Enthalpy Titrations with Temperature Adjustment

KURT SCHLYTER and
LARS GUNNAR SILLÉN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

With the revival of interest in complicated solution equilibria in the last two decades, a considerable amount of data has been collected about systems with several species formed (step-wise complex formation, polynuclear complexes) [1]. In many systems, there is very good evidence for the formulas of the species formed; the equilibrium constants of their formation, and thus the ΔG's of the reactions, are moreover known with a fair accuracy. In order to get a better understanding of such reactions, it would be desirable to break up the ΔG's into their ΔH and ΔS parts; many attempts have been made to calculate these from the variation of equilibrium constants with temperature. However, with the accuracy at present obtainable in systems with several species, and the limited temperature range available, the data of different careful workers very often disagree, even as to the sign of the quantities [2].

One might hope to get much better values for ΔH with a calorimeter, even of moderate accuracy. The traditional way of mixing two solutions, T and S, containing the reagents, would be keeping solution S and solution T in a sealed tube, in a calorimeter, until they have the same temperature, then mixing the solutions by breaking the tube with T and measuring the change of temperature. If only one reaction occurs, its ΔH may be obtained from the average of a relatively small number of such measurements.

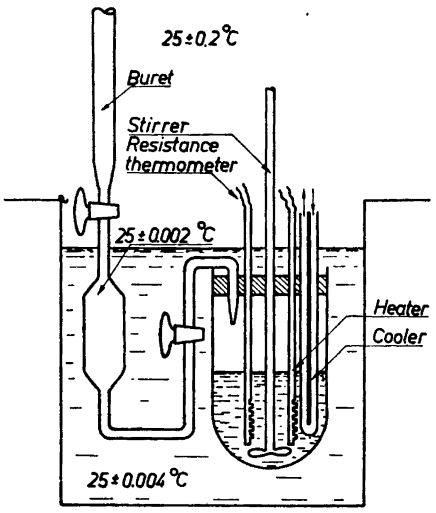

Fig. 1. Principle of calorimeter.

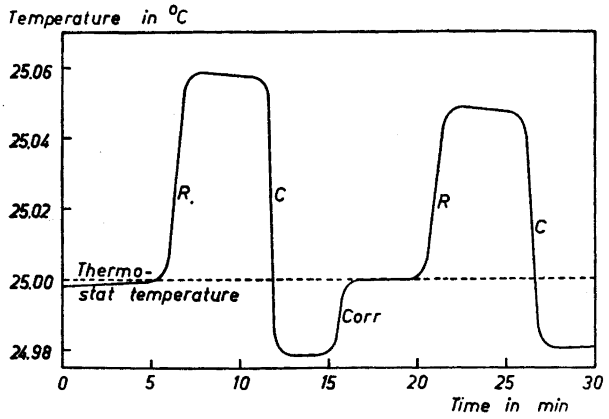

Fig. 2. Temperature history of part of a titration: R = reaction heat evolved; C=cooling applied; corr = temperature corrected by means of heater *etc.*

If, on the other hand, several reactions must be considered simultaneously, a much larger number of experiments of this type, varying the concentrations of both the reactants, would be needed and the method would become rather laborious and time-consuming.

We would suggest, for ΔH work, a titration technique which might give similar advantages over "point measurements" as does the titration technique introduced by Leden [3] for determining equilibrium constants: a much larger number of data for a given amount of time and labor, and a better check for small analytical errors.

It would, however, not be perfectly satisfactory to keep S in a calorimeter, and T in a buret (albeit thermostated), to add T portion-wise to S and measure the temperature in S after each addition. The temperature in S would naturally change during the reactions, so that one would have to make an increasing correction for the temperature difference between T and S. Moreover, the temperature in S might finally drift several degrees from the original one, say 25.0°C. Even if one knows the equilibrium constants for the various reactions at 25.0°C, the constants would now be different, which one would have to consider in the calculations.

These considerations have led us to try another simple device which we think has not been described before. The main parts are shown in Fig. 1, and a typical temperature history during the titration in Fig. 2.

The apparatus is kept in a thermostated room of approximately the standard temperature desired, 25.0°C. The upper part of the buret with solution T is thus air-thermostated. From the buret, T passes through a bulb, which is immersed in a water thermostat which keeps the temperature more accurately, and which also contains the calorimeter with S. The calorimeter is, as usual, provided with a thermometer and an electric heater, used for calibration. The unusual feature is a cooler of thin glass tubing, through which cool air may be blown; heat is then conducted away from the solution through the tube wall to the air. The temperature of S may be adjusted with any reasonable accuracy to equal the standard temperature of the thermostat bath and T; in practice, the final adjustment is best made with the heater, so the cooler is applied to produce a temperature somewhat below the standard one, after which the heat is applied.

The temperature history of the solution S will be as is seen in Fig. 2. Before each addition, the temperature in S is made equal to that in T; the addition is made, the temperature rise is recorded, and then the temperature of S is again brought back to the standard.

In this way, there will be practically no correction for temperature difference between S and T, and the temperature in S, even after an addition, may be kept within, say, 0.1° from the standard so that the equilibrium constants for the standard temperature may be used in the calculations.

An apparatus has been constructed according to these principles by one of us (K.S.) and is now being used to study a number of equilibrium systems. The main advantage is the increased speed of working, and the accuracy is quite satisfactory. A detailed description of the apparatus will appear elsewhere [4].

This work has been supported by *Statens Tekniska Forskningsråd (Swedish Technical Research Council)* and *Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council)*.

1. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Tables of stability constants, Chem. Soc. Spec. Publ.* **6** (1957) and **7** (1958).
2. Sillén, L. G. *J. Inorg. & Nuclear Chem. 8* (1958) 176.
3. Leden, I. *Z. physik. Chem.* **188 A** (1941) 160.
4. Schlyter, K. *Trans. Roy. Inst. Technol. Stockholm* (1959) no. 132 (=Chem. 2).

Received January 21, 1959.

The Occurrence of Endocrocin in *Penicillium islandicum*

STEN GATENBECK

Institute of Biochemistry, University of Lund, Lund, Sweden

Earlier investigations of the biogenesis of polyhydroxyanthraquinones have shown that the anthraquinone molecule originates from acetate through head to tail couplings of acetate units. As discussed in another paper the experiments with labelled acetate as substrate do not explain the formation of the ring system since the intramolecular