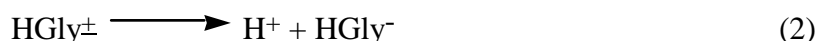
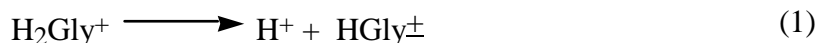


Glycine Proton - Transfer Enthalpies¹

Purpose: Determine the proton-transfer reaction enthalpies for the important aqueous species of the amino acid glycine.

Introduction

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



In these reactions, HGly^\pm represents the zwitter ionic form of glycine, $(^+\text{H}_3\text{NCH}_2\text{COO}^-)$. The zwitter ion is the predominant form at neutral pH. The enthalpy changes for chemical reactions are necessary for the calculation of Gibb's Free energies of reactions. Reaction enthalpies are particularly important for the prediction of the variation with temperature of equilibrium constants². The relationship is

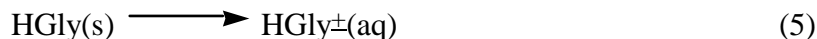
$$\frac{d \ln K_P}{dT} = \Delta_r H^\ominus / RT^2 \quad (3)$$

Therefore the enthalpies of reactions (1) and (2) are necessary to predict the concentrations of the different ionic forms of glycine under various environmental conditions.

The enthalpies of these two reactions cannot be measured directly. Rather, we will determine the reaction enthalpies indirectly using Hess's Law. The first reaction we will study gives the enthalpy of reaction of solid glycine with hydrochloric acid:

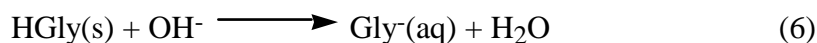


Note that reaction (4) is not simply the reverse of the desired reaction (1), because the glycine is added as a solid rather than being in the aqueous state. Therefore, it is necessary to make another calorimetric run to determine the enthalpy of solution of glycine:



Instead of pure water, however, we will use aqueous sodium chloride. Using aqueous sodium chloride will provide a similar ionic strength effect as reaction (4), but there will be no proton-transfer reaction. The enthalpy of reaction (1) is then $\Delta_r H_1 = \Delta_r H_5 - \Delta_r H_4$.

To obtain the enthalpy change for reaction (2), we first determine the enthalpy of reaction of solid glycine with aqueous sodium hydroxide:



To determine the enthalpy change for reaction (2), we combine the enthalpies for reactions (5) and (6), and also the enthalpy of formation of water:



The enthalpy change for reaction (7) is -55.81 kJ at zero ionic strength³, and -56.69 kJ at ionic strength 0.5.⁴ An interpolated value of -56.34 kJ may be used. The enthalpy of reaction (2) is then $\Delta_r H_2 = \Delta_r H_6 - \Delta_r H_5 - \Delta_r H_7$.

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

Theory

The enthalpy change of a chemical reaction in solution is most easily measured in a constant pressure solution calorimeter. In a constant pressure calorimeter (i.e. the solution is open to the atmosphere) the heat evolved is the enthalpy of the reaction. To calculate the heat evolved, the temperature change of the solution is measured and then

$$Q = C_{p,\text{sys}} \Delta T \quad (8)$$

where $C_{p,\text{sys}}$ is the combined heat capacity of the solution under study and the calorimeter. The molar enthalpy change for the reaction is:

$$\Delta_r H_m = Q/n \quad (9)$$

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

The heat capacity of the system is determined by passing a known amount of energy through a heating coil immersed in the solution and measuring the corresponding temperature change. If the electrical energy passed through the heating coil is w_{el} , and the corresponding temperature change is $\Delta T'$, then the heat capacity is calculated by

$$C_{p,\text{sys}} = \frac{-w_{el}}{\Delta T'} \quad (10)$$

The Problem of Incomplete Protonation of Glycine

In thermodynamic calculations of molar reaction enthalpies, we assume that the reactions run to completion. 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 to completion because the protonated species is not a very weak acid (its pK_a is about 2.3). The intermediate equilibrium position means that the heat change observed for reaction (4) should be interpreted as

$$Q_4 = Q_5 - Q_1$$

$$Q_4 = n \Delta_r H_{5,m} - \alpha n \Delta_r H_{1,m} \quad (11)$$

where α is the fraction of the glycine present as H_2Gly^+ in the equilibrium mixture. Therefore, we must use the equilibrium constant for reaction (4) to find $\Delta_r H_{4,m}$ from the measured reaction heat effect.

The number of moles of glycine added, n , and the volume of water in the calorimeter, 100 ml, gives the initial (pre-reaction) concentration of glycine as $n/0.100$ moles/L. Given the initial (pre-reaction) concentration of hydrochloric acid, 0.300 M, the value of α can be estimated from the following equilibrium relationship, which the reader should derive. Starting with the equilibrium expression:

$$K_1 = \frac{[\text{H}^+][\text{HGly}^\pm]}{[\text{H}_2\text{Gly}^+]} \quad (12)$$

and substituting in the concentrations gives:

$$K_1 = \frac{(0.3 - \alpha n/0.1)(n/0.1 - \alpha n/0.1)}{(\alpha n/0.1)}$$

This expression simplifies to:

$$K_1 = (0.3 - \alpha n/0.1) \frac{(1 - \alpha)}{\alpha} \quad (13)$$

The equilibrium constant values for the above reactions were reported for a range of temperatures by King² 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:

$$pK_1 = -46.7920 + 2378.22/T + 16.64 \log T \quad (14)$$

$$pK_2 = -16.1083 + 3165.76/T + 6.09 \log T \quad (15)$$

For T in degrees K. The appropriate value for K_1 at the temperature of your experiment can be found from King's results (equation (14)), and then expression (13) can be simplified and solved to find α by the quadratic formula or successive approximations. The value for $\Delta_r H_{1,m}$ then follows from rearrangement of equation (11).

Calorimeter

The constant pressure calorimeter is shown in Figure 1. The calorimeter is a Dewar flask containing a thermistor, used as a thermometer, the solids addition device, and a heating coil.

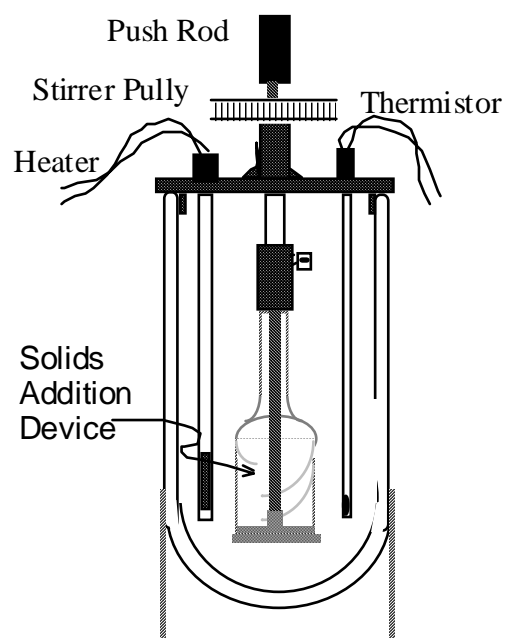


Figure 1. Solution Calorimeter

The heating coil is a $10\ \Omega$ resistor. The teflon bottom cup of the solids-addition device is loaded with the solid and is pressed into the glass top. To mix the reactants, the push rod is depressed, separating the teflon cup from the glass top. The solids-addition device also acts as a motor driven stirrer. The stirrer pulley is attached with a belt to a variable speed motor. The stirrer rate should be as high as possible. The temperature change is determined every second for several minutes before and after the reactants are mixed. Both before and after mixing, the temperature change is monitored until a slight but steady rate of temperature change due to stirring and heat leaks has been observed. After the reaction is complete, the heat capacity of the system is determined by passing a known current through the heating coil to cause a temperature change comparable to the reaction, monitoring the temperature as before.

During the time that current is flowing, the voltage across the heating coil and the current is monitored. Knowing the exact current flowing through the heating coil and the voltage across the heating

coil allows the electrical work to be calculated.

$$-w_{el} = \int_0^t V(t)I dt \quad (16)$$

Therefore, four things need to be measured in this experiment, the current supplied to the heater, the voltage across the heater, the time the current is supplied to the heater and finally the temperature of the solution

Procedure

A diagram of the heater circuit is shown in Figure 2. The four measurements needed are discussed below.

Time

The current and voltage are monitored as a function of time by the data acquisition software. Start the Logger Pro program and open the "heatsoln.cmb1" data acquisition program.

Current

The Hewlett Packard power supply used is capable of regulating the current or voltage supplied to an external circuit. Regulation in this sense means that the current will be held constant even though the external resistance is changing. However, the current output of the supply is measured continuously to keep track of small changes and the rapidly changing current at the beginning and end of the heating run. The current will be displayed from Logger Pro in the line below the top Icon bar. Depress the D.C. current selector switch on the power supply. With the voltage control of the power supply set at 3/4 maximum, adjust the current control to obtain approximately 0.500 amp, after turning on the heater switch. Keep the heater immersed in water during this procedure. Now turn off the heater switch.

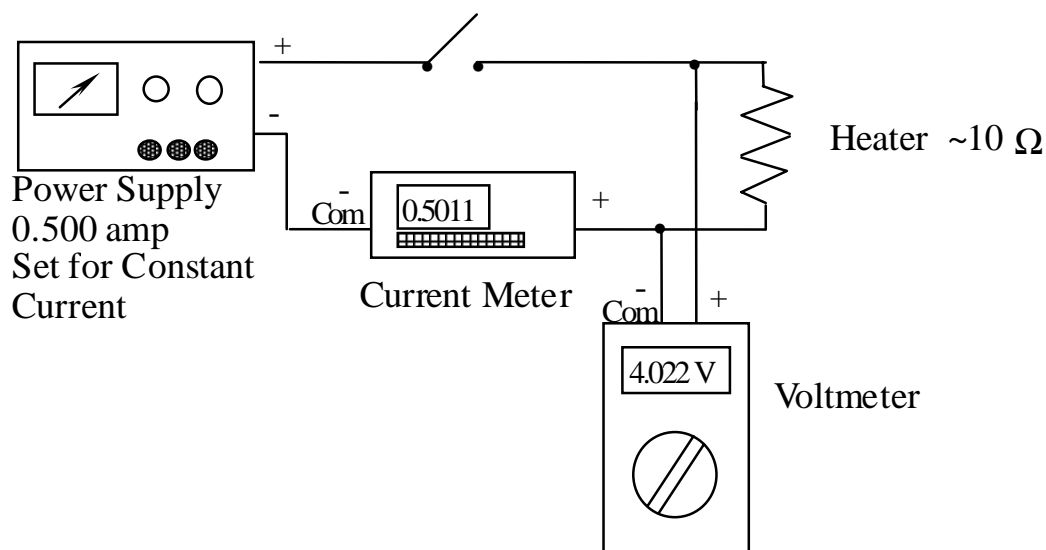


Figure 2. Heater Circuit for the Solution Calorimeter. The current and voltage measurements are probes for the data acquisition system. The values for these measurements are listed above the spreadsheet window in the Logger Pro data acquisition software.

Voltage

Attach the voltage probe across the heater. Turn on the current to observe the voltage across the heater. Note the polarity of the connections in the Figure 2 before turning on the current. This heater voltage is recorded in the data acquisition software as "potential 2".

Temperature

A thermistor is a convenient and accurate device for temperature measurement. The resistance of the thermistor varies as $1/T$ over a narrow temperature range. Over a broad temperature range,

$$R = B e^{a/T} \quad \text{or} \quad \ln R = \frac{a}{T} + b$$

where R is the resistance and a , b and B are constants. Small changes in temperature can be conveniently measured using the thermistor in a Wheatstone bridge circuit with the output of the bridge monitored by computer. For small changes in temperature, the output of the bridge is linear with temperature. The units of the output are in milli-volts (mV).

These are strange units for temperature, but the instrument is internally calibrated using the resistance heater and the units cancel in the final calculations. At the beginning of a run, the balance control is used to adjust the output voltage of the bridge to a convenient starting value (~80-120 mV). A diagram of the Wheatstone bridge circuit is shown in Figure 3. The output of the Wheatstone bridge is converted to a digital signal by the data acquisition system and recorded as the variable “potential”. Set the instrumentation amplifier to the 0-200 mV scale.

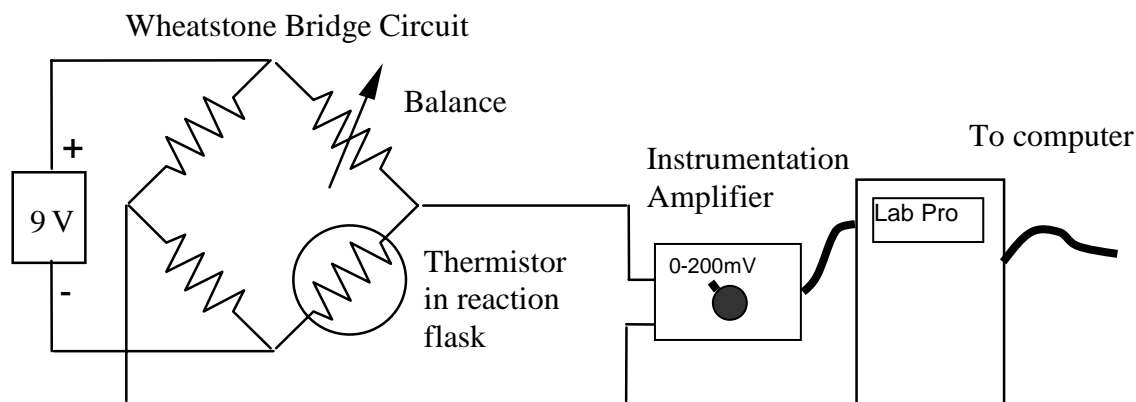


Figure 3. Wheatstone Bridge Circuit.

A typical plot of temperature versus time for an exothermic and endothermic reaction run is shown in Figure 4. 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 Figure 4 by dashed lines. This extrapolation procedure also compensates for the work of stirring and heat leaks.

The heat capacity of the calorimeter from equation 10 is then

$$C_{p,\text{sys}} = \frac{-w_{el}}{T_2' - T_1'} \quad (17)$$

The heat change associated with the chemical reaction, equation 8, is calculated by using the temperature change observed from the reaction thermogram:

$$Q = -C_{p,\text{sys}}(T_1 - T_0) \quad (18)$$

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

This experiment requires three separate runs, using 0.300 M solutions of hydrochloric acid, sodium chloride, and sodium hydroxide. Step-by-step details for instrument operation are provided in the next section. Do each of the following runs in **duplicate**.

Study of Reaction (1)

Run 1: To determine the enthalpy of reaction of solid glycine with HCl, set up the calorimeter cell with 100 ml of 0.3 M HCl in the Dewar compartment, and with about 1.5 g of glycine

(HGly) in the solids-addition device. Upon mixing, a temperature change will be observed because of reaction (4).

Run 2: To measure the enthalpy of solution of solid glycine, set up the calorimeter cell with 100 ml of 0.3 M NaCl and again add solid glycine. Upon mixing, a temperature change will be observed because of reaction (5). The 0.3 M NaCl is needed to keep the ionic strength the same for each reaction. The ionic strength is a measure of the total ionic concentration.

Study of Reaction (2)

Run 3: To determine the enthalpy of reaction of solid glycine with NaOH, set up the calorimeter cell with 100 ml of 0.3 M NaOH, and again add solid glycine. Upon mixing, a temperature change will be observed because of reaction (6).

Procedure for Each Run

Start the "heatsoln.cmb1" data acquisition program. A typical calorimeter run would go as follows:

- (1) Carefully add 1.5g of glycine (weighed to the nearest 0.001g) to the dry solids-addition device. Fill the Dewar with the appropriate solution using a 100-mL volumetric flask.
- (2) Turn on the stirrer. Adjust the thermistor bridge balance control so that the data trace is near the top of the chart. Click on "Stop watch" icon and then choose a data rate of 2 points per sec. Click on Collect. Monitor the temperature for at least 40 sec. until a small linear temperature drift is observed (see Figure 4).
- (3) Turn off the stirrer, briefly. Push the solids-addition device into the solution and turn the stirrer back on. The temperature should drop. Monitor the temperature for at least 30 sec. until a small linear temperature drift is observed.
- (4) Turn on the heater. Turn the heater off when the temperature approaches the starting temperature before addition of the solid. For the NaOH run, the temperature drop upon addition of glycine is very small. For this case, leave the heater on about the same length of time as the HCl run, otherwise you won't be able to calculate an accurate heat capacity.
- (5) Monitor the temperature for at least 40 sec. until a small linear temperature drift is observed. Then, stop the data acquisition and turn off the stirrer. Remember to save your data file (use a file name with your initials). Carefully rinse out the calorimeter, solids-addition device, stirrer, and heater coil. Dry the calorimeter and solids-addition device.

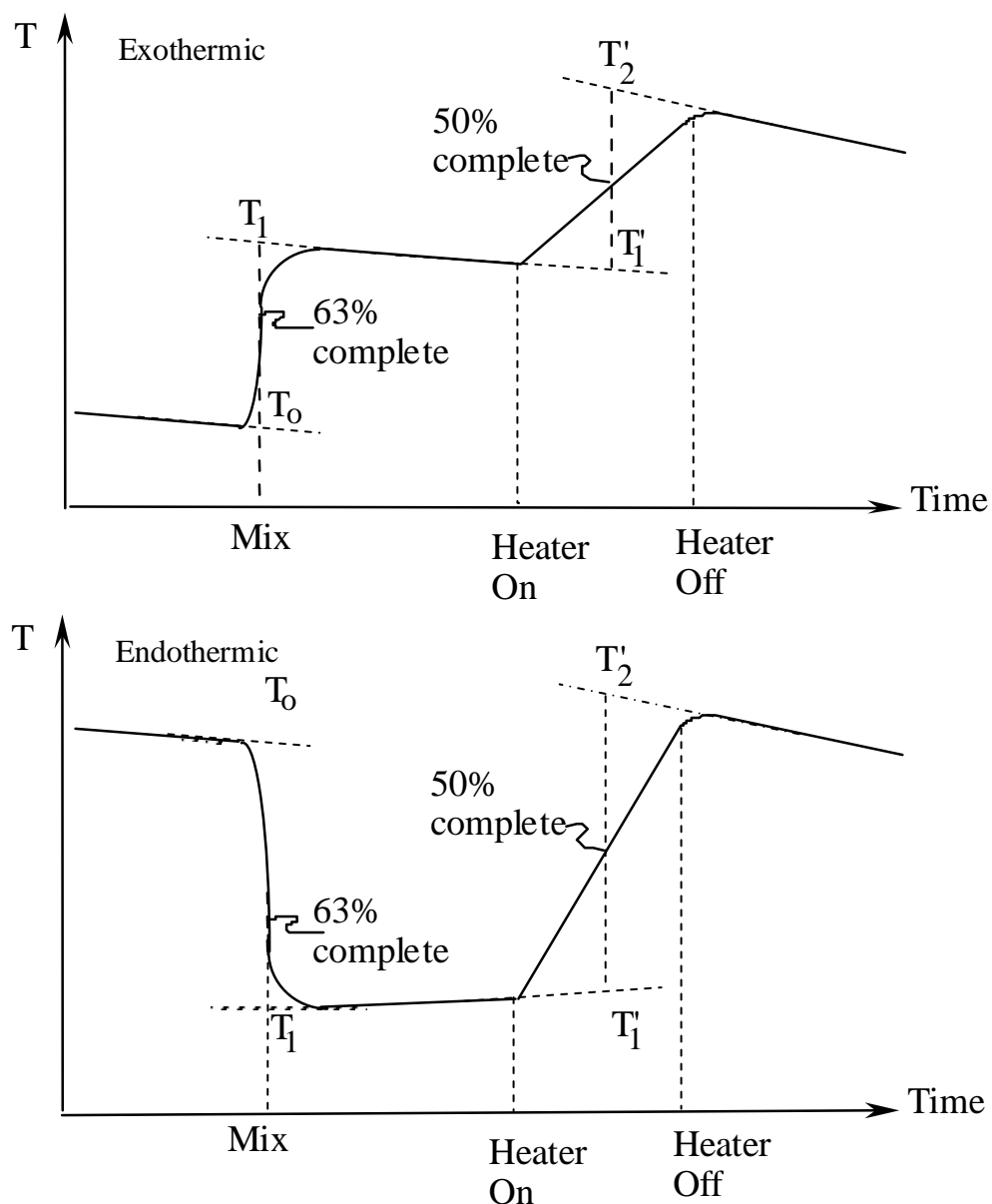


Figure 4. Schematic plot of temperature verses time.

Calculations

Perform the extrapolations shown in Figure 4 and obtain the temperature differences ($T_1 - T_0$) and ($T'_2 - T'_1$). To do the extrapolations, first highlight a linear portion of the thermogram and pull down the “Analysis” menu and choose “linear fit” for each of the three regions indicated in Figure 4. Then pull down the “Analysis” menu and choose “interpolate”. The readings along the extrapolated lines will be listed on the screen as you move the mouse across the thermogram. The heat capacity is calculated by use of equations (16) and (17). The integral for the electrical work can be done graphically by plotting $V(t)I$ versus time and determining the

area under the curve. In the "heatsoln.cmb1" program note that there is a column labeled "power". Double click on this column heading. You should see the following formula to calculate the power dissipated in the heater coil:

$$\text{Potential2} * \text{current} \quad (19)$$

A plot of the power versus time is shown in the bottom plot. Drag across the plot of power versus time during the heating interval. Pull down the "Analysis" menu and choose "integral". to determine the total heat delivered. Calculate the number of moles of reaction from the number of moles of the limiting reactant present and calculate each molar enthalpy change for reactions (5) and (6) using equations 17, 18, and 9. Get the molar enthalpy changes for each replicate separately and then average the results. The enthalpy change of reaction (2) is calculated from $\Delta_r H_{2,m} = \Delta_r H_{6,m} - \Delta_r H_{5,m} - \Delta_r H_{7,m}$. The enthalpy change of reaction (4) is calculated from equations 17 and 18. The K_1 is determined using equation (14), and α is calculated with equation (13). Determine α just once, for the average room temperature during your three runs. Substitution into equation (11) yields $\Delta_r H_{1,m}$.

For example, at 22.6°C $pK_1 = 2.365$ and $K_1 = 4.312 \times 10^{-3}$. Rearranging equation (13) gives

$$\alpha = (0.3 - \alpha n/0.1)/(K + (0.3 - \alpha n/0.1)) \quad (20)$$

To solve by successive approximations, start with $\alpha = 1$ on the right. After several iterations α converges to 0.9820.

Report

Prepare a tabular summary of glycine masses and number of moles, ΔT values deduced from the thermograms, w_{el} , C_p , Q and $\Delta_r H$ (if applicable). Give your average solution T , K_1 , and α . Report the enthalpy changes for the acid dissociation reactions (1) and (2), $\Delta_r H_{1,m}$ and $\Delta_r H_{2,m}$, and compare your results with those calculated from tabulated enthalpies of formation (at infinite dilution) and also with the values determined in the appendix using equations 14 and 15. Remember to use the standard deviations from multiple trials and significant figure rules to estimate the uncertainty of your final results. Discuss the predominant errors in the measurements. Discuss the chemical significance of your results. Derive equation 20.

Literature Cited

1. Excerpted from R. W. Ramette, J. Chem. Ed., 61 (1), 76 (1984).
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. and Hansen, L. D. and Izatt, R. M., "Handbook of Proton Ionization Heats," John Wiley & Sons, New York, 1976.

APPENDIX**Literature Value for Glycine Proton Transfer**

Equation 3 gives the relationship between the enthalpy change for a reaction, $\Delta_r H^\ominus$, and the temperature dependence of the equilibrium constant. The $pK(T)$ studies of King can be used, by comparison with equation (3), to calculate the corresponding values of the enthalpies of the reactions. To calculate $\Delta_r H^\ominus_{1,m}$ note that $pK = -\log K$ and that $\ln X = 2.303 \log X$, then equation 14 becomes:

$$\ln K_1 = 107.76 - 5477.04/T - 16.64 \ln T$$

Taking the derivative with respect to T gives:

$$\frac{d \ln K_1}{dT} = 5477.04/T^2 - 16.64/T = \Delta_r H^\ominus_{1,m} / RT^2$$

Solving for $\Delta_r H^\ominus_{1,m}$:

$$\Delta_r H^\ominus_{1,m} = 5477.04 R - 16.64 RT$$

Then, at 298.15°K

$$\Delta_r H^\ominus_{1,m} = 4.289 \text{ kJ mol}^{-1}$$

at 0.3 m ionic strength. In an analogous fashion from equation 15,

$$\ln K_2 = 37.0974 - 7290.75/T - 6.09 \ln T$$

$$\frac{d \ln K_2}{dT} = 7290.75/T^2 - 6.09/T = \Delta_r H^\ominus_{2,m} / RT^2$$

$$\Delta_r H^\ominus_{2,m} = 7290.75 R - 6.09 RT$$

$$\Delta_r H^\ominus_{2,m} = 45.52 \text{ kJ mol}^{-1}$$

Enthalpies of formation, $\Delta_f H^\ominus_m$, for each of the species in reaction (1) and (2), are available in Langes's Handbook, at infinite dilution. However, current editions of Lange's leave out the infinite dilution value for the zwitterionic form of glycine, which is -514.0 kJ/mol . Use those values to calculate $\Delta_r H^\ominus_{1,m}$ and $\Delta_r H^\ominus_{2,m}$, at infinite dilution, and compare with the values above and your experimental results.