

10.7: Measuring ΔH for Chemical Reactions- Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 10.7.1), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6}°C). Because the heat released or absorbed at constant pressure is equal to ΔH , the relationship between heat and ΔH_{rxn} is

$$\Delta H_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{calorimeter}} = -mC_s\Delta T \quad (10.7.1)$$

The use of a constant-pressure calorimeter is illustrated in Example 10.7.3

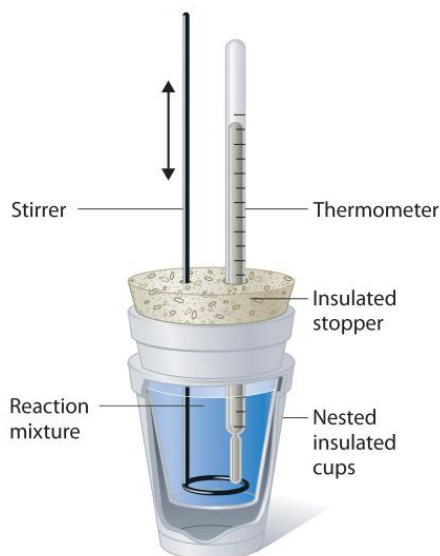


Figure 10.7.1: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants. (CC BY-NC-SA; anonymous)

Example 10.7.1

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C . The density of water in this temperature range averages 0.9969 g/cm^3 . What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

- Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
- Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.5.8.
- Use the molar mass of KOH to calculate ΔH_{soln} .

Solution:

A To calculate ΔH_{soln} , we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\text{ mL H}_2\text{O}) \left(0.9969\text{ g/mL} \right) + 5.03\text{ g KOH} = 104.72\text{ g} \quad (10.7.2)$$

The temperature change is $(34.7^{\circ}\text{C} - 23.0^{\circ}\text{C}) = +11.7^{\circ}\text{C}$.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{\text{calorimeter}} = mC_s\Delta T = \left(104.72 \text{ g}\right) \left(\frac{4.184 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}}\right) (11.7^{\circ}\text{C}) = 5130 \text{ J} = 5.13 \text{ kJ} \quad (10.7.3)$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 10.7.1, we see that

$$\Delta H_{\text{rxn}} = -q_{\text{calorimeter}} = -5.13 \text{ kJ}$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln} —the heat released when dissolving 1 mol of KOH:

$$\Delta H_{\text{soln}} = \left(\frac{5.13 \text{ kJ}}{5.03 \text{ g}}\right) \left(\frac{56.11 \text{ g}}{1 \text{ mol}}\right) = -57.2 \text{ kJ/mol} \quad (10.7.4)$$

Exercise 10.7.1

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C . Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C . Using the same assumptions as in Example 10.7.1, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

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