Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

DETERMINATION OF EQUILIBRIUM CONSTANTS BY TITRATION CALORIMETRY*

PART II. DATA REDUCTION AND CALCULATION TECHNIQUES

D. J. EATOUGH, J. J. CHRISTENSEN, AND R. M. IZATT

Departments of Chemical Engineering and Chemistry and Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601 (U. S. A.)

(Received July 9th, 1971)

This paper is the second in a series of three written to acquaint the reader with the general usefulness of titration calorimetry for the determination of equilibrium constants (K) for reactions in solution. In this paper the calculation procedures required to convert calorimetric data to the desired thermodynamic values are presented. In the first paper, an introduction to titration calorimetry was presented and in the third paper the application of the method to typical systems is presented and discussed.

General

The evaluation of K values from calorimetric data for reactions in solution involves four steps: (*a*) the experimental determination of the gross heat liberated in the reaction vessel, Q, as a function of titrant added, (*b*) the calculation of all correction terms for heat effects occurring in the reaction vessel other than those due to chemical reactions, (*c*) the evaluation of heat effects contributed from reactions other than the ones for which K values are to be evaluated, and (*d*) the calculation of the energy changes due to the reactions in question and the evaluation of K values. For simplicity and completeness the procedures given in this paper apply to measurements obtained from a continuous titration, constant-temperature environment, calorimeter[50], but with slight modifications it can be applied to either incremental titration[51] or isothermal titration[10] calorimetry data.

The principles presented here apply equally to studies in aqueous or non-aqueous solvents for a wide range of interactions such as proton ionization, metal–ligand interactions, oxidation-reduction reactions, and adduct formation as the heat produced by interactions in solution is dependent only on the types and quantities of species involved.

Determination of the gross heat liberated in the reaction vessel

The determination of the amount of heat produced as titrant is added to the reaction vessel involves the calibration of the calorimetric equipment and the analysis of the thermogram for the total heat produced as a function of the amount of titrant added.

---

*Contribution from the Departments of Chemical Engineering and Chemistry, and No. 19 from Center for Thermochemical Studies.

Calibration of equipment

Calibration of the equipment involves calibration of the titrant delivery system and the temperature sensing device and determination of the heat capacity of the reaction vessel.

Calibration of titrant delivery system. — In continuous titration calorimetry the titrant is added at a constant rate over the entire period of the run, necessitating the use of a precision, constant rate buret. The buret is calibrated by weighing the amounts of distilled water delivered by it over several measured time intervals. Consistence of the delivery rate can be confirmed by comparing the weights of water delivered over various time intervals. The delivery rate in units of volume (cc or liters) per unit of time (sec or min) can be calculated very accurately from the mass rate of delivery using the density of water at the calibration temperature.

Calibration of temperature sensing device. — The most common means of measuring temperature changes in the reaction vessel is by means of a thermistor incorporated into a Wheatstone bridge circuit[10,13,50]. The change in the output voltage of the bridge may be related to temperature change by calibration against a temperature standard. Either a calibrated platinum resistance thermometer or a one degree Beckman mercury-in-glass thermometer can be used with the latter being the most convenient and inexpensive. The calibration procedure consists of placing the thermistor and the thermometer in close proximity in a carefully controlled constant temperature water bath and measuring changes in the bridge voltage, E, as a function of bath temperature, T. Over a small temperature interval (~0.5°C) Eqn. (13) can be used to relate voltage to temperature

$$E = a + bT \tag{13}$$

where a and b are constants. The constant b is given by Eqn. (14)

$$b = \frac{m \sum_{i=1}^{m} E_i T_i - \sum_{i=1}^{m} T_i \sum_{i=1}^{m} E_i}{m \sum_{i=1}^{m} T_i^2 - (\sum_{i=1}^{m} T_i)^2} \tag{14}$$

where m is the number of data points taken. If a strip chart recorder is used to indicate voltage changes, the recorder output can be directly calibrated in terms of chart units per degree temperature change.

Determination of reaction vessel heat capacity. — In continuous titration calorimetry the total heat capacity of the system is a function of the amount of titrant added during a run. The total heat capacity of the reaction vessel and its contents can be determined by either (*a*) measuring the heat capacity for various additions of titrant and obtaining the heat capacity as a function of amount of titrant added or (*b*) measuring or evaluating the heat capacity of the empty reaction vessel, of the contents of the reaction vessel, and of the titrant and combining them to give the total heat capacity of the system as a function of the amount of titrant added. Method (*a*) is the more accurate of the two methods in that the heat capacity of the system is directly measured for each system but at the same time, it is also the most time consuming and laborious method. Method (*b*) depends on the total heat capacity being equal to the sum of the heat capacities of the parts which, for dilute solutions, is a very good assumption. This method has the advantage that once the heat capacity of the empty reaction vessel has been determined, no further calibrations are necessary as long as the heat capacities of the solutions used in the reaction vessel and as titrants can be evaluated from other sources. Method (*b*), because of its simplicity and versatility, will be used in this paper to evaluate the total capacity as a function of titrant added to the reaction vessel. Method (*b*) consists of measuring the heat capacity of the reaction vessel and its contents, subtracting the heat capacity of the contents to give the heat capacity of the empty reaction vessel and determining the total heat capacity for a given addition of titrant by adding the heat capacities of the empty reaction vessel, of the contents of the reaction vessel, and of the titrant.

The heat capacity of the reaction vessel and contents is most accurately measured electrically by introducing a constant current through a resistance heater over a measured period of time. Details of several heater circuits have been described[52]. Distilled water should be used in the reaction vessel as its heat capacity is accurately known as a function of temperature[53]. As electrical heaters have been known to give erroneous data for a multitude of reasons, electrical calibration should be checked periodically by chemical calibration. For solution calorimetry, the heat of neutralization of NaOH with $HClO_4$[54,55] or the heat of protonation of THAM [tris (hydroxy methyl) aminomethane][56,57] is sufficiently well known for this purpose. The heat capacity of the reaction vessel plus contents, Cp, is given by Eqn. (15)

$$Cp = Q_E/[\Delta T_T - (S_i + S_f)\theta/2] \tag{15}$$

where Q_E is the electrical or chemical energy introduced into the reaction vessel, ΔT_T is the total temperature rise, S_i and S_f are the initial and final rates of temperature rise, respectively, due to non-electrical heat contributions (stirring, radiation, conduction, etc.) and θ is the time of calibration. The heat capacity of the empty reaction vessel, Cp_r is found from Eqn. (16)

$$Cp_r = Cp - V\rho\, Cp_w \tag{16}$$

where V, ρ, and Cp_w are the volume, density and heat capacity of water, respectively, at the calibration temperature. Cp_r is a constant for a given volume of liquid in the reaction vessel but varies as the liquid volume changes as titrant is added. This change in Cp_r is due primarily to more of the reaction vessel wall coming into contact with the liquid as the liquid volume increases. For precision calorimeters[50] the change in Cp_r during the titration period is usually less than 1.0% of the value of Cp_r. This change can be evaluated by measuring Cp_r as a function of the volume of liquid in the reaction vessel. For volumes ranging from 100 to 106 ml in a 100 ml reaction vessel, it has been found that $(\delta Cp_r/\delta V)$ is a constant[58]. For a given amount of titrant added the total heat capacity of the reaction vessel and contents, Cp, is given by Eqn. (17)

$$Cp = Cp_r + (V\rho Cp)_s + (V\rho Cp)_t + \left(\frac{\delta Cp_r}{\delta V}\right) V_t \qquad (17)$$

where $(V\rho Cp)_s$ is the heat capacity of the initial solution in the reaction vessel, $(V\rho Cp)_t$ is the heat capacity of the titrant added and $(\delta Cp_r/\delta V)\, V_t$ is the increase in heat capacity due to the increase in the liquid–wall contact area in the reaction vessel. It should be emphasized that the quantities Cp_r and $(\delta Cp_r/\delta V)$ are independent of the liquid used in the calorimeter.

The total apparent heat, Q_p*, produced in the reaction vessel from the start of the titration, point x, to any data point p (see Fig. 6) is given by Eqn. (18)

$$Q_p = -Cp_p(T_p - T_x) \qquad (18)$$

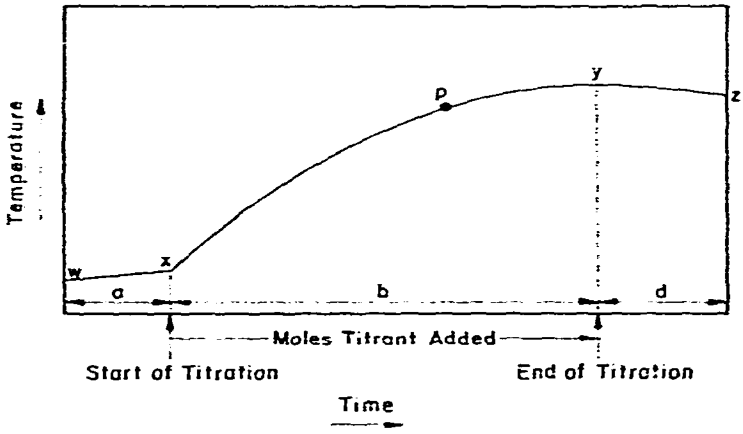

Fig. 6. Typical thermogram showing temperature *vs.* time trace for lead, trail, and reaction periods

where T_p is the temperature at point p and T_x is the temperature at point x. By combining Eqns. (13), (17) and (18), an expression for Q_p in terms of measurable quantities is obtained

$$Q_p = -\left[Cp_r + (V\rho Cp)_s + (V\rho Cp)_{t,p} + \left(\frac{\delta Cp_r}{\delta V}\right) V_{t,p}\right] [(E_p - E_x)/b] \qquad (19)$$

where $V_{t,p}$ is the volume of titrant added from point x to point p.

Analysis of the thermogram

The thermogram for a typical calorimetric run is given in Fig. 6. The lead (region a) and trail (region d) periods are a measure of the nonchemical heat effects

---

* Q_p is the quantity of heat which would be evolved by the system if reaction were started at temperature T_x and the temperature after reaction were reduced to the initial temperature, T_x.

due to stirring, resistance heating of the thermistor and heat losses to the surrounding in these periods. Titrant is added in region b with the resulting temperature rise being due to nonchemical heat effects, dilution of the titrant and titrate, and from chemical interactions as the titrant and titrate are mixed. In actual practice, point x is not the same as the time at which the titrant buret is turned on as a small air space is usually left at the tip of the titrant delivery tube to prevent premixing of the solutions. Point x may be found directly if a strip chart recorder is used to record the data. If the data are in the form of digital outpu. at set time intervals, then point x must be found by interpolation of the data points or from independent calibration.

The following data can be evaluated from the thermogram: the slopes of the fore period (S_i, °C/sec) and after period (S_f, °C/sec), the temperature of the titrate at the beginning of the reaction period, T_x, and the temperatures of the titrate at prescribed time intervals ($T_1, T_2, T_3, \ldots, T_p, \ldots, T_m$). A set of Q_p values corresponding to the T_p values can be calculated using Eqn. (19). These Q_p values represent the total heat produced in the reaction vessel from points x to p and must be corrected for all heat effects other than that due to the reaction of interest before they can be used to calculate equilibrium constants. These corrections are detailed in the next section.

Calculation of correction terms

Non-chemical energy terms. — Non-chemical contributions to the total energy change measured in the reaction vessel include those energy quantities associated with stirring of the solution, heat losses between the reaction vessel and its surroundings, and resistance heating of the thermistor. The initial and final equilibration slopes (S_i and S_f) can be used to calculate the rates of heat loss at points x and y if the assumption is made that the energy input from the thermistor and stirrer (w) is constant during the run and that the rate of heat loss is proportional to the temperature difference between the reaction vessel, T_p, and its surroundings, T_j. This final assumption is equivalent to saying that the reaction vessel obeys Newton's law of cooling[59]. Based on these assumptions, the following equations are obtained.

$$-S_i(Cp_x) = \frac{dQ_{HL,x}}{dt} = q_{HL,x} = -w-k(T_j-T_x) \tag{20}$$

$$-S_f(Cp_y) = \frac{dQ_{HL,y}}{dt} = q_{HL,y} = -w-k(T_j-T_y) \tag{21}$$

where both w and k are positive constants and $q_{HL,x}$ and $q_{HL,y}$ are rates of heat loss at points x and y, respectively. Eqns. (20) and (21) may be solved for w and k using the experimental values for S_i, S_f, T_x, T_y, and T_j. These values can then be used to calculated the value for q_{HL} at any point p.

$$q_{HL,p} = -w-k(T_j-T_p) \tag{22}$$

Eqns. (20), (21), and (22) can be combined to give an expression for $q_{\mathrm{HL,p}}$ which does not contain the somewhat ambiguous quantity, T_j.

$$q_{\mathrm{HL,p}} = q_{\mathrm{HL,x}} + (q_{\mathrm{HL,y}} - q_{\mathrm{HL,x}}) \left[\frac{T_p - T_x}{T_y - T_x} \right] \tag{23}$$

The total contribution of the non-chemical heat effects from the start of the titration (point x) to any time during the run (point p) is given by Eqn. (24)

$$Q_{\mathrm{HL,p}} = \int_{\theta_x}^{\theta_p} q_{\mathrm{HL}} \, \mathrm{d}\theta \tag{24}$$

Eqn. (24) may be solved by obtaining an analytical expression relating q_{HL} values calculated from Eqn. (23) for each data point and time, θ, and integrating the resulting function. A more simple and usually adequate method is to assume for the time interval ($\Delta\theta$) between data points that q_{HL} is a linear, first order expression in time. Eqn. (24) may then be expressed as a sum over all data points to point p

$$Q_{\mathrm{HL,p}} = \sum_{i=0}^{p} \frac{\Delta\theta_i}{2} (q_{\mathrm{HL},i} + q_{\mathrm{HL},i+1}) \tag{25}$$

where $Q_{\mathrm{HL,o}}$ is the initial rate of heat loss at point x. $Q_{\mathrm{HL,p}}$ values calculated from Eqn. (25) are used to correct Q_p values for the energy contributed by non-chemical terms. Examples of this calculation are given in the third paper of this series.

Temperature difference between titrant and titrate. — Ideally, the temperatures of the titrant, T_t, and titrate, T_x, at point x would be the same; however, in practice this identity is difficult to achieve. If the quantity $(T_x - T_t)$ is positive, there will be an endothermic heat effect as the colder titrant is added. Conversely, there will be an exothermic heat effect if the quantity $(T_x - T_t)$ is negative. The correction that must be made to the Q_p values for this heat effect is

$$Q_{\mathrm{TC,p}} = (V\rho\, Cp)_{t,p}(T_x - T_t) \tag{26}$$

It should be noted that the correction calculated using Eqn. (26) is only that energy that results from the titrant being introduced into the reaction vessel at a temperature different from the temperature of the contents of the reaction vessel at the beginning of the titration (T_x).

Dilution of titrant and titrate. — As the titrant is added to the titrate a heat effect will occur due to chemical changes such as solvation, hydrolysis, and ion pairing. The magnitude of the heat effect will also change as the relative concentrations of species present in the titrate solution change. This effect will be present even if an inert electrolyte is used to maintain a constant ionic strength. The magnitude of the dilution heat effects must be determined either by experimentation or from available tables[60-62].

Usually, the concentrations and changes in concentrations of the chemical species in the titrate are small enough that their contribution to the net correction for heat of dilution is negligible. The same, however, is not true for the heat of dilution of the titrant, ϕ_L. If ϕ_L values as a function of ionic strength, μ, are known for the titrant, then the heat effect due to dilution of the titrant, Q_D, is given by Eqn. (27).

$$Q_{D,p} = (\phi_{L,p} - \phi_{L,t})n_t \tag{27}$$

where $\phi_{L,p}$ refers to the titrant in the titrate at point p, $\phi_{L,t}$ refers to the titrant, and n_t is the moles of titrant added. If $(\phi_{L,p} - \phi_{L,t})$ values are not available in the literature, they must be measured; however, it is not necessary to determine absolute ϕ_L values as only the difference $(\phi_{L,t} - \phi_{L,p})$ need be known to calculate $Q_{D,p}$.

Heat contributed from other reactions. — If reactions other than the ones of interest occur in the calorimeter, their energy contributions must be corrected for in the Q_p values. ΔH values for proton ionization[63] and metal-ligand interactions[64] have been compiled. Hydrolysis of a ligand species is a commonly encountered reaction and will be used to illustrate this type of correction of Q_p. If one of the reactions being studied involves a basic ligand, L, then the reaction

$$L + H_2O \rightarrow HL^+ + OH^- \tag{28}$$

may contribute significantly to the total heat produced in the reaction vessel. The energy terms that arise from reaction (28) that must be corrected for in Q_p are those due to the formation of HL^+ and to the dissociation of water by the hydrolysis of L. In both cases the correction term will be the change in moles of the species involved times the appropriate ΔH values for the reaction. For the species HL^+ the correction term will be

$$\begin{aligned} Q_{RL,p} &= (C_{HL,p} V_p - C_{HL,x} V_x)\Delta H_{HL} \\ &= (n_{HL,p} - n_{HL,x})\Delta H_{HL} \end{aligned} \tag{29}$$

where ΔH_{HL} is the change in enthalpy for the reaction $H^+ + L = HL^+$ and the C and n terms refer to concentrations and moles of the HL^+ species, respectively. Since the number of moles of water hydrolyzed is the same as the number of moles of OH^- formed the correction for the formation of water is

$$Q_{RW,p} = (C_{OH,p} V_p - C_{OH,x} V_x)(-\Delta H_w) = (n_{OH,p} - n_{OH,x})(-\Delta H_w) \tag{30}$$

where ΔH_w is the change in enthalpy for the reaction $H^+ + OH^- = H_2O$. The conditions, V_x, $C_{HL,x}$ and $C_{OH,x}$ refer to the initial titrate solution if L is present in the titrate only. If L is present in the titrant, then the initial conditions in Eqns. (29) and (30) may refer either (*a*) to the initial titrant solution or, (*b*) to a hypothetical solution where the added titrant solution has been diluted to the volume of the titrate solution at point p but no interaction between titrant and titrate has occurred. Situation (*b*) applies to most of the ϕ_L values reported in the literature. It is important that the data for the heat of dilution and for the corrections for hydrolysis are consistent so that the correct heat effect is calculated.

Corrections for other side reactions such as ion pair formation, dimerization, etc., will involve terms of the form $(\Delta H_i)(\Delta n_i)$ where ΔH_i is the enthalpy change associated with the side reaction and Δn_i is the change in moles of the species involved from the start of the titration (point x) to the data point in question (point p).

Calculation of energy released by reactions for which K values are to be determined and the evaluation of K values.

Calculation of energy released by reactions for which K values are to be determined

The energy released, Q_c, due to the reactions of interest for a given amount of added titrant is determined by subtracting from the overall heat term, Q_p, the heat effects given by the previously described correction terms [see Eqns. (25), (26), and (27)].

$$Q_{c,p} = Q_p - Q_{HL,p} - Q_{TC,p} - Q_{D,p} - \sum_{1}^{R} \Delta H_R \Delta n_R \tag{31}$$

where the term $\Sigma \Delta H_R \Delta n_R$ refers to all other reactions occurring in the reaction vessel other than the ones for which the K values are to be determined. Q_c is a function only of the K values and ΔH values for the reactions of interest.

Evaluation of K values

The addition of titrant to the titrate solution produces one or more reactions where the extent of the reactions and the energy produced are related to the corresponding equilibrium constants and enthalpy changes for the reactions. The mathematical relationship between the heat produced, the equilibrium constants and the changes in enthalpy for the reactions is generally very complex. This was demonstrated for the simple reaction $A+B=AB$ in Part I of this series. It is, therefore, more convenient to express the relationship between these quantities for the general case of n reactions occurring in the reaction vessel in the form given by Eqn. (32)

$$Q_{c,p} = \sum_{i=1}^{n} \Delta H_i \Delta n_{i,p} \tag{32}$$

where $\Delta n_{i,p}$ is the number of moles of product i formed and is a function of the equilibrium constant for reaction i. A simple and moderately accurate method of solving Eqn. (32) for K and ΔH was outlined in Part I for the reaction $A+B=AB$ ($n=1$).

In general, the best values of K_i and ΔH_i are calculated by a least squares analysis of Eqn. (32). The error square sum over the m data points is given by Eqn. (33)

$$U(K_i, \Delta H_i) = \sum_{p=1}^{m} (Q_{c,p} - \sum_{i=1}^{n} (\Delta n_{i,p} \Delta H_i))^2 \tag{33}$$

where the subscript p is over all the data points and subscript i is over all the reactions being studied. The best values for K and ΔH for a given run are those which minimize $U(K_i, \Delta H_i)$, that is, those values which satisfy Eqns. (34) and (35)

$$\frac{\delta U(K_i, \Delta H_i)}{\delta \Delta H_k} = 0 = \sum_{p=1}^{m} Q_{c,p} \Delta n_{k,p} - \sum_{p=1}^{m} \Delta n_{k,p} \sum_{i=1}^{n} (\Delta n_{i,p} \Delta H_i) \tag{34}$$

$$\frac{\delta U(K_i, \Delta H_i)}{\delta K_k} = 0 = \sum_{p=1}^{m} \left(Q_{c,p} - \sum_{i=1}^{n} (\Delta n_{i,p} \Delta H_i)\right) \frac{\delta \sum_{i=1}^{n} (\Delta n_{i,p} \Delta H_i)}{\delta K_k} \tag{35}$$

where ($k = 1, \ldots\ldots n$). The n expressions given by Eqn. (34) are all homogeneous first order linear equations in the ΔH_i values and may be easily solved if K_i values, and therefore Δn_i values, are known. Eqn. (35) is a nonlinear expression in the K_i values and must either be solved by trial and error or by some iterative technique. A complete and accurate solution of Eqns. (32)–(35) involves five steps: (*1*) Assumption of initial K values, (*2*) calculation of the concentration of each species in the reaction vessel at each data point using the assumed K values, (*3*) calculation of the best value of each ΔH value corresponding to the K values chosen, (*4*) evaluation of the K and ΔH values to establish how well they fit the experimental data, (*5*) recalculation of steps (*2*), (*3*) and (*4*), using new K values until the best set of K and ΔH values are found. These five steps are detailed in the following sections.

(*1*) *Assuming K values.* — The shape of the titration curve is very dependent on the magnitude of the equilibrium constants of the reactions occurring in the reaction vessel as is illustrated in Fig. (3), Part I. The technique described here for determining K values requires fewer iterative calculations the closer the initial K values are to the calculated or best values. A good, initial estimate of the K values can be obtained from (*a*) values determined by other investigators for the same or similar reactions, many of which values have been compiled for proton ionization[63,66] and metal–ligand interaction[64,65,67] or (*b*) values determined by a simpler, less accurate method of evaluation K from titration data using Eqn. 9 or a similar equation applicable to the system being studied.

(*2*) *Calculating concentrations of species present in reaction vessel.* — The calculation of the species present in the reaction vessel at each data point is best illustrated by typical calculations. An example showing how the concentration of the various species at specific time intervals could be calculated was given in Part I for the reaction $A+B = AB$. Two additional examples will be given, one involving proton ionization of a weak acid and one involving metal–ligand interaction where n equilibrium constants are to be determined.

Proton ionization: Titration of a neutral base with a weak acid. The reactions to be considered are

$$H^+ + A^- = HA \qquad K_A, \Delta H_A \tag{36}$$

$$H^+ + B = HB^+ \qquad K_B, \Delta H_B \tag{37}$$

$$H_2O = H^+ + OH^- \qquad K_W, \Delta H_W \tag{38}$$

where the titrant, a solution of the weak acid, HA, is added to the titrate, a solution of the neutral base, B. The K_A and ΔH_A values are known and the values of K_B and ΔH_B are to be determined. For strong acid titrants (HCl or $HClO_4$) the calculations are identical to those given in Part I for the reaction $A+B=AB$ where $A=H^+$. The species present in the calorimeter at each data point (end of each time interval) can be calculated by combining Eqns. (36), (37), and (38) with the following mass and charge balance equations

$$[A_T] = [A^-]+[HA] \tag{39}$$

$$[B_T] = [B]+[HB^+] \tag{40}$$

$$[H^+]+[HB^+] = [OH^-]+[A^-] \tag{41}$$

where $[A_T]$ and $[B_T]$ refer to the total concentration in the reaction vessel of A and B, respectively, to give an expression which can be solved for the hydrogen ion concentration.

$$\begin{aligned}[H^+]^4 K_A K_B+[H^+]^3[K_B+K_A(1+K_B[B_T])]+[H^+]^2[1+K_B([B_T]-\\ -[A_T]-K_A K_W)]+[H^+](-[A_T]-K_W(K_A+K_B))-K_W = 0\end{aligned} \tag{42}$$

Eqn. (42) can be solved for the concentration of the hydrogen ion using Newton's method of approximation, where a reasonable approximation for the hydrogen ion concentration is made, and successive approximations made using Eqn. (43)

$$[H^+] = [H^+]_0 - \frac{f([H^+]_0)}{f'([H^+]_0)} \tag{43}$$

until a consistent value is obtained for $[H^+]$. The function, $f([H^+]_0)$, is given by Eqn. (42) and the function, $f'([H^+]_0)$, is the derivative of Eqn. (42) with respect to $[H^+]$. After $[H^+]$ has been calculated, the concentration of the other species present can be calculated using Eqns. (36)–(41). Once the concentrations of the various species are known at the various data points, p, corrections to the Q_p values for the formation of water and the disassociation of HA can be made as outlined in the previous section on Calculation of Correction Terms.

Metal–ligand interaction: Titration of a metal ion with a ligand. For simplicity it is assumed that the ligand, L, is not significantly hydrolyzed under the conditions of the titration. The system is then defined by the expressions for the *n* consecutive equilibrium constants, and for the total concentrations of the metal ion and the ligand.

$$M^{n+}+iL = ML_i^{n+} \qquad \beta_i,\ \Delta H_i\,(i=1,n) \tag{44}$$

$$[M_T] = [M^{n+}]+[ML^{n+}]+[ML_2^{n+}]+ \ldots [ML_n^{n+}] \tag{45}$$

$$[L_T] = [L]+[ML^{n+}]+2[ML_2^{n+}]+ \ldots n[ML_n^{n+}] \tag{46}$$

where β_i is the overall formation for the ith species

$$\beta_n = \frac{[\mathrm{ML}_n^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]^n}$$

Eqns. (44), (45), and (46) may be most easily solved for [L]. Using as an example the case where $n = 2$, the resulting expression is

$$[\mathrm{L}]^3\beta_2 + [\mathrm{L}]^2(\beta_1 + \beta_2(2[\mathrm{M_T}] - [\mathrm{L_T}])) + [\mathrm{L}](1 + \beta_1([\mathrm{M_T}] - [\mathrm{L_T}])) - [\mathrm{L_T}] = 0 \tag{47}$$

Eqn. (47) may be solved for [L] using Newton's method of approximation and the concentration of the other species present may be calculated from Eqns. (44)–(46). If hydrolysis or protonation of the ligand is important, then a charge balance expression similar to Eqn. (41) but including appropriate concentrations of the metal ion species must be included in the calculations. In the previous calculations of species concentrations it has been assumed that the values of the equilibrium constants are independent of concentrations or ionic strength (μ) or in other words, the activity coefficients were assumed to be independent of concentration and equal to 1. In most cases, however, the thermodynamic equilibrium constant valid at zero ionic strength must be converted to a concentration quotient for calculation of the species present. For dilute solutions ($\mu < 0.1$) the activity coefficient necessary to make this conversion can be approximated from an extended form of the Debye–Hückel equation given by Eqn. (48)

$$\log \gamma_{\pm} = \frac{-Z^2 A\sqrt{\mu}}{1 + \beta \mathring{a}\sqrt{\mu}} + C\mu \tag{48}$$

where the various terms have their usual significance[68]. If the ionic strength during an experimental run changes appreciably, then it becomes necessary at each point where a species concentration is desired to find the correct activity coefficient by an iterative technique. This involves assuming an ionic strength, calculating the activity coefficients from Eqn. (48), correcting equilibrium constants to concentration constants, calculating the species concentrations, comparing calculated and assumed ionic strength values to see if they are equal and repeating the above steps using the calculated ionic strength until the estimated and calculated ionic strengths agree to the desired degree. For aqueous solutions at 25°C, the values of A and β are 0.5092 and 0.3286 respectively. Values of $\mathring{a}$ and C of 4 Å and 0.2, respectively, used with the values of A and β given above have been shown to correctly calculate activity coefficients for many metal ion–ligand systems[19]. For concentrated solutions ($\mu > 0.1$) it is necessary to have either experimental activity coefficients or to calculate only concentration constants which are valid at the experimental ionic strengths.

(3) *Calculation of ΔH values.* — Once the concentrations of the various species have been calculated, the values of ΔH corresponding to the chosen K values may be

calculated using Eqn. (34). For the titration of B with HA, Eqn. (34) reduces to Eqn. (49)

$$\Delta H = \frac{\sum_{p=1}^{m} Q_{c,p}([HB^+]_p V_p - [HB^+]_x V_x)}{\sum_{p=1}^{m} ([HB^+]_p V_p - [HB^+]_x V_x)^2} \tag{49}$$

It should be pointed out that the ΔH value calculated from Eqn. (49) is not the same as that value calculated by taking the average of the ΔH values calculated at each data point as shown in Eqn. (50)

$$\Delta H_{avg} = \frac{1}{m} \sum_{p=1}^{m} Q_{c,p}/([HB^+]_p V_p - [HB^+]_x V_x) \tag{50}$$

If only random errors are present in the data, then the missing terms in Eqn. (50) as compared to Eqn. (49) will tend to cancel and ΔH_{avg} and ΔH values will be nearly equal. If, however, significant systematic errors are present in the Q_c data, then ΔH and ΔH_{avg} may be significantly different. It is the author's viewpoint that ΔH is best calculated by using Eqn. (49). For systems where there are two or more reactions for which K and ΔH values are to be determined, such as the titration of a metal ion solution with a ligand L to form ML^{n+} and ML_2^{n+} species, the best ΔH values are given by Eqns. (51) and (52)

$$\sum_{p=1}^{m} Q_{c,p}[ML^{n+}]_p V_p = \Delta H_1 \sum_{p=1}^{m} [ML^{n+}]_p^2 V_p^2 + \Delta H_2 \sum_{p=1}^{m} [ML^{n+}]_p [ML_2^{n+}]_p V_p^2 \tag{51}$$

$$\sum_{p=1}^{m} Q_{c,p}[ML_2^{n+}]_p V_p = \Delta H_1 \sum_{p=1}^{m} [ML^{n+}]_p [ML_2^{n+}]_p V_p^2 + \Delta H_2 \sum_{p=1}^{m} [ML_2^{n+}]_p^2 V_p^2 \tag{52}$$

The V_0, $[ML^{n+}]_0$, and $[ML_2^{n+}]_0$ terms do not appear in Eqns. (51) and (52) since there is no ligand present at the beginning of the run in the titrate.

(4) *Evaluation of error square sum.* — Once the ΔH values have been obtained an evaluation must be made of how well the assumed K and calculated ΔH values describe the data. This is accomplished by using ΔH and K values and species concentration values determined by the methods outlined above to evaluate the error square sum given by Eqn. (33).

(5) *Recalculation to find best value(s) of K and ΔH.* — The procedures outlined above of selecting a K value(s), evaluating $Q_{c,p}$ values, calculating a ΔH value(s), and calculating the error square sum is repeated until that set of K and ΔH values is

found which result in the minimum value of the error square sum. Various iterative procedures for locating this minimum have been described[5]. If the Q_c data are essentially free from random errors and the assumed reactions correspond to the reactions taking place in the reaction vessel, the value of the error square sum at the minimum should be close to that calculated from the known precision of the calorimeter. For example, if a given run produces 10 calories of heat in a calorimeter capable of a minimum detection level of 0.01 calories, then if 10 data points are analyzed one would expect the function $U(K, \Delta H)$ to approach the value

$$U(K, \Delta H) = \sum_{p=1}^{10} (0.01)^2 = 0.001 \text{ cal}^2 \tag{53}$$

Significant deviations of the minimum error square sum from this value usually indicates that either the assumed reactions do not correctly define the system or large systematic or random errors are present in the data. It should be noted that a small minimum value of $U(K, \Delta H)$ does not prove that the assumed species correctly describes the chemical system. If there are uncertainties about the actual species present runs should be made at several concentrations of titrate and/or titrant. Only if the same K and ΔH values are obtained at each of the different concentrations can it be assumed that the correct reactions have been used.

Summary

Techniques of data reduction and methods of calculation have been given for the determination of equilibrium constants by titration calorimetry. It has been shown how, starting with typical titration calorimetry data, the apparent heat liberated in the reaction vessel can be calculated, corrected for extraneous heat effects, and used to solve for the equilibrium constant and enthalpy change value(s) for the reaction(s) under investigation. Equations are given for calculating the energy contributed to the overall heat effects measured in the reaction vessel by processes other than chemical reactions such as heat of stirring, heat losses, heat of dilution, etc., and by chemical reactions other than the one(s) for which equilibrium constant(s) are sought. Mathematical techniques and equations are presented for calculating equilibrium constants and enthalpy change values from titration data by least squares analysis.

REFERENCES

1–49 See reference list for Part I, pp. 217–218.
50 J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instrum.*, 36 (1965) 779.
51 P. Gerding, J. Leden, and S. Sunner, *Acta. Chem. Scand.*, 17 (1968) 2190.
52 H. A. Skinner, *Experimental Thermochemistry*, Vol. II, Interscience, New York, 1962.
53 N. S. Osborne, H. F. Stimson, and P. C. Ginnings, *J. Res. Nat. Bur. Stand.*, 23 (1939) 261.
54 J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 67 (1963) 2605.
55 C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, 67 (1963) 2609.
56 J. O. Hill, G. Öjelund, and I. Wadsö, *J. Chem. Thermodyn.*, 1 (1969) 111.

57 L. D. Hansen and E. A. Lewis, *J. Chem. Thermodyn.*, 3 (1971) 35.
58 H. D. Johnston, Ph. D. Thesis, Brigham Young University, Provo, Utah, 1968.
59 F. D. Rossini, *Experimental Thermochemistry*, Vol. I, Interscience, New York, 1956, p. 30.
60 V. B. Parker, *Thermal Properties of Aqueous Uni-Univalent Electrolytes*, Nat. Bur. Stand., NSRDS-NBS 2, U. S. Government Printing Office, Washington, D. C., 1965.
61 F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, Nat. Bur. Stand., Circ. 500, U. S. Government Printing Office, Washington, D. C., 1952.
62 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties*, Nat. Bur. Stand., Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.
63 J. J. Christensen and R. M. Izatt, in H. A. Sober (Ed.), *Handbook of Biochemistry*, The Chemical Rubber Company, Cleveland, Ohio, 1970, pp. J-58–J-172.
64 J. J. Christensen and R. M. Izatt, *Handbook of Metal–Ligand Heats and Related Thermodynamic Quantities*, Marcel Dekker and Company, New York, 1970.
65 L. G. Sillen and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publication No. 17, The Chemical Society, London, 2nd edn., 1964.
66 G. Kortüm, W. Vogel, and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution*, International Union of Pure and Applied Chemistry, Butterworths, Washington, D. C., 1961.
67 K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Consultants Bureau, New York, 1960.
68 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Pub. Co., New York, 3rd edn., 1958.