

Calorimetric Determination of Enthalpies of Chemical Reactions

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OBJECTIVE: 1) To determine heat (enthalpy) change in the neutralization of hydrochloric acid (HCl) and acetic acid (CH₃COOH) with sodium hydroxide (NaOH).
2) To apply Hess's Law to calculate the enthalpy of dissociation of acetic acid in aqueous solution, from the values obtained for the enthalpies of neutralization of hydrochloric and acetic acid.

INTRODUCTION:

Chemical reactions are usually accompanied by a change in energy due to the breaking and forming of bonds. To keep track of energy changes during chemical reactions that occur under **constant atmospheric pressure**, we use a thermodynamic quantity called the enthalpy, H, which is defined in terms of energy, E, pressure, P, and volume, V, as

$$H = E + PV \quad (\text{Definition of Enthalpy})$$

At constant pressure, the enthalpy change ΔH is then

$$\Delta H = \Delta E + P\Delta V \quad (\text{Enthalpy change at const P}) \quad (1)$$

The first law of thermodynamics tells us that the change in energy of a system is the sum of **heat absorbed by** the system (q) and the **work done on** the system (w). If heat flows out of the system or the system does work on the surroundings, the signs of q or w will be correspondingly negative.

$$\Delta E = q_{\text{abs}} + w \quad (\text{First Law of Thermodynamics}) \quad (2)$$

In the absence of other forms of work (e.g., electrical, such as in a battery), the first law becomes

$$\Delta E = q_{\text{abs}} - P\Delta V \quad (\text{Assuming only PV work}) \quad (2a)$$

Substituting equation (2a) for ΔE in equation (1), the enthalpy change becomes

$$\Delta H = (q - P\Delta V) + P\Delta V = q_{\text{abs}} \quad (\text{Assuming only PV work}) \quad (3)$$

Thus for a chemical reaction at constant pressure, the enthalpy change is equal to the heat change.

When a chemical reaction occurs, the associated enthalpy change can be shown to be the difference between the enthalpy of the products and the reactants

$$\Delta H = H_{\text{product}} - H_{\text{reactant}}$$

When the enthalpy of the products of a reaction is greater than the enthalpy of the reactants, ΔH is positive, heat is absorbed and the reaction is called **endothermic**. On the other hand, if the enthalpy of the products is less than that of the reactants, ΔH is negative, and the reaction produces heat. Such reactions are called **exothermic**.

While heat cannot be measured directly, we can measure its effect on a system – namely the increase or decrease in temperature of the system when the system absorbs or liberates heat. We measure the heat associated with a chemical reaction by measuring the temperature change ($\Delta T = T_{\text{final}} - T_{\text{initial}}$) of the reaction mixture. To do so, requires knowledge of how the temperature of the reaction mixture changes when a given amount of heat is absorbed or liberated by the mixture. This quantity is generally called the **specific heat** (or heat capacity) of a system, C_{sys} – usually expressed as the quantity of heat in Joules (J) or Calories (cal) [1 cal = 4.186 joule], required to raise the temperature of one gram of the system by one Kelvin (which is the same as one Centigrade degree). Thus the heat (q_{sol}) absorbed by a solution of mass m_{sol} can be calculated as

$$q_{\text{sol}} = m_{\text{sol}} C_{\text{sol}} \Delta T \quad (4)$$

If we measure the volume of a solution rather than its mass, we must convert the volume to mass by using the density of the solution. The mass, m_{sol} , of a solution of volume v_{sol} and density d_{sol} is given by $m_{\text{sol}} = v_{\text{sol}} d_{\text{sol}}$. So the heat absorbed by the solution is:

$$q_{\text{sol}} = v_{\text{sol}} d_{\text{sol}} C_{\text{sol}} \Delta T \quad (4a)$$

Measurements of heat gain or loss are usually carried out in a **calorimeter**. Calorimeters can be expensive and complex to operate. The insulating properties of styrofoam cups make them reasonable substitutes for the more expensive devices. In this experiment, we will use nested styrofoam cups as a calorimeter to carry out neutralization reactions. Neutralization reactions are exothermic – i.e., they generate heat. Styrofoam calorimeters are reasonably insulated from their surroundings (the laboratory environment) but are not insulated from their contents. If a reaction generates heat in the calorimeter, some of the generated heat will warm the thermometer and calorimeter when the reaction is conducted.

We can account for this heat loss by *calibrating* the calorimeter. We do this by conducting a reaction or other process with known heat change in the calorimeter. This permits us to determine how much of the heat is exchanged between the contents and the calorimeter and thermometer, q_{cal} . The calibration process determines a quantity called the **calorimetric constant**, C_{cal} , which is basically the specific heat of the calorimeter – i.e., the amount of heat that is required to raise the temperature of the calorimeter by 1 Kelvin (= 1 C°). If we know the heat, q_{cal} , and the temperature change (ΔT) in the calibration process, the Calorimetric constant will be given by

$$C_{\text{cal}} = q_{\text{cal}} / \Delta T \quad (5)$$

We can then use this value of the calorimetric constant to compute the heat exchange with the same calorimeter (different calorimeters will generally have different calorimetric constants) in subsequent measurements. The amount of heat that will correspond to a change in the calorimeter temperature, ΔT , will be given by:

$$q_{\text{cal}} = C_{\text{cal}} \Delta T \quad (5a)$$

When we conduct an exothermic reaction in the calorimeter, the total heat **generated** by the reaction, q_{rxn} (since absorbed heat is positive, heat **generated** is a negative number) will be equal in magnitude to the sum of heat used in raising the temperature of the reaction mixture and that used to raise the temperature of the calorimeter.

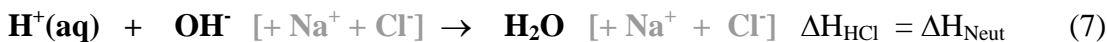
$$-q_{\text{rxn}} = q_{\text{sol}} + q_{\text{cal}} \quad (6)$$

In this exercise, we will determine C_{cal} by mixing a known mass of hot water with known mass of water at room temperature and use the known heat capacity of water.

Hess's Law

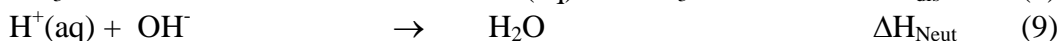
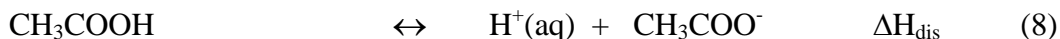
According to Hess's law, the enthalpy change of a reaction is the same whether the reaction is carried out directly or in a number of steps. It means that the enthalpy changes for chemical reactions are additive just like the chemical reactions themselves. In this exercise, we will use Hess's Law to calculate, ΔH_{dis} , the **enthalpy of dissociation of acetic acid** from the measured **enthalpy of neutralization** of hydrochloric acid (ΔH_{HCl}) and the **enthalpy of the reaction** of acetic acid (CH_3COOH), $\Delta H_{\text{CH}_3\text{COOH}}$ each with NaOH. We apply Hess's law to our experiment as follows:

First we will determine enthalpy of neutralization of HCl with NaOH. The net ionic equation for the reaction is



Reaction (7), assumes that the strong acid, HCl, is *completely dissociated* and the enthalpy of neutralization (ΔH_{HCl}) comes only from the combination of $\text{H}^+(\text{aq})$ and OH^- . We show the Na^+ and Cl^- ions in brackets because these ions play no role in the neutralization reaction for HCl. We would expect the enthalpy of neutralization of any other strong acid (e.g., HBr, HNO_3 , etc.) with any other strong base (KOH, RbOH, etc.) to be exactly the same. We call the general result ΔH_{Neut} .

Second we will determine the enthalpy of the reaction of acetic acid, CH_3COOH , with NaOH. Since CH_3COOH is a weak acid ($\text{pK}_a = 4.75$), its reaction with NaOH can be considered to be the result of two distinguishable chemical reactions. First, the dissociation of acetic acid to give $\text{H}^+(\text{aq})$, and acetate, CH_3COO^- , and then, the neutralization of $\text{H}^+(\text{aq})$ with OH^- . The net ionic equations for both steps are:



Adding equations (8) and (9) gives the overall neutralization reaction for acetic acid with hydroxide ion.



The reacting species in equation (9) are exactly the same as those in equation (7). Therefore, the enthalpy change associated with equation (9), must be the same as the enthalpy of neutralization of a strong acid by strong base represented by equation (7), (i.e., $\Delta H_{\text{Neut}} = \Delta H_{\text{HCl}}$).

Note that the chemical equation (8), the one whose enthalpy we ultimately seek, is the result of subtracting equation (9) (or equation (7), with which it is identical) from equation (10). Thus, by determining the enthalpy changes for the reactions (7) and (10) experimentally, we can calculate the enthalpy of dissociation (ΔH_{dis}) of acetic acid, equation (8), by applying the Hess's Law, namely

$$\Delta H_{\text{dis}} = \Delta H_{\text{CH}_3\text{COOH}} - \Delta H_{\text{Neut}} \quad (11)$$

Reaction enthalpies are normally reported in units of kJ/mol rather than kJ/g. Therefore, in both neutralization reactions it is the heat transferred when one mole of acid reacts with one mole of base. We will use the volume and molarity of acid to calculate the moles of HCl and CH₃COOH used in the exercise and calculate ΔH_{Neut} and $\Delta H_{\text{CH}_3\text{COOH}}$ as follows:

$$\Delta H_{\text{Rxn}} = \frac{q_{\text{Rxn}} (\text{kJ})}{\text{\# of moles of acid reacting}} \quad (12)$$

Remember that, in neutralization reactions, heat is *liberated* rather than *absorbed* in the neutralization reaction so q_{Rxn} must be negative.

The exercise consists of two parts. In **Part 1**, we determine the calorimeter constant (C_{cal}) for the styrofoam cup calorimeter. In **Part 2** we determine the enthalpy of neutralization of HCl and CH₃COOH, ΔH_{Neut} and $\Delta H_{\text{CH}_3\text{COOH}}$ respectively.

PROCEDURE:

You will be assigned a partner by your TA to do this experiment. The experiment may require the use of both the thermometer in your lab drawer and a second, thermometer accurate to ± 0.1 °C. Be particularly careful with the ± 0.1 °C thermometers. They are expensive and you will be charged if they are broken.

Part I: Determination of Calorimetric Constant

1. Obtain three styrofoam cups from your TA. Place two nested styrofoam cups into a 400-mL beaker. (We nest them to maximize insulation.) Measure out exactly **50.0**

mL of water at room temperature (unless instructed otherwise, do not use *tap water*) by using a graduated cylinder and pour into the nested styrofoam cups.

- Heat about 100 mL of water in a 250-mL beaker to approximately 50°C. (The maximum temperature for the precision thermometers is 50°C). **If the temperature of the laboratory's hot tap water is above 40°C, you may use hot tap water instead of heating water on the hot plate.** In either event, measure out exactly **50.0 mL** of hot water into the third styrofoam cup using a graduated cylinder.
- Cover the nested styrofoam cups with a cardboard lid with a hole in it. Insert a clamped 0.1°C thermometer vertically (a special thermometer clamp is provided) in the inner styrofoam cup adjusting the height of the thermometer so that its bulb is in the lower half portion of the liquid contents. Similarly, insert a second thermometer into the hot water Styrofoam cup. Try to insure the hot water is at a uniform temperature. Your TA will demonstrate the set-up in the lab.
- Measure the temperatures of the room temperature water in the calorimeter and the hot water in the styrofoam cup alternately at 30 second intervals for 3 minutes. Record these data on data sheet 1. One partner will measure and announce the temperature and the other partner will record time and temperature. Be sure to record the temperature to the full precision of the respective thermometers.
- Immediately after the reading at 3 minutes, add the hot water carefully to the cold water cup in the calorimeter and replace the cardboard cover. Mix by swirling the cups gently and *continue to read temperature at 30 second intervals* for the next two minutes and then at 1 minute intervals for another 5 minutes. Record these data on data sheet 1.

Part 2: Enthalpy of Neutralization of Hydrochloric acid and Acetic Acid with Sodium Hydroxide

- Dry the styrofoam cups used in Part 1 as well as possible. Rinse your cleaned 100-mL graduated cylinder with 5 mL of the hydrochloric acid provided in the laboratory and discard the rinse into the sink. Measure out exactly **50.0 mL** of HCl (note and record the exact concentration of HCl from the container) by using the graduated cylinder and pour the HCl into the nested styrofoam cups. Rinse the graduated cylinder twice with distilled water and then with 5 mL of sodium hydroxide solution. Measure out **55.0 mL** of sodium hydroxide solution (note and record the exact concentration from the bottle) in your graduated cylinder and pour it into a 250-mL beaker. The concentrations of the acid and base should have been adjusted so that using the above volumes will ensure that the acid is the limiting reagent.
- Measure the temperature of the liquids in both the Styrofoam cups and in the beaker alternately at 30 second intervals for 3 minutes. Record these data on Data Sheet 2. The temperature of both solutions should be within **0.5°C**. **If not, consult your teaching assistant about how to proceed.**

- Exactly on the 3rd minute, add the entire amount of NaOH to the HCl. Replace the cardboard cover and while continuing to swirl, measure the temperature at 30 second intervals for 2 minutes and at one minute intervals for 3 more minutes.
- Rinse out the containers and repeat steps 1, 2, and 3 using **50.0 mL** of acetic acid instead of hydrochloric acid in step 1.

GRAPHING AND CALCULATIONS:

Part 1: Calculation of Calorimetric constant

Plot the data from Data Sheet 1, with time as the horizontal-axis and temperature as the vertical axis. Draw a vertical line at the time of mixing. Draw straight lines through the three sets of points. Call the temperatures of the hot and cold water at three minutes T_{hot} and T_{cold} . Extrapolate the temperature of the mixture backward to where it crosses the vertical line at the time of mixing (3 minutes). Call that temperature T_{mix} . Make sure the plot permits reading these temperatures to the appropriate precision. (This will be simplest if the temperature scale on the graph is broken into three regions corresponding to the range of the three desired temperatures over their respective time intervals.)

Calculate heat **lost** by hot water (q_{hot}) and heat **gained** by cold water (q_{cold}) from hot water as follows (Note that, since $T_{\text{mix}} < T_{\text{hot}}$, q_{hot} will be negative.)

$$q_{\text{hot}} = (\text{vol of hot water, mL}) \times (\text{density of water, g/mL}) \times C_{\text{W}} \times (T_{\text{mix}} - T_{\text{hot}}) \quad (13)$$

$$q_{\text{cold}} = (\text{vol of cold water, mL}) \times (\text{density of water, g/mL}) \times C_{\text{W}} \times (T_{\text{mix}} - T_{\text{cold}}) \quad (14)$$

Assume the density of water is 1.00 g/mL and its heat capacity (C_{W}) is 4.18 J/g-°C. Since the magnitude of the heat lost by the hot water is equal to the magnitude heat gained by cold water and by the calorimeter

$$-q_{\text{hot}} = q_{\text{cold}} + q_{\text{cal}} \quad (15)$$

or

$$q_{\text{cal}} = -q_{\text{hot}} - q_{\text{cold}} \quad (16)$$

C_{cal} was defined in equation (5) as $C_{\text{cal}} = q_{\text{cal}} / \Delta T$, where ΔT is the change in temperature of the contents of the calorimeter. Since the calorimeter experienced the same temperature change as the cold water, this becomes

$$C_{\text{cal}} = q_{\text{cal}} / (T_{\text{mix}} - T_{\text{cold}}) \quad (17)$$

Note that q_{cal} (and therefore C_{cal}) must be positive. If you do not get a positive value for q_{cal} , you must repeat Part 1.

Part 2: Calculations of Heat of neutralization of HCl and CH₃COOH with NaOH.

Plot the data from Data Sheet 2 for each of the two acids on separate sheets of graph paper. In both cases, determine the temperature of the acid $T_{\text{ini}}(\text{acid})$ and of the base $T_{\text{ini}}(\text{base})$ at the time of mixing and temperature of the mixture (T_{mix}) at the time of mixing by the same extrapolation technique used in Part 1. Again, these plots should be prepared so as to obtain the appropriate precision in the extrapolated temperatures.

If the acid and base are at different temperatures at the time of mixing, use the average of their extrapolated temperatures as T_{ini} below.

Calculate heat (q_{Rxn}) produced in the neutralization reaction for both hydrochloric acid and acetic acid from equations (6), (4) and (5) as follows:

$$q_{\text{Rxn}} = (\text{vol of solution, mL})(\text{density, g/mL})(\text{heat capacity, J/g-}^{\circ}\text{C})(\Delta T) + C_{\text{cal}}\Delta T \quad (18)$$

$$\text{where } \Delta T = (T_{\text{mix}} - T_{\text{ini}}).$$

ΔT is called the “instantaneous temperature rise” in Data sheet 2

Assume the densities and heat capacities of the acids, the base and the resulting salt solutions are 1.02 g/mL, and 3.97 J/g-^oC respectively .

Use equation (12) to calculate molar enthalpies, ΔH_{Neut} and $\Delta H_{\text{CH}_3\text{COOH}}$. Be careful to report the correct sign for these quantities.

Finally use equation (11) to find enthalpy of dissociation, ΔH_{dis} , of acetic acid.

DATA SHEET 1
Calorimetric Determination of Enthalpy of Reactions

NAME: _____

SEC: _____

Partner's Name: _____

Time/Temperature data – Determination of Calorimetric Constant

Time (min.)	Temp. (°C) Hot Water	Temp. (°C) (Mix)	Temp. (°C) Cold Water
0.0	_____		_____
0.5	_____		_____
1.0	_____		_____
1.5	_____		_____
2.0	_____		_____
2.5	_____		_____
3.0	_____		_____
MIX			
3.5		_____	
4.0		_____	
4.5		_____	
5.0		_____	
6.0		_____	
7.0		_____	
8.0		_____	
9.0		_____	
10.0		_____	

Volume of hot water, mL _____

Volume of cold water, mL _____

Temperature of Hot water, (T_{hot} from graph), °C _____

Temperature of cold water, (T_{cold} from graph), °C _____

Temperature after Mixing (T_{mix} from graph), °C _____

Heat change for hot water (q_{hot}), J (eq. 13) _____

Heat change for cold water (q_{cold}), J (eq. 14) _____

Heat transferred to calorimeter (q_{cal}), J (eq. 16) _____

Calorimeter Constant of calorimeter (C_{cal}), J/°C (eq. 17) _____

DATA SHEET 2
Calorimetric Determination of Enthalpy of Reactions

NAME: _____

SEC: _____

Partner's Name: _____

**Time/Temperature data – Enthalpy of neutralization of HCl and CH₃COOH
 With NaOH**

Time (min.)	Mixture		Mixture	
	Temp. °C NaOH	Temp. °C HCl	Temp. °C NaOH	Temp. °C CH ₃ COOH
0.0	_____	_____	_____	_____
0.5	_____	_____	_____	_____
1.0	_____	_____	_____	_____
1.5	_____	_____	_____	_____
2.0	_____	_____	_____	_____
2.5	_____	_____	_____	_____
3.0	_____	_____	_____	_____
MIX				
3.5	_____		_____	
4.0	_____		_____	
4.5	_____		_____	
5.0	_____		_____	
6.0	_____		_____	
7.0	_____		_____	
8.0	_____		_____	
9.0	_____		_____	
10.0	_____		_____	

Calculations of Enthalpies of Neutralization:	<u>HCl</u>	<u>CH₃COOH</u>
Volume of NaOH, mL	_____	_____
Molarity of NaOH, M	_____	_____
Number of moles of NaOH	_____	_____
Volume of Acid, mL	_____	_____
Molarity of Acid, <u>M</u>	_____	_____
Number of moles of Acid	_____	_____
Instantaneous temperature rise (from graph) °C	_____	_____
Heat of neutralization (q_{Rxn}), J, (eq. 18)	_____	_____
Moles of Acid neutralized	_____	_____
Heat of neutralization (ΔH_{Rxn}), kJ mol ⁻¹ (eq 12)	_____	_____
Heat of dissociation of CH ₃ COOH (ΔH_{dis}), kJ mol ⁻¹ (eq11)	_____	_____

SUSB-053 Pre Lab

Name

Section

Date

- 1) If 50 mL of water at 22.3 °C is mixed with 50 mL of water at 47.7 °C in such a way that no heat is lost to the environment, what will be the temperature of the final mixture?
- 2) If 50 mL of water at 22.3 °C is mixed with 50 mL of water at 47.7 °C in a calorimeter with $C_{\text{cal}} = 20.0 \text{ J/}^\circ\text{C}$, what will be the temperature of the final mixture?
- 3) A student performed part 1 of the procedure. After plotting data as described in the calculations section, the student found the temperature of cold water, hot water, and temperature at time of mixing to be 22.3 °C , 47.7 °C , and 34.6 °C respectively. Calculate the calorimeter constant, C_{cal} for the calorimeter. Use the density and heat capacity values as shown in the calculations section.
- 3) The same student then performed the experiment according to Procedure 2 for HCl and obtained the following data:

Time (min)	Temp.(°C)		Time (min)	Temp. (°C)
	HCl	NaOH		
0.0	20.0	20.5	3.5	27.3
0.5	20.1	20.6	4.0	28.5
1.0	20.2	20.7	4.5	28.9
1.5	20.3	20.8	5.0	28.8
2.0	20.4	20.9	6.0	28.7
2.5	20.4	20.9	7.0	28.5
3.0	20.4	20.9	8.0	28.3
			9.0	28.1

MIX

- a) Graph data as described in the calculation section (attach graph)
- b) Extrapolate data and determine the temperature change (ΔT).at the time of mixing.

OVER

c) What is the total volume of the reaction mixture?

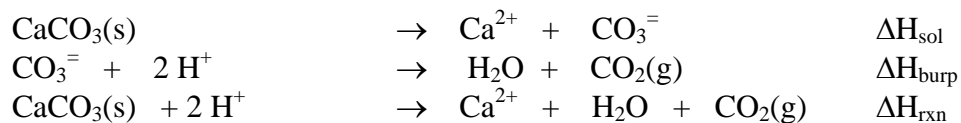
d) Calculate the heat (q_{ntnr}) liberated by the reaction using the densities and heat capacity values given in the calculation section. Use the value of C_{cal} calculated in question 1.

e) Suppose that molarity of HCl is 2.000 M, calculate the number of moles of acid neutralized. Assume the acid is the limiting reagent.

f) Calculate ΔH of neutralization for the reaction of HCl with NaOH.

4) Would the enthalpy of neutralization determined for HCl be the same if we replaced hydrochloric acid by nitric acid? Explain your answer.

5) The reaction of CaCO_3 with HCl to liberate CO_2 can be thought of as occurring in two steps;



How is the heat of solution ΔH_{sol} related to ΔH_{rxn} and ΔH_{burp} ?