

FIGURE 4 This is a diagram of a simple combustion calorimeter. A weighed sample is ignited by an electric spark and burned in the sample dish in an atmosphere of pure oxygen. The energy generated by the combustion reaction warms the steel bomb and the water surrounding it. The thermometer measures the initial and final temperatures of the water, and this temperature change is then used to calculate the energy evolved by the reaction as heat.

Enthalpy of combustion is defined in terms of *one mole of reactant*, whereas the enthalpy of formation is defined in terms of *one mole of product*. All substances are in their standard states. The general enthalpy notation,  $\Delta H$ , applies to enthalpies of reaction, but the addition of a subscripted c,  $\Delta H_c$ , refers specifically to enthalpy of combustion. A list of enthalpies of combustion can be found in Appendix Table A-5. A combustion calorimeter is a common instrument used to determine enthalpies of combustion. **Figure 4** shows a fixed-volume calorimeter. A similar apparatus under constant pressure is used to obtain enthalpy measurements.

## **Calculating Enthalpies of Reaction**

Thermochemical equations can be rearranged and added to give enthalpy changes for reactions not included in the data tables. The basis for calculating enthalpies of reaction is known as **Hess's law:** The overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process. The energy difference between reactants and products is independent of the route taken to get from one to the other. In fact, measured enthalpies of reaction can be combined to calculate enthalpies of reaction that are difficult or impossible to actually measure.

To demonstrate how to apply Hess's law, we will work through the calculation of the enthalpy of formation for the formation of methane gas, CH<sub>4</sub>, from its elements, hydrogen gas and solid carbon (graphite), at 298.15 K (25°C).

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta H_f^0 = ?$$