6.2 Reaction Enthalpy

- If only expansion work is done:

$$\Delta E = q + w = q - P_{ext}\Delta V$$

- At constant volume (rigid, sealed container):

$$\Delta V = 0 \quad \Rightarrow \quad \Delta E = q \quad \rightarrow \quad \boxed{\Delta E = q_v}$$

  – **The heat transferred at constant volume, q_v, is equal to the change in the internal energy**
- At constant pressure (open container), if the system pressure equals the external pressure:

$$P = P_{ext} \qquad \Delta E = q - P\Delta V$$

- **Enthalpy** (*H*) – a state function defined as:

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

- At constant pressure → $\Delta(PV) = P\Delta V$

$$\Delta H = \Delta E + P\Delta V \qquad \text{and} \qquad \Delta E = q - P\Delta V$$

$$\Delta H = q - P\Delta V + P\Delta V = q \quad \rightarrow \quad \boxed{\Delta H = q_p}$$

  – **The heat transferred at constant pressure, q_p, is equal to the change in the enthalpy**
- For processes at constant pressure

$$\Delta E = q_p - P\Delta V = \Delta H - P\Delta V$$

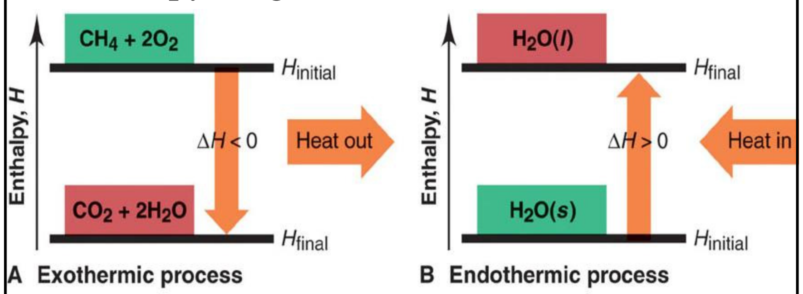
Exothermic and endothermic processes

- **Exothermic process** – the system releases heat in the surroundings (**$q < 0$**)
  – at constant pressure ($\Delta H = q_p$) $\Rightarrow$ $\Delta H < 0$
- **Endothermic process** – the system absorbs heat from the surroundings (**$q > 0$**)
  – at constant pressure ($\Delta H = q_p$) $\Rightarrow$ $\Delta H > 0$

$$NaOH(s) \xrightarrow{H_2O} NaOH(aq) + \text{heat} \qquad \text{(exo.)}$$

$$NH_4NO_3(s) + \text{heat} \xrightarrow{H_2O} NH_4NO_3(aq) \qquad \text{(endo.)}$$

- Enthalpy diagrams



$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{heat}$$

$$H_2O(s) + \text{heat} \rightarrow H_2O(l)$$

- The heat released or absorbed during a chemical change is due to differences in the bond strengths of reactants and products

6.3 Heat Measurements

- Heat transfer in or out of an object can be estimated by measuring the temperature change in the object
- **Heat capacity** – the heat required to increase the temperature of an object by **1 K** (or **°C**)

$$\text{Heat capacity} = q/\Delta T$$

  – units **J/K** or **J/°C**
- The heat capacity is an extensive property that increases with the size of the object

- **Specific heat capacity** (*c*) – the heat capacity per unit mass of the object

$$c = (\text{Heat capacity})/m \quad \rightarrow \quad c = q/m\Delta T$$

  – units **J/g·K** or **J/g·°C** (see Table 6.2)

$$q = mc\Delta T$$

- **Molar heat capacity** (*C*) – the heat capacity per one mole of a substance (units **J/mol·K**)

  Example: Calculate the heat needed to warm up **2.5 g** of ice from **-20** to **-5°C**. (c=**2.03 J/g·K**)

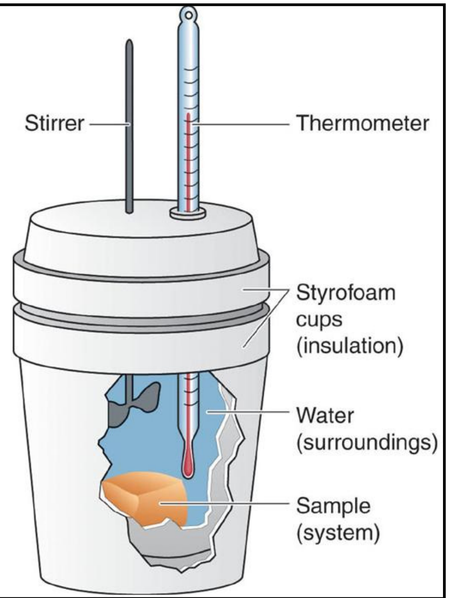
$\Delta T = T_f - T_i = -5°C - (-20°C) = 15°C$

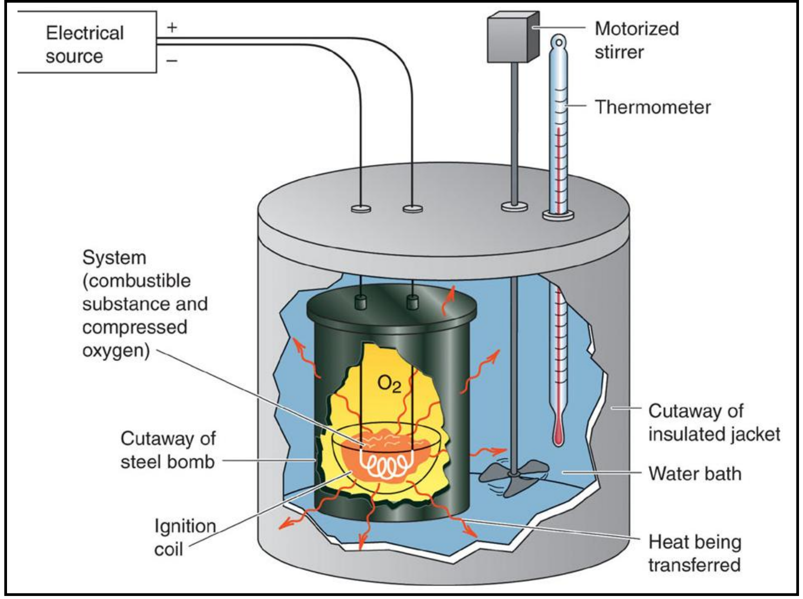
$q = mc\Delta T = 2.5\ g \times 2.03\ J/g{\cdot}°C \times 15°C = +76\ J$

- **Calorimeter** – a device used to measure heat transfers
  - thermally insulated container with a known heat capacity supplied with a thermometer
  - the system is placed in the calorimeter which serves as its surroundings
  - the heat transfer is estimated from the temperature change of the calorimeter contents
  - the system can be a chemical reaction
- Types of calorimeters
  - constant pressure calorimeters ($q_p = \Delta H$)
  - constant volume calorimeters ($q_v = \Delta E$)

- The heat released by the system is absorbed by the surroundings

$$q_{sys} = -\,q_{surr}$$





Example: **27 g** of brass at **105ºC** are placed in a coffee-cup calorimeter filled with **100 g** of water at **20ºC**. The water temperature increases to **22ºC**. Calculate the specific heat capacity of brass. (c_{water} = 4.18 J/g·ºC)

$$q_{water} = -q_{brass} \quad \Rightarrow \quad (mc\Delta T)_w = -(mc\Delta T)_b$$

$$(c)_b = -\frac{(mc\Delta T)_w}{(m\Delta T)_b} = -\frac{100\ \text{g} \times 4.18 \frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}} \times (22-20)\,{}^\circ\text{C}}{27\ \text{g} \times (22-105)\,{}^\circ\text{C}}$$

$$= -\frac{100 \times 4.18 \times 2}{27 \times (-83)} \frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}} = 0.37 \frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}$$

- Specific heats of dilute aqueous solutions are taken to be the same as that of water.

Example: A reaction between **50 g** of dilute HCl and **50 g** of dilute NaOH takes place in a coffee-cup calorimeter. The temperature rises by **2.1ºC**. What is the heat of the reaction.

$c \approx c_{water}$ = 4.18 J/g·ºC

m = 50 g + 50 g = 100 g $\quad \Delta T$ = +2.1ºC

$q_{sys} = -\,q_{surr} = -\,mc\Delta T$

= -100 g×4.18 J/g·ºC×2.1ºC = -8.8×10^2 J

= -0.88 kJ $\quad \rightarrow \quad q_p = \Delta H$ = -0.88 kJ

Example:

A sample of **1.82 g** sugar is burned in a bomb calorimeter with heat capacity **9.20 kJ/K**. The temperature rises by **3.2ºC**. What is the heat of the reaction per gram of sugar.

$q_{sys} = -\,q_{surr} = -$ *(Heat capacity)*$\times\Delta T$

= -9.20 kJ/ºC×3.2ºC = -29 kJ

$q_v = \Delta E$ = -29 kJ

Heat per gram = -29 kJ/1.82 g = -16 kJ/g