

Enthalpy of Neutralization

11.1 Background

All chemical processes involve energy. One form of chemical energy is heat, q . When a chemical process occurs at constant pressure (as most processes in the general chemistry laboratory occur) the heat released or absorbed is called the *enthalpy change*, ΔH , for that process. A process that releases heat to the surroundings has a negative change in enthalpy ($\Delta H < 0$) is termed *exothermic*; a process that absorbs heat from the surroundings has a positive change in enthalpy ($\Delta H > 0$) and is termed *endothermic*.

The enthalpy of a reaction can be experimentally determined by measuring the amount of heat (q) gained or lost in the reaction in comparison to the number of moles of the limiting reactant used:

$$\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{moles of limiting reactant}} \quad (11.1)$$

The experimental principle behind calorimetry is that the heat gained or lost by the reacting system (those molecules or ions directly involved in the chemical process) is exactly equal to the heat lost or gained by the surroundings:

$$q_{\text{rxn}} = -q_{\text{surr}} \quad (11.2)$$

While it's very difficult to measure the heat gained or lost by the reacting system, it's much easier to determine the heat lost or gained by the surroundings, particularly if we are careful in how we define the surroundings—we just need to know the temperature change (ΔT) of the surroundings, as well as its heat capacity (C), which is a measure of how much heat a system must absorb to change the temperature one degree:

$$q_{\text{surr}} = C_{\text{surr}}\Delta T_{\text{surr}} \quad (11.3)$$

In this experiment, the surroundings will include an aqueous solution and a styrofoam cup. As long as we assume that the styrofoam cup is a perfect insulator (does not absorb or give off heat), then we can limit our discussion of “surroundings” to the aqueous solution in which the reaction takes place, and further define the heat capacity in terms of the specific heat (s) of the solution, which describes how much heat it takes to increase the temperature of 1 g of a substance 1 degree, and the mass of the solution:

$$C_{\text{surr}} = s_{\text{soln}}m_{\text{soln}} \quad (11.4)$$

By combining Eqs. (11.3) and (11.4), we arrive at a central equation in thermochemistry:

$$q = ms\Delta T \quad (11.5)$$

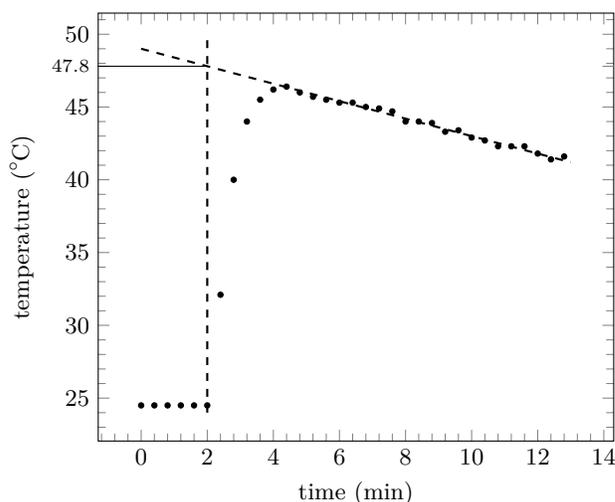


Fig. 11.1. Time versus temperature data. In this case, $T_f = 47.8\text{ }^\circ\text{C}$.

In other words, to determine q , you will need to know the total mass of your solution (m), its specific heat (s), and the temperature change due to the reaction (ΔT). The mass can easily be measured (for solids) or determined using density (for liquids), while the specific heat, s , can be looked up in a table for most common substances. **Because the temperature that we measure is the temperature of the surroundings, the q calculated by combining Eqs. (11.3) and (11.4) is q_{surr} .**

The temperature change of the reaction can be measured by using a calorimeter. A constant pressure calorimeter can be as simple of a device as an insulated container, such as a thermos or a styrofoam cup with loose-fitting lid, through which a thermometer is inserted. However, measuring the actual temperature change that could be achieved during a reaction is problematic for two reasons. First, these reactions do not occur instantaneously, so the maximum possible temperature cannot be measured directly. Second, because the system is slightly open (to maintain constant atmospheric pressure) and because the styrofoam cup is not a perfect insulator, heat loss to the surroundings is often a problem. This problem can be compensated for by measuring the temperature for several (as long as 10–15) minutes after initiating the reaction. The temperature can be plotted as a function of time and the maximum temperature found by extrapolating back to the time that the reaction was initiated. (See Fig. 11.1.)

If we examine this plot, we see that the reaction was initiated at $t = 2.0$ minutes, and the initial temperature was $24.5\text{ }^\circ\text{C}$. The temperature shows an immediate, but not instantaneous, rise as the reaction occurs, and then a slow decrease, as heat is lost to the surroundings. We can draw a best-fit straight line through the points where the temperature is linearly decreasing ($t > 5$ min) and determine the maximum possible temperature—the temperature from the extrapolation at $t = 2$ minutes. From the data in the figure we can determine that the “final temperature” would have been $47.8\text{ }^\circ\text{C}$. Therefore, for this reaction $\Delta T = 47.8\text{ }^\circ\text{C} - 24.5\text{ }^\circ\text{C} = 23.3\text{ }^\circ\text{C}$.

The enthalpy of a reaction can also be determined theoretically from the heats of formation of the reactants and products:

$$\Delta H_{\text{rxn}} = \Delta H_f^\circ[\text{products}] - \Delta H_f^\circ[\text{reactants}]$$

The standard heat of formation, ΔH_f° , of a substance is the enthalpy change involved in the formation of 1 mol of a substance from its component elements in their standard state. While this concept will be covered more in lecture, the important thing for lab is to know that these values are tallied for numerous substances, allowing for a quick and easy calculation of the enthalpy involved in any reaction. A worked example is on p. 333 of your textbook.

11.2 Procedure

In this experiment, each pair at a table will perform a single experiment, using the same acid but different bases, and then compare results.

Two styrofoam cups, one nested inside the other, and a plastic cover will serve as your calorimeter. If there is not already a small hole in the center of the plastic cover, make one with a pen cap. Then assemble the calorimeter by slipping the plastic cup cover over the temperature probe and slide it up the temperature probe. Stirring will be accomplished by swirling the cup without bumping the temperature probe.

1. Connect the GoTemp interface to one of the USB ports on the laptop and start the LoggerPro software from the shortcut on the desktop. The temperature should be displayed on the screen. Set up data collection in LoggerPro as follows:
 - a) Under the **Experiment** menu, select **Data Collection**.
 - b) Choose **Time Based** for mode.
 - c) Type in **720 seconds** for duration.
 - d) Type in **10 seconds** per sample.
 - e) Press **Done**.
2. Add 60 mL of your base (volume measured to the nearest 0.1 mL) to the calorimeter. Remember that you and the other pair at your table should use different bases.
3. Measure out 60 mL of your acid. Do NOT add it to the calorimeter yet.
4. Click **Collect** on the computer to start data collection. Swirl the cup (which should contain only the base) vigorously and constantly.
5. After about 60 seconds, or when you are sure the initial temperature reading is stable, lift the cover on the calorimeter and quickly add the acid. Continue to swirl the solution vigorously and constantly so it will completely react. This will provide the data for the determination of ΔH .
6. Your data is set to collect for 720 seconds. You may click **Stop** to end the data collection early if you are sure you have enough data to fit a line to the steadily decreasing portion.
7. Once data collection is complete, dispose of your solutions in the **Acid-Base Waste** container. Rinse the inner cup, and dry it out as best you can with a paper towel.

11.3 Analysis

1. Once you have collected your data, clean up the graph as follows:
 - a) Highlight the graph
 - b) Go to the **Options** menu and click **Graph Options**.
 - c) Enter an appropriate title in the blank space provided.
 - d) Unselect “Connect Points.”
 - e) Select “Point Symbols.”
 - f) Press **Done**.
2. To determine ΔT :
 - a) Draw a best-fit line through the points where the temperature is decreasing, by going to the Analyze menu and selecting Linear Fit.
 - b) Click and drag the brackets, [and], to select the points you want the best-fit line drawn through. *Record the equation of this line in your lab notebook.*
 - c) To find the “final” temperature, determine the time at which you added the acid, and substitute that into the equation for the best fit line.
 - d) The temperature on the graph at the time you added the acid is the initial temperature.
3. Copy/paste your graph into Word, and print a copy for each person. Label your initial and final temperatures on your graph.

11.4 Calculations and Analysis

Calculate the following for your trial:

1. q_{surr}
2. ΔH_{rxn} (make sure you know whether the acid or base is your limiting reactant!)
3. The theoretical ΔH_{rxn} (use the table at the end of this experiment) for
 - a) the molecular reaction
 - b) the net ionic reaction

Now you should compare your results with those of a pair that used the same acid but a different base than you (this should be the other pair at your table!). Prepare a summary table in your as follows:

	Our Data	[Names of other pair]’s Data
Acid used:		
Base used:		
ΔH_{rxn} (experimental)		
ΔH_{rxn} (calc; molecular)		
ΔH_{rxn} (calc; net ionic)		

Now use this information to answer the following questions in your lab notebook:

1. Does it make sense that ΔH_{rxn} (theoretical) is the same for both your reaction and the other pair's reaction? Why or why not?
2. Do your *experimental* ΔH_{rxn} values make sense relative to each other? Why or why not?

Useful Data

- $s = 3.71 \text{ J}/(\text{g } ^\circ\text{C})$

Densities of 2.0 M solutions:

- HCl: 1.03_3 g mL^{-1}
- HNO_3 : 1.06_5 g mL^{-1}
- NaOH: 1.07_9 g mL^{-1}
- KOH: 1.09_3 g mL^{-1}

Compound*	ΔH_f° (kJ mol ⁻¹)
HCl(aq)	-167.2
HNO ₃ (aq)	-207.4
NaOH(aq)	-470.1
KOH(aq)	-482.4
NaCl(aq)	-407.3
KCl(aq)	-419.6
NaNO ₃ (aq)	-447.5
KNO ₃ (aq)	-459.8
H ₂ O(l)	-285.8
OH ⁻ (aq)	-230.0
H ⁺ (aq)	0

References and Resources

Refer to Sections 9.6–9.7 and 9.9 (for heats of formation) of your textbook for more background on the topics covered in this experiment.

* Data from McMurry, J.; Fay, R.C. *Chemistry*, 4th Ed, Pearson Education: Upper Saddle River, NJ, 2004.

