

In this experiment, you will use calorimetry to experimentally determine the heat of neutralization of NaOH-HCl, or the enthalpy of the acid-base reaction between NaOH and HCl. The calorimeter is a thermos container equipped by a thermometer to monitor temperature and magnetic stirrer to ensure the contents are at uniform temperature. The thermos is assumed to be a perfect insulator such that no heat comes in or out of it. When a reaction is allowed to occur in it, the amount of heat absorbed or released by the reaction can be determined by monitoring the temperature change. If the reaction releases heat (exothermic), the solution in the thermos absorbs the heat released, thus showing a temperature increase. On the other hand, the reaction may absorb heat (endothermic) from the solution, which in turn shows a temperature decrease.

When aqueous solutions of NaOH and are mixed in the calorimeter, the chemical equation for the reaction that occurs is:

NaOH (aq) + HCl (aq)
$$\rightarrow$$
 H₂O (l) + NaCl (aq)

Assuming NaOH and HCl fully react, the solution in the calorimeter is composed of salt and water. Because the thermos is assumed to be a perfect insulator, the amount of heat absorbed or released by the reaction (q_{rxn}) is equal in magnitude, but opposite in direction, to the amount of heat released or absorbed by the solution (q_{soln}) , such that the q_{rxn} is just the negative of the q_{soln} as shown in Equation 1.

$$q_{rxn} = -q_{soln}$$
 Equation 1

The q_{soln} can be calculated from experimental data using Equation 2, where m_{soln} , $C_{s,soln}$, and ΔT_{soln} are the mass, specific heat and temperature change of the solution, respectively:

$$q_{soln} = m_{soln}C_{s,soln}\Delta T_{soln}$$
 Equation 2

As an example, let us calculate the enthalpy of the reaction below in kJ per mole of AgCl produced.

$$1 \operatorname{AgNO}_3(aq) + 1 \operatorname{HCl}(aq) \rightarrow 1 \operatorname{AgCl}(s) + 1 \operatorname{HNO}_3(aq)$$

In a calorimetry experiment, when 25.0 mL of 0.100 M AgNO₃ and 25.0 mL of 0.100 M HCl are mixed in a thermos container, an increase in temperature from 23.42 °C to 24.27 °C.

Since the solution warmed up, this means that the reaction released heat, and is thus exothermic. The q_{soln} is calculated from Equation 2, and q_{rxn} is the negative of q_{soln} by Equation 1. First, we will assume that volume is additive and that the density of the solution is the same as that of water at 1.00 g/mL, allowing us to calculate the m_{soln} . The $C_{s,soln}$ is also assumed to be the same as that of water which is 4.184 J/g·°C.

 $V_{soln} = 25.0 \text{ mL AgNO}_3 \text{ soln} + 25.0 \text{ mL HCl soln} = 50.0 \text{ mL solution}$ $m_{soln} = 50.0 \text{ mL } (1.00 \text{ g/mL}) = 50.0 \text{ g}$

$$q_{soln} = (50.0 \text{ g})(4.184 \text{ J/g} \circ \text{C})(24.27 \circ \text{C} - 23.42 \circ \text{C}) = 178\text{J}$$

 $q_{rxn} = -178 \text{ J}$

The reaction released 178 J of heat. However, we need to calculate the heat of reaction in kJ per mole of AgCl produced. For the reaction that released 178 J of heat, the number of moles of AgNO₃ and HCl that reacted are calculated from the molarities and volumes of the solutions before they were mixed:

moles
$$AgNO_3 = (0.100 \text{ M})(0.0250 \text{ L}) = 2.50 \times 10^{-3} \text{ moles } AgNO_3$$

moles $HCl = (0.100 \text{ M})(0.0250 \text{ L}) = 2.50 \times 10^{-3} \text{ moles } HCl$

Using the moles and molar relationships from the balanced chemical equation, the number of moles of AgCl can be calculated. But first, you must check if there is a limiting reagent in the reaction.

$$2.50 \times 10^{-3}$$
 moles AgNO₃ $\left(\frac{1 \ mol \ HCl}{1 \ mol \ AgNO_3}\right) = 2.50 \times 10^{-3}$ moles HCl

This is equal to the amount of HCl used; therefore, there is no limiting reagent. This means that the number of moles of either AgNO₃ or HCl can be used to calculate the number of moles of AgCl.

$$2.50 \times 10^{-3}$$
 moles AgNO₃ $\left(\frac{1 \ mol \ AgCl}{1 \ mol \ AgNO_3}\right) = 2.50 \times 10^{-3}$ moles AgCl

When 2.5 $\times 10^{-3}$ moles of both AgNO₃ and HCl react, 178 J of heat is released, which must be converted to kJ to calculate Δ H in kJ.

$$-178 \,\mathrm{J}\left(\frac{1 \,kJ}{1000 \,J}\right) = -0.178 \,\mathrm{kJ}$$

The enthalpy of reaction in terms of kJ per mole of AgCl produced can then be calculated as:

$$\Delta H = \frac{-0.178 \text{ kJ}}{2.50 \times 10^{-3} \text{ mol AgCl}} = -71.2 \frac{\text{kJ}}{\text{mol AgCl}}$$

PROCEDURE

- 1. Obtain ~150 mL each of NaOH and HCl in clean dry 250 mL beakers. Be sure to label the beakers, since both solutions are clear and colourless.
- 2. Dry the thermos and the thermometer with a paper towel. Using a dry, clean graduated cylinder, measure 50.0 mL of 1.0 M NaOH and pour it in the thermos. Put a dry, clean magnetic stirring bar into the thermos and put the thermos on top of a stirring plate.

CAUTION: You are provided with a combination heat/stir plate but will be using only the stirring function. **Do not turn the heat on as this will ruin the thermos.**

- 3. Rinse the graduated cylinder and wipe dry the inside. Measure 50.0 mL of 1.0 M HCl and pour it into a dry, clean beaker.
- 4. Measure the temperature of the acid. Rinse and wipe the thermometer, then measure the temperature of the base. The temperatures of the two solutions must be within 0.5 °C of each other. If not, warm the HCl by holding the beaker in your hands or cool by immersing the beaker in tap water.
- 5. Record the temperature of the NaOH solution; this will be your initial temperature and enter it as the temperature at 0 s.
- 6. Insert the thermometer into the thermos lid, making sure it passes through the top side of the lid then through the bottom side.
- 7. Add the HCl solution from the beaker to the NaOH solution in the thermos quickly, but taking care not to splash any solution to the sides of the thermos. Stir gently, close the lid, and lower the thermometer to the solution. Record the temperature 15 s after the addition of HCl. Continue recording the temperature every 15 s for 3 min.

The temperature rises at the beginning then stabilizes. Note the highest temperature that was achieved by the system; this will be the final temperature. If your readings show ΔT less than 4 °C, your thermometer is likely defective, and you need to repeat the experiment using another thermometer. Rinse and wipe the thermometer then turn it off when finished with the experiment.

- 8. Empty the thermos into the appropriate waste container and thoroughly rinse it and the stir bar.
- 9. Repeat Steps 1-7 two more times. Average the ΔT from all three trials.

CLEAN-UP

- Dispose of wastes in the container in the hood.
- Wash all glassware and the thermos container. Return all materials where they belong. Return the stir bar on top of the heat/stir plate.
- Make sure the thermometer is rinsed, wiped and turned off.

THERMOCHEMISTRY: HEAT OF NEUTRALIZATION

DATA

Trial 1

$T_{initial}$ (temperature at 0 seconds): NaOH _		HCl	
Time (s)	Temp (°C)	Time (s)	Temp (°C)
15		105	
30		120	
45		135	
60		150	
75		165	
90		180	
${ m T}_{ m final}$ (highest tem	p):		
$\Delta T (T_{\text{final}} - T_{\text{initial}})$:		_ (Use NaOH initial temperature)	
$T_{initial}$ (temperature at 0 seconds): NaOH _		HCl	
Time (s)	Temp (°C)	Time (s)	Temp (°C)
15		105	
30		120	
45		135	
60		150	
75		165	
90		180	
${ m T_{final}}$ (highest tem	p):		
$\Delta T (T_{\text{final}} - T_{\text{initial}})$:	_ (Use NaOH initial	temperature)

Trial 3

T _{initial} (temperature at 0 seconds): NaO	HCl			
Time (s) Temp (°C)	Time (s) Temp (°C)			
15	105			
30	120			
45	135			
60	150			
75	165			
90	180			
T _{final} (highest temp): ΔT (T _{final} – T _{initial}): (Use NaOH initial temperature)				

Average ΔT: _____

The specific heat (C_s) of water is $4.184 \text{ J/g} \cdot ^{\circ}\text{C}$

CALCULATIONS

Show clearly the complete calculations with correct number of significant figures and units.

 $\underline{\quad} \operatorname{NaOH} (aq) + \underline{\quad} \operatorname{HCl} (aq) \rightarrow \underline{\quad} \operatorname{H_2O} (l) + \underline{\quad} \operatorname{NaCl} (aq)$

1. Calculate the mass of the solution in g.

2. Calculate the q_{soln} in J using Equation 2. Use the average $\Delta T.$

3. Determine q_{rxn} in J using Equation 1.

4. Calculate the number of moles of NaCl produced.

5. Calculate the enthalpy of the reaction in kJ per mole NaCl produced.

6. The combustion of methylhydrazine (CH $_6N_2$), a liquid rocket fuel produces N $_2$ (g), CO $_2$ (g), and H $_2O$ (l):

 $\underline{\quad} CH_6N_2(l) + \underline{\quad} O_2(g) \rightarrow \underline{\quad} N_2(g) + \underline{\quad} CO_2(g) + \underline{\quad} H_2O(l)$

When 3.52 mL of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment, the heat capacity of the calorimeter is measured to be 1.95 kJ/ °C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2 . Density of methylhydrazine is 0.88 g/mL. (Hint: the heat is directly measured, not indirectly measured as in the experiment performed today)