

## 15.7: Measuring the Enthalpy Change

In an elementary laboratory, **enthalpy** changes are often measured in a “coffee-cup calorimeter” such as that shown in Figure 15.7.1. Suppose the reaction to be measured is between two solutions. One of these solutions is introduced into the coffee cup, and the temperature of both solutions is measured. The second solution is now introduced, the mixture stirred, and the rise in temperature recorded. Since the cup is made of polystyrene foam, a very good insulator, very little heat energy escapes. It may be measurable, however, and may be represented by the **calorimeter constant**.

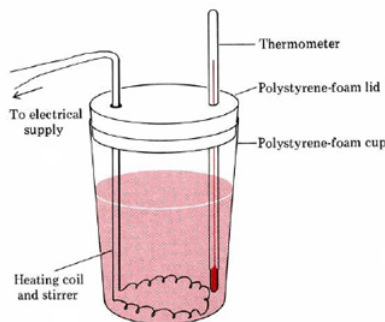


Figure 15.7.1 A coffee-cup calorimeter.

### The Calorimeter Constant

A simple experiment can be used to determine how much energy is lost to the calorimeter, the thermometer, and the surroundings. This energy loss, divided by the temperature change in the calorimeter that caused it, is often called the “calorimeter heat capacity” or “calorimeter constant” as illustrated by the following example:

#### ✓ Example 15.7.1: Calorimeter Constant

A styrofoam cup calorimeter contains 50 mL (50.00 g) of water at 22.00°C, and 40.00 mL (42.00 g) of water at 32.00°C is added. The mixture reaches a maximum temperature of 27.30°C. What is the calorimeter constant?

#### Solution

The hot water loses a quantity of heat  $q_{hot}$ ;

$$\begin{aligned} q_{hot} &= C m \Delta T \\ &= 4.18 \text{ J/g}^\circ\text{C} \times 50.0 \text{ g} \times (27.30^\circ\text{C} - 32.00^\circ\text{C}) \\ &= -982 \text{ J} \end{aligned}$$

The cold water gains a quantity of heat  $q_{cold}$ ;

$$\begin{aligned} q_{cold} &= C m \Delta T \\ &= 4.18 \text{ J/g}^\circ\text{C} \times 40.0 \text{ g} \times (27.30^\circ\text{C} - 22.00^\circ\text{C}) \\ &= 886 \text{ J} \end{aligned}$$

If no heat were lost to the surroundings,  $q_{hot}$  would equal  $-q_{cold}$  and their sum would be zero. However, it appears that more heat was lost by the hot water than was gained by the cold. The missing heat was absorbed by the calorimeter and surroundings:

$$\begin{aligned} q_{cal} &= q_{hot} + q_{cold} \\ &= 96 \text{ J.} \end{aligned} \tag{15.7.1}$$

The calorimeter heat capacity is this heat divided by the temperature change of the calorimeter:

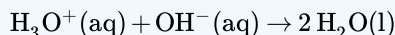
$$C_{cal} = q/\Delta T = 96 \text{ J} / 5.3^\circ\text{C} = 18.1 \text{ J/}^\circ\text{C}$$

## Using the Calorimeter Constant

The heat absorbed by the calorimeter *and* its contents is equal to the heat released by a chemical reaction, as illustrated by the following example:

### ✓ Example 15.7.2: $\Delta H$

The calorimeter above contains 250.0 cm<sup>3</sup> of 1.000 M HCl ( $D = 1.02 \text{ g/cm}^3$ ) at 20.38°C and to this is added, with stirring, 250.0 cm<sup>3</sup> of 1.000 M NaOH ( $D = 1.04 \text{ g/cm}^3$ ) also at 20.38°C. The temperature of the mixture rises to 27.80°C. Assuming that the specific heat capacity of the NaCl solution that results is 4.20 J/g°C, calculate  $\Delta H$ , for the reaction



#### Solution

The heat change for the solution is

$$q_{\text{solution}} = C m \Delta T = 4.20 \text{ J/g}^\circ\text{C} \times (250.0 \times 1.02 + 250 \times 1.04) \text{ g} \times (27.80^\circ\text{C} - 20.38^\circ\text{C}) = 16\,049 \text{ J}$$

The heat change for the calorimeter is

$$q_{\text{calorimeter}} = C_{\text{cal}} \Delta T = 18.1 \text{ J/}^\circ\text{C} \times 7.42^\circ\text{C} = 134 \text{ J}$$

The total heat change of the surroundings is

$$q_{\text{total}} = q_{\text{solution}} + q_{\text{calorimeter}} = 16\,183 \text{ J or } 16.2 \text{ kJ}$$

The heat change by the system is therefore

$$q_{\text{system}} = -q_{\text{surroundings}} = -16\,183 \text{ J or } -16.2 \text{ kJ}$$

To calculate  $\Delta H$ , we need to divide the enthalpy change by the amount of product, in moles. Since 250 mL of 1 M solutions of each reactant are mixed and they are in a 1:1 stoichiometric ratio, we will produce 0.250 mol ( $n = C \times V \text{ mol} = 0.250 \text{ L} \times 1.00 \text{ mol/L}$ ) of product, so:

$$\Delta H_m = \frac{-16.2 \text{ kJ}}{0.250 \text{ mol}} = 64.7 \text{ kJ mol}^{-1}$$

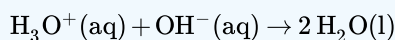
This value is slightly different from the accepted value (58.7 kJ/mol) because of inaccuracies in the heat capacity of the solution and crudeness of the method.

## Another Approach

In order to find the quantity of heat energy evolved, we need to know the rise in temperature but also the heat capacity of the calorimeter contents and calorimeter. These can be combined, and determined in a separate experiment: After the final solution has cooled to room temperature, it can be reheated to the higher temperature by means of an electrical coil. The heat supplied in this second experiment can be calculated in the usual way from the applied potential, the current flowing, and the time.

### ✓ Example 15.7.3: Coffee-cup Calorimeter

1.000 M HCl (250.0 cm<sup>3</sup>) at 20.38°C and 250.0 cm<sup>3</sup> of 1.000 M NaOH also at 20.38°C are mixed in a coffee-cup calorimeter similar to that shown in the Figure. The temperature of the mixture rises to 27.80°C. The mixture is then cooled to 20.45°C after which 24.06 V is applied to the heating coil, allowing 2.13 A to flow for 300.0 s. The temperature rises to 28.23°C. Find  $\Delta H$ , for the reaction



#### Solution

We first calculate the heat capacity of the contents of the calorimeter. The heat supplied by the coil  $q_{\text{coil}}$  is given by

$$q_2 = 24.06 \text{ V} \times 2.13 \text{ A} \times 300.0 \text{ s} = 15\,374 \text{ J}$$

so that

$$C = \frac{q_{\text{coil}}}{\Delta T} = \frac{15\,374 \text{ J}}{(28.23 - 20.45)\text{K}} = 1976 \text{ J K}^{-1}$$

Knowing the heat capacity, we can now calculate  $q_{\text{contents}}$ , the heat change in the contents of the experiment:

$$q_{\text{contents}} = C \Delta T = 1976 \text{ J K}^{-1} (27.80 - 20.38)\text{K} = 14.66 \text{ kJ}$$

where the sign is positive since the contents have gained energy.

The system (the chemical reactants) released the same amount of energy, so it is

$$q_{\text{system}} = -q_{\text{contents}} = -14.66 \text{ kJ}$$

The reaction was exothermic.

Because the change occurs at *constant pressure*, we can equate  $q_{\text{system}}$  to the enthalpy change  $\Delta H$ . However, the question asks for the enthalpy change per *mole* of acid (that is,  $\Delta H_m$ ), while only  $250 \text{ cm}^3 \times 1 \text{ mol dm}^{-3} = 0.250 \text{ mol}$  acid was used. Accordingly,

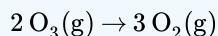
$$\Delta H_m = \frac{-14.66 \text{ kJ}}{0.250 \text{ mol}} = 58.7 \text{ kJ mol}^{-1}$$

### Constant Volume ("Bomb") Calorimetry

Even though most chemical reactions are more conveniently studied at constant [pressure](#) than at constant volume, there are some reactions for which the opposite is true. When one of the reactants is a gas, for instance, the reaction is much easier to carry out in a closed container called a **bomb** calorimeter. If a reaction is measured at constant volume, of course, we find  $\Delta U$  rather than  $\Delta H$ . However, almost all thermochemical data are recorded in terms of the [enthalpy](#) rather than the [internal energy](#). It is therefore often necessary to convert a measured  $\Delta U$  value to a  $\Delta H$  value. This is done as shown in the following example:

#### ✓ Example 15.7.4: Calculate $\Delta H$

Use the data in [Table 1 in the Internal Energy section](#) to find  $\Delta H$  for the reaction



25°C, 1 bar

#### Solution

$\Delta H$  for a constant-pressure change is given by

$$\Delta H = \Delta U + P \Delta V$$

Since  $\Delta U$  is known from [Table 1 in the Internal Energy section](#), we need only calculate  $P \Delta V$ . The initial volume of the system  $V_1$  is that of 2 mol  $\text{O}_3$  at 25°C.

$$V_1 = \frac{nRT}{P} = 2 \text{ mol} \frac{RT}{P}$$

Similarly, the final volume is that of 3 mol  $\text{O}_2$  at 25°C:

$$V_2 = 3 \text{ mol} \frac{RT}{P}$$

Thus

$$\Delta V = V_2 - V_1 = \frac{RT}{P} (3 - 2) \text{ mol}$$

and

$$P \Delta V = P \left[ \frac{RT}{P} (3-2)\text{mol} \right] = RT(3-2)\text{mol}$$

$$= 8.3143 \frac{\text{J}}{\text{K mol}} \times 298.15 \text{ K} \times 1 \text{ mol} = 2479 \text{ J} = 2.479 \text{ kJ}$$

Thus

$$\Delta H = \Delta U + P \Delta V = -287.9 \text{ kJ} + 2.5 \text{ kJ} = -285.5 \text{ kJ}$$

### $\Delta H$ vs. $\Delta U$

Perhaps because values of  $\Delta H$  are usually easier to measure than values of  $\Delta U$ , chemists have chosen to concentrate exclusively on  $\Delta H$  rather than on  $\Delta U$  as a way of recording thermochemical data. Though [enthalpies of formation](#) are easy to find, equivalent tables of internal energies are nonexistent. In many ways this insistence on  $\Delta H$  rather than on  $\Delta U$  is a pity. In particular, it suggests that somehow the enthalpy  $H$  has more fundamental significance on the molecular level than the internal energy  $U$ . It is important to realize that this is *not* the case. It is the internal energy which has a simple molecular interpretation, namely, the total energy of all the molecules in the system. By contrast the enthalpy includes not only the total energy of the molecules in the system but the potential energy of the atmosphere *outside the system* as well. We use the enthalpy so often because of its convenience rather than because of its molecular significance.

A further point worth making about the enthalpy is that the difference between  $\Delta H$  and  $\Delta U$  is not often of great chemical importance. This is particularly true of reactions which involve only gases, such as the decomposition of ozone. In a gaseous reaction the main factor determining both  $\Delta U$  and  $\Delta H$  is the *change in electronic energy*. Changes in molecular energy and also the expansion work  $P \Delta V$  are usually small compared with this change. In the decomposition of ozone, for example, the change in electronic energy is  $-290.7 \text{ kJ}$  per 2 mol ozone. The value of  $\Delta U$  is  $-287.9 \text{ kJ}$ , while that of  $\Delta H$  is  $-285.4 \text{ kJ}$ . The three quantities are all within a few percent of each other. For many purposes, differences of this order of magnitude are immaterial. When this is the case, we can equate both  $\Delta U$  and  $\Delta H$  to the change in electronic energy.

### Contributors

- Ed Vitz (Kutztown University), [John W. Moore](#) (UW-Madison), [Justin Shorb](#) (Hope College), [Xavier Prat-Resina](#) (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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