Experiment 3

HEAT OF REACTIONS

Objective

The purpose of this experiment is to investigate the heat of neutralization and solution by using a simple calorimeter. The molar enthalpy of formation of MgO is also determined by using Hess' law.

Lab techniques

- Weighing chemicals.
- Measuring volumes.
- Using a digital thermometer.

Introduction

I. The enthalpy of reaction

Chemical reactions are usually accompanied with a change in energy. The change of energy is reflected in the flow of heat (q) that can be determined experimentally. If the reaction occurs at constant pressure, the heat measured (q_p) is equal to the enthalpy (H) change of reaction, and is often called heat of reaction, denoted by ΔH. Reactions that release heat are said to be exothermic, and ΔH has a negative value ($\Delta H < 0$). On the other hand, reactions that absorb heat are said to be endothermic, and ΔH has a positive value ($\Delta H > 0$). If a reaction proceeds in an adiabatic calorimeter, we can calculate the heat that the reaction releases or absorbs by measuring the change in temperature (ΔT) of the calorimeter.

In this experiment, we set up a 'calorimeter' from simple Styrofoam cups and use it to measure the enthalpy changes of several reactions. Since the calorimeter itself can absorb or release heat from or into the reaction system, we first need to know the heat capacity of the device. The heat capacity of the calorimeter refers to the amount of heat absorbed or released in changing its temperature by 1^{o}C. To determine the heat capacity of the calorimeter, a known amount of warm water is added to a known amount of cold water in the calorimeter. The heat released by the warm water must be the same as the sum of the heat gained by the calorimeter and the cold water (3-1). This equality is illustrated below:

T_1: the temperature of the calorimeter with x mL cold water

T_2: the initial temperature of y mL warm water

T_f: the equilibrium temperature after mixing warm water with cold water

C: heat capacity of calorimeter in cal/^oC or J/^oC

q_1 = heat released from warm water

= $(T_2 - T_f)\ ^oC \cdot y\ mL \cdot 1.0\ g/mL \cdot 1\ cal/g{\cdot}^oC$

q_2 = heat gained by cold water

= $(T_f - T_1)\ ^oC \cdot x\ mL \cdot 1.0\ g/mL \cdot 1\ cal/g{\cdot}^oC$

q_3 = heat gained by calorimeter

= $(T_f - T_1)\ ^oC \cdot C\ cal/^oC$

$$q_1 = q_2 + q_3 \qquad (3\text{-}1)$$

Heat of reaction (ΔH) can therefore be calculated from the temperature change and the sum of the heat capacities of the calorimeter and its contents (3-2):

$$\Delta H = -[C \cdot \Delta T + m \cdot s \cdot \Delta T] \qquad (3\text{-}2)$$

II. Application of Hess' law - Enthalpy of formation of magnesium oxide

The enthalpy of a chemical reaction is path-independent. When a particular chemical reaction is expressed as the sum of two or more other chemical reactions, the enthalpy change of the former is equal to the sum of the enthalpy changes of the contributing steps. This principle, called Hess' law, is particularly useful to determine an enthalpy that is difficult to measure experimentally, since we can find its value from other known enthalpies or from those that are easy to measure by experiment. In this experiment, we will use Hess' law to determine the enthalpy of formation of magnesium oxide (3-3) by measuring the enthalpies of reaction of magnesium and magnesium oxide with hydrochloric acid (3-4 and 3-5), separately, as well as the enthalpy of formation of water (3-6), i.e. -285.8 kJ/mol or -68.4 kcal/mol.

$$Mg(s) + 1/2O_2(g) \rightarrow MgO(s) \qquad \Delta H_f^o(MgO) \qquad (3\text{-}3)$$

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad \Delta H_1 \qquad (3\text{-}4)$$

$$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l) \qquad \Delta H_2 \qquad (3\text{-}5)$$

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f^o(H_2O) \qquad (3\text{-}6)$$

Apparatus

Styrofoam cups (250 mL, 2), plastic lid, digital thermometer, beaker (400 mL), graduated cylinder (50 mL), timer, and electronic balance.

Chemicals

Magnesium strips, Mg

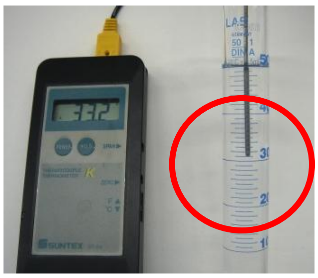
Ammonium nitrate, NH_4NO_3

Magnesium oxide, MgO

1.0 M Sodium hydroxide, NaOH

1.0 M Hydrochloric acid, HCl(aq)
1.0 M Acetic acid, CH_3COOH

Procedure

Procedure		Illustration
I. Heat capacity of the calorimeter		
1.	Construct a calorimeter by using a 400 mL beaker and two Styrofoam cups as shown in Fig. 3-1.	
2.	Measure exactly 50.0 mL of DI water and place it into the calorimeter. Let it stand for about 3 min. until thermal equilibrium is reached. Record the equilibrium temperature to one decimal place. Note: Refer to the experimental skills videos to learn how to use a graduated cylinder.	
3.	(1) Measure exactly 50.0 mL of warm water in a graduated cylinder (the temperature is ideally 10~15°C higher than that of the cold water). Let it stand for about 3 min. until the water and the graduated cylinder reach thermal equilibrium. Record the volume and the temperature of warm water. (2) Pour the warm water into the cold water in the calorimeter as quickly as possible. Note: Place the probe of thermometer in the center of solution and do not touch the wall of graduated cylinder.	 
4.	Cover the Styrofoam cup with the plastic lid and insert the thermometer. Swirl the cup so that the content is mixed and thermal equilibrium is reached. Record the equilibrium temperature. Note: The mixture reaches thermal equilibrium very quickly.	

II. Heat of neutralization - HCl/NaOH

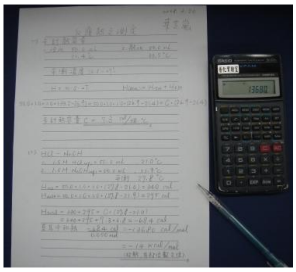
5.	Wash and wipe dry the thermometer and Styrofoam cups. Note: The thermometer probe and the Styrofoam cup must be washed after each use to prevent any remaining substances or heat from affecting the results of the next use.	
6.	Place exactly 50.0 mL of a 1.0 M HCl solution into the calorimeter. Measure and record the equilibrium temperature.	
7.	(1) Measure 50.0 mL of 1.0 M NaOH solution into a 50 mL graduated cylinder. Record the volume and equilibrium temperature. (2) Pour the NaOH solution into the calorimeter containing HCl solution.	
8.	Cover the Styrofoam cup and insert the thermometer. Swirl the cup to mix the solution thoroughly. Monitor the temperature of the solution and record it every 5 s. Determine the equilibrium temperature, i.e. the maximum or the minimum temperature for an exothermic or an endothermic reaction, respectively. Note: The reaction mixture reaches thermal equilibrium rapidly.	

III. Heat of neutralization – CH_3COOH/NaOH

9.	Repeat steps 5~8, using 50.0 mL of 1.0 M CH_3COOH and 50.0 mL of 1.0 M NaOH as reactants instead. Note: The reaction mixture reaches thermal equilibrium rapidly.	

IV. Heat of solution of ammonium nitrate

10.	Wash and wipe dry the thermometer and Styrofoam cups. Add exactly 50.0 mL of DI water into the calorimeter. Let it stand for about 3 min. until thermal equilibrium is reached. Record the equilibrium temperature.	
11.	Weigh ca. 4 g of NH_4NO_3 solid and record the exact weight. Add it into the calorimeter. Repeat step 8 and determine the equilibrium temperature. Note 1: The solid NH_4NO_3 dissolves in solution slowly. The reaction mixture should be swirled continuously until it reaches the minimum temperature, for this is an endothermic reaction. Note 2: Refer to the experimental skills videos to learn how to weigh chemicals.	
V.	Enthalpy of formation of magnesium oxide	
12.	(1) Wash and wipe dry the thermometer and Styrofoam cups. (2) Add exactly **100.0 mL** of 1.0 M HCl solution to the calorimeter. Let it stand for 3 min. until the calorimeter and its content are in thermal equilibrium. Record the temperature.	
13.	Weigh ca. 0.2 g of magnesium strip and record its exact weight. Add it to the calorimeter.	
14.	Repeat step 8 and determine the equilibrium temperature. Note: The reaction mixture should be swirled continuously until it reaches the maximum temperature, otherwise the reaction may not be completed.	

15.	(1) After the reaction completes, wash and wipe dry the thermometer and Styrofoam cups. (2) Add exactly **100.0 mL** of 1.0 M HCl solution to the calorimeter. Repeat step 13, but substitute the reactant with 0.7 g magnesium oxide. Determine the equilibrium temperature.	
16.	Calculate the molar enthalpy change of each reaction. In this experiment, the density and specific heat capacity of all aqueous solutions are assumed to be the same as that of water, i.e. 1.0 g/mL and 1 cal/g·°C (4.184 J/g·°C).	

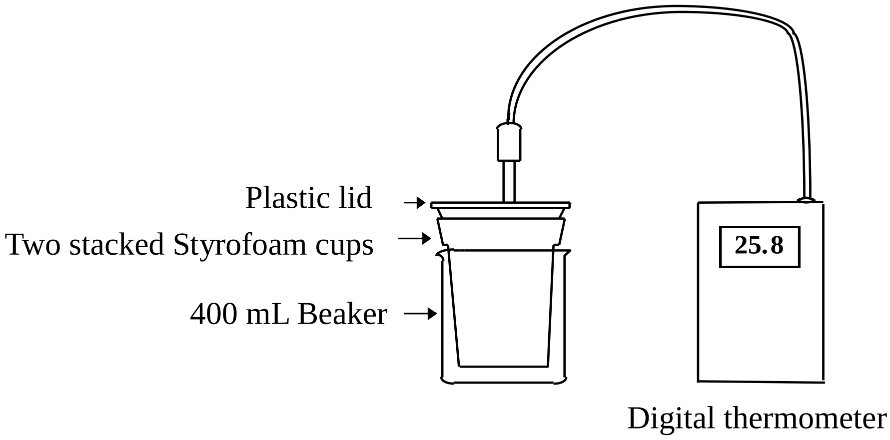


Figure 3-1 Coffee-cup calorimeter