EXPERIMENT A8: CALORIMETRY

Learning Outcomes

Upon completion of this lab, the student will be able to:

- 1) Measure the heat of a reaction under constant pressure conditions.
- 2) Calculate the enthalpy change for a reaction using the enthalpy change of two other reactions and Hess's law of heat summation.

Introduction

Enthalpy and Calorimetry

Enthalpy is defined as the heat of the reaction measured under constant pressure conditions. Since most reactions conducted in a laboratory are under constant pressure (i.e. atmospheric pressure), a measurement of the heat of the reaction is also a measure of the enthalpy change for that reaction. Heat of a reaction can be measured using a calorimeter.

A **calorimeter** requires two components: 1) an insulated container that minimizes loss of heat to the surroundings and 2) a thermometer to measure the temperature before and after a chemical reaction. A commonly used insulated container is a Styrofoam cup.

<u>Hess's Law</u>

According to the additive properties of enthalpy change (Δ H), **Hess's law** of heat summation states that states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps. For instance, assume the enthalpy change for reactions 1 and 2 below are respectively, Δ H₁ and Δ H₂.

Reaction 1:	A + B → C + D	ΔH_1
Reaction 2:	C + E → B + F	ΔH_2

Then according to Hess's law the enthalpy change for reaction 3, which is the sum of reactions 1 and 2, shown below:

Reaction 3: $A + E \rightarrow D + F \qquad \Delta H_3$

 ΔH_3 is the sum of ΔH_1 and ΔH_2

Therefore: $\Delta H_3 = \Delta H_1 + \Delta H_2$

Experimental Design

In this experiment two sets of reactions will be performed. The first set of reactions involves sodium hydroxide and hydrochloric acid. The enthalpy change for the following three reactions: 1) solubilization of solid sodium hydroxide in water 2) reaction between solid sodium hydroxide and aqueous hydrochloric acid and 3) reaction between aqueous solutions of sodium hydroxide and hydrochloric acid will be measured using the calorimetry method. The molecular equations for these three reactions are shown below:

1.	NaOH _(s)	→ NaOH _(aq)	ΔH_1
2.	$NaOH_{(s)} + HCl_{(aq)}$	→ NaCl _(aq) + H ₂ O _(l)	ΔH_2
3.	$NaOH_{(aq)} + HCl_{(aq)}$	→ NaCl _(aq) + H ₂ O _(l)	ΔH_3

Using the measured values of ΔH_1 and ΔH_2 , a calculated value of ΔH_3 can be obtained using Hess's law. The calculated and measured values of ΔH_3 will then be compared with each other to confirm Hess's law.

In the second set of reactions acetic acid will be used instead of hydrochloric acid. The molecular equations for the three reactions in this set are shown below:

4.	NaOH _(s)	\rightarrow NaOH _(aq)	ΔH_4
5.	NaOH(s) + CH ₃ COOH(aq)	→ NaCH ₃ COO _(aq) + H ₂ O _(l)	ΔH_5
6.	NaOH _(aq) + CH ₃ COOH _(aq)	→ NaCH ₃ COO _(aq) + H ₂ O _(l)	ΔH_6

Using the measured values of ΔH_4 and ΔH_5 , a calculated value of ΔH_6 can be obtained using Hess's law. The calculated and measured values of ΔH_6 will then be compared with each other to confirm Hess's law.

Note that reactions 1 and 4 are identical and will only need to be performed once.

Reagents and Supplies

Solid sodium hydroxide, 1.0 M NaOH, 1.0 M HCl, 1.0 M CH₃COOH

(See posted Material Safety Data Sheets)

Vernier kit with a temperature probe (from stockroom), laptop computer (from the lab)

Procedure

- 1. Obtain a Vernier kit containing a temperature probe and a Styrofoam cup with a lid from the stockroom. Obtain a laptop computer from the instructor.
- 2. Connect the Vernier kit and the laptop computer according to instructions provided in Appendix A.
- 3. Rinse the temperature probe with deionized water and wipe dry with a paper towel.
- 4. Set up the temperature probe and the Styrofoam cup as shown in the picture below. The Styrofoam cup should be placed inside a large beaker.



- 5. Measure exactly 100.0 mL of deionized water and add into the Styrofoam cup. Place the temperature probe in the liquid for one or two minutes to allow the probe to reach thermal equilibrium with the solution.
- 6. Measure about 2.0000 grams of solid sodium hydroxide (about 20 pellets) and record the exact mass. The mass will not be exactly two grams, but it should be as close as possible without breaking the pellets. Make sure to clean up any spills immediately. Make certain step 5 is complete before weighing the sodium hydroxide. Sodium hydroxide is hygroscopic and will absorb water from the air quickly.
- 7. Click the "collect" button on the computer.
- 8. After 2-3 seconds of temperature collection add the solid sodium hydroxide into the Styrofoam cup and mix the contents to dissolve the pellets in the water.

- 9. The temperature will begin to increase and reach a maximum value and then begin to plateau. When the temperature stays at this point for at least 30 seconds stop the collection and click the STAT button found on the menu bar above the graph. Record the minimum and maximum temperature as T_i and T_f . Calculate ΔT .
- 10. Dispose the contents of the Styrofoam cup into a large beaker and label this beaker as the "waste".
- 11. Rinse the Styrofoam cup and the temperature probe with deionized water and prepare for the next reaction.

- 12. Measure exactly 50.0 mL of deionized water and 50.0 mL of 1.0M HCl and add both into the Styrofoam cup. Place the temperature probe inside the beaker and allow it reach thermal equilibrium.
- 13. Measure about 2.0000 grams of solid sodium hydroxide (about 20 pellets) and record the exact mass. The mass will not be exactly two grams, but it should be as close as possible without breaking the pellets. Make sure to clean up any spills immediately. Make certain step 12 is complete before weighing the sodium hydroxide. Sodium hydroxide is hygroscopic and will absorb water from the air quickly.
- 14. Click the "collect" button on the computer.
- 15. After 2-3 seconds of temperature collection add the solid sodium hydroxide into the Styrofoam cup and mix the contents to dissolve the pellets in the solution.
- 16. The temperature will begin to increase and reach a maximum value and then begin to plateau. When the temperature stays at this point for at least 30 seconds stop the collection and click the STAT button found on the menu bar above the graph. Record the minimum and maximum temperature as T_i and T_f .
- 17. Dispose the contents of the Styrofoam cup into a large beaker and label this beaker as the "waste".
- 18. Rinse the Styrofoam cup and the temperature probe with deionized water and prepare for the next reaction.

- 19. For reaction 3, measure exactly 50.0 mL of 1.0 M HCl and 50.0 mL of 1.0M NaOH.
- 20. Add the 50.0 mL of 1.0M HCl into the Styrofoam cup. Place the temperature probe inside the beaker and allow it reach thermal equilibrium.
- 21. Click the "collect" button on the computer.
- 22. After 2-3 seconds of temperature collection add the 50.0 mL of 1.0M NaOH into the Styrofoam cup and mix the contents.
- 23. The temperature will begin to increase and reach a maximum value and then begin to plateau. When the temperature stays at this point for at least 30 seconds stop the collection and click the STAT button found on the menu bar above the graph. Record the minimum and maximum temperature as T_i and T_f .
- 24. Dispose the contents of the Styrofoam cup into a large beaker and label this beaker as the "waste".
- 25. Rinse the Styrofoam cup and the temperature probe with deionized water and prepare for the next reaction.
- 26. Your instructor will check your ΔT values and will indicate if reactions 1, 2 or 3 should be repeated.

REACTION 4

27. This reaction is actually the same as reaction 1. Copy the data from reaction 1 into the table for reaction 4. There is no need to repeat this reaction unless instructed to do so by your instructor

- 28. Measure exactly 50.0 mL of deionized water and 50.0 mL of 1.0M CH₃COOH and add both into the Styrofoam cup. Place the temperature probe inside the beaker and allow it reach thermal equilibrium.
- 29. Measure about 2.0000 grams of solid sodium hydroxide (about 20 pellets) and record the exact mass. The mass will not be exactly two grams, but it should be as close as possible without breaking the pellets. Make sure to clean up any spills immediately. Make certain step 28 is complete before weighing the sodium hydroxide. Sodium hydroxide is hygroscopic and will absorb water from the air quickly.

- 30. Click the "collect" button on the computer.
- 31. After 2-3 seconds of temperature collection add the solid sodium hydroxide into the Styrofoam cup and mix the contents to dissolve the pellets in the solution.
- 32. The temperature will begin to increase and reach a maximum value and then begin to plateau. When the temperature stays at this point for at least 30 seconds stop the collection and click the STAT button found on the menu bar above the graph. Record the minimum and maximum temperature as T_i and T_f . Calculate ΔT .
- 33. Dispose the contents of the Styrofoam cup into a large beaker and label this beaker as the "waste".
- 34. Rinse the Styrofoam cup and the temperature probe with deionized water and prepare for the next reaction.

- 35. For reaction 6, measure exactly 50.0 mL of 1.0 M CH₃COOH and 50.0 mL of 1.0M NaOH.
- 36. Add the 50.0 mL of 1.0M CH₃COOH into the Styrofoam cup. Place the temperature probe inside the beaker and allow it reach thermal equilibrium.
- 37. Click the "collect" button on the computer.
- 38. After 2-3 seconds of temperature collection add the 50.0 mL of 1.0M NaOH into the Styrofoam cup and mix the contents.
- 39. The temperature will begin to increase and reach a maximum value and then begin to plateau. When the temperature stays at this point for at least 30 seconds stop the collection and click the STAT button found on the menu bar above the graph. Record the minimum and maximum temperature as T_i and T_f . Calculate ΔT .
- 40. Dispose the contents of the Styrofoam cup into a large beaker and label this beaker as the "waste".
- 41. Rinse the Styrofoam cup and the temperature probe with deionized water and prepare for the next reaction.
- 42. Your instructor will check your ΔT values and will indicate if reactions 4, 5 or 6 should be repeated.

Data Table

	Reaction 1	Reaction 2	Reaction 3
Mass of solid			
sodium hydroxide			
(grams)			
Volume of			
deionized water			
(mL)			
Volume of 1.0 M			
HCl (mL)			
Volume of 1.0 M			
NaOH (mL)			
Initial			
temperature, T _i , °C			
Final temperature,			
T _f , °C			
Change in			
temperature ΔT , °C			

	Reaction 4	Reaction 5	Reaction 6
Mass of solid			
sodium hydroxide			
(grams)			
Volume of			
deionized water			
(mL)			
Volume of 1.0 M			
CH ₃ COOH (mL)			
Volume of 1.0 M			
NaOH (mL)			
Initial			
temperature, T _i , °C			
Final temperature,			
T _f , °C			
Change in			
temperature ΔT , °C			

Calculations

The enthalpy change, ΔH for each reaction studied will be calculated in units of kJ/mol of NaOH. As discussed in the "Introduction" section the ΔH for the reaction is identical to the heat flow or "q" for the reaction since the reactions are being conducted at constant pressure conditions.

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In general: q = mass \times specific heat \times \Delta T
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Since all the reactions in this experiment are being conducted in an aqueous medium, the specific heat will be assumed to be the same as the specific heat of water, which is 4.18 $\frac{Joules}{gram^{\circ}C}$.

The heat changes in this experiment involve three different components: 1) the chemical reaction 2) the aqueous medium and 3) the calorimeter.

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q_{reaction} + q_{water} + q_{calorimeter} = 0
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q_{\text{reaction}} = -(q_{\text{water}} + q_{\text{calorimeter}})
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A second assumption that will be made is that q_{calorimeter} is negligible and therefore can be ignored from these calculations. Therefore:

 $q_{reaction} = -q_{water} = -(mass_{water} \times specific heat_{water} \times \Delta T_{water})$

A third assumption that will be made in these calculations is that the density of the solution is the same as the density of water, which is 1.00 grams/mL. Therefore the mass of the water in each reaction is the same as the volume of the water.

A fourth assumption that will be made in these calculations is that when combining solutions the total final volume is the same as the sum of the volumes of the individual solutions.

Mass of water = _____ grams (Hint: Assume the density of water is close to 1.00g/mL)

$\Delta T = T_{\rm f} - T_{\rm i}$	=°C	
Specific heat	$= 4.18 \frac{Joules}{gram^{\circ}C}$	
q _{water} (Joules)	=	
q _{water} (kJ)	=	
Moles of NaOH	=	
q _{water} (kJ/mol)	=	
q _{reaction} (kJ/mol)	=	$= \Delta H_1$

REACTION 2

Mass of water= _____ grams(Hint: Assume that the solution is mostly water; therefore the density of the solution is close to the density of water 1.00g/mL)

$\Delta T = T_f - T_i$	=	_°C	
Specific heat	$= 4.18 \frac{Joules}{gram^{\circ}C}$		
q _{water} (Joules)	=		
q _{water} (kJ)	=		
Moles of NaOH	=		
Moles of HCl	=		
Limiting Reactant	=		
q _{water} (kJ/mol)	=		
qreaction (kJ/mol)	=		$= \Delta H_2$

Mass of water = _____ grams (Hint: Assume that the solution is mostly water; therefore the density of the solution is close to the density of water 1.00g/mL)

$\Delta T = T_{\rm f} - T_{\rm i}$	=	_°C	
Specific heat	$= 4.18 \frac{Joules}{gram^{\circ}C}$		
q _{water} (Joules)	=		
q _{water} (kJ)	=		
Moles of NaOH	=		
Moles of HCl	=		
Limiting Reactant	=		
q _{water} (kJ/mol)	=		
q _{reaction} (kJ/mol)	=		$= \Delta H_3$

EVALUATING THE VALIDITY OF HESS'S LAW

Measured value of ΔH for Reaction 3 = _____ (same as ΔH_3 above)

Value of ΔH for Reaction 3 based on Hess's law = $\Delta H_2 - \Delta H_1$ = _____

Percent error in the calculated value compared to the measured value: (show calculation below)

Also write equations to show how reactions 1 and 2 will be combined to obtain reaction 3:

REACTION 4 (SAME AS REACTION 1)

Mass of water = _____ grams (Hint: Assume the density of water is close to 1.00g/mL)

$\Delta T = T_{\rm f} - T_{\rm i}$	=°C	
Specific heat	$= 4.18 \frac{Joules}{gram^{\circ}C}$	
q _{water} (Joules)	=	
qwater (kJ)	=	
Moles of NaOH	=	
q _{water} (kJ/mol)	=	
q _{reaction} (kJ/mol)	=	$= \Delta H_4$

REACTION 5

Mass of water = _____ grams (Hint: Assume that the solution is mostly water; therefore the density of the solution is close to the density of water 1.00g/mL)

 $\Delta T = T_f - T_i = ____°C$

=

=

=

= 4.18 $\frac{Joules}{gram^{\circ}C}$

= _____

Specific heat

- q_{water} (Joules) =
- q_{water} (kJ)
- Moles of NaOH
- Moles of CH_3COOH =
- Limting Reactant

 $q_{water} (kJ/mol) =$

qreaction (kJ/mol)

 $= \Delta H_5$

Mass of water = _____ grams (Hint: Assume that the solution is mostly water; therefore the density of the solution is close to the density of water 1.00g/mL)

$\Delta T = T_{\rm f} - T_{\rm i}$	=	_°C	
Specific heat	$= 4.18 \frac{Joules}{gram^{\circ}C}$		
q _{water} (Joules)	=		
q _{water} (kJ)	=		
Moles of NaOH	=		
Moles of CH ₃ COOH	=		
Limting Reactant	=		
q _{water} (kJ/mol)	=		
q _{reaction} (kJ/mol)	=		$= \Delta H_6$

EVALUATING THE VALIDITY OF HESS'S LAW

Measured value of ΔH for Reaction 6 = _____ (same as ΔH_6 above)

Value of ΔH for Reaction 6 based on Hess's law = $\Delta H_5 - \Delta H_4$ = _____

Percent error in the calculated value compared to the measured value: (show calculation below)

Also write equations to show how reactions 4 and 5 will be combined to obtain reaction 6: