Entropy Titration. A Calorimetric Method for the Determination of $\Delta G°$ (K), $\Delta H°$ and $\Delta S°$ [1]

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THE thermodynamic values $\Delta G°$, $\Delta H°$, and $\Delta S°$ can be determined for a reaction in aqueous media from a single thermometric titration calorimetry experiment. The method is applicable for a

reaction or combination of reactions in which the equilibrium constant (K) is less than approximately 10^3, and has an appreciable ΔH value. Under these conditions the thermometric titration curve will be a function of both the overall heat of reaction and the overall equilibrium constant. That function is described for the idealized reaction, Reactants (R) + Titrant (T) = Products (P), by equations 1—4 which contain ΔH, K, and the various reaction variables. It is assumed that the solution present initially in the calorimeter contains only reactants (R).

$$Q_c = \Delta H[P]V \tag{1}$$

$$K = [P]\gamma_P/[R]\gamma_R\,[T]\gamma_T \tag{2}$$

$$[R_t] = [R] + [P] \tag{3}$$

$$[T_t] = [T] + [P] \tag{4}$$

where Q_c is the energy produced by the reaction, i.e., the total heat produced corrected for heat losses, heats of dilution, etc.; the [R], [T], and [P] concentrations of R_t, T_t, and P, respectively in the calorimeter; R and T the total concentrations of R and T, respectively, in the calorimeter; V = the volume of solution in the calorimeter; and γ = activity coefficient.

Simultaneous solution of equations 1—4 results in equation 5 which, since the γ values are a function of the ionic strength, μ, which is in turn a function of K, includes only two unknowns, ΔH and K.

Self-consistency between K, μ, and γ values is obtained by using K to calculate the concentrations of the species present which are then used to calculate new μ and γ values. These μ and γ values are then used to calculate a better K value, and the process repeated until successive K values agree to within 0·1%. The calculations are aided by use of an IBM 7040 computer.

This procedure requires accurate calorimetric data. A thermometric titration apparatus having accuracy comparable to that of a conventional solution calorimeter has been designed and constructed[2] to obtain these data. Using this apparatus, the heat of ionization of water was determined to ±0·2%, the value obtained, 13·34 kcal./mole, being identical with that reported previously.[3,4]

The method was tested on the reactions [approximate values for log$K$ and ΔH (kcal./mole), respectively, given in parentheses] $H^+ + SO_4^{2-} = HSO_4^-$ (2·0, 5·2) and $HPO_4^{2-} + OH^- = PO_4^{3-} + H_2O$ (1·6, −9). In the first reaction several solutions of sodium sulphate were titrated with perchloric acid. The second reaction illustrates how, by proper selection of titrant, in this case, sodium hydroxide, the method has general applicability provided the overall values of K and ΔH are of the correct magnitude.

The agreement of the thermodynamic quantities calculated from the thermometric titration calorimetry curves with those given in the literature is

$$\frac{\Delta H}{K} = \left(V\,[T_t][R_t]\,\frac{\gamma_R\,\gamma_T}{\gamma_P\,Q_c} \right)\left(\Delta H \right)^2 - \left\{ \left([T_t] + [R_t] \right)\left(\frac{\gamma_R\,\gamma_T}{\gamma_P} \right) \right\}\,\Delta H + \left(Q_c\,\frac{\gamma_R\,\gamma_T}{\gamma_P V} \right) \tag{5}$$

or

$$\Delta H/K = A(\Delta H)^2 + B\Delta H + C \tag{6}$$

Since $\Delta H/K$ has the same value at any point on the titration curve equation 6 can in principle be solved for ΔH by combining any two points on the curve, giving

seen in the Table to be good. The estimated uncertainty of the pK values is ±0·03 unit, and that of the $\Delta H°$ values, ±0·2 kcal./mole.

This method for determining pK and ΔH

$$(A_2 - A_1)\,(\Delta H)^2 + (B_2 - B_1)\,\Delta H + (C_2 - C_1) = 0 \tag{7}$$

Having determined ΔH, $K(\Delta G)$ can be obtained from equation 6 and ΔS calculated from the relationship $\Delta S = (\Delta H - \Delta G)/T$.

simultaneously should have wide applicability in both aqueous and nonaqueous solvents, especially to very weak and very strong acids in aqueous

[1] Supported by the U.S. Atomic Energy Commission and National Institutes of Health. Presented at the 19th Calorimetry Conference, Washington, D.C., October, 1964.
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pK, ΔH°, and ΔS° values for the indicated reactions in aqueous solution at 25°

Reaction	pK	$\Delta H°$ (kcal./mole)	$\Delta S°$ (e.u.)
$HSO_4^- = H^+ + SO_4^{2-}$	1·90	−5·6	−27
	(1·98)[5,6]	(−5·2)[5,6]	
$HPO_4^{2-} + OH^- = PO_4^{3-} + H_2O$	−1·61	−9·0	−23
	(−1·625)[7]		

solution where the pK values are difficult to measure accurately with methods presently available.