Experiment 5

HEAT OF REACTIONS

Objective

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

Lab techniques

➢ Using a digital thermometer
➢ Weighing chemicals
➢ Measuring volumes

Introduction

I. The enthalpy of reaction

All substances have specific energies. When reactions are carried out, they are often accompanied by changes in energy. This change in energy is often exchanged with the surroundings in the form of thermal energy, which is called heat (q). When the reaction is carried out under constant pressure, the measured heat (q_p, p represents constant pressure) is the change in enthalpy (H) of the reaction system, ΔH, which is called the enthalpy of reaction or heat of reaction. A reaction that absorbs energy from surroundings is said to be endothermic, and its ΔH has a positive value ($\Delta H > 0$). On the contrary, a reaction that releases energy is said to be exothermic, and its ΔH has a negative value ($\Delta H < 0$), as shown in Fig. 5-1. If the reaction proceeds in an adiabatic calorimeter, we can calculate the energy that the reaction releases or absorbs by measuring the change in temperature of the calorimeter.
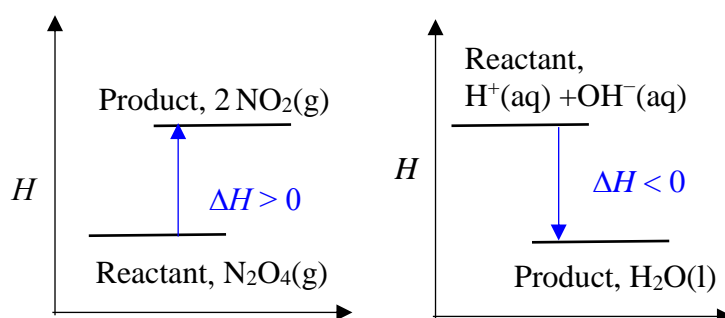

Figure 5-1　Enthalpy changes of reactions

In this experiment, we set up a 'coffee-cup calorimeter' from Styrofoam cups (Fig. 5-2), and use it to measure the heat of several reactions. Assuming that the calorimeter is an adiabatic system ($q_{sys} = 0$), the heat released (or absorbed) by the reaction (q_{rxn}) is absorbed (or released) by the calorimeter (q_{cal}) and its content solution (q_{soln}), as shown in Equation 5-1. The heat of the reaction can therefore be calculated from the temperature change ($\Delta T = T_f - T_i$), the sum of the heat changes of the calorimeter, and the aqueous solution contained in it (5-2). Then, the molar enthalpy of reaction, ΔH, can be obtained by q_{rxn} divided by number of mole of limiting reagent, n, as shown in equation 5-3.

$$q_{sys} = q_{rxn} + q_{cal} + q_{soln} = 0 \tag{5-1}$$

$$q_{rxn} = -[\, q_{cal} + q_{soln}] = -[C \cdot \Delta T + m \cdot s \cdot \Delta T\,] \tag{5-2}$$

$$\Delta H = q_{rxn} \div n \tag{5-3}$$

where m is the mass and s is the specific heat of the aqueous solution, respectively. C is the heat capacity of the calorimeter, which refers to the amount of energy absorbed or released in changing its temperature by 1°C.

II. Heat capacity of calorimeter

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 (5-4). This equality is illustrated below:

$$q_w + q_c + q_{cal} = 0$$

$$q_w = -[\, q_c + q_{cal}] = -[\, m_c \cdot s \cdot \Delta T_c + C \cdot \Delta T_c] \tag{5-4}$$

$$q_w = m_w \cdot s \cdot \Delta T_w = (1.0 \text{ g/mL} \cdot V_w \text{ mL}) \cdot 1 \text{ cal/g·°C} \cdot (T_f - T_w)\,°C$$

$$q_c = m_c \cdot s \cdot \Delta T_c = (1.0 \text{ g/mL} \cdot V_c \text{ mL}) \cdot 1 \text{ cal/g·°C} \cdot (T_f - T_c)\,°C$$

$$q_{cal} = C \cdot \Delta T_c = C \text{ cal/°C} \cdot (T_f - T_c)\,°C$$

where

s: the specific heat of water, 1 cal/g·°C

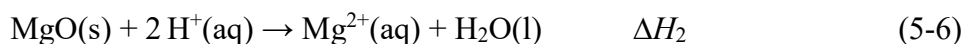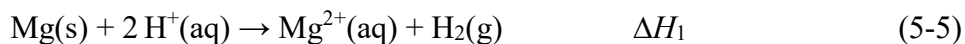T_c: the temperature of the calorimeter with V_c mL cold water

T_w: the temperature of V_w mL warm water

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

III. 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 of the former is equal to the sum of the enthalpies of the contributing steps. This principle is called Hess' law or law of constant heat summation. It is particularly useful to determine an enthalpy that is difficult to measure experimentally, since its

value can be calculated from other known enthalpies or those that are easy to be measured. In this experiment, we will measure the enthalpies of reactions of magnesium and magnesium oxide with hydrochloric acid (5-5 and 5-6), respectively, and use Hess' law with the known enthalpy of formation of water (5-7), *i.e.* −285.8 kJ/mol or −68.4 kcal/mol, to determine the enthalpy of formation of magnesium oxide (5-8).

$$\text{Mg(s)} + 2\,\text{H}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \qquad \Delta H_1 \qquad (5\text{-}5)$$

$$\text{MgO(s)} + 2\,\text{H}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{H}_2\text{O(l)} \qquad \Delta H_2 \qquad (5\text{-}6)$$

$$\text{H}_2(\text{g}) + 1/2\,\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} \qquad \Delta H_f^\circ(\text{H}_2\text{O}) \qquad (5\text{-}7)$$

$$\text{Mg(s)} + 1/2\,\text{O}_2(\text{g}) \rightarrow \text{MgO(s)} \qquad \Delta H_f^\circ(\text{MgO}) \qquad (5\text{-}8)$$

Apparatus

Styrofoam cup (250 mL, 2), plastic lid, digital thermometer, dropper, beaker (100, 400 mL), graduated cylinder (50 mL), and timer.
Shared: electronic balance.

Chemicals

Magnesium strips, Mg

Ammonium chloride, NH_4Cl

Magnesium oxide, MgO

1.0 *M* Sodium hydroxide, NaOH

1.0 *M* Hydrochloric acid, HCl(aq)

1.0 *M* Acetic acid, CH_3COOH
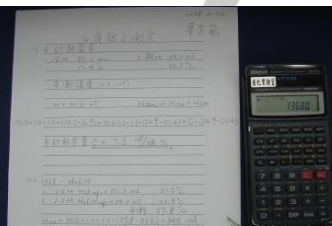
Procedure

Procedure		Illustration
I. Heat capacity of the calorimeter		
1.	Construct a calorimeter by using a 400 mL beaker, two Styrofoam cups, and a lid as shown in Fig. 5-2.	
2.	Measure *ca.* 50 mL of DI water, record the exact volume, and pour it into the calorimeter. Let it stand for 1~2 min until thermal equilibrium is reached. Record the equilibrium temperature.	

3.	(1) Mix the hot water and cold water in a 100 mL beaker to get warm water with a temperature about 10~15°C higher than the cold water. (2) Measure 50 mL of the warm water in a graduated cylinder. Let it stand for 1~2 min until the water and the graduated cylinder reach thermal equilibrium. Record the volume and the temperature of the warm water. (3) Pour the warm water into the cold water in the calorimeter as quickly as possible. Note1: Rinse the thermometer probe with water to bring its temperature to room temperature. Note 2: Place the thermometer probe in the center of the liquid and do not touch the wall of the graduated cylinder.	
4.	Quickly cover the Styrofoam cup with the plastic lid and insert the thermometer. Swirl the calorimeter so that the content is mixed and thermal equilibrium is reached. Record the equilibrium temperature. Note: The mixture reaches thermal equilibrium rapidly.	

II. Heat of neutralization – HCl/NaOH

5.	Wash and wipe dry the thermometer probe 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 measurement.	
6.	Place *ca.* 50 mL of 1.0 M HCl into the calorimeter. Measure and record the equilibrium temperature and volume.	

7.	(1) Measure *ca.* 50 mL of 1.0 *M* NaOH with a 50 mL graduated cylinder, and record the volume and equilibrium temperature. (2) Pour the NaOH solution into the calorimeter containing the HCl solution. Note: Rinse the graduated cylinder with a small amount of reagent when changing the solution.	
8.	Quickly cover the Styrofoam cup and insert the thermometer. Swirl the calorimeter to mix the solution thoroughly. Monitor the temperature evolution of the solution and record it. Determine the equilibrium temperature, *i.e.* the maximum or the minimum temperature for an exothermic or an endothermic reaction, respectively. Note: The aqueous solution reaction reaches thermal equilibrium rapidly.	

III. Heat of neutralization – CH₃COOH/NaOH

9.	Repeat steps 5~8 using 50 mL of 1.0 *M* CH₃COOH and 50 mL of 1.0 *M* NaOH as reactants instead.	

IV. Heat of solution of ammonium chloride

10.	Wash and wipe dry the thermometer and Styrofoam cups. Add *ca.* 50 mL of DI water into the calorimeter. Measure the equilibrium temperature, then record the temperature and the volume.	
11.	Weigh *ca.* 3 g of NH₄Cl solid and record the exact weight. Add it into the calorimeter. Repeat step 8 and determine the equilibrium temperature. Note: For solid reactants, the reaction mixture should be swirled continuously to react completely.	

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	V. Enthalpy of formation of magnesium oxide	
12.	(1) Wash and wipe dry the thermometer and Styrofoam cups. (2) Add 100 mL of 1.0 M HCl to the calorimeter. (3) Measure and record the equilibrium temperature.	
13.	Weigh *ca.* 0.2 g of magnesium strip and record its exact weight. Add it into the calorimeter. Repeat step 8 and determine the equilibrium temperature.	
14.	After the reaction completes, wash and wipe dry the thermometer and Styrofoam cups. Add 100 mL of 1.0 M HCl to the calorimeter. Repeat step 13, but substitute the reactant with 0.7 g magnesium oxide. Determine the equilibrium temperature. Note: Swirl the reaction mixture continuously to react completely.	
15.	Calculate the molar enthalpy of each reaction. Note: The density and the specific heat capacity of all aqueous solutions are assumed to be the same as those of water, *i.e.* 1.0 g/mL and 1 cal/g·°C (4.184 J/g·°C), respectively.	
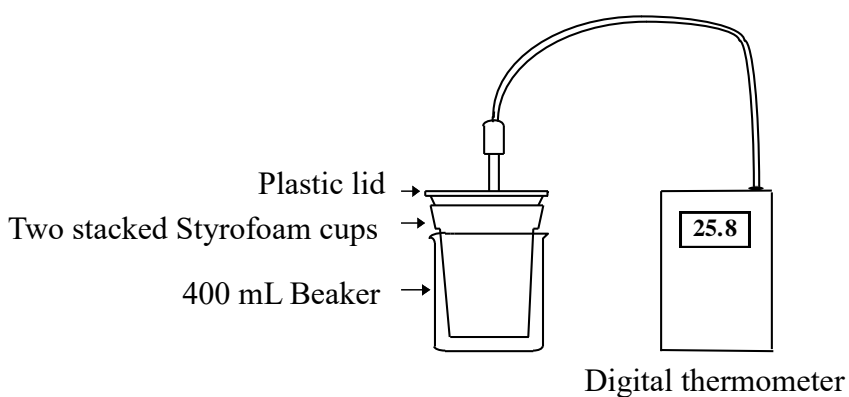
Figure 5-2   Coffee-cup calorimeter