

# Solution Calorimetry in the Advanced Laboratory

## A Study of Glycine Proton-Transfer Enthalpies

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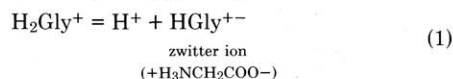
Heat effects accompanying chemical reactions are among the most fundamental and informative phenomena encountered by chemists, both in the classroom and in the laboratory. Yet, except for numerous general chemistry experiments, typically involving expanded-polystyrene-cup reaction vessels and relatively insensitive thermometers, students gain little experience with solution calorimetry. A major reason for this in the past has been the unavailability of reliable calorimetric equipment that is both reasonable in cost and high in accuracy. The introduction of a moderately priced solution calorimeter (1) has made it convenient to use this technique in the advanced laboratory. In our experience over a few years, the Parr Model 1451 calorimeter has performed reliably and in accord with its high specifications. The experiment described in this paper requires precise measurement of temperature changes of a few tenths of a degree. The Model 1451 generates a voltage output with a sensitivity of 100 mV per degree, and a strip chart recorder provides a convenient record.

In addition to a variety of acid-base reactions we have used powdered zinc metal in the rotating glass cell with copper perchlorate solution in the Dewar flask to determine the enthalpy change for the redox reaction. We have also measured the heat of complexation when a solution of ethylenediamine is added in excess to a solution of nickel chloride and the heat of reaction between permanganate and ferrous ion. A variation is to use the cell compartment as a titration vessel, using a dispensing pipet to add titrant. A plot of temperature versus volume added may be used to find the titration endpoint.

This paper discusses a fairly rigorous investigation of the heat effects accompanying the acid-base reactions of glycine. Adaptation to studies of other amino acids should be straightforward. A good reason for using glycine is that the calculated enthalpy values may readily be compared with those derived entirely from Gibbs free-energy measurements. This has the value of encouraging physical chemistry students to see key relationships in an integrated way. The entire experiment can be performed by a pair of students in one afternoon, and in our experience the results have been quite good.

Stock solutions of 0.300 *M* hydrochloric acid, sodium hydroxide, and sodium chloride are needed. Glycine, recrystallized from water and dried overnight at 80°C, is finely ground before use. What follows is an abridged version of the handout for students. Complete details on the experimental procedure are available from the author.

The purpose of this experiment is to determine the molar enthalpies for the two stages of glycine proton-transfer:



The calorimeter will be used to find the quantities of heat absorbed or liberated when known amounts of glycine are mixed with sodium chloride, with hydrochloric acid, and with sodium hydroxide. The calculated enthalpy changes will not be the standard values because the experiments are carried out at electrolyte concentrations of about 0.3 *M*. However, the effect of ionic strength on the values is not large.

The equilibrium constant values for the above reactions were reported for a range of temperatures by King (2) who used precise measurements of galvanic cells based on the hydrogen electrode. Least-squares fits for results obtained at ionic strength 0.30 are as follows:

$$\text{p}K_1 = -46.7920 + 2378.22/T + 16.64 \log T \quad (3)$$

$$\text{p}K_2 = -16.1083 + 3165.76/T + 6.09 \log T \quad (4)$$

Values for  $\Delta H$  are readily inferred from these equations by using the thermodynamic relationship:

$$d \ln K/dt = \Delta H/RT^2 \quad (5)$$

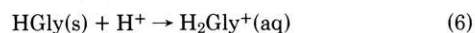
Such values may then be compared with the calorimetric results of this experiment.

### Experimental Procedure

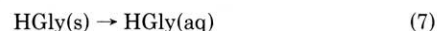
This experiment requires three separate runs, using 0.300 *M* solutions of sodium chloride, hydrochloric acid, and sodium hydroxide. Step-by-step details for instrument operation are provided in a separate handout.

#### Study of Reaction (1)

Set up the calorimeter cell with 100 mL of 0.3 *M* hydrochloric acid in the Dewar compartment, and with about 20 mmol of glycine (HGly) in the solid sample compartment. Upon mixing, a temperature change will be observed because of the reaction:



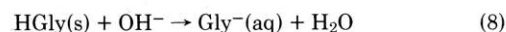
Note that reaction (6) is not simply the reverse of the desired reaction (1), because the glycine is added as a solid rather than being in the aqueous state. Therefore, it is necessary to make another calorimetric run, using 100 mL of 0.3 *M* sodium chloride. This will provide a similar ionic strength effect on the heat of solution of glycine, but there will be no proton-transfer reaction:



If the observed molar enthalpy change for reaction (6) is subtracted from that for reaction (7), the result is the enthalpy change for reaction (1).

#### Study of Reaction (2)

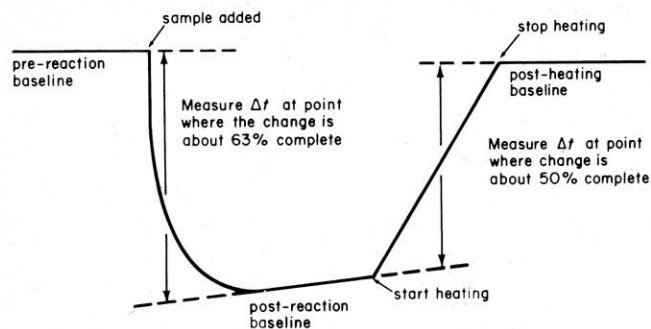
Set up the calorimeter cell with 100 mL of 0.3 *M* sodium hydroxide, and again add solid glycine. The reaction is



To obtain the enthalpy change for reaction (2) it is necessary not only to use the heat of solution determined for reaction (7), but also to introduce the heat of formation of water:



Note that  $\Delta H_2 = \Delta H_8 - \Delta H_7 - \Delta H_9$ . The enthalpy change for reaction (9) is  $-13,340$  cal at zero ionic strength (3), and  $-13,550$  cal at ionic strength 0.5 (4). An interpolated value of  $-13,465$  may be used.



Typical thermogram for an endothermic reaction.

### Interpretation of Data

Each thermogram has five parts: pre-reaction baseline, temperature change due to reaction, post-reaction baseline, temperature rise due to heating calibration, and post-heating baseline. To determine the precise temperature changes it is necessary to extrapolate the baselines as shown in the figure.

The purpose of the electrical heating is to determine the heat capacity,  $C_p$ , of the calorimeter under conditions identical to those used for the chemical reaction. The current and voltage through a heater is monitored to calibrate the calorimeter and its contents.

The heat change associated with the chemical reaction is calculated by using the temperature change  $\Delta t$  observed for the reaction thermogram:

$$Q = -C_p \Delta t \quad (10)$$

where the minus sign is used to satisfy the convention that heat evolved is given a negative sign.

Finally, to find the enthalpy change per mole of glycine

$$\Delta H = Q/n \quad (11)$$

where  $n$  is the amount (moles) of solid glycine used for the run.

### The Problem of Incomplete Protonation of Glycine

When solid glycine is added to a slight excess of hydrochloric acid the reaction  $\text{HGly} + \text{H}^+ \rightarrow \text{H}_2\text{Gly}^+$  does not proceed quantitatively because the protonated species is not a very weak acid ( $\text{p}K_a$  about 2.3). This means that the heat change observed for reaction (6) should be interpreted as

$$\begin{aligned} Q_6 &= Q_7 - Q_1 \\ &= n \cdot \Delta H_7 - \alpha n \cdot \Delta H_1 \end{aligned} \quad (12)$$

where  $\alpha$  is the fraction of the glycine present as  $\text{H}_2\text{Gly}^+$  in the equilibrium mixture.

Given the initial (pre-reaction) concentrations of hydrochloric acid and glycine, 0.300 and  $n/0.1$ , respectively, the value of  $\alpha$  can be estimated from the stoichiometric/equilibrium relationship, which the reader should derive

$$\begin{aligned} K_1 &= [\text{H}^+][\text{HGly}]/[\text{H}_2\text{Gly}^+] \\ &= (0.3 - (\alpha n/0.1))((n/0.1) - (\alpha n/0.1))/(\alpha n/0.1) \\ &= (0.3 - n/0.1)(1 - \alpha)/\alpha \end{aligned} \quad (13)$$

The appropriate value for  $K_1$  can be found from King's results (eqn. (3)), and then this expression can be simplified and solved by the quadratic formula. The value for  $\Delta H_1$  then follows from rearrangement of equation (12).

### Report

Prepare a tabular summary of glycine masses,  $\Delta t$  values deduced from thermograms, values of  $Q$ ,  $Q_h$ ,  $C_p$  and  $\Delta H$ . Calculate the enthalpy changes for the acid dissociation reactions (1) and (2), and compare your results with those inferred from the  $\text{p}K(T)$  studies by King. Look up the enthalpy of formation of solid glycine, and calculate the enthalpy of formation of glycine(aq). Calculate the entropy changes for reactions (1) and (2) and suggest an explanation for their algebraic signs. Make suggestions for improvement of the experiment.

### Literature Cited

- (1) Bulletin 1451, Parr Instrument Co., 211 Fifty-Third St., Moline, IL 61265.
- (2) King, E. J., *J. Amer. Chem. Soc.*, **73**, 155 (1951).
- (3) Olofsson, G., and Hepler, L., *J. Solution Chem.*, **4**, 127 (1975).
- (4) Christensen, J. J., Hansen, L. D. and Izatt, R. M., "Handbook of Proton Ionization Heats," John Wiley & Sons, New York, 1976.