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V. MISCELLANEOUS

COMPUTER CALCULATION OF STEPWISE STABILITY CONSTANTS AND HEAT CHANGES FROM CALORIMETRIC DATA: SYSTEM SILVER(I)-PYRIDINE

P. PAOLETTI, A. VACCA AND D. ARENARE

Istituto di Chimica Generale dell'Università, Via J. Nardi 39, Firenze (Italy)

This communication reports on a general direct calorimetric method for the determination of stepwise stability constants and enthalpies of formation of complexes. A few studies based on related methods have been reported by others[1,2].

Our method differs from these works in both method of calculation and calorimetric technique. Indeed we have used a simple calorimeter instead of the commonly employed titration apparatus. This method has been successfully applied to the stepwise equilibrium:

$$Ag^+ + py \rightleftarrows Agpy^+$$
$$Ag^+ + 2py \rightleftarrows Agpy_2{}^+$$

If ΔH_1 and ΔH_{1-2} are the enthalpies of formation of complexes $Agpy^+$ and $Agpy_2{}^+$ from the aqueous solutions of the reagents, the heat calculated for each experiment is given by equation:

$$Q_{calc} = -V\{[Agpy^+]\Delta H_1 + [Agpy_2{}^+]\Delta H_{1-2}\} \quad (1)$$

where V is the volume of the solution and the terms between parentheses are the concentrations of complexes formed. These values may be calculated from the concentrations of the reagents provided that the formation constants β are known. Also partial hydrolysis of the pyridine in aqueous solution

$$py + H_2O \rightleftarrows pyH^+ + OH^-$$

must be accounted for, and the mass balance equations are:

$$\begin{aligned} [H^+]_{tot} &= [H^+] + K_b[H^+][py] - K_w[H^+]^{-1} \\ [py]_{tot} &= [py] + K_b[H^+][py] + \beta_1[Ag^+][py] + 2\beta_2[Ag^+][py]^2 \quad (2) \\ [Ag^+]_{tot} &= [Ag^+] + \beta_1[Ag^+][py] + \beta_2[Ag^+][py]^2 \end{aligned}$$

From a series of calorimetric data Q_{exp}, values of the two enthalpies are calculated. As a consequence of the experimental errors, in each measurement the difference function $S = Q_{calc} - Q_{exp}$ differs from zero. The value of S depends on several factors which include the values of β used. It may be shown that in a homogeneous series of measurements the sum of difference functions squared $U = \Sigma S^2$ is a function of the constants of formation only. This fact provides the basis of calorimetrical determination of the formation constants. The best pair of values of β_1 and β_2 is that which minimizes U.

COMPUTER PROGRAM

We have applied in this case the calculation method of "pit mapping", proposed by Sillén[3]. An appropriate Fortran program for the IBM 1620 computer has been written which is shown in simple block form in Fig. 1. With BETA the computer is furnished a set of approximate constants β_1 and β_2, with values of K_b and K_w taken from the literature[4,5]. In DATA, the computer is furnished the following quantities for the first measurement: the number of moles of reagents present in the calorimeter, the volume of the solution before and after the reaction and the heat evolved Q_{exp}.

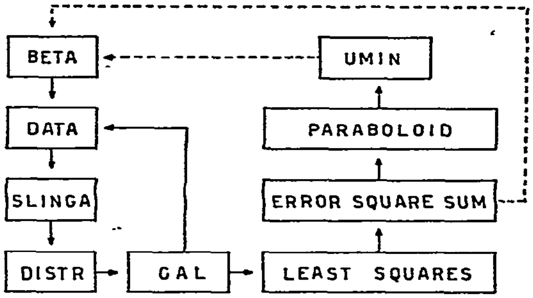

Fig. 1. Block diagram of the computer program.

In SLINGA the concentration of hydrogen ion, free metal ion and free ligand before and after the reaction are calculated by trial and error via successive approximations (eqn. 2).

The block SLINGA has been translated, with some modifications into Fortran from the analogous block of the Algol program "Letagrop"[3].

The number of moles of species pyH^+, OH^-, $Agpy^+$ and $Agpy_2{}^+$ present before and after the reaction are calculated in DISTR. In CAL the total heat is corrected for the thermal effect of the hydrolysis reactions calculated from the heats of the two reactions[6,7]

$$pyH^+ \rightleftarrows py + H^+$$

$$H^+ + OH^- \rightleftarrows H_2O$$

Really this correction was small for all measurements. At this point one returns to DATA, where the related data for another measurement are read. The described procedure is repeated for all measurements.

Next, the system of m linear equations, of type (1), in the two unknowns ΔH_1 and ΔH_{1-2} is entered in the block LEAST SQUARES

$$x_{j1}\Delta H_1 + x_{j2}\Delta H_{1-2} = -Q_{\mathrm{cor}\,j} \qquad (j = 1, 2, \ldots m)$$

x_{j1} and x_{j2} are the numbers of moles of complexes Agpy^+ and $\mathrm{Agpy_2}^+$ formed in the jth measurement and calculated in DISTR. $Q_{\mathrm{cor}\,j}$ is the corrected heat.

This system of equations may be written in a matrix form

$$\mathbf{X}H = Q$$

where $\mathbf{X}$ is the rectangular matrix $m \times 2$ of the coefficients x_{j1} and x_{j2}: H is the vector of the unknowns ΔH_1 and ΔH_{1-2}, and Q is a vector consisting from m known terms $-Q_{\mathrm{cor}\,j}$.

Applying the method of least squares one obtains

$$\mathbf{X}^T\mathbf{X}H = \mathbf{X}^T Q$$

where $\mathbf{X}^T$ is the transposed matrix of $\mathbf{X}$; $\mathbf{X}^T\mathbf{X}$ is a square matrix 2×2 and $\mathbf{X}^T Q$ is a two terms vector. The unknowns H are calculated by inversion of the matrix $\mathbf{X}^T\mathbf{X}$

$$H = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T Q$$

With the values of ΔH_1 and ΔH_{1-2} calculated one computes, in the block ERROR SQUARE SUM, the value of the error square sum U

$$U = \sum_{j=1}^{m} S_j^2 = \sum_{j=1}^{m} (x_{j1}\Delta H_1 + x_{j2}\Delta H_{1-2} + Q_{\mathrm{cor}\,j})^2$$

and the standard deviations of ΔH_1 and ΔH_{1-2} by external consistency[8] via

$$\sigma_{\Delta H_i} = [\mathrm{I}_{ii}U/(m-2)]^{\frac{1}{2}} \qquad i = 1, 2$$

where I_{11} and I_{22} are the diagonal terms of the inverse matrix $(\mathbf{X}^T\mathbf{X})^{-1}$.

At this point the constants are modified and one returns to the block BETA. The procedure described above is repeated with the new values of β.

This method enables, via successive approximations, the determination of the region with the lowest values of U, even if initial constants are considerably in error. We may assume, as Sillèn has done, that in the neighborhood of the minimum, U is approximately a second degree function (specifically an elliptical paraboloid) of β_1 and β_2.

It is now sufficient to evaluate the function U for six different pairs of β in order to determine the six coefficients of the equation for a paraboloid

$$U = A + B\beta_1 + C\beta_2 + D\beta_1^2 + E\beta_2^2 + F\beta_1\beta_2$$

This portion of the calculation proceeds in the block PARABOLOID.

Differentiating this equation with respect to the variables β_1 and β_2 and setting the derivative equal to zero, one calculates in UMIN, the coordinates β_1' and β_2' of the minimum of the surface, the value of U at this point $U_{\min}$ and the standard deviations of β_1 and β_2.

From these values and their variations six other values of U may be calculated, and thus the coordinates of a new minimum β_1'' and β_2'', and consequently a new value of U_{min} are obtained. The latter values do not agree with those calculated in the preceding cycle since the function U contains terms of order higher than two which are neglected. In any case three cycles were sufficient to reach converging values of β_1, β_2 and $U_{\min}$.

RESULTS AND DISCUSSION

The number of moles of reagents present in the calorimeter and the heat evolved for each measurement, Q_{exp}, are reported in Table I. Table II shows values of U, ΔH_1 and ΔH_{1-2} for various pairs of log β_1 and log β_2. As may be observed from Table II, after a certain number of cycles we have rejected those measurements (Table I, Nos. 7, 9, 14, 24) where the error S was greater than three times the estimated error in calorimetric measurement (0.1 cal.). Fig. 2 shows some sections of the paraboloid in the vicinity of the minimum. In particular the section shown in solid line represents the D-boundary from which are estimated[3] also the standard deviations of the constants. We established that inside this boundary all the points determined lie accurately on the surface of the calculated paraboloid. Table III shows the values of the constants, the enthalpy and entropy changes, at 25.0° in 0.5 M potassium nitrate, relative to the equilibria of formation of the

TABLE I

CALORIMETRIC DATA*

No.	*$AgNO_3$ (moles · 10^{-3})*	*Pyridine (moles · 10^{-3})*	*Q (cal.)*	*No.*	*$AgNO_3$ (moles · 10^{-3})*	*Pyridine (moles · 10^{-3})*	*Q (cal.)*
1	4.1604	33.0991	45.54	13	3.7221	11.0578	34.63
2	4.1585	33.0974	45.65	14	3.7440	11.0909	35.35
3	4.1581	33.1016	45.87	15	3.8003	11.0911	35.34
4	4.0297	25.2344	43.57	16	4.0197	8.8910	32.41
5	4.0337	25.6848	43.89	17	4.0585	8.9251	32.93
6	3.9830	19.7697	42.09	18	4.0282	6.7766	26.21
7	4.0352	19.7414	43.15	19	4.0303	6.9041	26.86
8	3.9917	17.2156	41.53	20**	3.6764	4.9383	19.23
9	4.0273	17.0426	41.48	21**	3.6772	4.9379	19.33
10	4.0143	14.1345	39.85	22**	3.6819	4.9385	19.16
11	4.0259	14.1330	40.14	23**	3.6340	4.9383	19.22
12	3.7225	11.0631	34.90	24**	3.6762	4.9380	19.54

* The total volume of the resulting solution was 165.3 cm^3.

** Nitric acid buffer ($4.2 \cdot 10^{-6}$ moles) was used to prevent the precipitation of silver oxide.

TABLE II

SOME REPRESENTATIVE VALUES FOR CALCULATION OF THE CONSTANTS

log β_1	*log* β_2	$-\Delta H_1$ *(kcal/mole)*	$-\Delta H_{1-2}$ *(kcal/mole)*	*U* *(cal²)*
1.970	4.22	4.09	11.20	2.105
2.040	4.22	4.24	11.27	1.310
2.110	4.150	4.78	11.44	1.119
2.110	4.22	4.38	11.35	0.904
2.080	4.180	4.57	11.36	0.865
2.040	4.150	4.67	11.35	0.857
2.018	4.135	4.75	11.33	0.872
2.019	4.127	4.80	11.35	0.838
2.019	4.127	4.76	11.34	0.266*
2.010	4.117	4.81	11.34	0.265*
2.017	4.117	4.82	11.35	0.267*
2.010	4.107	4.87	11.35	0.272*
2.004	4.107	4.87	11.34	0.266*
2.005	4.113	4.84	11.34	0.264*

* Calculations based on twenty measurements only.

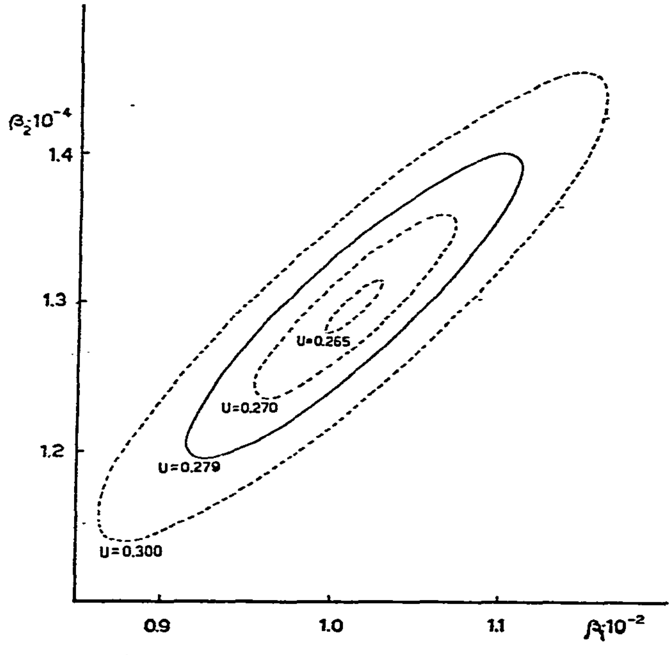

Fig. 2. Schematic map of the paraboloid.

complexes Agpy$^+$ and Agpy$_2$$^+$, together with the calculated standard deviations.

The agreement between the calculated values of stability constants and those determined potentiometrically at the same ionic strength and temperature[4] is very good.

TABLE III

THERMODYNAMIC FUNCTIONS FOR THE EQUILIBRIA: $Ag^{+}+xL = AgL_x^{+}$

Reaction	*log K*	$-\Delta F$ *(kcal/mole)*	$-\Delta H$ *(kcal/mole)*	$-\Delta S$ *(e.u.)*
$Ag^{+}+py \rightleftarrows Agpy^{+}$	2.00 ± 0.04	2.73 ± 0.05	4.83 ± 0.05	7.0 ± 0.3
$Agpy^{+}+py \rightleftarrows Agpy_2^{+}$	2.11 ± 0.08	2.88 ± 0.10	6.51 ± 0.06	12.2 ± 0.5
$Ag^{+}+2py \rightleftarrows Agpy_2^{+}$	4.11 ± 0.04	5.61 ± 0.05	11.34 ± 0.01	19.2 ± 0.2

It may be observed that the value of $-\Delta H_2$ is larger than $-\Delta H_1$. This trend is not common in the stepwise formation of complexes. However this tendency is evident in the case of complexes of manganese(II) with ethylenediamine[9].

The decreasing trend of entropies of formation is sufficiently regular, especially since it is always found that the initially positive entropy becomes increasingly negative with successive steps. With silver(I), however, the value of ΔS is already negative for the monocomplex. In conclusion, one may thus state that it is the enthalpy term which determines the trend of successive formation constants, while the entropy influences the stability of successive complexes negatively.

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