Thermochemistry (Chapter 5)

- Is the study of the energy changes that accompany physical and chemical changes.
- Energy is defined as the ability to do work or the capacity to produce change. The forms of energy that are chemistry related include:

(1) Potential Energy

(2) Thermal Energy

(3) Chemical Energy

(4) Nuclear Energy

(5) Radiant Energy

- During chemical reactions, chemical energy may be *stored, released* as heat, or *converted* to other forms of energy. Regardless of the change, energy is always conserved, that is the ***Law of Conservation of Energy,*** which states that "energy can neither be created nor destroyed, but may be converted to other form", is always obeyed.

- When studying the transfer of energy, a distinction between the **chemical system**, which is the reactants and products being studied and the s**urroundings**, which is everything else that is capable of absorbing or releasing heat to the system, must be made

- A chemical system is usually represented by a chemical reaction. For example: sodium hydroxide react with sulfuric acid. Sodium hydroxide and sulfuric acid is chemical system whereas the water bath is surrounding.

Classification of Changes

Exothermic change = one in which heat, **q,** is transferred from the system to the surroundings → an increase in the thermal energy of the molecules in the surroundings → an increases in the kinetic energy of the molecules → an increase in the temperature of the surroundings

Endothermic change = one in which heat is absorbed by the system from the surroundings

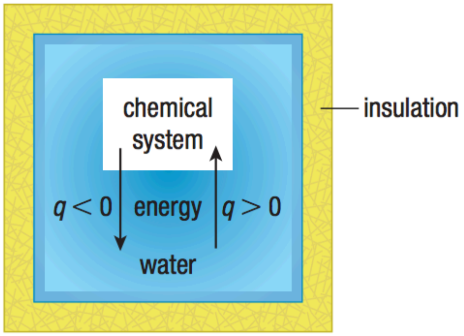


Figure 3 The chemical system undergoes either a physical change or a chemical change. Energy is either absorbed from, or released to, the surroundings (the water in the calorimeter). An increase in the temperature of the water indicates an exothermic reaction, whereas a decrease in the temperature of the water indicates an endothermic reaction.

Types of Systems

Closed system = one in which there is no transfer of matter between the system and the surroundings

Open system = one in which there is a transfer of matter + energy between the system and the surroundings

Isolated system = one in which no matter nor energy is transferred between the system and the surroundings

Caloriometry

- A process of measuring the energy changes (heat) in a chemical system
- Process depends on three important things: mass (m); temperature change (ΔT), and the types of substance:

$$\boxed{q = m c \Delta T}$$

Here **"c"** is the *specific heat capacity* = the quantity of heat required to raise the temperature of one **gram** of a substance by one degree Celcius or one kelvin.

See Table 1 on page 292 for the specific heat capacities of certain substances.

Water has a "c" of 4.18 $J/g.^0C$

Example 1:

When 600 ml of water in an electric kettle is heated from 20^oC to 85^oC to make a cup of tea, how much heat flows into the water?

Practice:

If water is heated from 0^oC to 50^oC, calculate the mass of water that could be warmed by the addition of 8.00 kJ of heat.

Enthalpy (5.2)

- Enthalpy: the total amount of thermal energy in a substance
- Enthalpy change can be measured by calorimetry.
- ΔH = enthalpy **after** the change in the system – **before** the change

or

- Enthalpy change = quantity of heat that flows from a system to its surroundings or from the surroundings to the system

$$\boxed{\Delta H_{system} = +/- \, \mathbf{q}_{surroundings}}$$

Enthalpy, ΔH, is ultimately the change in potential energy of the system.

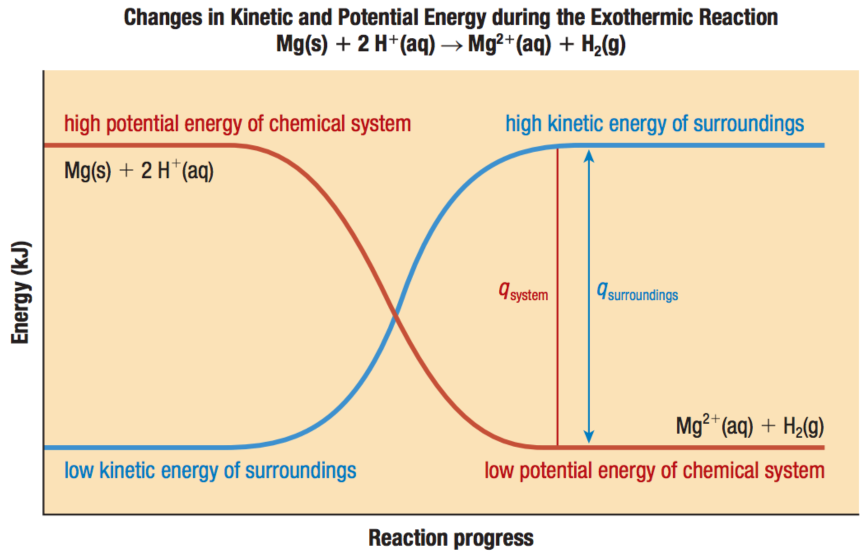


Figure 4 As this exothermic reaction progresses, the quantity of energy in the chemical system, q_{system}, decreases as the system releases energy to the surroundings. Consistent with the law of conservation of energy, this same quantity of energy, $q_{surroundings}$, is absorbed by the surroundings.

Observing Enthalpy Changes: Enthalpy changes may occur when:

a) A *physical change* occurs (change in the form of the substance, but involves no breakage of chemical bonds e.g phase changes or dissolution)

b) *Chemical change* = a change in the chemical bonds between atoms, resulting in the rearrangement of atoms for form new substances

c) *Nuclear change* = a change in the protons or neutrons in an atom resulting in the formation of new atoms

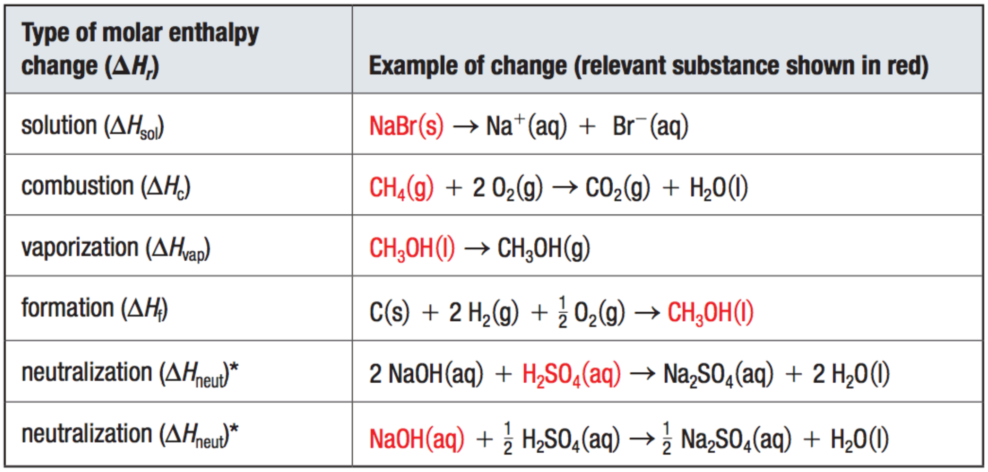
Molar Enthalpies: (5.2)

Molar Enthalpy, ΔH_x = the enthalpy change per mole of a substance, where x indicates the type of change. The unit is then kJ/mol.

- A - sign in front of ΔH = an exothermic change
- A + sign in front of ΔH = an endothermic change

Note that a linear relationship exists between enthalpy and moles. 2 mole will have 2 folds the enthalpy change than 1 mole $\boxed{\rightarrow}$ $\mathbf{\Delta H = n\Delta H_x}$

Table 2 Molar Enthalpies of Reaction



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.

Using Molar Enthalpies in Heat Calculations:

Example 1:
Freon, a common refrigerant (molar mass is 120.91g/mol) is alternately vaporized in tubes inside a refrigerator, hence absorbing heat, and condensed in tubes outside the refrigerator, thus releasing heat. This results in energy being transferred from inside to the outside of the refrigerator. The molar enthalpy of vaporization of freon is 34.99 kJ/mol. If 500.0 g of refrigerant is vaporized, what is the expected enthalpy change?

Given : $\Delta H_{vap} = 34.99 kJ/mol$
ΔH = + because heat is absorbed by the system during vaporization

Steps:
1) $n_{freon} = m/M$ 2) $\Delta H = n\Delta H_{vap}$

Example 2: Calculate the enthalpy change, ΔH, for the vaporization of 100.0 g of water?

Steps:

1) ΔH_{vap} of water = (Google it up)
2) n_{water} =
3) $\Delta H = n\Delta H_{vap}$

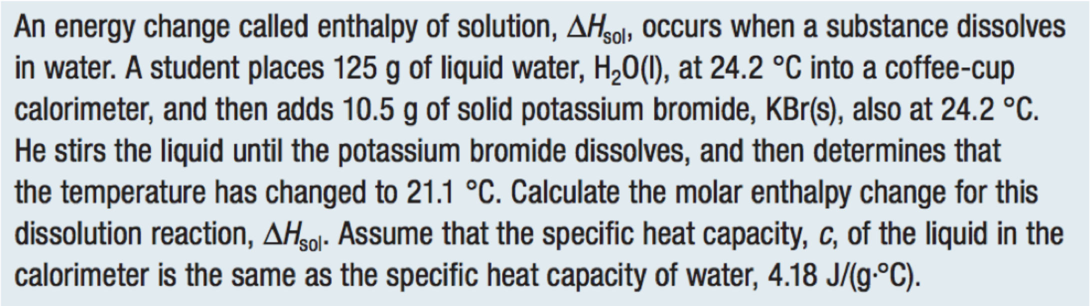
Using Calorimetry to Determine Molar Enthalpies

- Requires a calorimeter consists of an insulated container for the chemical system (nested Styrofoam cups are perfectly OK)

- Involves some underlying assumptions:
  a) No heat is transferred between the calorimeter and the outside environment
  b) Any heat absorbed or released by the calorimeter materials is negligible
  c) Dilute aqueous solutions is assumed to have a density and specific heat capacity equal to that of pure water

- Water is often the **surrounding**, thus energy changes between the chemical system and the surrounding are monitored by changes in temperature of the water.

Example 3: Calculate enthalpy change for dissolution reactions



An energy change called enthalpy of solution, ΔH_{sol}, occurs when a substance dissolves in water. A student places 125 g of liquid water, $H_2O(l)$, at 24.2 °C into a coffee-cup calorimeter, and then adds 10.5 g of solid potassium bromide, KBr(s), also at 24.2 °C. He stirs the liquid until the potassium bromide dissolves, and then determines that the temperature has changed to 21.1 °C. Calculate the molar enthalpy change for this dissolution reaction, ΔH_{sol}. Assume that the specific heat capacity, c, of the liquid in the calorimeter is the same as the specific heat capacity of water, 4.18 J/(g·°C).

You could check the answer on
pg 300 – sample problem 2

Practice 1:
In a calorimetry experiment, 7.46g of potassium chloride is dissolved in 100 ml (100 g) of water at an initial temperature of 24.1^0C. If the final temperature of the solution is 20^0C, what is the molar enthalpy of solution for potassium chloride?

Practice 2:
What mass of lithium chloride must have dissolved if the temperature of 200.0 g of water increased by 6.0^oC? The molar enthalpy of solution of lithium chloride is –37 kJ/mol

Representing Enthalpy Changes (5.2)

Method 1 = Writing thermochemical Equations with energy terms

Method 2 – Thermochemical Equations with ΔH values

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285 \text{ kJ}$$

$$H_2O(l) + 285 \text{ kJ} \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H = 285 \text{ kJ}$$

Method 3 – Molar Enthalpies of Reactions = the energy change associated with the reaction of one mole of a substance. If the molar enthalpy was determined at SATP conditions, it is called a standard molar enthalpy of reaction and given the symbol, ΔH^o_r.

Method 4 – potential energy diagrams

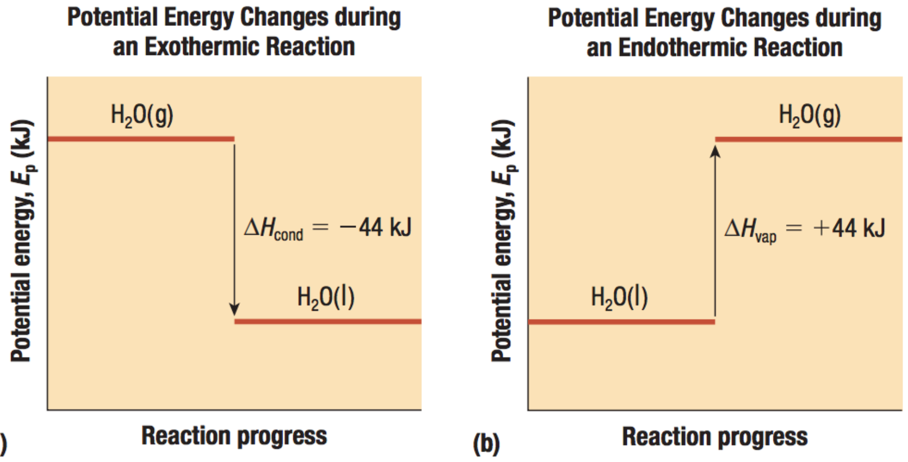


Figure 6 (a) The condensation reaction of 1 mol of water vapour is exothermic. The reactant has a higher potential energy than the product. (b) The vaporization reaction of liquid water to water vapour is endothermic. The reactant has a lower potential energy than the product.

Example 4:

Write a thermochemical equation to represent the exothermic reaction that occurs when two moles of butane burn in excess oxygen gas. The molar enthalpy of combustion of butane is

–2871 kJ/mol.

$2C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)}$

$\Delta H = n\Delta H_{com}$

$2C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} + 5742\ \text{kJ}$

Could you use 2 more methods to represent enthalpy change?