Enthalpy of Neutralization

Introduction

Energy changes always accompany chemical reactions. If energy, in the form of heat, is liberated the reaction is exothermic and if energy is absorbed the reaction is endothermic. Thermochemistry is concerned with the measurement of the amount of heat evolved or absorbed. The heat (or enthalpy) of neutralization (∆H) is the heat evolved when an acid and a base react to form a salt plus water.

\[
\text{Eq. 1} \quad \text{HNO}_2(aq) + \text{NAOH}(aq) \rightarrow \text{NaNO}_2(aq) + \text{H}_2\text{O}(l) + \text{Q}
\]

Q in the above equation is -∆H and is expressed in kJ/mol of water. Neutralization reactions are generally exothermic and thus ∆H is negative.

Heat measurements are performed by carrying out the reaction in a special container called a calorimeter. The heat (Q) given off by the neutralization reaction is absorbed by the reaction solution and the calorimeter. Both the solution and calorimeter increase in temperature due to the absorbed heat and this increase can be measured with a thermometer. ∆H is negative if heat is evolved and positive if heat is absorbed.

\[
\text{Eq. 2} \quad -\Delta H_{\text{neutralization}} = Q_{\text{Solution}} + Q_{\text{Calorimeter}}
\]

To evaluate the calorimeter constant (also known as its heat capacity) in J/°C, one adds a known mass of hot water to a known mass of cold water which is in the calorimeter. Heat (Q) is lost by the hot water and is absorbed by the cold water and the calorimeter. Thus the heat absorbed by the calorimeter is the heat lost by the hot water minus the heat gained by the cold water.

\[
\text{Eq. 3} \quad Q_{\text{calorimeter}} = Q_{\text{Hot water}} - Q_{\text{Cold water}}
\]

It should be noted that we assume that the temperature of the calorimeter is the same as the solution inside it at all times. Q for both the hot and cold water is given by:

\[
\text{Eq. 4} \quad Q = (4.184\text{J/g-°C})(\text{Mass in g})(\Delta t)
\]

∆t is found by plotting temperature versus time for the system in the calorimeter and extrapolating the results to find ∆t at the instant of mixing (in this experiment, 5 minutes). A typical graph is shown in Figure 1.
The heat gained by the calorimeter is the difference between the heat lost by the hot water and the heat gained by the cold water. The calorimeter constant is this difference divided by the temperature change of the calorimeter (temperature change of the cold water).

**Eq. 5** Calorimeter constant $= \frac{Q_{\text{calorimeter}}}{\Delta t_{\text{cold water}}}$

The $\Delta H$ of neutralization is found by mixing known quantities (moles) of an acid and a base (both initially at the same temperature) in a calorimeter and measuring $\Delta t$ of the mixture and the calorimeter. A typical graph for neutralization is shown in Figure 2.
The heat given off by the neutralization reaction, $\Delta H$, is the sum of the heat absorbed by the solution and calorimeter.

\[ \text{Eq. 6 } \quad -\Delta H = + Q_{\text{solution}} + Q_{\text{calorimeter}} \]

\[ \text{Eq. 7 } \quad Q_{\text{solution}} = (\text{Sp. Ht.})(\text{Volume})(\text{Density})(\Delta t) \]

\[ \text{Eq. 8 } \quad Q_{\text{calorimeter}} = (\text{Calorimeter Constant})(\Delta t) \]

The specific heat (Sp. Ht.) and the density of the solution of the salt formed from your assigned acid and base. You must calculate the $\Delta H$ for one mole of water formed in your system in order to compare it to the theoretical value. $\Delta t$ is the same for the solution and the calorimeter.

**Procedure**

**Calorimeter Constant**

Weigh 50.0 grams of distilled water into your assigned calorimeter. Be sure it is clean and dry. This is the cold water. Suspend the supplied 50°C thermometer into the water from a paper clip on a ring stand. Be sure to note the thermometer can be read to 0.01°C.

Weigh 50.0 grams of distilled water into a 100 mL beaker. Heat this water to 15 – 20°C above the temperature of the cold water. Remove from the hot plate and place on the bench. Suspend a 110°C thermometer (in your locker) from a ring stand with a paper clip.

Be sure to note the starting time when measuring temperatures. Starting with the hot water, alternately measure the hot and cold water temperatures for a 4.5 minute period. You will have 5 measurements of each water sample. At the 5.0 minute mark quickly add the hot water to the cold water (in the calorimeter) and record the temperature of the mixture at 1 minute intervals for a 10 minutes for a total of 15 readings.

Clean and dry the beaker and calorimeter and repeat the above procedure for a second trial. Clean and dry the beaker and calorimeter for the neutralization reaction.

Plot graphs of temperature vs time for the two calorimeter constant trials. Extrapolate the three lines beyond the data points and evaluate the hot and cold water temperature changes ($\Delta t$) at the 5 minute mark as shown in Figure 1. Evaluate the average calorimeter constant on page 9.
Procedure

Acid-Base Neutralization

Each student will be assigned an acid and a base from the following list.

Acids:  
2.00 M HCl  
2.00 M HNO₃  
1.00 M H₂SO₄  
0.667 M H₃PO₄

Bases:  
2.00 M NaOH  
2.00 M KOH  
2.00 M NH₄OH

Pipet 50.00 mL of your assigned acid into the clean dry calorimeter. Suspend the 50°C thermometer in the acid. Pipet 50.00 mL of your assigned base into a 100 mL beaker. Since both the acid and base have been at room temperature for several hours, we can safely assume that both are at the same temperature. Record the acid (and base) temperature every one half minutes for 4.5 minutes. At the 5 minute mark quickly add the base to the acid in the calorimeter. Record the solution temperature every minute for 10 minutes giving a total of 15 minutes of readings. **Record all temperatures to the nearest 0.01°C.**

Clean and dry the beaker and calorimeter and repeat the above procedure for a second trial.

Plot graphs of temperature vs time for the two neutralization reaction trials. Extrapolate the two lines beyond the data points and determine the temperature changes (Δt) at the 5 minute mark as shown in Figure 2. Evaluate the average ΔH for the reaction on page 10.

Write a balanced equation for you assigned acid-base mixture, be sure to neutralize all of the acidic hydrogens of your acid. Determine the moles of water formed in your system from the molarity and volumes of acid and base used and correct your ΔH for the formation of one mole of water.

Using standard thermodynamic tables calculate the theoretical enthalpy change in kJ/1 mole water and compare to you experimentally determined value.
### Data

**Calorimeter Constant, Trial 1**

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<th>Time, Minutes</th>
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## Data

### Acid-Base Neutralization, Trial 2

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### Calculations and Results

#### Calorimeter Constant Determination

**Trial 1.**

1. Mass of hot water (g) ________________________________
2. $\Delta t$ of hot water ($^\circ$C) (absolute value) __________________
3. Heat lost by hot water (J) ____________________________
4. Mass of cold water (g) _______________________________
5. $\Delta t$ of cold water ($^\circ$C) _________________________
6. Heat gained by cold water (J) _________________________
7. Heat gained by calorimeter (J) ($3 - 6$) _______________
8. Calorimeter Constant ($J/^\circ$C) ($7/5$) ________________

**Trial 2**

1. Mass of hot water (g) ________________________________
2. $\Delta t$ of hot water ($^\circ$C) (absolute value) __________
3. Heat lost by hot water (J) _____________________________
4. Mass of cold water (g) _______________________________
5. $\Delta t$ of cold water ($^\circ$C) _________________________
6. Heat gained by cold water (J) _________________________
7. Heat gained by calorimeter (J) ($3 - 6$) _______________
8. Calorimeter Constant ($J/^\circ$C) ($7/5$) ________________

**Average Calorimeter Constant Value ($J/^\circ$C) ___________**
Calculations and Results

Enthalpy of Neutralization

Assigned Acid and Base: ____________ ________________

Balanced Equation for Complete Neutralization

Density of Salt Solution (g/mL) ____________________________

Specific Heat of Salt Solution (J/g-°C) _____________________

Trial 1

1. Volume of Salt Solution (mL) ____________________________
2. Mass of Salt Solution (g) ________________________________
3. Δt of Salt Solution (°C) (from graph) ____________________
4. Heat Gained by Salt Solution (J) ________________________
5. Heat Gained by Calorimeter (J) (Cal. Const. x 3) __________
6. Total heat Evolved by Reaction (J) (4 + 5) ________________

Trial 2

1. Volume of Salt Solution (mL) ____________________________
2. Mass of Salt Solution (g) ________________________________
3. Δt of Salt Solution °C) (from graph) ____________________
4. Heat Gained by Salt Solution (J) ________________________
5. Heat Gained by Calorimeter (J) (Cal. Const. x 3) __________
6. Total Heat Evolved by Reaction (J) (4 + 5) ________________

Average Heat Evolved by Reaction (Q) (Trials 1&2) ________________
Name:_________________________________

Calculations and Results

Moles of Acid Used in the Neutralization Reaction

Moles Base of Used in the Neutralization Reaction

Moles of Water Formed in the Neutralization Reaction

Enthalpy of Neutralization (ΔH) (Average Heat Evolved in kJ/ Moles Water Formed)

Theoretical Enthalpy of Neutralization

From Standard Heat of Formation Data and calculate ΔH in kJ per one mole of H₂O. Remember $\Delta H^0 = \Sigma n\Delta H_f$ Products – $\Sigma n\Delta H_f$ Reactants

Physical Properties of 1.00 M Salt Solutions
<table>
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<th>Solution</th>
<th>Density, g/mL</th>
<th>Specific Heat, J/g-°C</th>
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**Heat of Formation Data for 1.00 M Solutions at 25°C**

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Name:_________________________________

**Enthalpy of Neutralization**

12
Prestudy Page 1

A student studied the enthalpy of neutralization of HClO₄ and NaOH by reacting 50.0 mL of 2.00 M HClO₄ with 50.0 mL of 2.00 M NaOH in a calorimeter. He measured the temperature versus time for 15 minutes. The first 4.5 minutes show the temperature of the acid and base before mixing. The solutions were mixed at the 5 minute mark and the temperature of the resulting salt solution measured for 10 minutes to give the following data.

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<th>Time, Minutes</th>
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<td>(Acid/Base) 23.28</td>
</tr>
<tr>
<td>1.5</td>
<td>(Acid/Base) 23.30</td>
</tr>
<tr>
<td>2.0</td>
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</tr>
<tr>
<td>3.0</td>
<td>(Acid/Base) 23.35</td>
</tr>
<tr>
<td>4.0</td>
<td>(Acid/Base) 23.44</td>
</tr>
<tr>
<td>4.5</td>
<td>(Acid/Base) 23.47</td>
</tr>
<tr>
<td>5.0</td>
<td>Acid &amp; Base Mixed</td>
</tr>
<tr>
<td>6.0</td>
<td>(Salt Solution) 33.50</td>
</tr>
<tr>
<td>7.0</td>
<td>(Salt Solution) 33.55</td>
</tr>
<tr>
<td>8.0</td>
<td>(Salt Solution) 33.48</td>
</tr>
<tr>
<td>9.0</td>
<td>(Salt Solution) 33.32</td>
</tr>
<tr>
<td>10.0</td>
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<tr>
<td>11.0</td>
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<tr>
<td>12.0</td>
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<tr>
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</tr>
<tr>
<td>14.0</td>
<td>(Salt Solution) 32.80</td>
</tr>
<tr>
<td>15.0</td>
<td>(Salt Solution) 32.75</td>
</tr>
</tbody>
</table>

Plot a graph of temperature versus time and determine the Δt at the time of mixing, 5.0 minutes. See Figure 2.

The density of the final solution is 1.07 g/mL and its specific heat is 3.85 J/g-°C. The calorimeter constant is 85.8 J/°C.

Write a balanced equation for the reaction and calculate the moles of water formed.

Name:______________________________

Enthalpy of Neutralization

13
Calculate the enthalpy ($\Delta H$) of neutralization in kJ per 1.00 mole of water formed. Remember $\Delta H =$ heated absorbed by the final salt solution plus the heat absorbed by the calorimeter.

Calculate the theoretical (true) enthalpy of neutralization in kJ per 1.00 mole water from heats of formation data given on page 12. $\Delta H = \Sigma n\Delta H_f$ products $– \Sigma n\Delta_f$ reactants.

Calculate the % error between the two results. 
% Error = \frac{(Exptl \ Value - True \ Value) \times 100\%}{True \ Value} 
% Error can be + or – depending whether the experimental value is greater or less than the true value.