

## Modification of Procedure for Experiments 17 and 18

### I. Calorimeter Constant

Obtain two polystyrene cups, a lid for one of the cups and a magnetic stirrer. Rinse everything with distilled water and dry thoroughly. (Note: Do not use acetone to rinse cups.) Place one cup within the other and place the stir bar in the top cup. The lid will be placed over the cups after the solutions have been added. It is very important to keep the same cups, lid, stirrer, and thermometer for which the calorimeter constant has been determined because the calorimeter constant is specific to those particular components.

From a buret, dispense 50.0 ml of 2.00 M HCl at room temperature into your calorimeter. Dispense 50.0 ml of 2.05 M NaOH at room temperature from a second buret into a clean, dry 100 ml beaker.

Place the lid on the inner cup and insert a high precision thermometer through the hole in the lid. Adjust the thermometer so that it doesn't touch the bottom or sides of the calorimeter. Start the stirrer spinning gently, making sure that the stir bar does not hit the thermometer as it spins. A second high precision thermometer should be used to measure the temperature of the NaOH solution. If the two solutions' temperatures are more than 1°C apart, adjust the temperature of the NaOH solution by running the outside of the beaker under warm or cold tap water, taking care not to get any water into the solution. For all temperature measurements, the reading should be estimated to  $\pm 0.01^\circ\text{C}$ .

For a 5 minute period, record the temperature/time data for each solution at one minute intervals. Then rapidly pour the entire NaOH solution into the calorimeter, quickly replace the lid, and begin stirring. Record the time of mixing and continue to record the temperature for a further 10 minutes at 1 minute intervals.. Plot this data using Sigma Plot as was done in the first

computer project to obtain  $T$  for each trial. Repeat this experiment twice more for a total of three trials.

### **Calorimeter constant calculations.**

For this experiment, the system, defined as the calorimeter (thermometer, stirrer, cups, and lid) and the mixed solution, will be considered to be adiabatic. This means that there is no heat transferred between the system and the surroundings (i.e., everything outside the system). Therefore, all heat produced or absorbed by this reaction,  $q_{\text{rxn}}$ , will be confined to the system,  $q_{\text{system}}$ . For an adiabatic process, the total sum of heat transferred within the system must be equal to zero; therefore,

$$0 = q_{\text{rxn}} + q_{\text{system}} \quad (1)$$

For example, if the neutralization process produces 4.0 kJ of heat upon mixing the acid and base solutions (i.e.,  $q_{\text{rxn}} = -4.0$  kJ), then this heat must be absorbed by the various components of the system (i.e.,  $q_{\text{system}} = +4.0$  kJ). The heat absorbed by the various components of the calorimeter can be broken down into individual components. For a reaction of this type, the solution itself absorbs some of the energy,  $q_{\text{soln}}$ , thereby increasing its internal energy, and its temperature rises (i.e.,  $T > 0$ ). Further, the other components of the system also absorb some of the energy,  $q_{\text{calor}}$ , released by the reaction,  $q_{\text{rxn}}$  and their temperature will also increase. Therefore, equation 1 can be rewritten as

$$0 = q_{\text{rxn}} + q_{\text{soln}} + q_{\text{calor}} \quad (2)$$

The heat absorbed by the solution is given by equation 3.

$$q_{\text{soln}} = m_{\text{soln}} \cdot c_{p,\text{soln}} \cdot T \quad (3)$$

where  $m_{\text{soln}}$  is the mass of solution in grams,  $c_{p,\text{soln}}$  is the specific heat capacity of the solution, and  $T$  is the change in temperature of this process.

The heat absorbed by the components of the calorimeter is given by equation 4.

$$q_{\text{calor}} = C_{\text{calor}} \cdot T \quad (4)$$

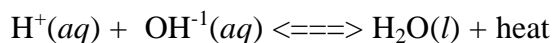
where  $C_{\text{calor}}$  is the heat capacity of the calorimeter or the calorimeter constant. Since these components of the calorimeter are in contact with the solution, it is assumed that the temperature of the solution is also the temperature of these other components of the system. Thus, the value of  $T$  is the same for the solution and the calorimeter.

In order for your calorimeter to be useful, it is necessary to determine the value of the calorimeter constant, which is assumed to be independent of the reaction run in the calorimeter as long as the volume of the resulting solution is kept approximately the same from run to run. To do this, a reaction whose heat is known must be run in the calorimeter. Further, the specific heat capacity of the resulting solution must also be known. In this case, the neutralization of the acid and base produces a solution of sodium and chloride ions with a slight excess of hydroxide ion. If we neglect this slight excess of hydroxide ions, the resulting solution is approximately a 1.00 M NaCl solution whose density is 1.037 g/mL and specific heat capacity of  $0.932 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ , and equation 3 can be written as

$$q_{\text{soln}} = V_{\text{soln}} \cdot d_{\text{soln}} \cdot c_{p,\text{soln}} \cdot T \quad (5)$$

where  $V_{\text{soln}}$  and  $d_{\text{soln}}$  are the solution volume and density, respectively.

The net equation for an acid/base neutralization reaction is



The accepted value for the change in the enthalpy,  $H$ , for the formation of one mole of water molecules is  $-13,600 \text{ cal mol}^{-1}$ . Therefore, if the number of moles of water molecules actually formed during the experiment can be determined through the stoichiometry of this reaction, then the heat produced during of the experiment can be determined by equation 6.

$$q_{\text{rxn}} = H \cdot (\# \text{ mol H}_2\text{O produced}) \quad (6)$$

The value for the calorimeter constant can then be determined by rearranging equation 1 with the proper substitutions. Determine a mean and standard deviation for the calorimeter constant.

## II. Enthalpy of Neutralization

The objective of next experiment is to study the heat of neutralization produced during the reaction of nitric acid and potassium hydroxide. Essentially, this experiment is performed by repeating the previous procedure except  $\text{HNO}_3$  and  $\text{KOH}$  are substituted for  $\text{HCl}$  and  $\text{NaOH}$ , respectively. Plot this data using Sigma Plot as was done in the first computer project to obtain  $T$  for each trial. Repeat this experiment at least once more. If there is not good agreement in the heat of neutralization among the trials, then repeat the experiment again. Calculate a mean and standard deviation for the heat of neutralization of this reaction.

### Enthalpy of neutralization calculations.

For this experiment, the neutralization of the acid and base produces a solution of potassium and nitrate ions with a slight excess of hydroxide ion. If we neglect this slight excess of hydroxide ions, the resulting solution is approximately a 1.00 M  $\text{KNO}_3$  solution whose density is 1.059 g/mL and specific heat capacity is  $0.9001 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ . The enthalpy of neutralization for this reaction can be found by the using this information, the calorimeter constant determined in the previous experiment, and the previously developed equations. Since  $\text{HNO}_3$  is the limiting reagent in this experiment and it is assumed that this reaction goes to completion, the number of moles of  $\text{HNO}_3$  consumed is equal to the number of moles of water produced during the reaction.

How does your calculated value of the heat of neutralization compare to the literature value? Does it matter which spectator ions are involved in this reaction?

### **III. Enthalpy of Dissolution**

In this experiment, the enthalpy of dissolving solid  $\text{KNO}_3$ , the salt formed in the above reaction, in water will be determined. To do this, first calculate the concentration of  $\text{KNO}_3$  formed in the previous experiment and determine the mass of  $\text{KNO}_3$  and the mass of water required to make a 100 ml solution with this same concentration.

Tare your dry, inner calorimeter cup on the analytical balance and carefully add the mass of water, to  $\pm 0.01$  g, of the value calculated to prepare the 100 mL solution. Place this cup back into the outer cup. Carefully place the magnetic stir bar in the cup and replace the lid. Insert the thermometer through the hole in the lid. Clamp the thermometer in place so that it doesn't touch the bottom or sides of the calorimeter or the stir bar. With the stirrer turned on gently, record the water temperature for a 5 minute period at 1 minute intervals.

After 5 minutes, rapidly add the required mass of  $\text{KNO}_3$  to the water, replace the lid, and begin stirring the solution. Record the time of mixing and continue to record the temperature for a further 10 minutes at 1 minute intervals. Plot this data using Sigma Plot as was done in the first computer project to obtain  $\Delta T$  for each trial.

Perform this experiment at least twice. If there is not good agreement in the heats of dissolution, then repeat for a third trial. Calculate a mean and standard deviation of the heat of dissolution. Is this process endo- or exothermic? What must be happening at the molecular level that might explain this process?

### Enthalpy of dissolution calculations.

Equation 2, with the proper substitutions, can be rearranged and used to find the heat of dissolution of the  $\text{KNO}_3$ . The change in enthalpy of dissolution can be found according to the equation

$$H_{\text{diss}} = q_{\text{rxn}} / (\# \text{ mol KNO}_3) \quad (7)$$

Hopefully, it should be apparent that  $H_{\text{diss}}$  varies as a function of the  $\text{KNO}_3$  concentration.

### References:

1. Neiding, H.A., Enthalpy of Formation, Chemical Education Resources, Inc., 1983.
2. Brown, M. G., Prentiss, P. G., Wolf, A. V., Concentrative Properties of Aqueous Solutions: Conversion Tables, D-246.
3. Combet, S., Tuech, J., 'Etude Thermodynamique Des Solutions Aqueuses De Nitrate De Potassium Jusqu'au-Dela De La Saturation', *Journal De Chimie Physique*, 1976, 73, n<sup>o</sup> 9-10.

NAME \_\_\_\_\_

**Calculation Sheet****I. Calorimeter Constant**

	First	Determination Second	Third
T (°C)	_____	_____	_____
Volume of solution ( $V_{\text{soln}}$ ), mL	_____	_____	_____
Mass of solution ( $m_{\text{soln}}$ ), g	_____	_____	_____
Heat of solution ( $q_{\text{soln}}$ ), cal	_____	_____	_____
Moles of water produced	_____	_____	_____
Heat of reaction ( $q_{\text{rxn}}$ ), cal	_____	_____	_____
Heat of calorimeter ( $q_{\text{calor}}$ ), cal	_____	_____	_____
Calorimeter constant ( $C_{\text{calor}}$ ), cal/deg	_____	_____	_____
Calorimeter constant ( $C_{\text{calor}}$ ), cal/deg		Mean _____	sd _____

**II. Enthalpy of Neutralization**

	First	Determination Second	Third
T (°C)	_____	_____	_____
Volume of solution ( $V_{\text{soln}}$ ), mL	_____	_____	_____
Mass of solution ( $m_{\text{soln}}$ ), g	_____	_____	_____
Heat of solution ( $q_{\text{soln}}$ ), cal	_____	_____	_____
Heat of calorimeter ( $q_{\text{calor}}$ ), cal	_____	_____	_____
Heat of reaction ( $q_{\text{rxn}}$ ), cal	_____	_____	_____
Moles of water produced	_____	_____	_____
Enthalpy of neutralization (H), cal/mol	_____	_____	_____
Enthalpy of neutralization (H), cal/mol		Mean _____	sd _____

Name \_\_\_\_\_

### III. Enthalpy of Dissolution

	First	Determination Second	Third
Calculated mass $\text{KNO}_3$ , g	_____	_____	_____
Actual mass $\text{KNO}_3$ , g	_____	_____	_____
Moles $\text{KNO}_3$ , mol	_____	_____	_____
Calculated mass $\text{H}_2\text{O}$ , g	_____	_____	_____
Actual mass $\text{H}_2\text{O}$ , g	_____	_____	_____
Mass of solution ( $m_{\text{soln}}$ ), g	_____	_____	_____
T ( $^{\circ}\text{C}$ )	_____	_____	_____
Heat of calorimeter ( $q_{\text{calor}}$ ), cal	_____	_____	_____
Heat of solution ( $q_{\text{soln}}$ ), cal	_____	_____	_____
Heat of reaction ( $q_{\text{rxn}}$ ), cal	_____	_____	_____
Enthalpy of dissolution ( $H_{\text{diss}}$ ), cal/mol	_____	_____	_____
Enthalpy of dissolution ( $H_{\text{diss}}$ ), cal/mol		Mean _____	sd _____

Name \_\_\_\_\_

**DataSheet 1**

<i>Time min.</i>	<i>First Determination</i>		<i>Second Determination</i>		<i>Third Determination</i>	
	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>
0	_____	_____	_____	_____	_____	_____
1	_____	_____	_____	_____	_____	_____
2	_____	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____	_____
5	_____	_____	_____	_____	_____	_____
(mix)						
6		_____		_____		_____
7		_____		_____		_____
8		_____		_____		_____
9		_____		_____		_____
10		_____		_____		_____
11		_____		_____		_____
12		_____		_____		_____
13		_____		_____		_____
14		_____		_____		_____
15		_____		_____		_____

Name \_\_\_\_\_

**DataSheet 2**

<i>Time min.</i>	<i>First Determination</i>		<i>Second Determination</i>		<i>Third Determination</i>	
	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>
0	_____	_____	_____	_____	_____	_____
1	_____	_____	_____	_____	_____	_____
2	_____	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____	_____
5 (mix)	_____	_____	_____	_____	_____	_____
6		_____		_____		_____
7		_____		_____		_____
8		_____		_____		_____
9		_____		_____		_____
10		_____		_____		_____
11		_____		_____		_____
12		_____		_____		_____
13		_____		_____		_____
14		_____		_____		_____
15		_____		_____		_____

Name \_\_\_\_\_

**DataSheet 3**

<i>Time min.</i>	<i>First Determination</i>		<i>Second Determination</i>		<i>Third Determination</i>	
	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>	<i>Temp <u>NaOH</u></i>	<i>Temp <u>HCl</u></i>
0	_____	_____	_____	_____	_____	_____
1	_____	_____	_____	_____	_____	_____
2	_____	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____	_____
5 (mix)	_____	_____	_____	_____	_____	_____
6		_____		_____		_____
7		_____		_____		_____
8		_____		_____		_____
9		_____		_____		_____
10		_____		_____		_____
11		_____		_____		_____
12		_____		_____		_____
13		_____		_____		_____
14		_____		_____		_____
15		_____		_____		_____