Chapters 1-5 study matter, now we study energy.

Warming your hands with chemical hand warmers involves many of the principles of thermochemistry, the study of the relationships between chemistry and energy. When you open the package that contains the hand warmer, the contents are exposed to air, and a reaction that gives off heat to its surroundings occurs. Most handwarmers involve the oxidation of iron:

$$4\,\text{Fe(s)} + 3\,\text{O}_2\text{(g)} \longrightarrow 2\,\text{Fe}_2\text{O}_3\text{(s)}$$
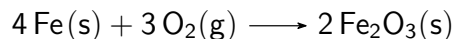
In this chapter, we look at how chemical reactions can exchange energy with their surroundings and how we can quantify the magnitude of those exchanges.

### 6.0.1 Applications

- Heating of homes

- Production of energy

## 6.1 Key Definitions

**Energy** Capacity to do work

**Work** Result of a force active through a distance

**Examples of work**

- Pushing a box across the floor
- a billiard ball rolling across a billiard table and colliding with a second, stationary ball

**Potential energy** Associated with position or composition. Example: Raising a billiard ball off the table increases its potential energy.

**Chemical energy** Associated with relative positions of electrons and nuclei in atoms and molecules

**Law of conservation of energy** energy can be neither created nor destroyed; it can assume different forms

**System** chemicals in a beaker (or handwarmers) for example

**Surrounding** water that the chemicals are dissolved in, the beaker, the lab bench, air in the room, etc.

- Surroundings gain the exact amount of energy lost by the system and vice versa.
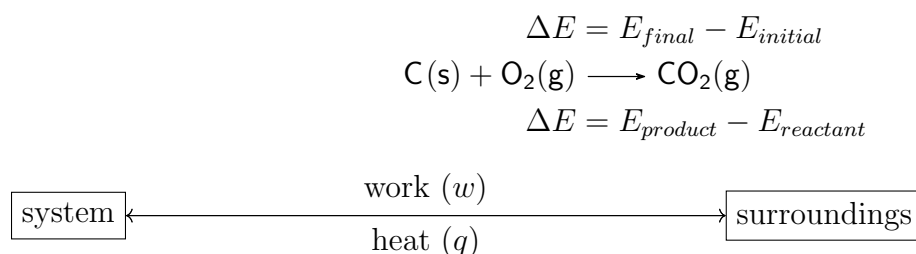
## 6.2   Units of Energy

- $KE = \frac{1}{2}mv^2$, $[KE] = [m][v] = \text{kg} \times \frac{m}{s}$

- 1 Joule (J) $= 1 \ \frac{\text{kg m}^2}{\text{s}^2}$

- 1 calorie $= 4.184$ J

## 6.3   1st law of thermodynamics

- The total energy of the universe is constant $\rightarrow$ Energy is neither created, nor destroyed, universe does not exchange energy with anything else.

- According to the 1st law, a device that continually produces energy with no energy input cannot exist.

### 6.3.1   Internal Energy (IE)

- The internal energy of a system is the sum of the kinetic and potential energies of all the particles that compose the systems.

- It is a "state function".

- State of a chemical system is specified by parameters such as temperature, pressure, concentration, and phase (solid, liquid, or gas)

- Elevation of 10,000 ft, for example, is a state function no matter how you climbed it; the distance, however, is not a state function as you can take any route.

$$\Delta E = E_{final} - E_{initial}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
$$\Delta E = E_{product} - E_{reactant}$$

$$\boxed{\text{system}} \xleftarrow{\quad\quad} \overset{\text{work } (w)}{\underset{\text{heat } (q)}{\xrightarrow{\hspace{5cm}}}} \boxed{\text{surroundings}}$$

- System can exchange energy with its surrounding through heat and work.

- According to 1st law of thermodynamics

$$\Delta E = q + w \tag{6.1}$$

## 6.4 Quantifying Heat and Work

Experimentally, $q \propto \Delta t$ where $q$ is heat absorbed by the system and $\Delta t$ is the change of temperature.

$$q = c \times \Delta t \tag{6.2}$$

where $c$ is the heat capacity (quantity of heat required to change temperature by 1°C).

$$q = m \times s \times \Delta t$$
$$[J] = [g] \times \left[\frac{J}{gC}\right] \times [C] \tag{6.3}$$

where $m$ is the mass and $s$ is the specific heat.

## 6.5 Work: Pressure Volume Work

$$W = -P\Delta V$$
$$= -P(V_f - V_i) \tag{6.4}$$
$$= P(V_i - V_f)$$

Combustion of gasoline causes gases within the cylinders of an automobile engine to expand, pushing the piston outward and moving the car wheels.

## 6.6 Enthalpy

Enthalpy – Heat evolved in a chemical reaction at constant pressure.
Firstly, at constant volume (chemical rxn [reaction] in a sealed container):

$$W = -P\Delta V$$
$$= 0$$
$$\Delta E_{rxn} = q_v + w$$
$$= q_v$$

When chemical reactions occur open to the atmosphere at constant pressure, both $q$ and $w$ are involved in $\Delta E_{rxn}$.
We are often interested only in $q$, not $w$. For example, when we burn natural gas in the furnace to heat our homes.
Enthalpy $H$, a new thermodynamic quantity, is thus introduced.

$$H = E + PV$$
$$\Delta H = \Delta E + P\Delta V \quad \text{(at constant pressure)}$$
$$= (q_p + W) + P\Delta V \tag{6.5}$$
$$= q_p + W - W$$
$$= q_p$$

## 6.7 $\Delta E$ and $\Delta H$

- Conceptually they are similar

- $\Delta E$ is a measure of all of the energy ($q$ and $w$) exchanged with the surroundings

- $\Delta H$ is only a measure of heat exchanged ($q$) under conditions of constant pressure.

- For chemical rxns that do not exchange much work with the surroundings, i.e., $W = -P\Delta V$ is small as $\Delta V$ is small, $\Delta H \approx \Delta E$ (nearly identical)

- For chemical reactions that produce or consume large amounts of gas, hence have large $\Delta V$ (and hence large $W$), $\Delta H \neq \Delta E$ (significantly different)

## 6.8 Exothermic and Endothermic Reactions

- $\Delta H > 0$ is an endothermic reaction, chemical reaction absorbs heat from the surroundings.

  - Example: The reaction that occurs in the chemical cold packs used to ice athletic injuries $\to$ The surroundings, including the bruised wrist, get colder as the cold pack absorbs energy.

- $\Delta H < 0$ is an exothermic reaction, chemical reaction radiates heat to its surroundings.

  - Example: Chemical handwarmers.

## 6.9 Stoichiometry involving $\Delta H$: Thermochemical Equations

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$$
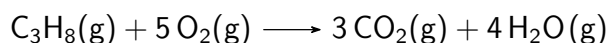
$$\Delta H_{rxn} = -2044kJ$$
$$1 \text{ mol } C_3H_8 = -2044kJ$$
$$5 \text{ mol } O_2 = -2044kJ$$
$$1 \text{ mol } O_2 = \frac{-2044}{5}kJ$$
$$= -408.8kJ$$

## 6.10 Hess' Law

## 6.11 Enthalpies of Reaction From Standard Heats of Formation

- Standard state

- For a gas: pure gas at 1 atm

- For a liquid or solid: pure substance in its most stable form at 1 atm (and other 25°C).

- For a substance in solution: 1M concentration.

- Standard enthalpy change $(\Delta H°) \to \Delta H$ for a process when all reactants and products are in their standard states

- Standard Enthalpy of Formation $(\Delta H_f°)$

  - For a pure compound: $\Delta H$ when 1 mole of the compound forms from its constituent elements in their standard states

  - For a pure element: $(\Delta H_f°) = 0$

$$C(s, graphite) + 2\,H_2(g) \longrightarrow CH_4(g) \quad (\Delta H_f°) = -74.6 \text{ kJ/mol}$$
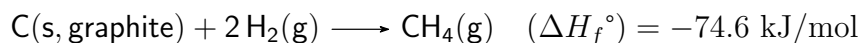
- Standard enthalpy change for a reaction $(\Delta H_{rxn})$

$$aA + bB \longrightarrow cC + dD$$
$$\Delta H_{rxn} = [] - []$$