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HEAT EXCHANGE TYPE OF TITRATION CALORIMETRY WITH ON-LINE ANALOGUE COMPENSATION FOR THE EFFECT OF TITRANT ADDITION

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ABSTRACT

A theoretically exact method of compensation for the effect of titrant addition is developed for the previously reported heat exchange type of calorimetry. An adequate modification is made on the calorimeter vessel, covering a part of the heat exchange surface for thermal insulation, to make the relevant differential equations simpler. The differential equations are realized in the form of an operational amplifier circuit, where the resistance of a variable resistor increases in parallel with the movement of the piston of a burette. The effect of titrant addition at a rate up to 7 cm^3 min^{-1} can be completely compensated. For illustration the heat of reaction of THAM with a standard HCl solution is estimated in a titrimetric procedure and a satisfactory result is obtained.

INTRODUCTION

Our previously reported technique of the heat exchange type of calorimetry [1] permitted free exchange of heat with the ambient water and involved on-line analogue treatment of the resulting temperature change to estimate the net heat evolved. This technique was characterized by a simple apparatus and a much shorter time for the establishment of thermal equilibrium before the start of each run. The technique afforded reliable data on the heat of solution of optical isomers of ruthenium complexes [2] and metal perchlorates in aqueous acetonitrile [3].

However, the theoretically perfect treatment was not given for the case where an appreciable volume change of the solution, such as a volume increase in titrations, was involved. In conventional titrations sometimes a very concentrated titrant solution, usually 50—100 times as concentrated as the titrand, is used to approximate a constant volume. But it is not easy to measure precisely a small volume of titrant and a more concentrated solution may produce more heat of dilution.

In this paper the effect of volume increase is theoretically considered and the problem is solved on a strictly mathematical basis. This allows the use of dilute solutions as titrant, which leads to convenience in practice and improved accuracy.

CALORIMETER

As illustrated in the previous paper [1], the principal part of the calorimeter consists of two glass vessels of identical configuration of which one is for the sample and the other is for reference. A thermistor is incorporated into each vessel. The two vessels are immersed in a large bath of water. Solutions in the vessels and the ambient water are stirred vigorously enough to assure uniformity of temperature. Titration takes place in the sample vessel and the temperature difference between the two vessels is observed as unbalanced output voltage of a Wheatstone bridge. The voltage is directly treated with an appropriately designed operational amplifier circuit, as described later.

THEORETICAL

When heat is being evolved in the sample vessel at the rate of q (in J sec^{-1}), fundamental relations between q and the resulting temperature change are expressed by the following equations

$$\frac{\mathrm{d}T_s}{\mathrm{d}t} = \frac{q + q'}{W} - \alpha(T_s - T_a) \tag{1}$$

$$\frac{\mathrm{d}T_r}{\mathrm{d}t} = -\alpha(T_r - T_a) \tag{2}$$

where T_s and T_r are the temperatures at time t in the sample and the reference vessels, respectively, q' is the heat equivalent produced by adding the titrant which is at a temperature different from T_s, W is the effective heat capacity, α is a constant relating to the efficiency of heat exchange, and T_a is the temperature of the ambient water. In practice T_a is usually controlled to be constant, and therefore T_r also remains nearly constant. T_s, q', W and α should vary with time, when the volume of solution increases by the addition of titrant. For simplicity, a constant delivery rate of the titrant solution is assumed throughout.

As long as the heat exchange occurs at an appreciable rate, α is considered closely proportional to the heat exchange area A and reciprocally proportional to the effective heat capacity. Thus

$$\alpha \propto A/W \tag{3}$$

The heat exchange area is the sum of the area of the side wall of the vessels below the level of the inner liquid, A_s, and the area of the base, A_b. Therefore, $A = A_s + A_b$.

If the base is covered with an absolutely insulating material, $A_b = 0$; hence $A = A_s$. Since the vessels are cylindrical, A_s is proportional to the volume of inner liquid, V. Thus, $A = kV$, where k is a proportionality constant. On the other hand, the solution inside the vessel contributes to a large extent to the effective heat capacity W, so that W is closely proportional to V. These conclusions are combined with eqn. (3) to lead to a constant value of α, regardless of a volume increase. This is realized in actual cases, as described in a later section.

The effective heat capacity, W, of the sample vessel is substantially close to the heat capacity of the solution itself, as long as heat is exchanged rapidly enough, as in the present case. When a titrant is added at a constant rate v for a period of time t, the heat capacity of the solution, hence the effective heat capacity W, is given as follows

$$W = W_0 + \rho cvt = W_0 + k_v vt \tag{4}$$

where W_0 is the initial value of W, ρ and c are density and specific heat capacity, respectively, of the titrant solution, and k_v is the product of ρ and c.

Since the titrant is kept at the temperature of the ambient water T_a, addition of the titrant at a rate of v is thermally equivalent to evolving heat at a rate of $-\rho cv(T_s - T_r)$. In actual experiments, T_r is mostly equal to T_a. Therefore

$$q' = -\rho cv(T_s - T_r) = -k_v vT \tag{5}$$

where $T = T_s - T_r$.

Substituting W and q' in eqns. (4) and (5) for those in eqn. (1) and subtracting eqn. (2) from eqn. (1), we obtain

$$\mathrm{d}T/\mathrm{d}t = (q - k_v vT)/(W_0 + k_v vt) - \alpha T \tag{6}$$

This is then rearranged into the following expression

$$q/W_0 = (\mathrm{d}T/\mathrm{d}t + \alpha T)\,(1 + (k_v v/W_0)t) + (k_v v/W_0)T \tag{7}$$

The quantity, $\mathrm{d}T/\mathrm{d}t + \alpha T$, is the rate of temperature change which could be expected when heat was not dissipated. This quantity is corrected for the volume increase by the first term on the right-hand side of eqn. (7), and further for the effect of different temperatures of titrant by the second term.

In practice we use a pair of thermistors to measure the temperature difference θ $(=\theta_s - \theta_r)$ which is different from the actual temperature difference T. T and θ are simply connected [1] by

$$\mathrm{d}\theta/\mathrm{d}t = \beta(T - \theta) \tag{8}$$

This expression permits T values to be calculated from observed θ values. Thus

$$T = (1/\beta)\,(\mathrm{d}\theta/\mathrm{d}t) + \theta \tag{9}$$

The analogue circuit for computing q from observed θ is basically made up to be concordant with eqns. (7) and (9).

COMPUTATION CIRCUIT

Figure 1 is the analogue computation circuit which realizes eqns. (7) and (9). The whole circuit consists of five sections, as shown by the broken lines.

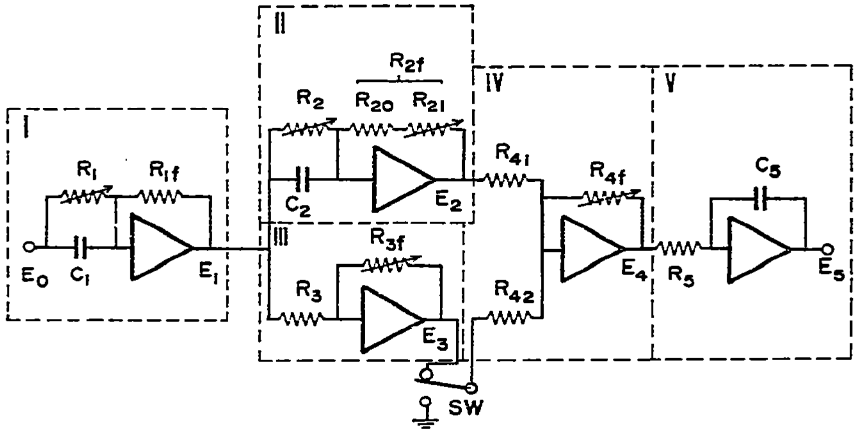

Fig. 1. Analogue computation circuit.

Each section contains an operational amplifier and the input—output characteristics [4] are summarized in Table 1.

The output voltage of the Wheatstone bridge, θ, is applied to E_0, input of section I. If the variable resistors are adjusted accordingly, as described later, the voltage at E_4, output of section IV, gives an estimate of q at the particular moment and the voltage at E_5, output of section V, is proportional to the heat integrated up to that moment.

For illustration, Fig. 2 shows variation of voltage, during a titration, to be observed at several points in the circuit, E_0 through E_5, which are either inputs or outputs of a section. A titrant solution is added between the arrows and q is assumed to be constant. The observed voltage θ which is applied to E_0 varies along the curve E_0 in Fig. 2. The corresponding variation of voltage at E_1, output of section I, is shown by the curve E_1 in Fig. 2. The relation between E_0 and E_1 is found as (I — E) in column 2 (Electrical expression) of Table 1. If the time constant R_1C_1 is so adjusted [1] in calibration runs as to be equal to $1/\beta$ (Requirement), (I — E) can be rewritten to give (I — P) (Physical expression). In (I — P), E_1 proves to be proportional to T. Thus, section I serves to convert θ into T.

Similarly, the first term on the right-hand side of eqn. (7) is computed in section II, whose electrical function is expressed as (II — E) in Table 1. The time constant R_2C_2 has to be adjusted beforehand to be reciprocally equal to α. Resistance R_{2f} consists of fixed (R_{20}) and variable (R_{21}) resistors, so that $R_{2f} = R_{20} + R_{21}$. The shaft of the latter is rotated in linkage with the motion of a burette, so that $R_{21} = rt$ at time t. R_{2f} [$=R_{20} + rt = R_{20}(1 + rt/R_{20})$] is kept at any time proportional to the effective heat capacity W [$=W_0 + k_v vt = W_0(1 + k_v vt/W_0)$]. Therefore $r/R_{20} = k_v v/W_0$, as appears in column 3, Table 1. The output voltage E_2 varies, for example, along the curve E_2 in Fig. 2.

Section III corresponds to the second term of the right-hand side of eqn. (7) and simply contributes to correction for the effect of difference in temperature and the addition rate of the titrant. The output voltage varies like E_3 in Fig. 2.

Voltages at E_2 and E_3 are added in section IV to obtain the output at E_4

TABLE 1

Input—output characteristics of the sections in Fig. 1

Section	Electrical expression	Requirement	Physical expression	Remark
I	$E_1 = \frac{R_{1f}}{R_1}\left(R_1 C_1 \frac{dE_0}{dt} + E_0\right)$ ····· (I − E)	$E_0 = k_0 \theta$ $R_1 C_1 = 1/\beta$	$E_1 = -k_1((1/\beta)(d\theta/dt) + \theta)$ $= -k_1 T$ ····· (I − P)	$k_1 = (R_{1f}/R_1)$
II	$E_2 = -R_{2f} C_2 \left(\frac{dE_1}{dt} + \frac{E_1}{R_2 C_2}\right)$ ····· (II − E)	$R_2 C_2 = 1/\alpha$ $r/R_{20} = k_v v/W_0$ $R_{2f} = R_{20}\left(1 + \frac{rt}{R_{20}}\right)$	$E_2 = k_2\left(\frac{dT}{dt} + \alpha T\right)\left(1 + \frac{k_v v t}{W_0}\right)$ ····· (II − P)	$k_2 = k_1 R_{20} C_2$ $k_v = \rho c$
III	$E_3 = -\frac{R_{3f}}{R_3} E_1$ ····· (III − E)	$R_{3f}/R_3 = \frac{k_2 k_v v}{k_1 W_0}$	$E_3 = k_2\left(\frac{k_v v T}{W_0}\right)$ ··· (III − P)	
IV	$E_4 = -R_{4f}\left(\frac{E_2}{R_{41}} + \frac{E_3}{R_{42}}\right)$ ····· (IV − E)	$R_{41} = R_{42}$	$E_4 = -k_4\left(\frac{dT}{dt} + T\right)\left(1 + \frac{k_v v t}{W_0}\right) + \frac{k_v v T}{W_0}$ $= -k_4 \frac{q}{W_0}$ ····· (IV − P)	$k_4 = k_2 \frac{R_{4f}}{R_{41}}$
V	$E_5 = -\frac{1}{R_5 C_5}\int E_4\, dt$ ····· (V − E)		$E_5 = k_5 \int q\, dt$ ····· (V − P)	$k_5 = \frac{k_4}{R_5 C_5 W_0}$

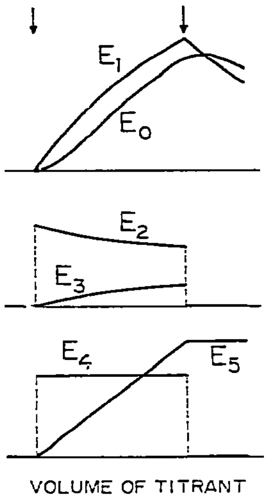

Fig. 2. Variation of voltage at various points in Fig. 1.

which proportionally represents q in eqn. (7).

In principle, the voltage at E_4 will give an important estimate of differential heat, instead of integral heat, at any particular moment of time. But since the analogue differentiation with an operational amplifier (sections I and II) usually suffers from noises, and the output E_4 hardly gives a reliable result, an integration circuit (section V) is included to obtain noise-free output voltages at E_5 for the integral heats. Values of unknown heat can be calculated as usual referring to electrically generated known heats.

EXPERIMENTAL

The fundamental setup of the calorimeter assembly was generally the same as that previously reported [1], except for several modifications on the vessels and the computation circuit. The circuitry is mostly self-evident from Fig. 1 and Table 1. Operational amplifiers are LF356 (National Semiconductor). As capacitors, those of polystyrene or polycarbonate are chosen on account of their low dielectric losses.

The value of α could be made constant, regardless of the increased volume of solution, by appropriately restricting the heat exchange surface on the walls of the vessels (Theoretical). In practice, polystyrene foam was used for covering the wall. The appropriate coverage should be determined experimentally for particular vessels, as described below. Further, it is necessary to this end to maintain a flat, instead of concave, surface of the inside solution while it is stirred vigorously. This is accomplished by using a thin plastic strip with several narrow, vertically long openings which is held half-immersed in the solution with its surface in the direction perpendicular to the flow of solution. The dimensional factors are experimentally determined.

In Fig. 3, variation of the constant α with increase in volume is illustrated for four different extents of coverage, A—D. Each experimental run was

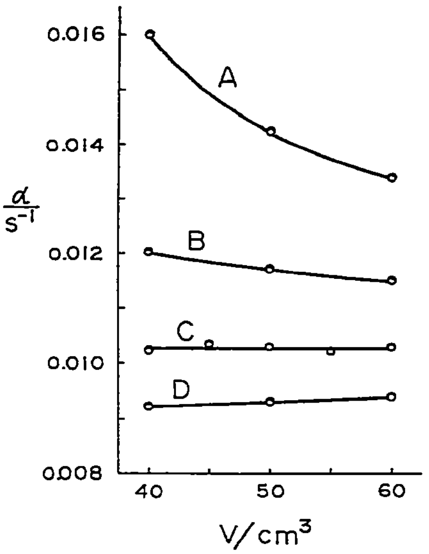

Fig. 3. Dependence of α on the varied volume of solution in the cylindrical vessel when different areas on the heat exchange surface were covered with a thermally insulating material. A, No covering; B, only the base covered; C, covered to the level of 6 cm^3 content; D, covered to the level of 10 cm^3 content.

carried out by the batch process using 40, 50 or 60 cm^3 of water in the vessel and the electrically evolved heat. Only C includes experiments with 45 and 55 cm^3 of water. Values of α were estimated from the time constant of the cooling curves. As seen in C, α could be made practically constant when the base plus a small fraction of the side wall was covered. In fact, the covered areas in C and D were so large as to enclose about 6 and 10 cm^3, respectively, of the content.

Strictly speaking, exchange of heat also occurs through that part of the wall which is above the level of the inside solution. But the contribution may be reasonably ignored in our case, as long as the exchange proceeds with a relatively high efficiency. The vessels thus covered so as to produce the effect as in C (Fig. 3) were employed in later experiments.

The resistor R_{21} is a precision 10-turn variable resistor (100 kΩ) of linearity 0.3%. The resistance is increased by a set of gears which are synchronized with the motion of the burette. Thus, $R_{2f} = R_{20} + rt$, corresponding to $W = W_0 + k_v v t$. If an increase by 1 cm^3 in volume corresponds to an increase in resistance by, for example, 5 kΩ, and v is expressed in cm^3 sec^{-1}, then numerically $r = 5v$.

Resistance R_{20} should satisfy the relation

$$r/R_{20} = k_v v/W_0 \quad \text{or} \quad 5/R_{20} = k_v/W_0$$

The value of W_0 is approximated by the heat capacity of the initial 40 cm^3 solution. Since a 1 cm^3 increase of solution was made equivalent to a 5 kΩ increase in R_{2f}, as defined above, R_{20} should be approximately $5 \times 40 = 200$ kΩ.

The exact value of R_{20} was decided using several different volumes of solution in the vessels. R_{2f} was manually adjusted so as to produce an identical value of voltage at E_5 for a given heat, regardless of the volume of solution, V cm^3. R_{2f} minus $5(V-40)$ kΩ gave an estimate of R_{20}. The most probable value of R_{20} was 212.7 kΩ. This value corresponds to 212.7/5 = 42.5 cm^3 of solution. The surplus 2.5 cm^3 can be considered mainly as being the water equivalent of the stirrer rod, thermistor, heater element and the undefined contribution of the base of the vessel.

Resistance R_{3f} depends on the titration speed v and is so selected as to satisfy the relation $R_{3f}/R_3 = k_2k_vv/k_1W_0$ (Requirement, Table 1). The ratio need not be very precise because usually section III contributes far less than section II.

Before the start of a titration, R_{21} is returned to the zero position and kept at the standby, the switch (SW) is turned to common, R_{3f} is given a value as just mentioned, and C_5 is completely discharged. The switch is turned on only while the burette is being operated.

In the following discussion, it is assumed that titrations start with a volume of 40 cm^3 and up to 20 cm^3 of a titrant solution is added and only dilute aqueous solutions are considered. The rate of titrant addition, v, should not be so high as to disturb the practical uniformity of temperature in the vessel, but may be varied up to 7 cm^3 min^{-1} with our calorimeter assembly.

The above discussions mostly concern aqueous solutions, but the process could be extended to non-aqueous solutions only with some numerical modifications on specific heat, density and the non-additivity of volumes of those solutions.

EXAMPLE OF APPLICATION

The accuracy and reliability of the proposed method were demonstrated using tris(hydroxymethyl)aminomethane (THAM) as a test material. For ease of comparison with literature values, the heat of reaction of THAM with aqueous hydrochloric acid was estimated according to the following process

$$\text{THAM(s, 0.25 g)} + \text{HCl(aq, 50 cm}^3\text{, 0.1 mole dm}^{-3}\text{)} \rightarrow \text{THAM}\cdot\text{H}^+\text{Cl}^-\text{(aq, 50 cm}^3\text{, 0.1 mole HCl dm}^{-3}\text{)};\ \Delta H \quad (10)$$

In this paper, process (10) was intentionally resolved into the following three component processes to include titrimetric procedures, (12) and (13), where an aqueous solution of THAM and 40 cm^3 of water, respectively, were titrated with a hydrochloric acid solution.

$$\text{THAM(s, 0.25 g)} + \text{H}_2\text{O (40 cm}^3\text{)} \rightarrow \text{THAM(aq, 40 cm}^3\text{)};\ \Delta H_\text{S} \quad (11)$$

$$\text{THAM(aq, 40 cm}^3\text{)} + \text{HCl(aq, 10 cm}^3\text{, 0.5 mole dm}^{-3}\text{)} \rightarrow \text{THAM}\cdot\text{H}^+\text{Cl}^-\text{(aq, 50 cm}^3\text{, 0.1 mole HCl dm}^{-3}\text{)};\ \Delta H_\text{N} \quad (12)$$

$$\text{HCl(aq, 10 cm}^3\text{, 0.5 mole dm}^{-3}\text{)} + \text{H}_2\text{O(40 cm}^3\text{)} \rightarrow \text{HCl(aq, 50 cm}^3\text{, 0.1 mole HCl dm}^{-3}\text{)};\ \Delta H_\text{D} \quad (13)$$

Process (10) can be numerically realized by adding (11) and (12) followed by subtracting (13). Thus,

$$\Delta H = \Delta H_S + \Delta H_N - \Delta H_D \tag{14}$$

Since the present method postulates a uniform temperature in each vessel (Theoretical) and therefore does not accept abrupt evolution of a large quantity of heat, the solid THAM and the HCl solution are added in increments with pauses in between. The temperature changes on adding an increment, but, as a result of exchange of heat, it gradually returns to the original value until a further increment is added.

All the experiments were carried out at 298.15 ± 0.1 K by controlling the temperature of the ambient water. Titrant solutions were added at a rate of 1 cm^3 min^{-1}. A total of 0.25 g of purified THAM was added in about 10 fractions to 40 cm^3 of water [process (11)]. The result was absorption of 36.40 J (ΔH_s = 36.40 J/0.25 g THAM).

The 40 cm^3 solution of 0.25 g THAM was then titrated with a 0.500 mole dm^{-3} solution of HCl until 10 cm^3 of the titrant was added [process (12)]. The HCl was excessive in equivalent. The procedure was followed very carefully and the mean heat evolved in five runs amounted to 101.67 ± 0.07 J as calculated to 0.25 g of THAM (ΔH_N = —101.67 J/0.25 g THAM). The final solution was the same as if 0.25 g of THAM was dissolved in 50 cm^3 of a 0.1 mole dm^{-3} solution of HCl, except for the heat effect. Process (13) was included to correct the difference in the heat effect. In this process 3.849 J was evolved (ΔH_D = —3.849 J).

It therefore follows from (14) that ΔH = 36.40 + (—101.67) — (—3.849) = —61.42 J/0.25 g THAM or —245.68 J/g THAM. Presumably this value is accompanied by a relative standard deviation of 0.4% at most for a single estimate instead of for the mean.

A number of literature values are found for the heat of reaction of THAM with aqueous hydrochloric acid [process (10)]. Prosen and Kilday [5] reported a value of 245.76 ± 0.26 J g^{-1} which was obtainable with standard reference material of THAM issued by the National Bureau of Standards. Montgomery et al. [6] summarized the results obtained up to 1975 under specified conditions at 298.15 K. The weighted mean of these values was 245.54 ± 0.04 J g^{-1}, where the uncertainty was twice the overall standard deviation of the mean. Our present value well agrees with these values.

Allowing for the involvement of the titrimetric process which is liable to lead to erroneous results, the agreement is satisfactory for demonstrating the usefulness of the present type of titration calorimetry. As an advantage of titration calorimetry, this calorimeter can be successfully employed for obtaining a number of data from a single experimental run. However, the present investigation has not succeeded in directly obtaining instantaneous heats because of serious noise disturbances at E_4 in Fig. 1. A different approach to this problem is under examination.

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