heat exchange integration.

eqn. (4) in the form:

$$Q_{p,j} = \frac{C_p + v_j}{\tau} \Delta t \sum_{i=1}^{j} \frac{\Delta T_{i-1} + \Delta T_{b,i-1} + \Delta T_i + \Delta T_{b,i}}{2} \tag{7}$$

Equation (7) can be rewritten as follows:

$$\Delta T_{p,j} = \frac{Q_{p,j}}{C_p + v_j} = -\frac{\Delta t}{2\tau}\left[\Delta T_j + \Delta T_{b,j} - 2\sum_{i=1}^{j} (\Delta T_i + \Delta T_{b,i})\right] \tag{8}$$

and substitution of eqns. (3) and (8) into eqn. (1) leads to:

$$C_p = -v_j \frac{\Delta T_j + C_v \Delta H_w - \Delta T_d + \Delta T_{p,j}}{\Delta T_j - v_j \Delta T_d + \Delta T_{p,j}} \tag{9}$$

Alternatively, instead of using the cooling curve to determine τ previously, the values of C_p and τ can be obtained simultaneously, rearranging eqn. (9) and carrying out a linear least-squares fit of the data points of the titration. However, much less reproducible results are obtained by this method.

On the other hand, the calculation of τ from the cooling curve also leads to a partial correction of the error coming from the extrapolation of the baseline. Thus, for example, a positive error in the slope of the baseline gives a higher value of τ, leading to a greater correction of the heat leaks, which tends to compensate the error.

DETERMINATION OF NEUTRALIZATION ENTHALPIES

Expressions for the heat evolved along the titration of an acid solution with a strong base were given in a previous work [12]. For the equilibrium:

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad \Delta H_N$$

$$Q_{g,j} = C_0 V\left(\frac{1}{1 + K_0 h_0} - \frac{1}{1 + K_j h_j}\right)\Delta H_N + \left[h_j(V + v_j) - \frac{C_0 V}{1 + K_0 h_0}\right]\Delta H_w \tag{10}$$

where C_0 is the initial concentration of the acid, K_0 and h_0 are its protonation constant and the free hydrogen ion concentration at the beginning of the experiment, and K_j and h_j the values along the titration, which are corrected at each point for the titrant added and the ionic strength. Substituting eqn. (10) into eqn. (1) we obtain:

$$\Delta H_N = \frac{\Delta T_j(C_\mathrm{p} + v_j) - \left[h_j(V + v_j) - \dfrac{C_0 V}{1 + K_0 h_0}\right]\Delta H_\mathrm{w} - Q_{\mathrm{d},j} + Q_{\mathrm{p},j}}{C_0 V\left(\dfrac{1}{1 + K_0 h_0} - \dfrac{1}{1 + K_j h_j}\right)} \tag{11}$$

where the values of $Q_{\mathrm{d},j}$ and $Q_{\mathrm{p},j}$ are given by eqns. (2) and (7).

Similarly, for a diprotic acid:

$$\mathrm{H_2A + OH^- \rightleftharpoons HA^- + H_2O} \qquad \Delta H_{N2}$$

$$\mathrm{HA^- + OH^- \rightleftharpoons A^{2-} + H_2O} \qquad \Delta H_{N1}$$

Substituting the corresponding expression of the heat evolved in eqn. (1) and rearranging, the equation of a straight line is obtained:

$$Y = \frac{\Delta H_{N1}}{\Delta H_{N2}} + \frac{1}{\Delta H_{N2}} X \tag{12}$$

where

$$X = \frac{\Delta T_j(C_\mathrm{p} + v_j) + M}{C_0 V\left(\dfrac{1}{P(h_j)} - \dfrac{1}{P(h_0)}\right)}$$

$$Y = -\frac{\beta_{1,j} h_j + 1}{P(h_j)} - \frac{\beta_{1,0} h_0 + 1}{P(h_0)} \Bigg/ \left[\frac{1}{P(h_j)} - \frac{1}{P(h_0)}\right]$$

with $P(h) = 1 + \beta_1 h + \beta_2 h^2$ and

$$M = \left[C_0 V \frac{\beta_{1,0} + 2}{P(h_0)} - h_j(V + v_j)\right]\Delta H_\mathrm{w} - Q_{\mathrm{d},j} + Q_{\mathrm{p},j}$$

The neutralization enthalpies of a triprotic acid are determined in a similar way, by means of a multiple linear regression.

EXPERIMENTAL

The Wheatstone bridge and the DC constant power supply have been built according to the design of Lumbiarres et al. [13], using a thermistor of 5 KΩ nominal resistance. The applied voltage was 1.000 ± 0.001 V.

The polypropylene cylindrical cell, with a wall thickness smaller than 0.5 mm and a volume of 30 ml, is surrounded by a controlled mild air stream in a plastic tube. The solution was magnetically stirred. The experiments are carried out in a 25.0 ± 0.1°C thermostated room, using a RADIOMETER Abu-80 autoburette provided with a 2.5-ml cylinder. Enthalpigrams are plotted with a Linseis L600/1 recorder. With a recorder sensitivity of 10 mV, a 198 mm $^{\circ}C^{-1}$ pen deflection was obtained.

The heat capacity of the system has been determined by titration of 20 ml HCl (0.100 M) with NaOH (2.000 M). The value $\Delta H_w = -13.47 \pm 0.04$ kcal mol^{-1} has been calculated from the data of Palmer [14], taking into account the concentrations and temperature [15] along the titration. The value $\Delta T_d = 0.017°C$ has been obtained for the titrant solution by direct injection enthalpimetry. For a given titration τ is calculated taking points from the cooling curve at 0.1-min intervals. The resulting values of τ range between 12 and 14 min.

RESULTS

The value of C_p was determined according to eqns. (8) and (9), taking points from the titration curve at 0.05-ml intervals. From five titrations, using an injection speed of 1.0 ml min^{-1}, we found $C_p = 21.0 \pm 0.3$ cal $^{\circ}C^{-1}$. The same result has been obtained at 0.5 and 1.5 ml min^{-1}.

The determination of the neutralization enthalpies of acetic, oxalic and citric acids has been performed in an analogous experimental way by

TABLE 1
Neutralization enthalpies (kcal mol^{-1})

Acid		This work	Literature data	I (M)	Ref.
Acetic	$-\Delta H_N$	13.51 ± 0.19	13.57 [a]	0	16
			12.72 ± 0.03 [a]	3	16
			13.5		17
Oxalic	$-\Delta H_{N1}$	15.25 ± 0.17	15.07 [a]	0	16
			13.99 [a]	1	16
			15.13 [a]	0	18
	$-\Delta H_{N2}$	13.12 ± 0.20	14.37 [a]	0	16
Citric	$-\Delta H_{N1}$	14.14 ± 0.21	14.27 [a]	0	16
			14.00 ± 0.03	0.05	19
	$-\Delta H_{N2}$	12.63 ± 0.21	12.89 [a]	0	16
			12.75 ± 0.03	0.05	19
	$-\Delta H_{N3}$	12.18 ± 0.11	12.47 [a]	0	16
			12.41 ± 0.03	0.05	19

[a] Calculated making use of the value $\Delta H_w = -13.47$ kcal mol^{-1}.

titration with 20 ml NaOH (0.1 N). The results obtained from six titrations for each acid are compared in Table 1 with some literature data.

The good agreement achieved indicates the validity of the system and the heat leak corrections and its applicability to thermometric titrimetry.

REFERENCES

1 P.W. Carr, Thermochim. Acta, 3 (1972) 427.
2 H. Kehlen, Wiss. Z. Tech. Hochsch. Chem. Carl Schorlemmer Leuna-Merseburg, 19 (1977) 276.
3 D.J. Eatough, J.J. Christensen and R.M. Izatt, Thermochim. Acta, 3 (1972) 219.
4 M.V. Kilday, J. Res. Natl. Bur. Stand., 85 (1980) 449.
5 C.E. Vanderzee, J. Chem. Thermodyn., 13 (1981) 1139.
6 L.D. Hansen, T.E. Jensen, S. Mayne, D.J. Eatough, R.M. Izatt and J.J. Christensen, J. Chem. Thermodyn., 7 (1975) 919.
7 J. Brandstetr, J. Therm. Anal., 21 (1981) 357.
8 J. Jordan, J.D. Stutts and W.J. Brattlie, Natl. Bur. Stand. (U.S.), Spec. Publ., 580 (1980) 149.
9 P.W. Carr, CRC Crit. Rev. Anal. Chem., (1972) 491.
10 C.J. Martin, B.R. Sreenathan and M.A. Marini, Biopolymers, 19 (1980) 2047.
11 P.C. Gravelle, Netsu-Ondo Sokutei to Netsu Bunseki (1980) 21.
12 C. Mongay, M.C. Garcia and G. Ramis, Thermochim. Acta, 56 (1982) 307.
13 J. Lumbiarres, C. Mongay and V. Cerdà, Analusis, 8 (1980) 62.
14 W.G. Palmer, Experimental Physical Chemistry, 2nd edn., Cambridge University Press, Cambridge, 1964.
15 R. Livingstone, Physico Chemical Experiments, Macmillan, New York, 1944.
16 R.M. Smith and A.E. Martell, Critical Stability Constants, Plenum Press, New York, 1976.
17 J. Jordan and W.M.H. Dumbaugh, Jr., Anal. Chem., 31 (1959) 210.
18 L.G. Sillén and A.E. Martell, Stability Constants of Metal–Ion Complexes, The Chemical Society, London, 1964.
19 G. Arena, R. Cali, M. Grasso, S. Musumeci and S. Sammartano, Thermochim. Acta, 36 (1980) 329.