Calorimetry and Enthalpy

Chapter 5.2

Heat Capacity

- **Specific heat capacity (c)** is the quantity of thermal energy required to raise the temperature of 1g of a substance by $1^{o}C$
- The units for specific heat capacity are **J/(g•^{o}C)**

The water has a higher specific heat capacity so it requires more thermal energy to raise its temperature

The sand has a lower specific heat capacity so it requires a less thermal energy to raise its temperature

Heat Capacity

- Specific heat capacity values can be looked up in tables
- There is one in your textbook on page 292

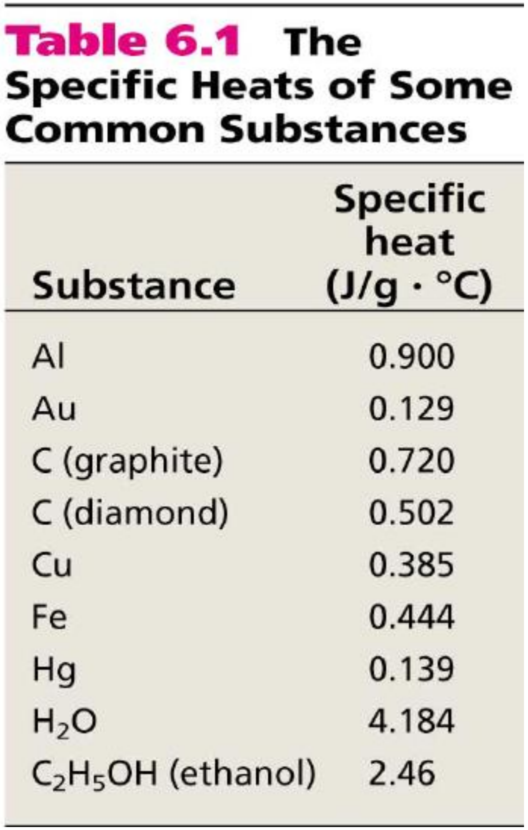
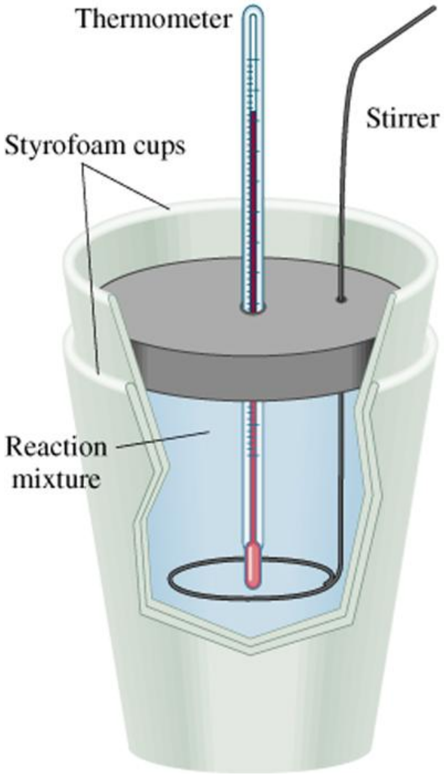


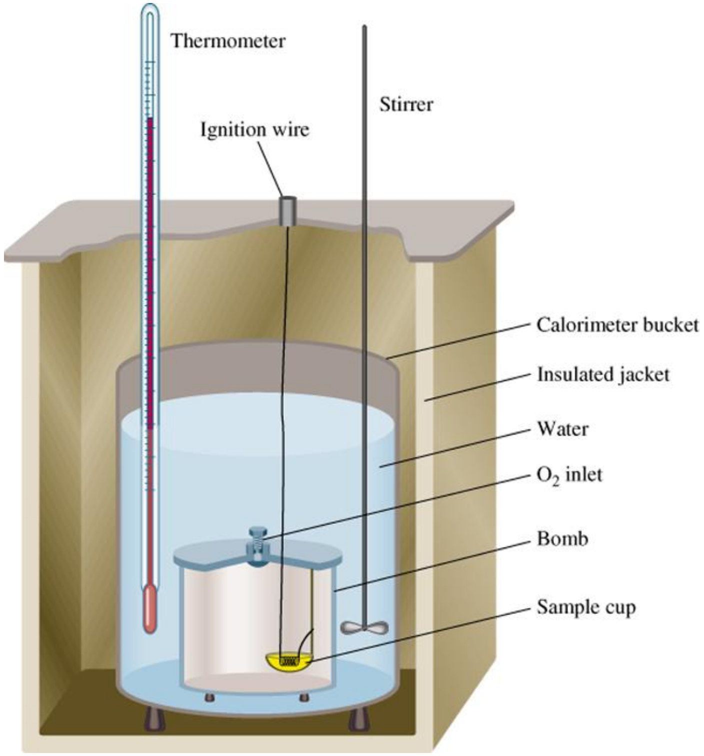
Table 6.1 **The Specific Heats of Some Common Substances**

Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

Calorimetry and Thermal Energy Transfer

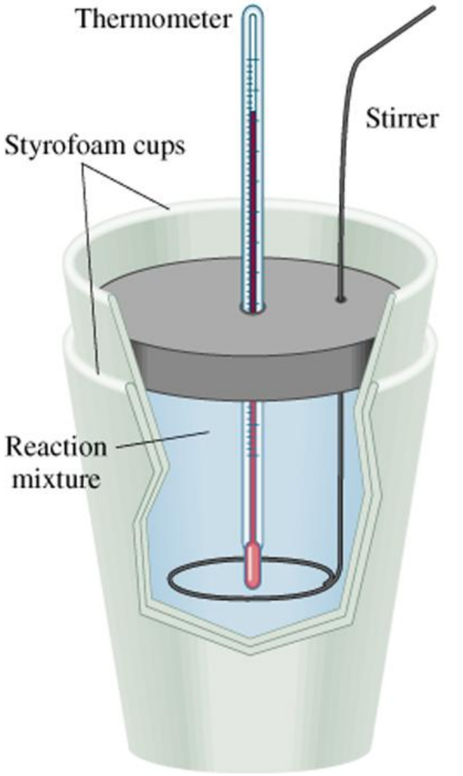
- **Calorimetry** is the experimental process of measuring the thermal energy change in a chemical or physical change
- A **calorimeter** is a device that is used to measure thermal energy changes in a chemical or physical change





Calorimetry Calculations

- To simplify our calculations we will make three **assumptions**:
  1. Any thermal energy transferred from the calorimeter to the outside environment is negligible
  2. Any thermal energy absorbed by the calorimeter itself is negligible
  3. All dilute, aqueous solutions have the same density (1.00g/mL) and specific heat capacity (4.18 J/(g•^{o}C)) as water



Calorimetry Calculations

- We will use the following equation:

q is the total amount of **thermal energy** absorbed or released by a chemical system in **joules**

$$q = mc\Delta T$$

ΔT is the **temperature change** experienced by the substance as it warms or cools in **°C**

note: $\Delta T = T_{final} - T_{initial}$

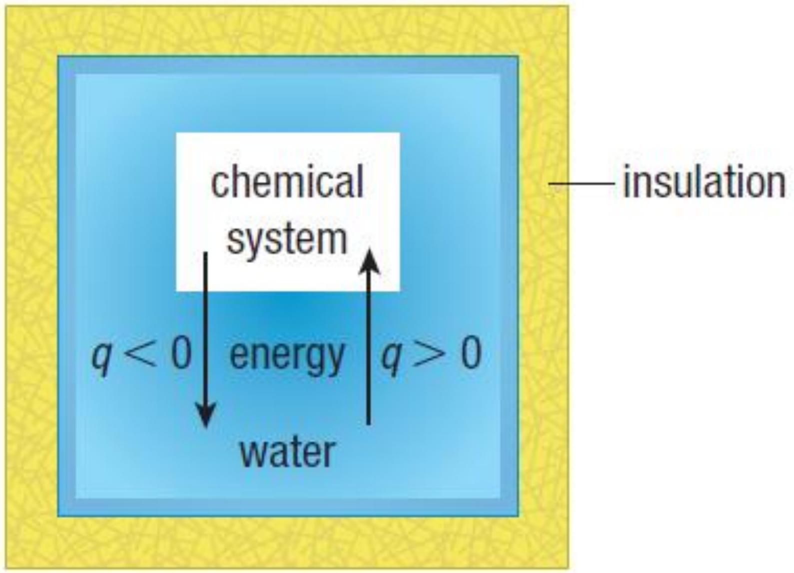
m is the **mass** of the substance in **grams**

c is the **specific heat capacity** of the substance in **J/(g•°C)**

The value of *q* has two parts:

$q = -\ 237\text{J}$

1. The magnitude tells us how much energy is involved
2. The sign tells us the direction of energy transfer



Because of the law of conservation of energy, the total thermal energy of the system and its surroundings remains constant:

$$q_{system} + q_{surroundings} = 0$$

$$q_{system} = -\ q_{surroundings}$$

The chemical system undergoes either a physical change or a chemical change

Energy is either absorbed from, or released to, the surroundings (the water in the calorimeter)

An increase in the temperature of the water indicates an exothermic reaction, whereas a decrease in the temperature of the water indicates an endothermic reaction

Practice Problem 1

- 600mL of water in an electric kettle is heated from 20°C to 85°C to make a cup of tea. How much thermal energy is absorbed by the water?

Practice Problem 2

- The temperature of an aluminum fence post at 5pm is 20^{o}C. The same fence post has a temperature of 6^{o}C by 11pm. If the fence post releases 315kJ of thermal energy to its surroundings, what is the mass of the fence post?

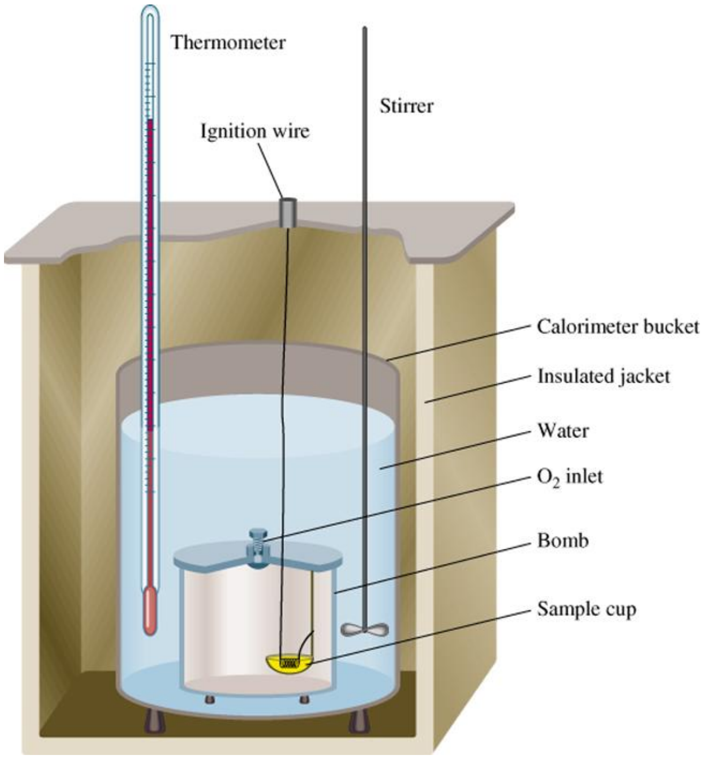
Practice Problem 3

- 50.00mL of aqueous copper (II) sulfate reacts with 50.00mL of aqueous sodium hydroxide in a calorimeter. The initial temperature of both solutions is 21.40^{o}C and the highest temperature reached in the calorimeter is 24.60^{o}C. Determine the quantity of thermal energy transferred by the reaction to the water, and state whether the reaction was endothermic or exothermic.

Enthalpy Change

- **Enthalpy (H)** is the total amount of thermal energy in a substance
- **Enthalpy Change (ΔH)** is the energy released to or absorbed from the surroundings during a chemical or physical change

Enthalpy Change Can be Measured



Enthalpy change can be measured using calorimetry data

As long as pressure is kept constant, the enthalpy change of a chemical system is equal to the flow of thermal energy into or out of the system

$$\Delta H_{\text{system}} = |q_{\text{system}}|$$

Calculating the enthalpy change can give us information about type of reaction

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If $\Delta H > 0$, the reaction is **endothermic**

If $\Delta H < 0$, the reaction is **exothermic**

For example, suppose we use a bomb calorimeter to determine the enthalpy of the reaction in which magnesium metal, Mg(s), reacts with an aqueous solution of hydrochloric acid, HCl(aq), according to the net ionic equation

$$\text{Mg(s)} + 2\,\text{H}^{+}\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$$

The chemical system consists of solid magnesium, aqueous hydrochloric acid, magnesium ions, and hydrogen gas. The surroundings are the liquid water in the calorimeter. During the reaction, the water temperature increases. You can infer from the temperature increase that energy is transferred from the chemical system to the surroundings (**Figure 4**). Therefore, the products have a lower enthalpy than the reactants, so $\Delta H < 0$ and this is an exothermic reaction.

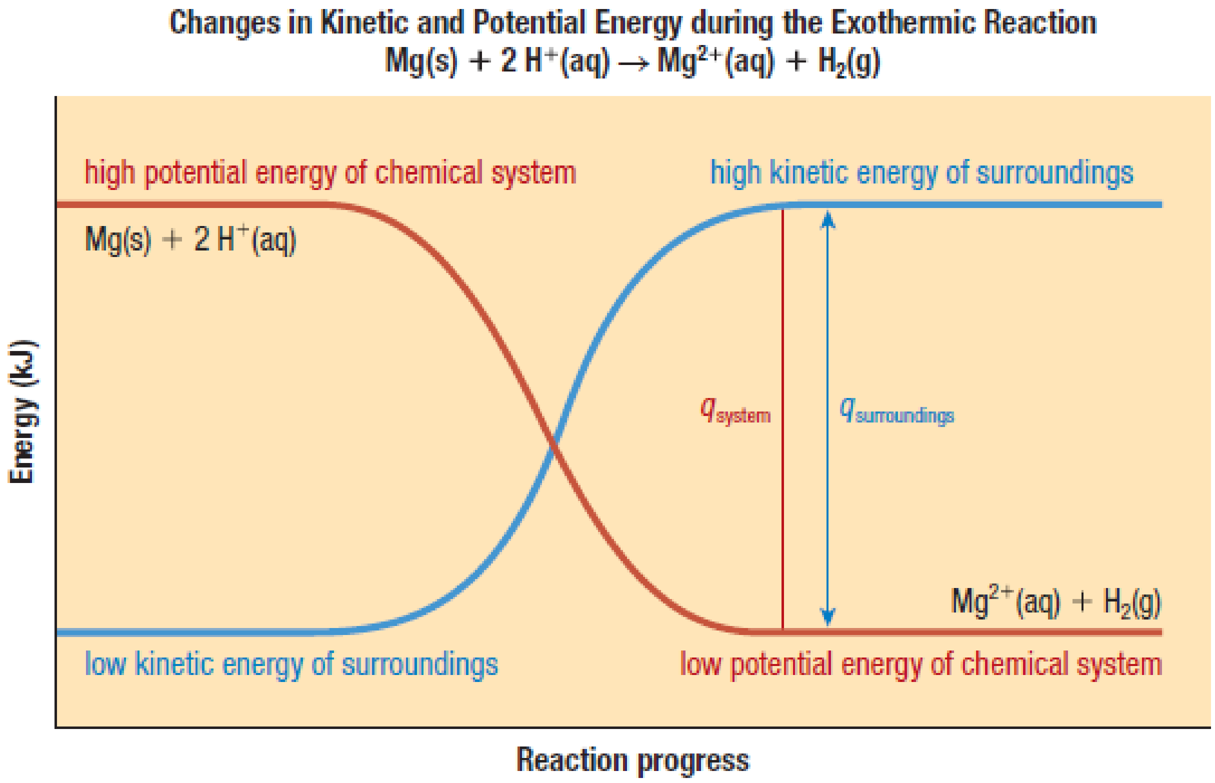
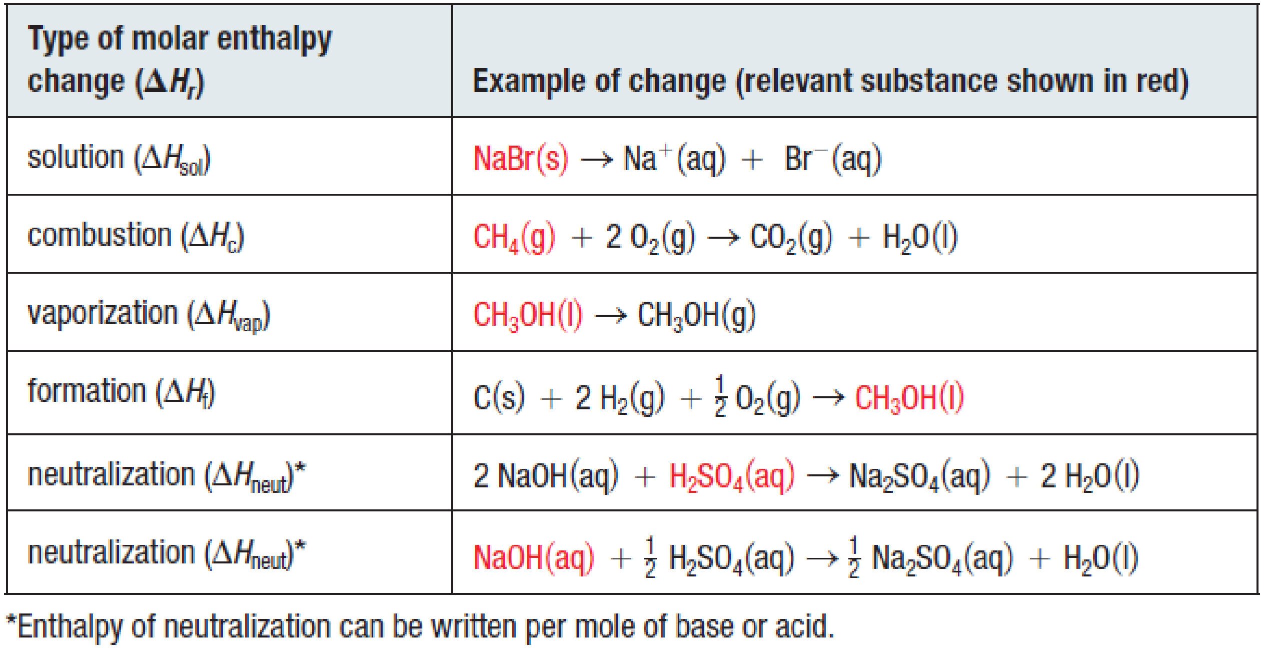

Changes in Kinetic and Potential Energy during the Exothermic Reaction
$\text{Mg(s)} + 2\,\text{H}^{+}\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$

Figure 4 As this exothermic reaction progresses, the quantity of energy in the chemical system, q_{system}, decreases as the system releases energy to the surroundings. Consistent with the law of conservation of energy, this same quantity of energy, $q_{\text{surroundings}}$, is absorbed by the surroundings.

Molar Enthalpy Change

- **Molar enthlapy change (ΔH_r)** is the enthalpy change associated with a physical, chemical, or nuclear change involving one mole of a substance
- The units for molar enthalpy change are **J/mol**



Type of molar enthalpy change (ΔH_r)	Example of change (relevant substance shown in red)
solution (ΔH_{sol})	$NaBr(s) \rightarrow Na^+(aq) + Br^-(aq)$
combustion (ΔH_c)	$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + H_2O(l)$
vaporization (ΔH_{vap})	$CH_3OH(l) \rightarrow CH_3OH(g)$
formation (ΔH_f)	$C(s) + 2\,H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow CH_3OH(l)$
neutralization (ΔH_{neut})*	$2\,NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\,H_2O(l)$
neutralization (ΔH_{neut})*	$NaOH(aq) + \frac{1}{2}\,H_2SO_4(aq) \rightarrow \frac{1}{2}\,Na_2SO_4(aq) + H_2O(l)$

*Enthalpy of neutralization can be written per mole of base or acid.

Molar Enthalpy Change

Many molar enthalpy changes have been carefully measured by scientists and the values are published in tables like the one below and can easily be looked up

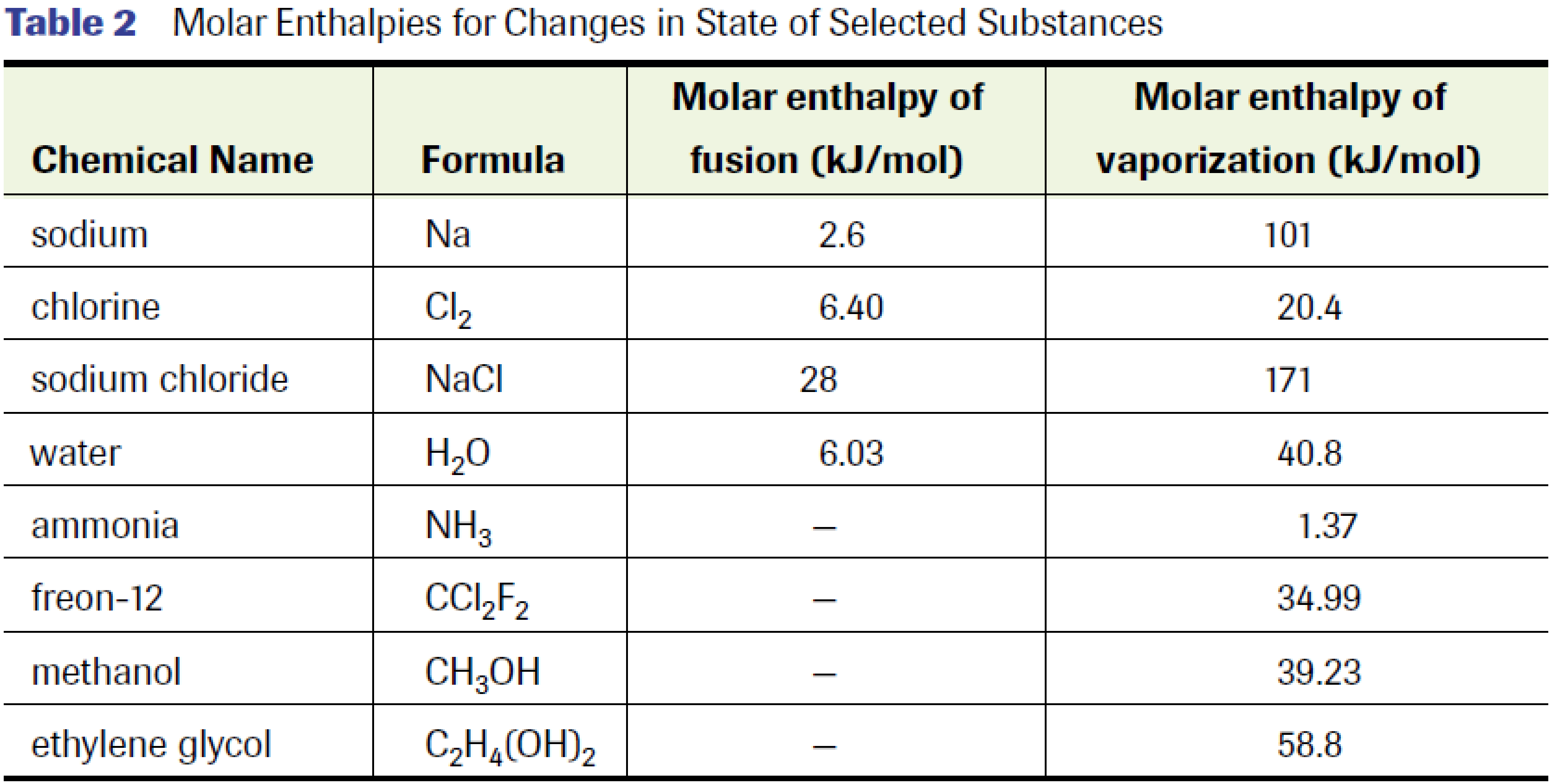


Table 2 Molar Enthalpies for Changes in State of Selected Substances

Chemical Name	Formula	Molar enthalpy of fusion (kJ/mol)	Molar enthalpy of vaporization (kJ/mol)
sodium	Na	2.6	101
chlorine	Cl_2	6.40	20.4
sodium chloride	NaCl	28	171
water	H_2O	6.03	40.8
ammonia	NH_3	–	1.37
freon-12	CCl_2F_2	–	34.99
methanol	CH_3OH	–	39.23
ethylene glycol	$C_2H_4(OH)_2$	–	58.8

Using Molar Enthalpy Change

- Molar enthlapy values (**ΔH_r**) can help us calculate an enthalpy change (**ΔH**)
- To calculate an enthalpy change (**ΔH**) for some amount of substance other than one mol, we need to look up the molar enthalpy value (**ΔH_r**) and then multiply it by the number of moles **(n)** using the formula below

$$\Delta H = n\Delta H_r$$

Practice Problem 4

- A common refrigerant (Freon-12 with molar mass 120.91g/mol) is alternately vaporized in tubes inside a refrigerator, absorbing heat, and condensing in tubes outside the refrigerator, releasing heat. This results in energy being transferred from the inside to the outside of the refrigerator. The molar enthalpy of vaporization for the refrigerant is 34.99kJ/mol. If 500.0g of the refrigerant is vaporized, what is the expected enthalpy change?

Representing Enthalpy Changes

- There are **four** ways to represent enthalpy changes:
  1. Thermochemical equations with energy terms
  2. Thermochemical equations with **ΔH** values
  3. Molar Enthalpies
  4. Potential Energy Diagrams

SUMMARY Communicating Enthalpy Changes

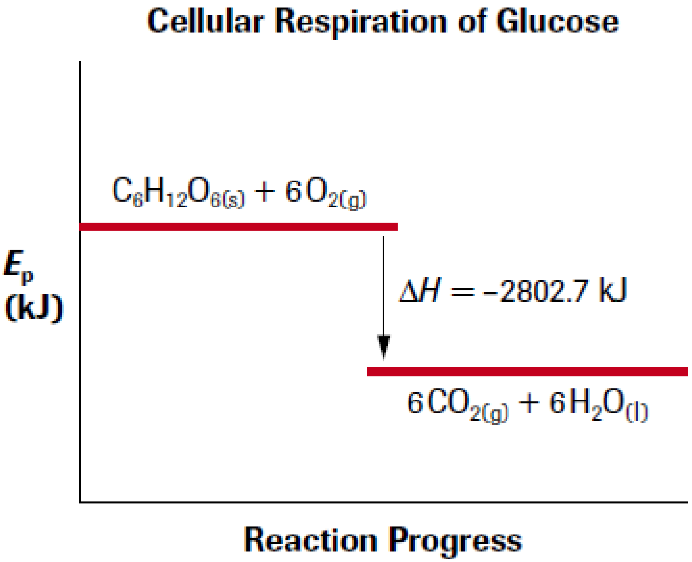
Figure 8 uses the chemical reactions for photosynthesis and respiration to summarize the four methods of communicating the molar enthalpy or change in enthalpy of a chemical reaction. Each method has advantages and disadvantages. To best communicate energy changes in chemical reactions, you should learn all four methods.

1 $C_6H_{12}O_{6(s)} + 6\,O_{2(g)} \longrightarrow 6\,CO_{2(g)} + 6\,H_2O_{(l)} + 2802.7\ kJ$

2 $C_6H_{12}O_{6(s)} + 6\,O_{2(g)} \longrightarrow 6\,CO_{2(g)} + 6\,H_20_{(l)} \quad \Delta H = -2802.7\ kJ$

3 Molar enthalpy for cellular respiration:
$\Delta H_{respiration} = -2802.7\ kJ/mol\ glucose$

4 Potential energy diagram for **cellular respiration:**

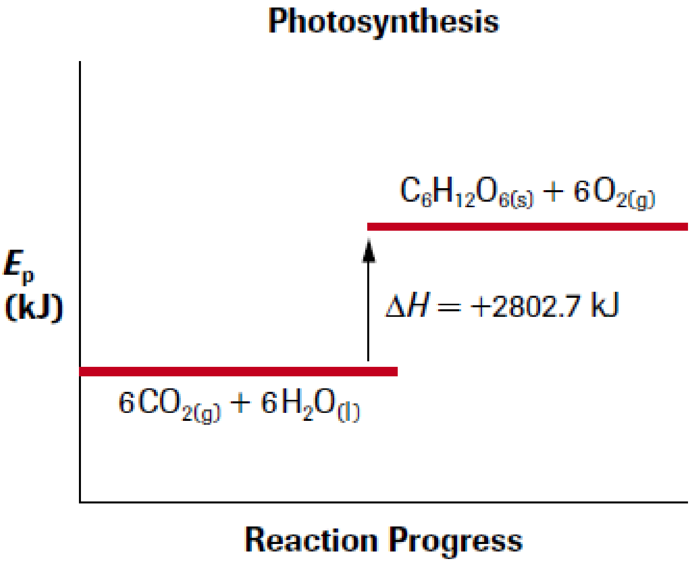


1 $6\,CO_{2(g)} + 6\,H_2O_{(l)} + 2802.7\ kJ \longrightarrow C_6H_{12}O_{6(s)} + 6\,O_{2(g)}$

2 $6\,CO_{2(g)} + 6\,H_2O_{(l)} \longrightarrow C_6H_{12}O_{6(s)} + 6\,O_{2(g)} \quad \Delta H = +2802.7\ kJ$

3 Molar enthalpy for photosynthesis:
$\Delta H_{photosynthesis} = +2802.7\ kJ/mol\ glucose$

4 Potential energy diagram for **photosynthesis:**



HOMEWORK

Required Reading:

p. 292-306

(remember to supplement your notes!)

Questions:

p. 297 #1-3

p. 301 #1-4

p. 304 #1-4

p. 306 #1-7