Thermochimica Acta, 25 (1978) 261–268
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

ESTIMATION OF ERRORS IN DIFFERENTIAL THERMOMETRIC TITRIMETRY

ALAN E. VAN TIL* AND DENNIS C. JOHNSON
Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)
(Received 1 September 1977)

ABSTRACT

Equations are derived predicting the error for applications of thermistors as temperature sensors in differential thermometric. titrimetry. The predictions are compared with the error measured experimentally for a circuit with NTC thermistors.

INTRODUCTION

A new thermometric circuit constructed from operational amplifiers was described by Van Til and Johnson[1]. The sensitivity of the circuit output, when used with NTC thermistors, was shown to be nearly equal to the theoretical value. This circuit, together with a new differential calorimeter described by Van Til and Johnson[2], was applied to a series of thermometric titrations of 4-aminopyridine, a proposed calorimetric standard, with standard solutions of $HClO_4$[3]. The application of differential thermometric titrimetry for precise determination of heats of chemical reactions in solution is presently restricted by the lack of a theoretical understanding of the primary sources of experimental error and their minimization. An estimation of error for differential thermometric titrimetry as applied in ref. 3 is derived here.

THEORY

Consideration of the heat of dilution in differential thermometric titrimetry is, in principle, eliminated since titrant is added simultaneously and at identical rates to both the reaction vessel, containing solvent and reactant, and the reference vessel, containing only solvent. This simplification presumes identical values of the final ionic strength for both solutions. Also ignored as a source of determinate error in this discussion is error in the heat capacity determined for the reaction and reference vessels at the equivalence point in the thermometric titration. The thrust of this derivation is the estimation of random error.

---

* Present address: Corporate Research, UOP Inc., Des Plaines, IL 60016. Author to whom correspondence should be sent.

In the course of a differential thermometric titration for the determination of heats of exothermic chemical reactions, heat is generated electrically in the reference cell to increase the temperature by an amount equal, hopefully, to that of the reaction cell. The heat of the chemical reaction, ΔH_r, is calculated on the basis of the electrical heat equivalent, $\Delta q_{e,1}$ and the ratio of heat capacities for the reaction and reference vessels, c_2/c_1, according to eqn. (1).

$$\Delta H_r = \left(\frac{\Delta q_{e,1}}{c_{rl} m_{rl}}\right)\left(\frac{c_2}{c_1}\right) \tag{1}$$

In eqn. (1) the subscript rl denotes that the designated quantity corresponds to the limiting reactant. $\Delta q_{e,1}$ is calculated for the time interval, t, from the product of current and potential for the standard resistor used as the heating element in the reference vessel.

$$\Delta q_{e,1} = \frac{E_1 I_1 t}{J} \tag{2}$$

The symbol J in eqn. (2) is the Joule mechanical equivalent of heat (4.184 joule cal^{-1}).

The ratio of heat capacities in eqn. (1) is determined by comparison of the electrical equivalent of heat required in both vessels to produce nearly identical changes in temperature for the two vessels.

$$\Delta q'_{e,1} = \frac{E'_1 I'_1 t'_1}{J} = c_1 \Delta T'_1 \tag{3}$$

$$\Delta q'_{e,2} = \frac{E'_2 I'_2 t'_2}{J} = c_2 \Delta T'_2 \tag{4}$$

The prime notation in eqns. (3) and (4) denotes that the values of designated quantities for the calibration of heat capacity are not necessarily equal to corresponding values for a thermal titration. The standard heating resistors of the two cells are connected in series for determination of heat capacity ratio and, consequently, $I'_1 = I'_2$ and $t'_1 = t'_2$. Hence, the ratio of heat capacities is given by eqn. (5).

$$\frac{c_2}{c_1} = \frac{E'_2 \Delta T'_1}{E'_1 \Delta T'_2} \tag{5}$$

The constant current used for balancing the cell temperatures during the titration is equal to the current used for determination of heat capacities and, consequently, $E_1 = E'_1$. The constant current is monitored by measurement of the potential drop across a standard resistor in series with the heaters and I_1 in eqn. (2) is calculated according to eqn. (6).

$$I_1 = \frac{E_{std}}{R_{std}} \tag{6}$$

Eqn. (1) for ΔH_r may now be rewritten as given by eqn. (7).

$$\Delta H_r = \left(\frac{E_{std}E'_2}{R_{std}J}\right)\left(\frac{t}{c_{rl}m_{rl}}\right)\left(\frac{\Delta T'_1}{\Delta T'_2}\right) \tag{7}$$

The conventional method of error analysis is applied to eqn. (7) to estimate the standard deviation of ΔH_r, $S_{\Delta H'_r}$, as described by eqn. (8).

$$S^2_{\Delta H_r} = \left(\frac{\Delta H_r}{E'_2}\right)^2 S^2_{E_2'} + \left(\frac{\Delta H_r}{I_{std}}\right)^2 S^2_{I_{std}} + \left(\frac{\Delta H_r}{t}\right)^2 S^2_t + \left(\frac{\Delta H_r}{\Delta T'_1}\right)^2 S^2_{\Delta T_1'}$$

$$+ \left(\frac{\Delta H_r}{\Delta T'_2}\right)^2 S^2_{\Delta T_2'} + \left(\frac{\Delta H_r}{J}\right)^2 S^2_J + \left(\frac{\Delta H_r}{m_{rl}}\right)^2 S^2_{m_{rl}} + \left(\frac{\Delta H_r}{c_{rl}}\right)^2 S^2_{c_{rl}} \tag{8}$$

The value of S_J is zero since there is assumed to be no fluctuation in the value of J. The remaining variables in eqn. (8) involve the five primary quantities measured: energy, time, temperature, mass, and concentration of the limiting reactant in the calorimetric determination. The conclusion that is evident, from examination of eqn. (8), is that $S_{\Delta H_r}$ is minimized when the values of the denominators of each quantity are maximized, assuming of course that ΔH_r is constant over the range of concentrations studied.

Temperature imbalance between the reaction and reference vessel in thermometric calorimetry is frequently followed by recording on a strip-chart recorder the potential imbalance for the thermistor bridge (see ref. 1). The bridge potential is observed to drift slowly, even in the absence of chemical or electrical heating, when the thermometric cells are not in thermal equilibrium with their surroundings and the rate of heat exchange is not identical for the two vessels. The rate of drift is expected to be a function of the magnitude of the temperature difference between the vessels and their surroundings and, hence, the baselines recorded before and after the thermometric titration or electrical calibration are not expected to have identical slopes. Determination of the net change in temperature resulting from the chemical or electrical heating involves a graphical procedure requiring extrapolation of the baseline regions. Uncertainty in the baseline estimates is a major source of uncertainty in ΔH_r.

Theoretical examination of error resulting from baseline uncertainty begins with the equation for the output of the thermistor bridge reported in ref. 1.

$$e_{0,3} = -\left(\frac{R_f}{R_1}\right)e_- - \left(\frac{R_f}{R_2}\right)e_+ \tag{9}$$

The response of a thermistor to a small change of temperature is approximated by eqn. (10).

$$\frac{1}{R_t}\left(\frac{\Delta R_t}{\Delta T_t}\right) \cong -\frac{\beta_t}{T_t^2} \tag{10}$$

Assumptions beneficial to this derivation result when the temperatures of the calorimetric cells are closely matched before and after the determination of the heat capacity ratio and the thermometric titration ($\Delta T < 5$ m°C). Assuming also that the two thermistors are matched for resistance and sensitivity, $T_1 - T_2$ is small, $R_1 \simeq R_2$, $e_{+} = -e_{-} = e$, and $\mathrm{d}R_1/\mathrm{d}T_1 \simeq \mathrm{d}R_2/\mathrm{d}T_2$. Equation (9) can now be written as given by eqn. (11).

$$e_{0,3} = \left(\frac{R_2 - R_1}{R_1 R_2}\right) R_f e = \left(\frac{\Delta R}{R^2}\right) R_f e - \left[\frac{\beta(T_2 - T_1)}{T^2}\right] \left(\frac{R_f}{R}\right) e = - \left[\frac{\beta \Delta T}{T^2}\right] \left(\frac{R_f}{R}\right) e \tag{11}$$

The substitutions $R = \sqrt{R_1 R_2}$, $\beta = \sqrt{\beta_1 \beta_2}$ and $T = \sqrt{T_1 T_2}$ are made in eqn. (11) for the purpose of simplification of the nomenclature. The temperature change in each cell for the total calorimetric experiment does not exceed 0.5°C and the sensitivity of the thermistors can be considered constant.

During the initial period in the calibration procedure, $e_{0,3}$ is given by eqn. (12).

$$e'_{0,3,i} = - \left[\frac{\beta(T'_{2,i} - T'_{1,i})}{T_i'^2}\right] \left(\frac{R_f}{R}\right) e \tag{12}$$

During the final period eqn. (13) applies.

$$e'_{0,3,f} = - \left[\frac{\beta(T'_{2,f} - T'_{1,f})}{T_f'^2}\right] \left(\frac{R_f}{R}\right) e \tag{13}$$

The primes in eqns. (11) and (12) signify that the designated quantities correspond to the calibration as specified previously. Since $T_f - T_i \leq 0.05$°C, the substitution $T_i'^2 = T_f'^2 = T'^2$ is accurate. Subtraction of eqn. (11) from (12) yields eqn. (14) describing the net change of $e'_{0,3}$, $\Delta e'_{0,3}$, during the calibration.

$$\begin{aligned} \Delta e'_{0,3} &= e'_{0,3,f} - e'_{0,3,i} \\ &= [(T'_{2,i} - T'_{2,f}) + (T'_{1,f} - T'_{1,i})] \frac{R_f \beta e}{R T'^2} \end{aligned} \tag{14}$$

Equation (14) is rearranged to give the ratio temperature change in vessels 1 and 2.

$$\frac{\Delta T'_1}{\Delta T'_2} = \frac{T'_{1,f} - T'_{1,i}}{T'_{2,f} - T'_{2,i}} = 1 + \left(\frac{R T'^2}{R_f \beta e}\right) \left(\frac{\Delta e'_{0,3}}{\Delta T'_2}\right) \tag{15}$$

An equation similar to the above can be written for the temperature change occurring during the chemical reaction (titration).

$$\frac{\Delta T_2}{\Delta T_1} = 1 - \left(\frac{R T^2}{R_f \beta e}\right) \left(\frac{\Delta e_{0,3}}{\Delta T_1}\right) \tag{16}$$

The values of temperature ratios described by eqns. (15) and (16) may differ from unity because of any mismatch of the heat capacities of the cells and operator judgement in evaluating $\Delta e_{0,3}$. The parameters R_f, β, and e are virtually constant for the conditions prescribed. The product RT^2 is not a constant, however, because R

decreases at a rate of approximately 4 pph°C^{-1} while T^2 increases at a rate of 4 ppt°C^{-1}. Consequently, the ratios are likely to pass through a value of unity during the course of the experiment.

The desirability of minimizing the values of the second terms in eqns. (15) and (16) should be emphasized. R and T are calculated from the average values of R_1, R_2, T_1 and T_2 for the range of experimental temperature in each cell during electrical heating. $\Delta T_2'$ is determined from the result of a separate heating by electrical means of the reaction vessel, cell 2, following determination of the heat capacity ratio. Values calculated for $\Delta T_1'$ can be checked and the circuits calibrated by monitoring the reference vessel, cell 1, by a precision mercury thermometer. The heat capacity of cell 2 can be matched with that of cell 1 by adjusting the quantity of mercury placed in a glass tube with the bottom end sealed and submerged in the liquid of cell 2.

The largest contribution to the error calculated by eqn. (8) is from the terms $(\Delta H_r/\Delta T_1')^2 S^2_{\Delta T'_1}$ and $(\Delta H_r/\Delta T_2')^2 S^2_{\Delta T'_2}$. Probably a more realistic estimation of error requires the multiplication of these terms by the ratio $\Delta T_2/\Delta T_1$. The corresponding terms become $(\Delta H_r/\eta)^2 S_\eta^2$ and $(\Delta H_r/\xi)^2 S_\xi^2$, respectively, where $\eta = \Delta T_1'/\Delta T_2'$ and $\xi = \Delta T_2/\Delta T_1$. The value of S_η is given by eqn. (17) since the error in the first term of η is zero and no cross correlation exists between the first and second terms. The value of

$$S_\eta^2 = \left(\frac{\eta - 1}{\Delta e_{0,3}}\right)^2 S^2_{e0,3} + \left(\frac{\eta - 1}{e}\right)^2 S_e^2 + \left(\frac{\eta - 1}{\Delta T_2'}\right)^2 S^2_{\Delta T_2'} \tag{17}$$

S_ξ is calculated from an equation nearly identical to eqn. (17) with $\xi + 1$ replacing $\eta - 1$. The room temperature, T_a, is considered to be constant and S_{R_f} is assumed to be zero. The terms $\eta/2T$, η/R and η/β are negligible since η can be adjusted to 1 ± 0.02.

Hence, the final form of eqn. (8) for calculating the standard deviation of ΔH_r as determined from differential thermometric titrimetry is given by eqn. (18).

$$S^2_{\Delta H_r} = \left(\frac{\Delta H_r}{E_2'}\right)^2 S^2_{E_2'} + \left(\frac{\Delta H_r}{I_{std}}\right)^2 S^2_{I_{std}} + \left(\frac{\Delta H_r}{t}\right)^2 S_t^2 + \left(\frac{\Delta H_r}{\eta}\right)^2 S_\eta^2$$
$$+ \left(\frac{\Delta H_r}{\xi}\right)^2 S_\xi^2 + \left(\frac{\Delta H_r}{m_{rl}}\right)^2 S^2_{m_{rl}} + \left(\frac{\Delta H_r}{c_{rl}}\right)^2 S^2_{c_{rl}} \tag{18}$$

RESULTS AND DISCUSSION

Data are given in Tables 1 and 2 which were obtained from a series of thermometric titrations of 4-aminopyridine (4-AP) with $HClO_4$ as described in ref. 3. This data is used here for theoretical evaluation of $S_{\Delta H_r}$. Comparison is made to experimental deviation determined from $-\Delta H_N$ data by the least squares method.

The numerical evaluation of S_η by eqn. (17) is given in eqn. (19).

TABLE 1

PARAMETERS FOR THERMOMETRIC TITRATIONS OF 4-AMINOPYRIDINE(AQ) BY $HClO_4$(AQ). (DATA FROM TRIAL # 1 IN REF. 3)

Parameter	*Value*	*Standard deviation*	*Units*
E_2'	1.457860	7.7×10^{-5}	volt
I_{std}	4.8358×10^{-2}	2.0×10^{-6}	amp
e	1.00000	2.0×10^{-5}	volt
t	1309.43	$1.9 \times 10^{-5}\ t$	sec
$\Delta T_2'$	3.59×10^{-2}	2.0×10^{-4}	°C
$e_{0,3}$	variable	5.9×10^{-5}	volt
ΔH_r	11.243	to be calculated	kcal
$m_{rt,4-AP}$	0.185985	3.0×10^{-6}	g
Purity$_{4-AP}$	99.983	3.4×10^{-2}	per cent

TABLE 2

RATIO OF HEAT CAPACITIES AND END-POINT VALUES FOR THERMOMETRIC TITRATIONS OF 4-AMINOPYRIDINE (AQ) WITH $HClO_4$(AQ). (DATA FROM REF. 3)

Trial	$10^2(\eta - 1)$	$10^2\Delta T_2'$ (°C)	$10^3\Delta e_{0,3}$ (volts)	$10^3(\xi + 1)$	$\Delta T_1'$ (°C)	$10^3\Delta E_0$
1	1.17	3.59	1.67	0.50	0.110	0.22
2	1.15	3.36	1.55	2.48	0.089	0.89
3	1.40	3.67	2.05	2.90	0.064	0.74
4	0.65	3.63	0.95	2.91	0.038	0.44
5	0.58	3.83	0.88	28.77	0.015	1.73
6	0.011	3.70	0.017	1.21	0.146	0.71
7	0.55	3.99	0.87	1.46	0.125	0.36

$$S_\eta^2 = \left(\frac{1.17 \times 10^{-2}}{1.67 \times 10^{-3}}\right)^2 (1.18 \times 10^{-4})^2 + \left(\frac{1.17 \times 10^{-2}}{1}\right)^2 (2 \times 10^{-5})^2$$

$$+ \left(\frac{1.17 \times 10^{-2}}{3.59 \times 10^{-2}}\right)^2 (2 \times 10^{-4})^2 = 6.82 \times 10^{-7} + 5.5 \times 10^{-14} + 4.2 \times 10^{-9}$$

$$= 6.83 \times 10^{-7} \qquad (19)$$

The numerical evaluation of S_ξ is given in eqn. (20).

$$S_\xi^2 = \left(\frac{5.0 \times 10^{-4}}{2.2 \times 10^{-4}}\right)^2 (1.18 \times 10^{-4})^2 + \left(\frac{5.0 \times 10^{-4}}{1}\right)^2 (2 \times 10^{-5})^2$$

$$+ \left(\frac{5.0 \times 10^{-4}}{1.1 \times 10^{-1}}\right)^2 (2 \times 10^{-3})^2 = 7.19 \times 10^{-8} + 1 \times 10^{-16} + 8 \times 10^{-11}$$

$$= 7.19 \times 10^{-8} \qquad (20)$$

TABLE 3

HEAT OF NEUTRALIZATION OF 4-AMINOPYRIDINE(AQ) (DATA FROM REF. 3)

Trial	$10^3 m_{4\text{-}AP}$ (mole kg^{-1})	$-\Delta H_{N,exp}$ (kcal mol^{-1})	$-\Delta H_{N,cal}$ (kcal mol^{-1})	R (cal)	$S_{\Delta H_r,theory}$ (cal)
1	7.8673	11.243	11.250	− 7	10
2	6.1978	11.249	11.238	11	11
3	4.4655	11.236	11.225	11	11
4	2.6067	11.192	11.200	−16	13
5	0.90892	11.192	11.189	3	24
6	12.468	11.284	11.279	5	10
7	10.407	11.257	11.266	− 9	11

These calculations illustrate that the only important contributions in the present case are from the first terms which result from deviations in e_0.

The evaluation of $S_{\Delta H_r}$ is given in eqn. (21).

$$S^2_{\Delta H_r} = \left(\frac{1.12 \times 10^4}{1.46}\right)^2 (7.7 \times 10^{-5})^2 + \left(\frac{1.12 \times 10^4}{9.84 \times 10^{-2}}\right)^2 (2 \times 10^{-6})^2$$

$$+ \left(\frac{1.12 \times 10^4}{1.3 \times 10^3}\right)^2 (2.49 \times 10^{-2})^2 + \left(\frac{1.12 \times 10^4}{1.01}\right)^2 (6.83 \times 10^{-7})$$

$$+ \left(\frac{1.12 \times 10^4}{0.999}\right)^2 (7.19 \times 10^{-8}) + \left(\frac{1.12 \times 10^4}{1.86 \times 10^{-1}}\right)^2 (3 \times 10^{-6})^2$$

$$+ \left(\frac{1.12 \times 10^4}{0.99983}\right) (3.4 \times 10^{-4})^2 = 0.35 + 0.2 + 0.045 + 84 + 9 + 0.033$$

$$+ 14.5 = 108 \qquad S_{\Delta H_r} = 10\,cal \tag{21}$$

This calculation illustrates that the error in ΔH_r results primarily from η and ξ and the uncertainty in the purity of the 4-AP. Hence, careful measurement of these quantities is of paramount importance. Uncertainty in the quantity m_{rl} is not serious based on measurements made with available microbalances unless sample weights are less than 2 mg.

Table 3 is a compilation of data from ref. 3 calculated by the least squares method using eqn. (22) for the heat of neutralization of 4-AP. The calculated standard

$$-\Delta H_N = 1.1164 \times 10^4 + 7.37740 \times 10^2\, m^{1/2} + 2.58834 \times 10^3\, m \tag{22}$$

deviation is in fair agreement with the residuals between calculated and experimental values of $-\Delta H_N$ for individual experiments. When the standard deviation for the entire series of thermometric titrations is calculated from eqn. (23), the result is $S_{\Delta H_r,exp} = 12$ cal which is in good agreement with $S_{\Delta H_r,theor} = 13$ cal. If we consider

$$S_{\Delta H_{r,\mathrm{exp}}} = \frac{\Sigma R_i^2}{n-2} \tag{23}$$

the values of $S_{\Delta H_r,\mathrm{theor}}$ to be theoretically derived residuals, the corresponding value of the overall $S_{\Delta H_r,\mathrm{theor}}$ is 16 cal which is still in good agreement with $S_{\Delta H_r,\mathrm{exp}}$.

In conclusion, the agreement between theoretically and experimentally determined estimates of calorimetric error for a series of differential thermometric titrations is satisfactory. This suggests that reliable a priori estimates of error can be made for a variety of experimental conditions using the error equation derived here.

REFERENCES

1 A. E. Van Til and D. C. Johnson, *Thermochim. Acta*, 20 (1977) 115.
2 A. E. Van Til and D. C. Johnson, *Thermochim. Acta*, 20 (1977) 141.
3 A. E. Van Til and D. C. Johnson, *Thermochim. Acta*, 20 (1977) 177.