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DETERMINATION OF EQUILIBRIUM CONSTANTS BY TITRATION CALORIMETRY*

PART III. APPLICATION OF METHOD TO SEVERAL CHEMICAL SYSTEMS

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This paper is the third and final in a series of three papers 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 experimentation and calculation concepts discussed in the two previous papers are applied to three typical chemical systems. Calorimetric data and computer programs used in the examples have been deposited and are available from ASIS National Auxiliary Publication Service.

General

Reactions for which equilibrium constants can be determined by titration calorimetry generally fall into one of two types:

(*a*) The replacement reaction of the form

$$AB + C = AC + B, \quad K_{\text{overall}} = \frac{[AC][B]}{[AB][C]} \tag{54}$$

or (*b*) The addition reaction of the form

$$A + B = AB, \quad K = [AB]/[A][B] \tag{55}$$

Replacement reactions have been extensively studied with respect to the effect on the determined value of K of random[2,4,48] and systematic[48] errors in the titrant and solution concentrations and in the heat data. The studies indicated, as discussed in Part I (see p. 203), that the most accurate log K_{overall} values are obtained, all other experimental conditions being equal, when log K_{overall} is greater than 0 and less than 4. By combining the appropriate addition reactions to obtain a replacement reaction where the overall constant is in the appropriate range it is theoretically possible to determine the equilibrium constant for any given reaction.

The experimentation and calculation concepts discussed in the previous two papers are applied to three representative chemical systems in the following examples. The first system represents an addition reaction where K is determined for the protonation of *o*-bromo-aniline using a strong acid ($HClO_4$) as titrant. The second system represents a replacement reaction where K is determined for proton ionization from

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imidazole using a weak acid (acetic acid) titrant. The third system represents a two-step addition reaction where K is determined for the first and second stepwise additions of thiourea to $Hg(CN)_2$. The data used in these examples together with the appropriate computer programs used to make the necessary calculations have been compiled and are available*.

The determination of K and ΔH values for an addition reaction: The titration of o-bromo-aniline with $HClO_4$

The log K value for the protonation of *o*-bromo-aniline, A, is within the range required for its determination by titration calorimetry and the corresponding ΔH^0 value is large enough to produce an easily detected heat change.

$$H^+ + A = HA^+, \qquad \log K = 2.7 \qquad \Delta H = -4.4 \text{ kcal/mole.}$$

The K value for protonation of *o*-bromo-aniline can therefore be conveniently determined using a strong acid titrant such as $HClO_4$. The thermogram for the titration of 0.10005 l of a 0.00729 F *o*-bromo-aniline solution with a 0.1952 F $HClO_4$ solution is given in Fig. 7. For this run (Run No. 441, Ref. 71) Cp, Cp_t, b, and the titrant delivery rate† are 103.73 cal/°C, 0.995 cal/°C·ml, 1502.9 mV/°C, and 0.0005127 l/min

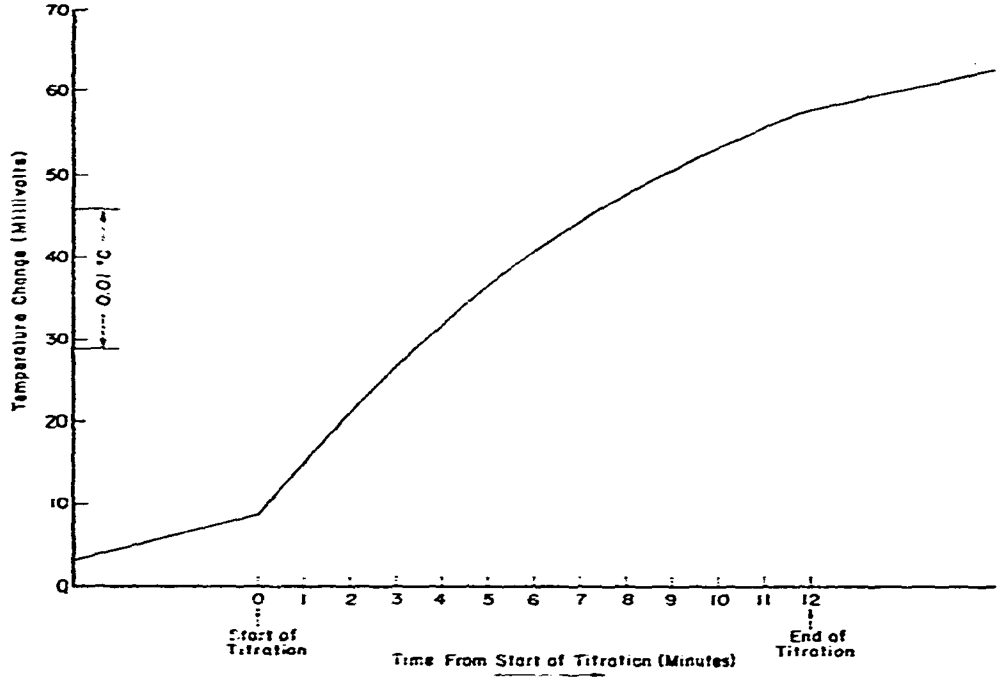

Fig. 7. Thermogram for the titration of *o*-bromo-aniline with $HClO_4$.

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*Material supplementary to this Article has been deposited as Document No. NAPS 01626 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave, New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC-NAPS.

†See Part II for definition of terms and symbols used in this paper.

respectively. Analysis of the thermogram gives the following values: $S_i = 1.283$ mV/min, $S_f = 1.176$ mV/min, $(T_x - T_t) = 0.300$ mV, $T_x = 8.60$ mV, $T_y = 57.60$ mV and the temperatures, T_p, at one minute intervals along the thermogram from x are 14.75, 21.00, 26.75, 31.95, 36.60, 40.70, 44.30, 47.60, 50.50, 53.10, and 55.45 mV. The time from x to y is 11.95 min.

Following the procedure outlined in the preceeding two papers, the experimental temperature rise values, T_p, must first be converted to heat values, Q_p, which in turn must be corrected for all heat effects other than that due to protonation of the *o*-bromo-aniline. For illustrative purposes these procedures will be carried out for the first data point, p = 1, corresponding to the end of the first one minute time interval. The change in temperature from x to p = 1 is $\Delta T = (14.75-8.60) \times (1/1502.9) = 0.00409\,^{\circ}\mathrm{C}$. During the first minute 0.513 ml of titrant is added increasing the heat capacity of the reaction vessel from 103.73 to 104.24 cal/°C. The heat produced from point x to point p is $Q_1 = -0.00409 \times 104.24 = -0.427$ cal*. The Q_1 value must be corrected for the heat effects due to non-chemical energy terms, Eqn. (25), the temperature difference between the titrant and titrate at point x, Eqn. (26), and the dilution of the titrant, Eqn. (27). To correct for the non-chemical energy terms from x to p, $q_{HL,x}$ and $q_{HL,y}$ must first be calculated by means of Eqns. (20) and (21). The resulting values are $-1.283 \times (1/1502.9) \times 103.73 = -0.088$ and $-1.176 \times (1/1502.9) \times (103.73 + 11.95 \times 0.5127 \times 0.99533) = -0.086$ cal/min, respectively. Using Eqn. (23), $Q_{HL,1}$ is then calculated to be $-0.088 + (-0.086 + 0.088) \times \frac{(14.75-8.60)}{46.85} = -0.088$ cal/min and the correction term $Q_{HL,1}$ is then calculated from Eqn. (25).

$$Q_{HL,1} = \frac{(-0.088-0.088)}{2} \times 1.0 = -0.088 \text{ cal.}$$

The heat correction term arising from the temperature difference between the titrant and titrate at point x is calculated from Eqn. (26).

$$Q_{TC,1} = 0.5127 \times 0.995 \times (0.300/1502.9) = 0.0001 \text{ cal.}$$

The corrections for dilution of the titrant solution can be made using ϕ_L values in the literature[60] and Eqn. (27). The ionic strength of the titrant is 0.1952 *M* and of the titrate at p_1 is $0.1952 \times 0.513/100.56 = 0.00997$ *M*. The corresponding ϕ_L values are 60.1 and 13.9 cal/mol, respectively. During the first minute time period $0.1952 \times 0.000513 = 0.000100$ moles of $HClO_4$ titrant was added to the titrate solution. The heat correction for dilution of the titrant is therefore

$$Q_{D,1} = 0.000100 \times (13.9 - 60.1) = -0.0005 \text{ cal.}$$

The corrected heat, $Q_{c,1}$, due only to protonation of the *o*-bromo-aniline is

$$Q_{c,1} = Q_1 - Q_{HL,1} - Q_{TC,1} - Q_{D,1} = -0.334 \text{ cal.}$$

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*See Part II, Eqn. (18) for calculation and explanation of the sign of *Q*. See Part II also for Eqns. (13)–(53).

$Q_{c,p}$ values can be calculated at each of the other 10 data points in an analogous manner. The complete array of values obtained is given in Table VIII.

TABLE VIII

TITRATION CALORIMETRIC DATA AND HEAT CORRECTIONS FOR THE TITRATION OF *o*-BROMO-ANILINE WITH $HClO_4$

Time (min)	Q_p *(cal)*	Q_{HL} *(cal)*	Q_{TC} *(cal)*	Q_D *(cal)*	Q_c *(cal)*
1.00	−0.427	−0.088	0.000	−0.005	−0.334
2.00	−0.864	−0.175	0.000	−0.008	−0.681
3.00	−1.270	−0.262	0.001	−0.011	−0.998
4.00	−1.643	−0.348	0.001	−0.014	−1.282
5.00	−1.980	−0.434	0.001	−0.016	−1.531
6.00	−2.281	−0.519	0.001	−0.018	−1.745
7.00	−2.549	−0.604	0.001	−0.019	−1.927
8.00	−2.797	−0.689	0.002	−0.021	−2.089
9.00	−3.020	−0.775	0.002	−0.022	−2.225
10.00	−3.228	−0.866	0.002	−0.023	−2.341
11.00	−3.409	−0.946	0.002	−0.024	−2.441

The Q_c values given in Table VIII are a function of the pK and ΔH values for proton ionization from the *o*-bromo-anilinium ion as shown by Eqn. (32). The pK and ΔH values which best describe the titration curve are found as outlined in Part II of this series by least squares analysis of the error square sum given in Eqn. (33). The first step in this procedure is the assumption of a pK value for *o*-bromo-aniline (in this example a first guess value of 2.76 will be used) and the calculation of the concentration of the various chemical species in the reaction vessel for each point p. The pK value is small enough that hydrolysis of A may be neglected and the expression for the hydrogen concentration, Eqn. (42), reduces to

$$[H^+] = \frac{-[1+K([A_T]-[H_T^+])]+\sqrt{[1+K([A_T]-[H_T^+])]^2+4K[H_T^+]}}{2K} \qquad (56)$$

The concentrations of *o*-bromo-aniline and of *o*-bromo-anilinium ion are calculated from Eqns. (57) and (58)

$$[A] = \frac{[A_T]}{(1+K[H^+])} \qquad (57)$$

$$[HA^+] = K[A][H^+] \qquad (58)$$

The moles of *o*-bromo-anilinium ion at each data point are then the product of $[HA^+]$ and the volume in the reaction vessel at that data point. The moles of *o*-bromo-anilinium ion formed at each data point are given in Table IX.

A ΔH value of 4.449 is calculated using Eqn. (49), the experimental Q_c values and the n_{HA} values given in Table IX. A Q_c value can then be calculated at each of the

TABLE IX

RESULTS OF CALCULATIONS TO DETERMINE K AND ΔH FROM TITRATION CALORIMETRIC DATA FOR THE IONIZATION OF *o*-BROMO-ANILINE

Time (min)	Q_c *(cal)* *Experimental*	*pK* *Assumed*	$n_{HA^+} = [HA^+]_p V_p$ *(mmole)*	ΔH *Calculated*	Q_c *(cal)* *Calculated*	$Q_{c_{exp}} - Q_{c_{calc.}}$ *(cal)*
1.00	−0.334	2.76	0.0789		−0.351	0.017
2.00	−0.681	2.76	0.1534		−0.682	0.001
3.00	−0.998	2.76	0.2226		−0.990	−0.008
4.00	−1.282	2.76	0.2859		−1.272	−0.010
5.00	−1.531	2.76	0.3425		−1.523	−0.008
6.00	−1.745	2.76	0.3921	4.449	−1.744	−0.001
7.00	−1.927	2.76	0.4347		−1.934	0.007
8.00	−2.089	2.76	0.4709		−2.095	0.006
9.00	−2.225	2.76	0.5012		−2.230	0.005
10.00	−2.341	2.76	0.5265		−2.342	0.001
11.00	−2.441	2.76	0.5476		−2.436	−0.005

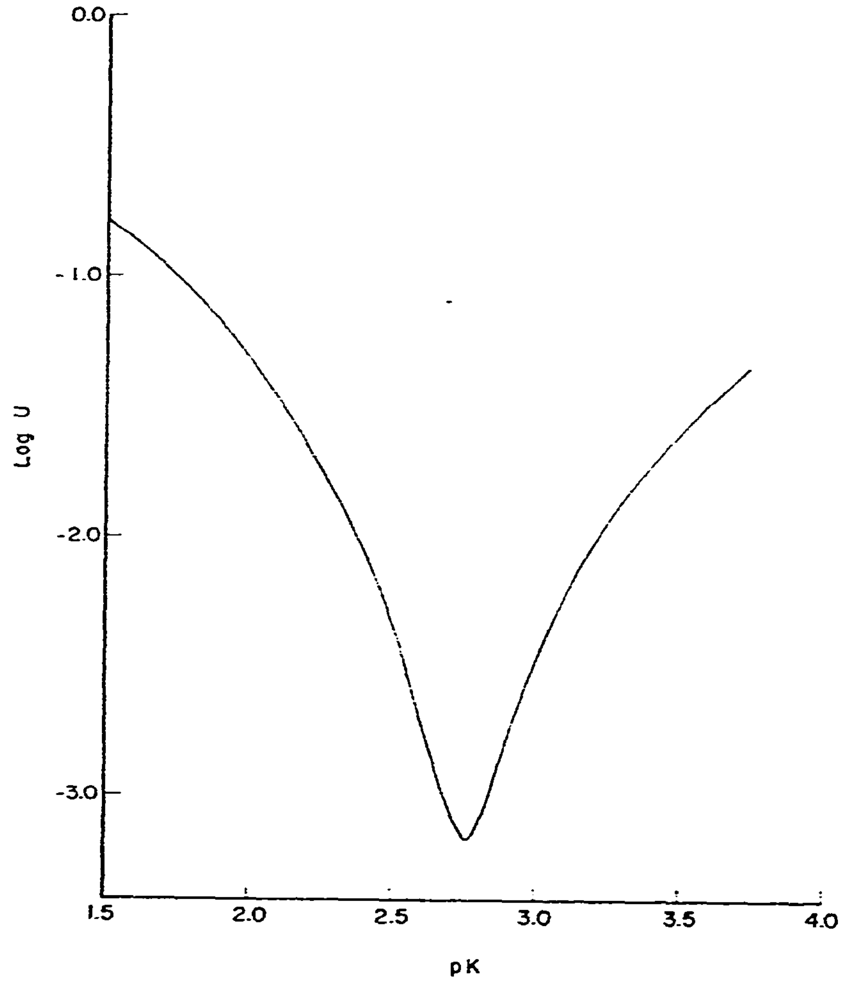

Fig. 8. Plot of assumed values of pK vs. log U for the titration of *o*-bromo-aniline with $HClO_4$.

data points using Eqn. (32) and compared with the experimentally measured Q_c value at that point. Table IX gives the results of such a calculation.

The error square sum, U [Eqn. (33)] gives an indication of how well the chosen p*K* value and corresponding calculated ΔH value describes the data. The p*K* value may be systematically varied until p*K* and ΔH values are found which give the minimum value of the error square sum and, therefore, best describe the experimental data. A plot of U *vs.* p*K* for the *o*-bromo-aniline illustration is given in Fig. 8. The minimum U value of $0.000664\ \text{cal}^2$ occurs at $pK = 2.76$. This corresponds to an average difference between the calculated Q_c values and experimental Q_c values of 0.008 cal, well under the estimated accuracy of the calorimeter of ± 0.01 cal.

Fig. 9 gives as a function of time a plot of the Q_c values and the corresponding species distribution calculated using a p*K* value of 2.76.

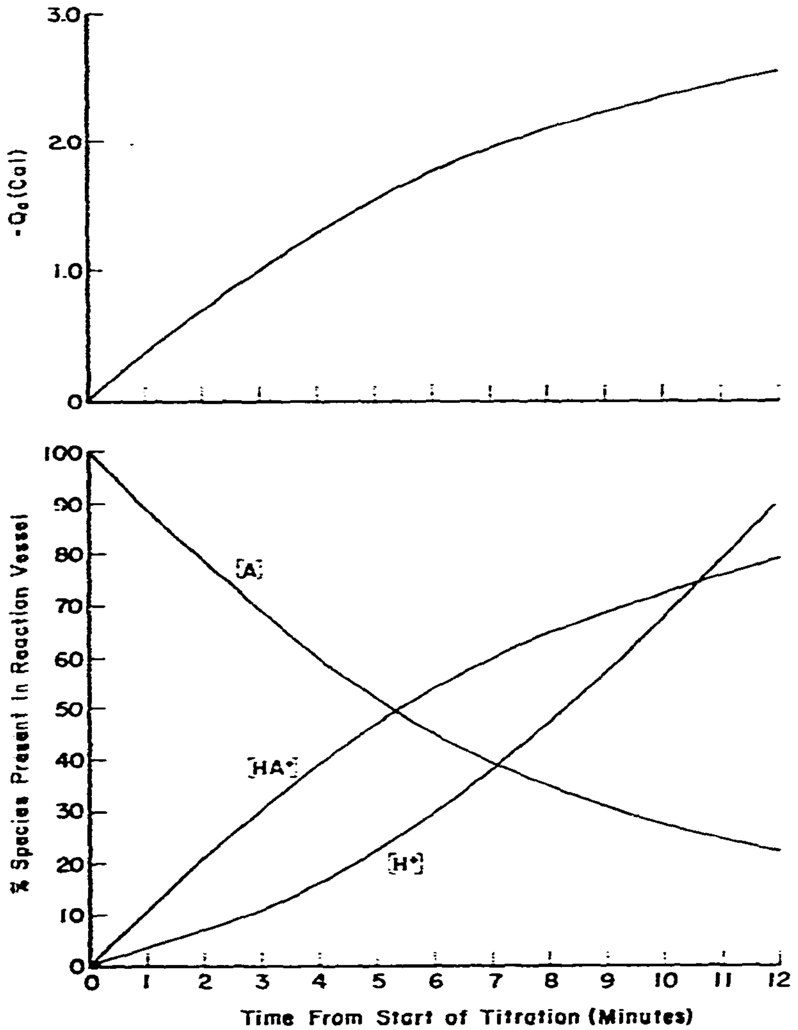

Fig. 9. Plots of Q_c values and species distribution as a function of time for the titration of *o*-bromo-aniline with $HClO_4$.

Four runs for the titration of *o*-bromo-aniline with $HClO_4$ were analyzed as outlined above, giving the thermodynamic values: $pK = 2.76 \pm 0.07$, $\Delta H = 4.43 \pm 0.07$ kcal/mole and $\Delta S = 2.4 \pm 0.2$ gibbs/mole, where the uncertainties are expressed as standard deviations. The value of the p*K* for *o*-bromo-aniline is in good agreement with the value determined by pH titration[69] and higher than that (2.53) determined spectrophotometrically[70].

The determination of K and ΔH values for a replacement reaction: The titration of imidazole with acetic acid

In the following example of a replacement reaction B and HB^+ refer to imidazole and its protonated ion, respectively and HA and A^- refer to acetic acid and the acetate anion, respectively. A replacement reaction can be thought of as consisting of two reactions as discussed in Part I under sections on Proton ionization: Extension to intermediate regions and Metal ion–ligand interactions in aqueous solution: Strong interactions. The competitive reaction in this example is

$$HA + B = HB^+ + A^- \tag{59}$$

which is comprised of the following two reactions.

$$HA = H^+ + A^- \tag{60}$$

$$H^+ + B = HB^+ \tag{61}$$

Reaction (59) is the reaction occuring in the reaction vessel and is the one for which thermodynamic values are determined by titration calorimetry. However since the *K* and ΔH values are known for reaction (60) the *K* and ΔH values for reaction (61) can be obtained by difference. The p*K* values of imidazole (7.0) and acetic acid (4.7) differ by 2.3 p*K* units which gives rise to competitive equilibria [Eqn. (59)] with the overall equilibrium constant ($\log K = 2.3$) within the required limit for equilibrium constant determination by means of titration calorimetry. The ΔH value for the replacement reaction is 8.8 kcal/mole. The *Q* values as a function of time (amount of titrant added) were calculated as outlined in the previous section from the calorimetric data reported by Ref. 71 for run 147 and are reported in Table X together with the other heat terms necessary to correct *Q* values to Q_c values. The heat corrections for the dilution of the titrant, including the dissociation of acetic acid and for the hydrolysis of imidazole at each data point were calculated as follows.

The concentration of the various species in solution were calculated using Eqns. (36)–(42) and a first guess value of 7.00 for the p*K* of imidazole. ϕ_L values for acetic acid as a function of ionic strength have been reported[60]. Since the reported ϕ_L values have not been corrected for the dissociation of acetic acid upon dilution, this correction was calculated from the difference between the moles of acetic acid at each data point and the moles present in a hypothetical diluted titrate before interaction with the imadazole. The corrections for hydrolysis of the imidazole,

$$B + H_2O = HB^+ + OH^-,$$

TABLE X

DATA AND RESULTS OF CALCULATIONS FOR THE DETERMINATION OF K AND ΔH FROM TITRATION CALORIMETRIC DATA FOR THE IONIZATION OF IMIDAZOLE

Time (min)	[a]*mmoles* HB^+	Q_p *(cal)*	Q_{HL} *(cal)*	Q_{TC} *(cal)*	Q_D *(cal)*	Q_{H_2O} *(cal)*	Q_{HAc} *(cal)*	Q_c *(cal) Experimental*	Q_c *(cal) Calculated*
1.120	0.0820	−0.762	−0.015	0.000	−0.003	−0.046	−0.001	−0.697	−0.721
2.120	0.1581	−1.412	−0.028	0.000	−0.004	−0.047	−0.002	−1.371	−1.390
3.120	0.2342	−2.131	−0.039	0.000	−0.005	−0.047	−0.002	−2.038	−2.058
4.120	0.3102	−2.825	−0.049	0.000	−0.006	−0.047	−0.003	−2.720	−2.727
5.120	0.3861	−3.498	−0.057	0.000	−0.007	−0.047	−0.004	−3.383	−3.394
6.120	0.4619	−4.176	−0.065	0.000	−0.008	−0.047	−0.005	−4.051	−4.060
7.120	0.5375	−4.848	−0.072	0.000	−0.009	−0.047	−0.005	−4.715	−4.724
8.120	0.6128	−5.531	−0.077	0.000	−0.010	−0.047	−0.006	−5.391	−5.386
9.120	0.6878	−6.200	−0.081	0.000	−0.012	−0.048	−0.007	−6.052	−6.046
10.120	0.7623	−6.859	−0.084	0.000	−0.013	−0.048	−0.008	−6.706	−6.701
11.120	0.8361	−7.505	−0.087	0.000	−0.014	−0.048	−0.008	−7.348	−7.349
12.120	0.9087	−8.148	−0.088	0.000	−0.015	−0.048	−0.009	−7.988	−7.987
13.120	0.9793	−8.784	−0.088	0.000	−0.017	−0.048	−0.010	−8.621	−8.608
14.120	1.0463	−9.375	−0.087	0.000	−0.018	−0.048	−0.010	−9.212	−9.197
15.120	1.1065	−9.894	−0.085	−0.001	−0.019	−0.048	−0.011	−9.730	−9.727
16.120	1.1546	−10.313	−0.082	−0.001	−0.021	−0.048	−0.012	−10.149	−10.149
17.120	1.1867	−10.590	−0.079	−0.001	−0.022	−0.048	−0.012	−10.428	−10.431
18.120	1.2054	−10.745	−0.076	−0.001	−0.024	−0.048	−0.012	−10.584	−10.595

[a] The mmoles HB^+ values were calculated using the value pK = 7.000. The resulting ΔH value from which the Q_p values were calculated is 8.790 kcal/mol. The data are those given in run 147 in Ref. 71. The data are for the titration of 0.099951 of 0.01251 F B with 0.2235 F HA. The titrant delivery rate is 0.0003413 l/min.

can be made by calculating the changes in hydroxide ion concentration. The initial concentration of hydroxide ion is calculated to be 0.00316 mmole. At the first data point (p = 1) there are 0.00013 mmole of hydroxide ion present. The correction at this point for hydrolysis is given by Eqn. (30) and has a value of

$$Q_{H_2O} = (0.00316-0.00013)(-13.35) = -0.046 \text{ cal.}$$

The ΔH value for ionization of water was taken from the literature[54]. Similarly corrections can be calculated at each data point in the titration.

Once all the Q_c values have been obtained, the ΔH value for the ionization process can be calculated using Eqn. (49). For the first guess pK value of 7.00, the calculated ΔH value is 8.790 kcal/mole. The best pK and ΔH values are found by varying the pK value until the minimum in the error square sum is found. For this run the minimum occurs at a pK value of 7.00. The variation in the error square sum with pK is given in Fig. 10 and a plot of the Q_c values and the corresponding species

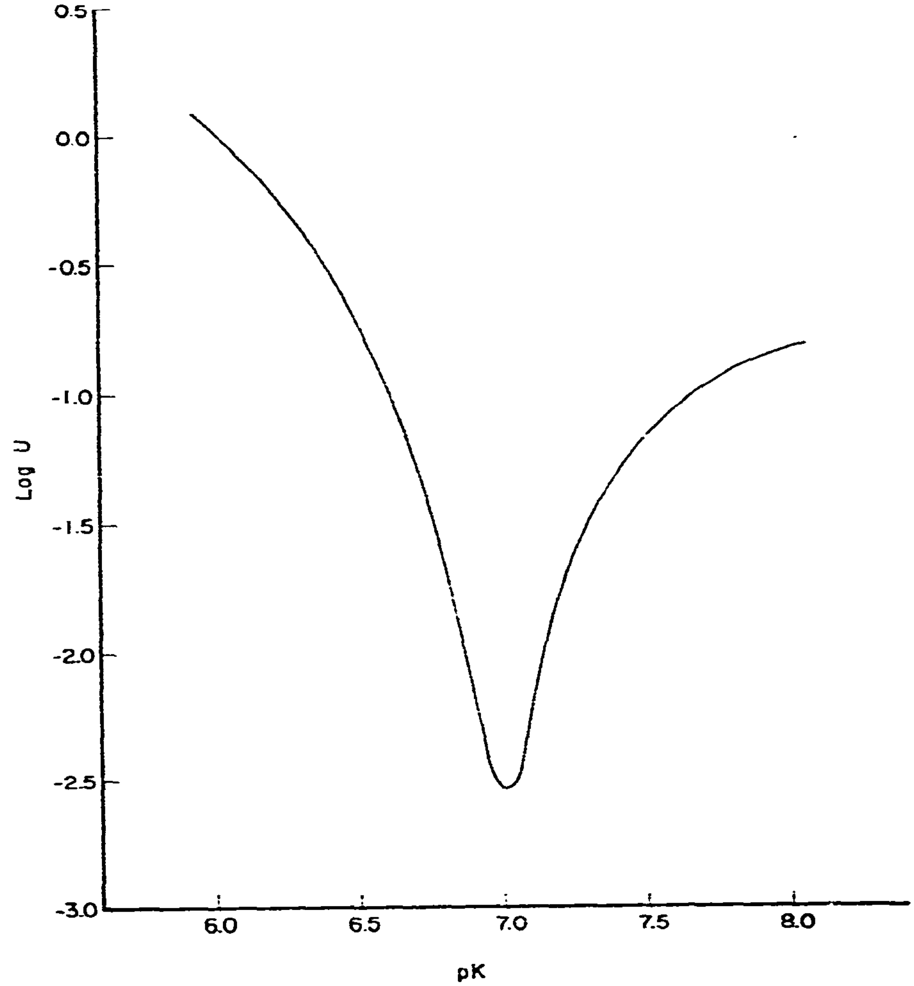

Fig. 10. Plot of assumed values of log U *vs.* pK for the titration of imidazole with acetic acid.

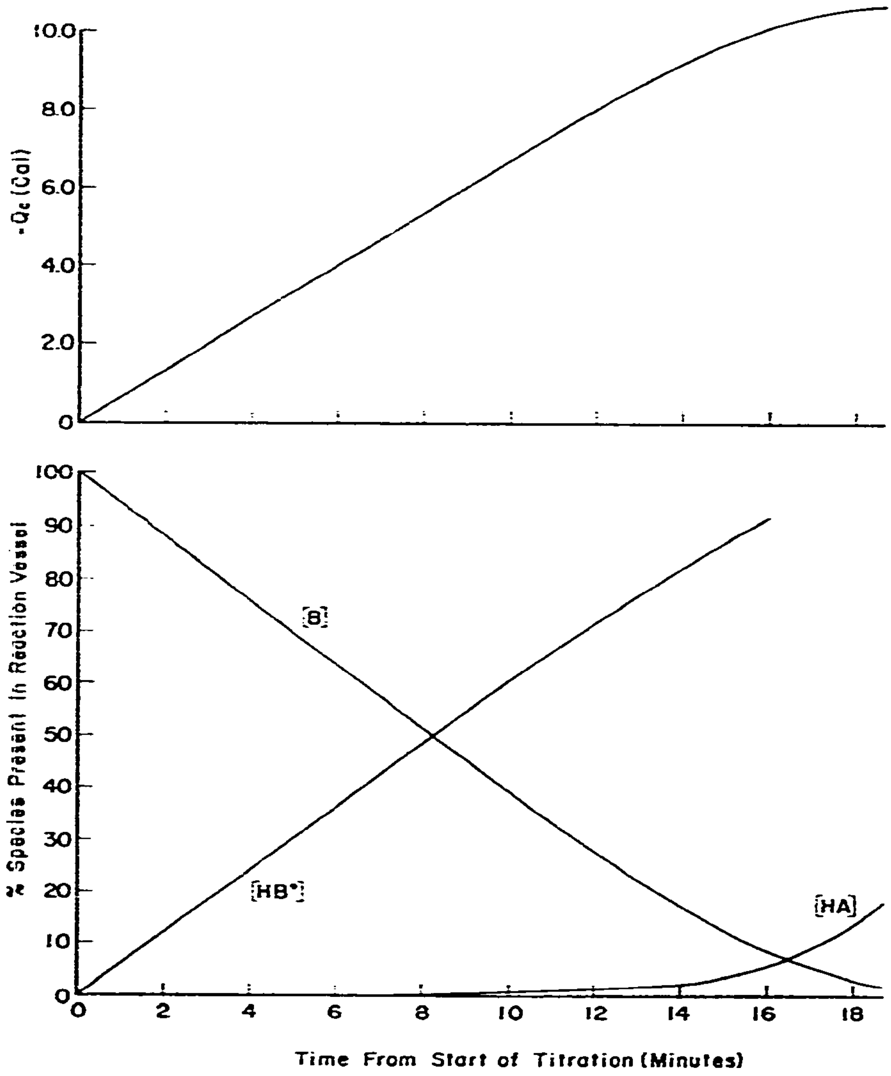

Fig. 11. Plot of Q_C values and species distribution as a function of time for the titration of imidazole with acetic acid.

distribution calculated using a p*K* value of 7.00 is given in Fig. 11. A total of seven runs were analyzed, and gave the following thermodynamic values for proton ionization from the imidazolinium ion: $pK = 7.00 \pm 0.02$, $\Delta H^0 = 8.80 \pm 0.02$ kcal/mol and $\Delta S = -2.52 \pm 0.06$ gibbs/mol, where the uncertainties are expressed as the standard deviation from the mean. These results indicate the high precision which can be obtained with the titration calorimeter procedure.

The determination of log K and ΔH values for a two step addition reaction: The titration of $Hg(CN)_2$ with thiourea

The system considered here is the stepwise interaction of thiourea, Tu, with $Hg(CN)_2$ to form $Hg(CN)_2$ Tu and $Hg(CN)_2$ Tu_2. The calorimetric data[72] can be

TABLE XI

DATA AND RESULTS OF CALCULATIONS FOR THE DETERMINATION OF K AND ΔH FROM TITRATION CALORIMETRIC DATA FOR THE STEPWISE INTERACTION OF THIOUREA WITH $Hg(CN)_2$

Time (*min*)	$[MA]/[M_T]^a$	$[MA_2]/[M_T]^a$	Q_p (*cal*)	Q_{HL} (*cal*)	Q_{TC} (*cal*)	Q_D (*cal*)	Q_c (*cal*) *Experimental*	Q_c (*cal*) *Calculated*
0.901	0.110	0.000	−0.34	−0.03	0.00	0.13	−0.44	−0.42
1.901	0.222	0.002	−0.70	−0.06	0.00	0.27	−0.91	−0.92
2.901	0.323	0.005	−1.06	−0.09	0.00	0.42	−1.39	−1.39
3.901	0.411	0.009	−1.41	−0.12	0.00	0.56	−1.85	−1.85
4.901	0.485	0.015	−1.75	−0.14	0.00	0.70	−2.31	−2.32
5.901	0.547	0.022	−2.08	−0.17	0.00	0.85	−2.76	−2.76
6.901	0.597	0.030	−2.40	−0.20	0.01	0.99	−3.20	−3.20
7.901	0.636	0.039	−2.70	−0.23	0.01	1.13	−3.61	−3.62
8.901	0.666	0.049	−3.00	−0.26	0.01	1.27	−4.02	−4.03
9.901	0.689	0.059	−3.29	−0.29	0.01	1.41	−4.42	−4.42
10.901	0.706	0.070	−3.56	−0.32	0.01	1.56	−4.81	−4.82
11.901	0.719	0.081	−3.82	−0.35	0.01	1.70	−5.18	−5.20
12.901	0.727	0.091	−4.07	−0.38	0.01	1.84	−5.54	−5.53
13.901	0.733	0.102	−4.30	−0.40	0.01	1.98	−5.89	−5.88
14.901	0.737	0.113	−4.53	−0.43	0.01	2.12	−6.23	−6.22
15.901	0.738	0.124	−4.75	−0.46	0.01	2.26	−6.56	−6.56
16.901	0.738	0.135	−4.96	−0.49	0.01	2.40	−6.88	−6.89
17.901	0.739	0.145	−5.14	−0.52	0.02	2.54	−7.18	−7.18

[a] The concentration ratios were calculated using the values $\log \beta_1 = 2.074$ and $\log \beta_2 = 2.644$. The data[72] are for the titration of 0.09999 l of 0.03010 *F* $Hg(CN)_2$ with 1.422 *F* thiourea. The titrant delivery rate is 0.005688 ml/sec.

converted to Q_c values as previously outlined. Heat of dilution data have been reported[72]. The pK value, 2.03, for protonation of the thiourea molecule[73] is small enough that hydrolysis may be neglected. The Q_c values and calculated correction terms are given in Table XI. A set of β_1 and β_2 values are assumed and the species in solution are calculated using Eqns. (44)–(47). The determination of the β and ΔH values which best describe the thermometric titration curve is complicated by the presence of two simultaneous equilibria; however, the details of the procedure are similar to those for the study of a single equilibria. Using the β_1 and β_2 values previously assumed for calculating the species in solution ΔH_1 and ΔH_2 are calculated from Eqns. (51) and (52) and the magnitude of the error square sum calculated from Eqn. (33). Repeatedly new β_1 and β_2 values are chosen and concentrations of species in solution and ΔH_1 and ΔH_2 values are calculated until the β_1, β_2, ΔH_1 and ΔH_2 values are found which give the minimum value for the error square sum.

The minimum error square sum for the data occurs at $\log \beta_1 = 2.074$ and $\log \beta_2 = 2.644$. The schematic map of $U(K_i, \Delta H_i)$ *vs.* $\log K_1$ with $\log K_2$ as a second parameter is given in Fig. 12. The corresponding ΔH values are -1.279 and -9.957 kcal/mole, respectively. A plot of the Q_c values and the corresponding species distribution calculated using $\log \beta_1 = 2.074$ and $\log \beta_2 = 2.644$ are given in Fig. 13.

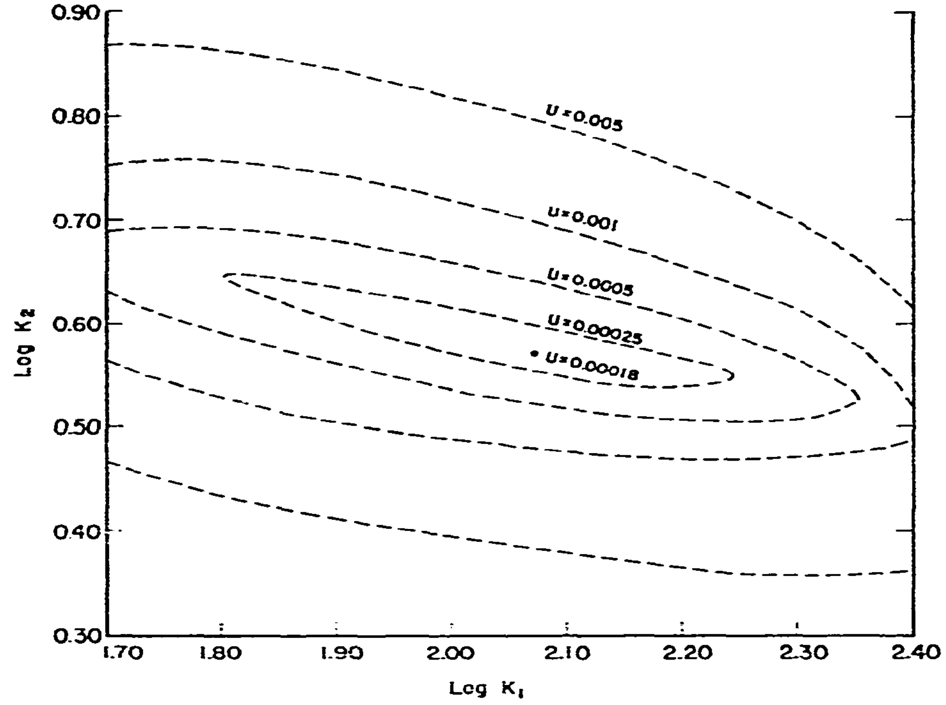

Fig. 12. Plot of assumed values of K_1 and K_2 *vs.* U for the titration of $Hg(CN)_2$ with thiourea.

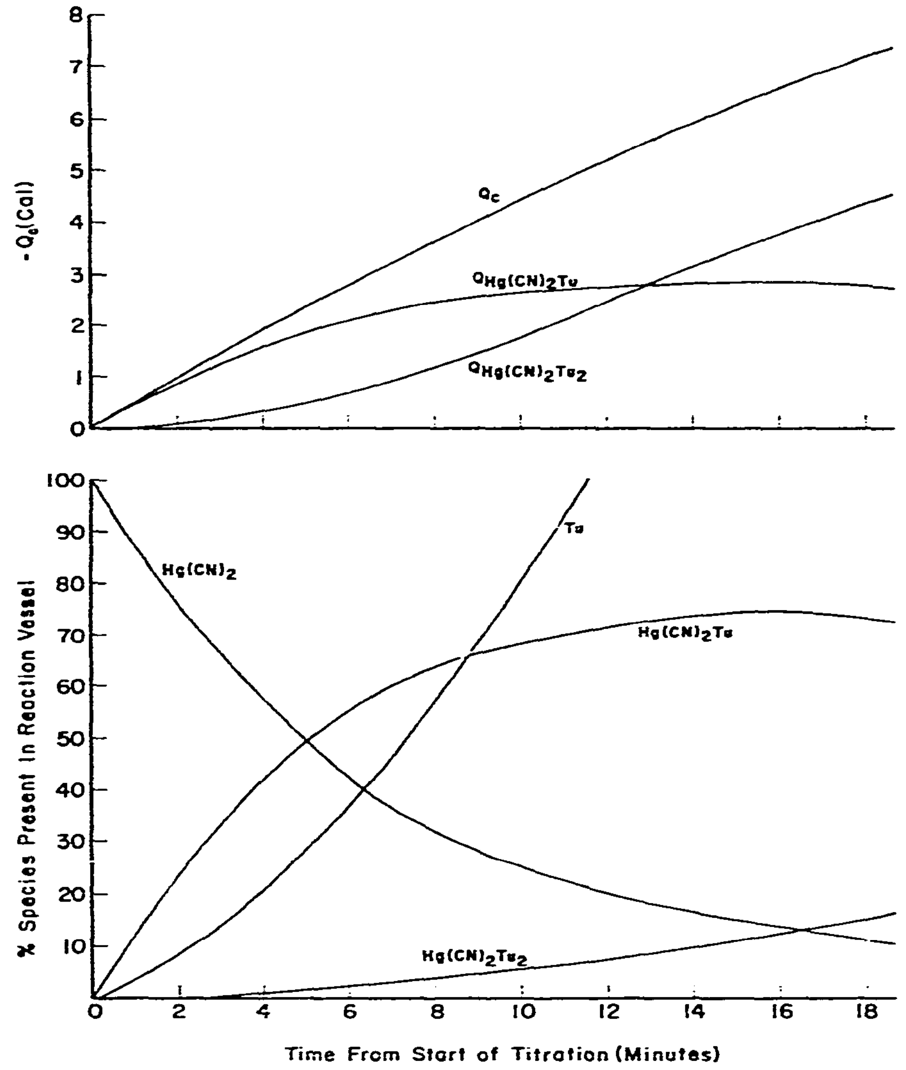

Fig. 13. Plot of Q_C values and species distribution as a function of time for the titration of $Hg(CN)_2$ with Tu.

Summary

The determination of equilibrium constants and enthalpy change values from titration calorimetry data has been demonstrated for three chemical systems. It has been shown how, starting with the calorimetric data, the computational methods outlined in the previous papers of this series can be used to calculate the heat, Q_c, produced, due to the reaction(s) of interest and from these Q_c values the K and ΔH values can be calculated for the interactions occurring in the calorimeter. Sources of computer programs used in the calculations have been given.

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