

## 11.5: Reaction Calorimetry

Reaction calorimetry is used to evaluate the molar integral reaction enthalpy  $\Delta H_m(\text{rxn})$  of a reaction or other chemical process at constant temperature and pressure. The measurement actually made, however, is a temperature change.

Sections 11.5.1 and 11.5.2 will describe two common types of calorimeters designed for reactions taking place at either constant pressure or constant volume. The constant-pressure type is usually called a *reaction calorimeter*, and the constant-volume type is known as a *bomb calorimeter* or *combustion calorimeter*.

In either type of calorimeter, the chemical process takes place in a reaction vessel surrounded by an outer jacket. The jacket may be of either the adiabatic type or the isothermal-jacket type described in Sec. 7.3.2 in connection with heat capacity measurements. A temperature-measuring device is immersed either in the vessel or in a phase in thermal contact with it. The measured temperature change is caused by the chemical process, instead of by electrical work as in the determination of heat capacity. One important way in which these calorimeters differ from ones used for heat capacity measurements is that work is kept deliberately small, in order to minimize changes of internal energy and enthalpy during the experimental process.

### 11.5.1 The constant-pressure reaction calorimeter

The contents of a constant-pressure calorimeter are usually open to the atmosphere, so this type of calorimeter is unsuitable for processes involving gases. It is, however, a convenient apparatus in which to study a liquid-phase chemical reaction, the dissolution of a solid or liquid solute in a liquid solvent, or the dilution of a solution with solvent.

The process is initiated in the calorimeter by allowing the reactants to come into contact. The temperature in the reaction vessel is measured over a period of time starting before the process initiation and ending after the advancement has reached a final value with no further change.

The heating or cooling curve (temperature as a function of time) is observed over a period of time that includes the period during which the advancement  $\xi$  changes. For an exothermic reaction occurring in an adiabatic calorimeter, the heating curve may resemble that shown in Fig. 7.3, and the heating curve in an isothermal-jacket calorimeter may resemble that shown in Fig. 7.4. Two points are designated on the heating or cooling curve: one at temperature  $T_1$ , before the reaction is initiated, and the other at  $T_2$ , after  $\xi$  has reached its final value. These points are indicated by open circles in Figs. 7.3 and 7.4.

The relations derived here parallel those of Sec. 11.5.1 for a constant-pressure calorimeter. The three paths depicted in Fig. 11.13 are similar to those in Fig. 11.11, except that instead of being at constant pressure they are at constant volume. We shall assume the combustion reaction is exothermic, with  $T_2$  being greater than  $T_1$ .

The internal energy change of the experimental process that actually occurs in the calorimeter between times  $t_1$  and  $t_2$  is denoted  $\Delta U(\text{expt})$  in the figure. Conceptually, the overall change of state during this process would be duplicated by a path in which the temperature of the system with the reactants present increases from  $T_1$  to  $T_2$ , followed by the isothermal bomb process at temperature  $T_2$ . (When one investigates a combustion reaction, the path in which temperature changes without reaction is best taken with reactants rather than products present because the reactants are more easily characterized.) In the figure these paths are labeled with the internal energy changes  $\Delta U(\text{R})$  and  $\Delta U(\text{IBP}, T_2)$ , and we can write

$$\Delta U(\text{expt}) = \Delta U(\text{R}) + \Delta U(\text{IBP}, T_2) \quad (11.5.4)$$

To evaluate  $\Delta U(\text{R})$ , we can use the energy equivalent  $\epsilon_R$  of the calorimeter with reactants present in the bomb vessel.  $\epsilon_R$  is the average heat capacity of the system between  $T_1$  and  $T_2$ —that is, the ratio  $q/(T_2 - T_1)$ , where  $q$  is the heat that would be needed to change the temperature from  $T_1$  to  $T_2$ . From the first law, with expansion work assumed negligible, the internal energy change equals this heat, giving us the relation

$$\Delta U(\text{R}) = \epsilon_R(T_2 - T_1) \quad (11.5.5)$$

The initial and final states of the path are assumed to be equilibrium states, and there may be some transfer of reactants or  $\text{H}_2\text{O}$  from one phase to another within the bomb vessel during the heating process.

The value of  $\epsilon_R$  is obtained in a separate calibration experiment. The calibration is usually carried out with the combustion of a reference substance, such as benzoic acid, whose internal energy of combustion under controlled conditions is precisely known from standardization based on electrical work. If the bomb vessel is immersed in the same mass of water in both experiments and

other conditions are similar, the difference in the values of  $\epsilon_R$  in the two experiments is equal to the known difference in the heat capacities of the initial contents (reactants, water, etc.) of the bomb vessel in the two experiments.

The internal energy change we wish to find is  $\Delta U(\text{IBP}, T_2)$ , that of the isothermal bomb process in which reactants change to products at temperature  $T_2$ , accompanied perhaps by some further transfer of substances between phases. From Eqs. 11.5.4 and 11.5.5, we obtain

$$\Delta U(\text{IBP}, T_2) = -\epsilon(T_2 - T_1) + \Delta U(\text{expt}) \quad (11.5.6)$$

The value of  $\Delta U(\text{expt})$  is small. To evaluate it, we must look in detail at the possible sources of energy transfer between the system and the surroundings during the experimental process. These sources are

1. The ignition work occurs during only a short time interval at the beginning of the process, and its value is known. The effects of heat transfer, stirring work, and temperature measurement continue throughout the course of the experiment. With these considerations, Eq. 11.5.6 becomes

$$\Delta U(\text{IBP}, T_2) = -\epsilon(T_2 - T_1) + w_{\text{ign}} + \Delta U'(\text{expt}) \quad (11.5.7)$$

where  $\Delta U'(\text{expt})$  is the internal energy change due to heat, stirring, and temperature measurement.  $\Delta U'(\text{expt})$  can be evaluated from the energy equivalent and the observed rates of temperature change at times  $t_1$  and  $t_2$ ; the relevant relations for an isothermal jacket are Eq. 7.3.24 (with  $w_{\text{el}}$  set equal to zero) and Eq. 7.3.32.

### Correction to the reference temperature

#### Reduction to standard states

We want to obtain the value of  $\Delta_c U^\circ(T_{\text{ref}})$ , the molar internal energy change for the main combustion reaction at the reference temperature under standard-state conditions. Once we have this value, it is an easy matter to find the molar *enthalpy* change under standard-state conditions, our ultimate goal.

Consider a hypothetical process with the following three isothermal steps carried out at the reference temperature  $T_{\text{ref}}$ :

1. The net change is a decrease in the amount of each reactant in its standard state and an increase in the amount of each product in its standard state. The internal energy change of step 2 is  $\Delta U(\text{IBP}, T_{\text{ref}})$ , whose value is found from Eq. 11.5.8. The internal energy changes of steps 1 and 3 are called **Washburn corrections** (Edward W. Washburn, *J. Res. Natl. Bur. Stand. (U.S.)*, **10**, 525–558, 1933).

Thus, we calculate the standard internal energy change of the main combustion reaction at temperature  $T_{\text{ref}}$  from

$$\Delta U^\circ(\text{cmb}, T_{\text{ref}}) = \Delta U(\text{IBP}, T_{\text{ref}}) + (\text{Washburn corrections}) - \sum_i \Delta \xi_i \Delta_r U^\circ(i) \quad (11.5.9)$$

where the sum over  $i$  is for side reactions and auxiliary reactions if present. Finally, we calculate the standard *molar* internal energy of combustion from

$$\Delta_c U^\circ(T_{\text{ref}}) = \frac{\Delta U^\circ(\text{cmb}, T_{\text{ref}})}{\Delta \xi_c} \quad (11.5.10)$$

where  $\Delta \xi_c$  is the advancement of the main combustion reaction in the bomb vessel.

### Standard molar enthalpy change

#### Washburn corrections

The Washburn corrections needed in Eq. 11.5.9 are internal energy changes for certain hypothetical physical processes occurring at the reference temperature  $T_{\text{ref}}$  involving the substances present in the bomb vessel. In these processes, substances change from their standard states to the initial state of the isothermal bomb process, or change from the final state of the isothermal bomb process to their standard states.

For example, consider the complete combustion of a solid or liquid compound of carbon, hydrogen, and oxygen in which the combustion products are  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and there are no side reactions or auxiliary reactions. In the initial state of the isothermal bomb process, the bomb vessel contains the pure reactant, liquid water with  $\text{O}_2$  dissolved in it, and a gaseous mixture of  $\text{O}_2$  and  $\text{H}_2\text{O}$ , all at a high pressure  $p_1$ . In the final state, the bomb vessel contains liquid water with  $\text{O}_2$  and  $\text{CO}_2$

dissolved in it and a gaseous mixture of  $O_2$ ,  $H_2O$ , and  $CO_2$ , all at pressure  $p_2$ . In addition, the bomb vessel contains internal parts of constant mass such as the sample holder and ignition wires.

In making Washburn corrections, we must use a single standard state for each substance in order for Eq. 11.5.9 to correctly give the standard internal energy of combustion. In the present example we choose the following standard states: pure solid or liquid for the reactant compound, pure liquid for the  $H_2O$ , and pure ideal gases for the  $O_2$  and  $CO_2$ , each at pressure  $p^\circ = 1 \text{ bar}$ .

We can calculate the amount of each substance in each phase, in both the initial state and final state of the isothermal bomb process, from the following information: the internal volume of the bomb vessel; the mass of solid or liquid reactant initially placed in the vessel; the initial amount of  $H_2O$ ; the initial  $O_2$  pressure; the water vapor pressure; the solubilities (estimated from Henry's law constants) of  $O_2$  and  $CO_2$  in the water; and the stoichiometry of the combustion reaction. Problem 11.7 guides you through these calculations.

### 11.5.3 Other calorimeters

Experimenters have used great ingenuity in designing calorimeters to measure reaction enthalpies and to improve their precision. In addition to the constant-pressure reaction calorimeter and bomb calorimeter described above, three additional types will be briefly mentioned.

A *phase-change calorimeter* has two coexisting phases of a pure substance in thermal contact with the reaction vessel and an adiabatic outer jacket. The two coexisting phases constitute a univariant subsystem that at constant pressure is at the fixed temperature of the equilibrium phase transition. The thermal energy released or absorbed by the reaction, instead of changing the temperature, is transferred isothermally to or from the coexisting phases and can be measured by the volume change of the phase transition. A reaction enthalpy, of course, can only be measured by this method at the temperature of the equilibrium phase transition. The well-known Bunsen ice calorimeter uses the ice–water transition at  $0^\circ\text{C}$ . The solid–liquid transition of diphenyl ether has a relatively large volume change and is useful for measurements at  $26.9^\circ\text{C}$ . Phase-transition calorimeters are especially useful for slow reactions.

A *heat-flow calorimeter* is a variation of an isothermal-jacket calorimeter. It uses a thermopile (Fig. 2.7) to continuously measure the temperature difference between the reaction vessel and an outer jacket acting as a constant-temperature heat sink. The heat transfer takes place mostly through the thermocouple wires, and to a high degree of accuracy is proportional to the temperature difference integrated over time. This is the best method for an extremely slow reaction, and it can also be used for rapid reactions.

A *flame calorimeter* is a flow system in which oxygen, fluorine, or another gaseous oxidant reacts with a gaseous fuel. The heat transfer between the flow tube and a heat sink can be measured with a thermopile, as in a heat-flow calorimeter.

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