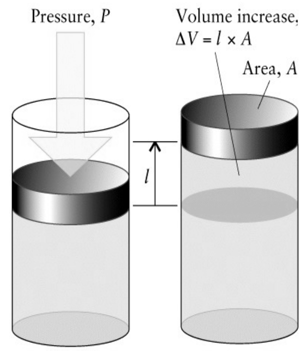
6.5 Transferring Energy as Work

- **Expansion work** – due to changes in the volume of the system (important for reactions involving gases)
- If an object is moved over a distance (***l***) against an opposing force (***F***), the work is:

$$w = F \times l$$

- If a system expands against an external pressure (P_{ext}) applied over an area (***A***), the opposing force (***F***) is:

$$F = P_{ext} \times A \quad \Rightarrow \quad w = P_{ext} \times A \times l$$



$$w = P_{ext} \times A \times l$$

$$A \times l = DV$$

$$\Rightarrow \quad w = P_{ext}\, DV$$

$$DV = V_f - V_i$$

– when the system expands $DV > 0$, but ***w*** must be negative because the system does work

$$\Rightarrow \quad w = -P_{ext}\, DV$$

- Units of work
  - If P_{ext} is in **Pa** and DV is in **m^3**, than ***w*** is in **J**

1 Pa·m^3 = 1 (kg/m·s^2)×1 m^3 = 1 kg·m^2/s^2 = 1 J

  - If P_{ext} is in **atm** and DV is in **L**, than ***w*** is in **L·atm**

1 L·atm = 10^{-3} m^3×101325 Pa = 101.325 J

Example: Calculate the work done when a gas is compressed from **12.0 L** to **5.0 L** by an external pressure of **2.6 atm.**

$$w = -P_{ext}\, DV = -2.6 \text{ atm} \times (5.0 \text{ L} - 12.0 \text{ L}) =$$

$$= -2.6 \times (-7.0) \text{ L·atm} = 18 \text{ L·atm}$$

18 L·atm×(101.325 J/1 L·atm) = 1.8×10^3 J = 1.8 kJ

6.6 Transferring Energy as Heat

- Assuming that only expansion work is done:

$$DU = q + w = q - P_{ext} DV$$

- At constant volume (rigid, sealed container):

$$DV = 0 \quad \Rightarrow \quad DU = q \quad \rightarrow \quad DU = q_v$$

  – **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:

$$P = P_{ext} \qquad DU = q - PDV$$

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

$$H = U + PV$$

$$DH = DU + PDV + VDP$$

- At constant pressure ($DP = 0$):

$$DH = DU + PDV \quad \text{and} \quad DU = q - PDV$$

$$DH = q - PDV + PDV = q \quad \rightarrow \quad DH = q_p$$

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

- At constant pressure:

$$DU = q - PDV = DH - PDV$$

Example: In a given chemical reaction carried out in an open container at **1.0 atm**, **75 kJ** of heat are released in the surroundings and the system expands by **10 L** due to the gaseous products. Calculate the internal energy change.

$$P = \text{constant} \quad \Rightarrow \quad DH = q_p = -75 \text{ kJ}$$

$$\Rightarrow \quad DU = DH - PDV$$

$$DV = +10 \text{ L} \qquad PDV = 1.0 \text{ atm} \times 10 \text{ L} = 10 \text{ L·atm}$$

10 L·atm×(101.325 J/1 L·atm) = 1.0×10^3 J = 1.0 kJ

$$DU = DH - PDV = -75 \text{ kJ} - 1.0 \text{ kJ} = -76 \text{ kJ}$$

6.7 Exothermic and Endothermic Processes

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

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

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

6.8 Measuring Heat

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

$$C = q/DT$$

  - units **J/K** or **J/ºC**
- The heat capacity is an extensive property (**C** increases with the size of the object)

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

$$C_s = C/m$$

  - units **J/g·K** or **J/g·ºC** (see Table 6.1)

$$C = mC_s \quad \text{and} \quad C = q/DT \quad \Rightarrow \quad q/DT = mC_s$$

$$\Rightarrow \quad q = mC_sDT$$

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

$DT = T_f - T_i$ = -5ºC – (-20ºC) = 15ºC

$q = mC_sDT$ = 2.5 g×2.03 J/g·ºC×15ºC = +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 ($q_p = DH$)
  - constant volume calorimeters ($q_v = DU$)

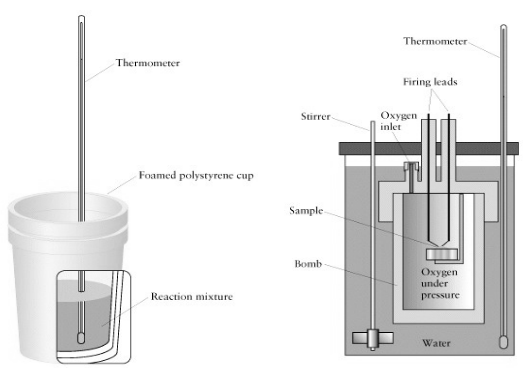


Fig. 6.21, 6.22

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

$$q_{water} = -q_{brass} \quad \Rightarrow \quad (mC_sDT)_w = -(mC_sDT)_b$$

$$(C_s)_b = -\frac{(mC_s\Delta T)_w}{(m\Delta T)_b} = -\frac{100\text{ g}\times 4.18\frac{\text{J}}{\text{g}\cdot°\text{C}}\times(22-20)°\text{C}}{27\text{ g}\times(22-105)°\text{C}} =$$

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

- 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.

  $C_s \cong (C_s)_{water} = 4.18$ **J/g·ºC**

  $m = 50$ **g** $+ 50$ **g** $= 100$ **g**

  $DT = +2.1$**ºC**

  $q = mC_sDT = 100$ **g** $\times 4.18$ **J/g·ºC** $\times 2.1$**ºC** $=$
  $= 8.4\times10^2$ **J** $= 0.84$ **kJ**