Week 7 Fast and Slow Chemistry

What is chemical energy (of a substance)?

The sum of the potential (stored) energy and the kinetic (movement) energy.

These energies result from events such as:

- attractions between electrons and protons
- repulsions between nuclei
- Repulsions between electrons
- Movement of electrons
- Vibrations of and rotations around bonds

The chemical energy of a substance is called its heat content or **enthalpy** (*H*)

Energy changes during reactions

The total chemical energy of the products might be less than the energy of the reactants. The difference in energy between the reactants and products is released into the environment. This is an exothermic reaction.

The total chemical energy of the products might be greater than the energy of the reactants. Energy must be absorbed from the environment around the reactants for the reaction to occur. This is an endothermic reaction.

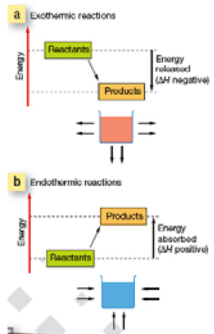

Figure 15.2
Possible energy changes for a chemical reaction.

The energy released or absorbed during a chemical reaction is called the **heat of reaction** (ΔH) where:
$\Delta H = H(\text{products}) - H(\text{reactants})$

For exothermic reactions ΔH will be negative *i.e.* $\Delta H < 0$

For endothermic reactions ΔH will be positive *i.e.* $\Delta H > 0$

Thermochemical equations

These show the energy released or absorbed during a chemical reaction.
Energy is measured in Joules (J) or Kilojoules (kJ)
ΔH has the units J mol^{-1} or kJ mol^{-1}

Photosynthesis

$6CO_2\ (g) + 6H_2O\ (l) \longrightarrow C_6H_{12}O_6\ (aq) + 6O_2\ (g)$; $\Delta H = +2803$ kJ mol^{-1}

Combustion of glucose

$C_6H_{12}O_6\ (aq) + 6O_2\ (g) \longrightarrow 6CO_2\ (g) + 6H_2O\ (l)$; $\Delta H = -2803$ kJ mol^{-1}

Activation energies

Combustion of natural gas
CH4 (g) + 2O2 (g) → CO2 (g) + 2H2O (g); $\Delta H = -890$ kJ mol-1

Why doesn't methane gas combust spontaneously when it comes into contact with oxygen? Why must a spark or match be required?
In a reaction:

- Bonds in the reactants must be broken. Energy is required for this.
- As products are formed new bonds are made. Energy is released during this formation.

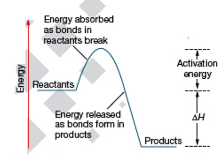

Figure 15.4
Energy profile of an exothermic reaction.

The energy required to break bonds of reactants so that reactions may proceed is called the **activation energy** (E_A).

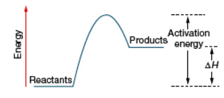

Figure 15.5
Energy profile of an endothermic reaction.

Making reactions go faster

In manufacturing maximizing chemical reactions rates is an important consideration for processes to be profitable.

Collision theory

For reactions to occurs reactants must collide with sufficient energy to overcome the activation energy barrier.
The rate of a chemical reaction is dependant on the proportion of 'successful' collision where the energy of collision is greater than the activation energy.

There are 4 main ways in which reaction rates can be increased:

- Increasing the surface area of solids
- Increasing the concentration of reactants in solution (or pressure of gases)
- Increasing the temperature
- Adding a catalyst

Increasing the surface area of solids

In a solid only the particles at the surface can participate in a reaction. Crushing a solid into smaller particles means that more particles are present at the surface *e.g.*

in sherbet, fine-grained powders are used to create a fast reaction between malic acid and sodium hydrogen carbonate.

Figure 15.6
Sherbet 'fizzes' on the tongue as the finely powdered mixture of a weak acid and sodium hydrogen carbonate reacts rapidly to form carbon dioxide gas.

The surface area of solid reactants in fireworks are chosen for particular effects. Finely divided aluminium confined in a shell explodes violent. If larger pieces are used, the reaction is slower and sparks from burning metal are seen.

Increasing the concentration of reactants

With more particles in a given volume of solution, the frequency of collisions is increased and so more successful collisions occur.
Acid rain is an example of the effect of concentration.

Increasing the pressure of gases increases the concentration of gas molecules, causing more frequent collisions.
This fact is used in the design of chemical plants.

Increasing the temperature

As temperature increases the average kinetic energy of the particles increases as well, as does the rate of reaction.

Cooking using temperature above the boiling point of water is an example of the effect of temperature as is the use of water to douse fires.

Extending collision theory

The effect of temperature on reaction rate cannot be simply explained by the increased frequency of collisions.

A temperature increase of 10°C causes the rate of many reactions to double but collisions have increased by 1/50th of this amount.

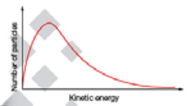

Figure 15.10
The distribution of energies of particles at a particular temperature.

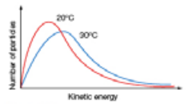

Figure 15.11
The distribution of energies of particles at two temperatures. Raising the temperature increases the proportion of particles with higher energies.

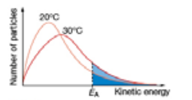

Figure 15.12
The energies of particles at two temperatures. E_A represents the activation energy for the reaction. The shaded area under the graph represents the proportion of particles with sufficient energy to react.

It is the proportion of particles with more energy than E_A that is the factor that causes disproportionality between temperature increase and rate of reaction.

Catalysts

The chemical industry uses catalysts extensively. Without them, many reactions would be too slow for products to be obtained at an economical rate

TABLE 15.1 Some industrial processes that involve the use of catalysts

Product	Name of process	Catalyst
Polyethene	Low-pressure polymerisation	Titanium/aluminium compound
Ammonia	Haber process	Iron
Sulfuric acid	Contact process	Vanadium(V) oxide
Gasoline	Catalytic cracking	Zeolite
Nitric acid	Ostwald process	Platinum/rhodium
Margarine	Hydrogenation	Nickel
Wine	Fermentation	Enzyme in yeast

Homogeneous catalysts: in the same state as reactants and products.
Heterogeneous catalysts: in different states as reactants and products.

How do catalysts work?

In the Haber process particles at the surface of a solid with high surface energy tend to absorb gas molecules that strike it.

Absorption distorts bonds in the gas molecules and may even break them.

Therefore, a reaction can proceed faster.
Reaction rate is proportional to the surface area available of the solid.

In the Haber process, a catalyst of powdered iron allows the manufacture of ammonia to proceed at an economical 500 instead of 3000ºC.

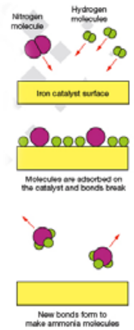

Figure 15.15 The catalyst in the Haber process allows the bonds in the nitrogen and hydrogen molecules to be broken more easily.

The catalyst provides an alternative reaction pathway that reduces the activation energy barrier to break covalent bonds in nitrogen and hydrogen.

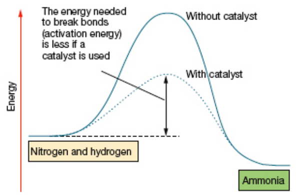

Figure 15.16 Energy changes in the uncatalysed and the catalysed reaction of nitrogen and hydrogen to form ammonia.

Consequently, a greater proportion of reactant particles collide with sufficient energy to overcome the activation energy barrier.

Providing such a pathway increases the proportion of successful collisions and therefore the rate of reaction increases.

A catalyst only alter the activation energy of the reaction and not the heat of reaction.

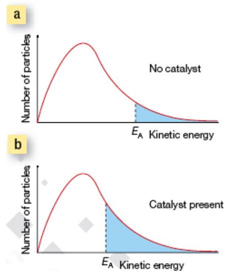

Figure 15.17 A higher proportion of particles have sufficient energy to react when a catalyst is added b, compared with no catalyst a.

3 Consider the examples of reactions mentioned on page 251—wood burning on a camp fire, bathroom tiles being cleaned, a cake baking, and a tomato plant growing.
  a How would you speed up the rates of these reactions?
  b Explain why the methods you suggested would produce an increase in the reaction rate.

4 Explain the following observations in terms of the behaviour of particles.
  a There have been many explosions in coal mines.
  b Refrigeration slows down the browning of sliced apples.
  c Bushfires often start during lightning storms.
  d Iron anchors from shipwrecks can show little corrosion after years in the sea.
  e A burning match is used to light a candle, but the candle continues to burn when the match is extinguished.

Chemical energy

6 Decide, giving reasons for your answers, whether the following processes are endothermic or exothermic:
  a burning of wood
  b melting of ice
  c recharging of a car battery
  d decomposition of plants in a compost heap

8 Hydrogen reacts explosively with oxygen to form water.
  a What chemical bonds are broken in the reaction?
  b What chemical bonds are formed?
  c Explain how the energy changes during bond-breaking and bond-forming affect the energy change for the reaction.
  d Why is there no reaction until the reaction mixture is ignited?

10 Many major car makers have unveiled hydrogen-powered cars. In the engines of these cars hydrogen reacts with oxygen from the air to produce water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Energy changes for the reaction are shown in Figure 15.22.
  a What is the magnitude of the activation energy of this reaction?
  b What is ΔH for this reaction?

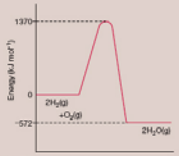

Figure 15.22
Energy changes for the reaction of hydrogen and oxygen.

  c Several groups of scientists have claimed to have split water into hydrogen and oxygen using a molybdenum catalyst:

$$2H_2O(g) \xrightarrow{Mo} 2H_2(g) + O_2(g)$$

Sketch energy change graphs for this reaction with and without the presence of a catalyst.
  d What is the value of ΔH for this water-splitting equation?

Rates of reaction

13 Account for the following observations with reference to the collision model of particle behaviour.
  a Surfboard manufacturers find that fibreglass plastics set within hours in summer but may remain tacky for days in winter.
  b A bottle of fine aluminium powder has a caution sticker warning that it is 'highly flammable, dust explosion possible'.
  c A potato cooks much more slowly in a billy of boiling water on a trekking holiday in Nepal than a potato boiled in a similar way in the Australian bush. Hint: at high altitudes pressure is lower so water boils at a lower temperature than at sea level.

15 Explain the meaning of the terms:
  a catalyst
  b activation energy

16 If a sugar cube is held in the flame of a candle, the sugar melts and browns but does not burn. However, the cube will burn if salt is first rubbed into it, even though the salt does not react. Explain the effect of the salt on the activation energy of this combustion reaction.

20 The reaction of hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$$

is shown on the energy level diagram Figure 15.24.

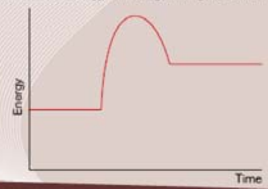

Figure 15.24
Energy level diagram for the production of hydrogen iodide.

a Copy Figure 15.24 and label the following: $H_2(g)$ and $I_2(s)$; HI(g); ΔH; activation energy.
b Is the reaction endothermic or exothermic?
c Draw on the diagram the energy profile that would result if a catalyst was used in the reaction.