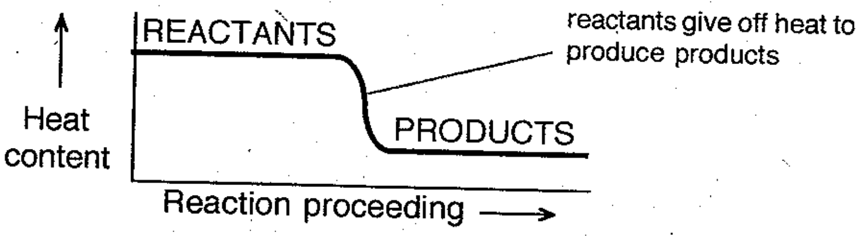
# UNIT I : REACTION KINETICS

## I.1. INTRODUCTION

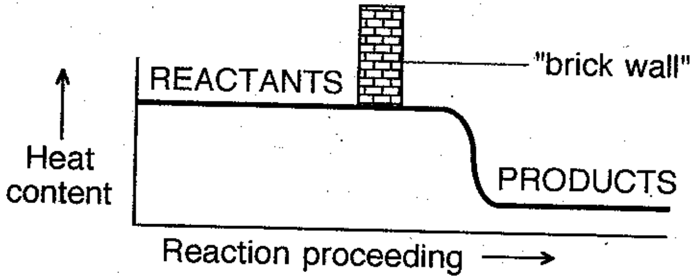
Recall that EXOTHERMIC reactions give off heat.



You might expect that such a reaction would proceed spontaneously, like a ball rolling downhill. However, the reaction

$$2\,N_2(g) + 5\,O_2(g) + 2\,H_2O(l) \longrightarrow 4\,HNO_3(l) + 121\text{ kJ}$$

is exothermic, giving off 121 kJ. If this reaction went on its own, as expected, then the air ($N_2$ and $O_2$) and water of the world would combine to form nitric acid, thus destroying the world and all life! Since swimming in a lake is not generally considered an act of suicide, some type of "wall" must prevent the oxygen, nitrogen and water from forming nitric acid, as shown below.



Since the reaction does not appear to go at all or at least seems to have a VERY SLOW rate, there must be a problem. In an effort to find a clue to this mysterious "wall", the following sections will define what is meant by a "reaction rate", find ways to measure the rate of a reaction, and then look at some of the factors which can affect the reaction rate.

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**REACTION KINETICS** is the study of the rates of reactions and the factors which affect the rates.

***Definition***: REACTION RATE $= \dfrac{\text{amount of product formed}}{\text{time interval}}$

or $= \dfrac{\text{amount of reactant used}}{\text{time interval}}$

or $= \dfrac{\Delta\text{amount}}{\Delta t}$, where "Δ" means "the change in"; "t" stands for "time"

**EXAMPLE:** If 16 g of HCl are used up after 12 min in a certain reaction, then the average reaction rate is:

$$\text{Rate of using HCl} = \frac{16\text{ g}}{12\text{ min}} = \mathbf{1.3\ g/min}\ .$$

If a reaction between $CaCO_3$ and HCl produces 245 mL of $CO_2(g)$ in 17 s, the average reaction rate is:

$$\text{Rate of producing } CO_2 = \frac{245\text{ mL}}{17\text{ s}} = \mathbf{14\ mL/s}\ .$$

**EXERCISES:**

1. A 5.0 g sample of magnesium reacts completely with a hydrochloric acid solution after 150 s. Express the average rate of consumption of magnesium, in units of g/min.
2. How long will it take to completely react 45.0 g of $CaCO_3(s)$ with dilute HCl(aq) if the reaction proceeds at an average rate of 2.35 g $CaCO_3(s)$/min under a given set of conditions?
3. The electrolysis of water produces oxygen gas at the rate of 32.5 mL/min in a certain experiment. What volume of oxygen gas can be produced in 7.50 min?
4. Which of the following are acceptable units for expressing reaction rate?

   (a) moles/second
   (b) minutes/metre
   (c) (moles/litre)/second
   (d) grams/litre
   (e) millilitres/hour
   (f) grams/minute

5. Hydrogen and oxygen gas react in a fuel cell to produce water according to the equation:

   $$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)\,.$$

   If the rate of water ***production*** is 1.34 mol/min, what is the rate of oxygen gas ***consumption*** expressed in mol/min?

## I.2. METHODS OF MEASURING REACTION RATES

If an Alka Seltzer™ tablet is "plopped" into a beaker of water, you will see bubbles of $CO_2(g)$ forming. The reaction producing the gas is:

$$NaHCO_3(s) + H^+(aq) \longrightarrow CO_2(g) + Na^+(aq) + H_2O(l)\,.$$

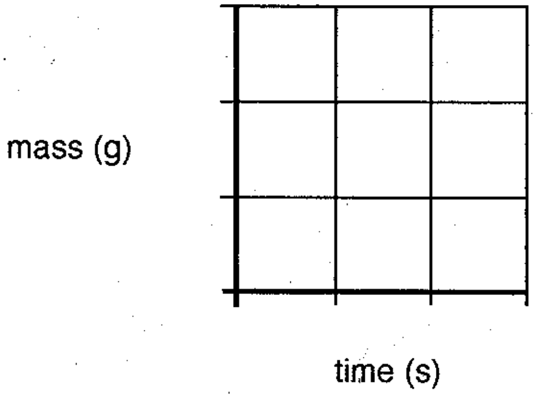
The $H^+(aq)$ is produced by the contents of the tablet; $NaHCO_3$ ("baking soda") is another of the tablet's ingredients.

***EXERCISE:***

6. The following data was obtained for the above reaction (mass includes beaker and contents).

| Time (s) | Mass (g) |
|---|---|
| 0 | 150.00 |
| 10 | 149.94 |
| 20 | 149.88 |
| 30 | 149.82 |

Plot the above data on the graph below.



Now answer the following questions.

(a) Why is the mass decreasing?
(b) What is the slope of the line in the above graph, using: slope = RISE / RUN ?
(c) What are the units of: (i) the RISE? (ii) the RUN? (iii) the slope?
(d) What units would you expect to use for the rate of this reaction?
(e) What relationship exists between the slope of the graph and the rate of the reaction? State the value found for the experimentally–determined reaction rate.

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In order to illustrate the methods used to determine the rate of a reaction, consider a specific reaction: the reaction of copper metal with nitric acid.

$$\underset{\text{red–brown}}{Cu(s)} + \underset{\text{colourless}}{4\,HNO_3(aq)} \longrightarrow \underset{\text{blue}}{Cu(NO_3)_2(aq)} + 2\,H_2O(l) + \underset{\text{brown}}{2\,NO_2(g)} + \text{heat}$$

The rate of the above reaction can be found by measuring any one of at least four different properties.

## a) Colour change

The $Cu(NO_3)_2(aq)$ has a characteristic blue colour. The intensity of the blue colour can be measured with a spectrophotometer.

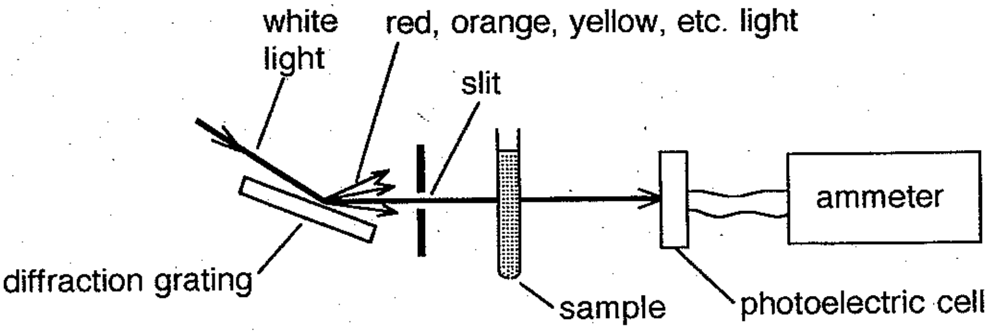


DIAGRAM OF A SIMPLE SPECTROPHOTOMETER

The diffraction grating acts like a prism and splits up the incoming light into the colours of the rainbow. When the diffraction grating is tilted the incoming light is reflected at a particular angle, allowing a specific colour, for example green, to pass through the slit. The amount of light which is absorbed by the sample is directly proportional to the concentration of the light–absorbing chemical. Changes in the amount of light hitting the photocell allow measurement of changes in the concentration of **dissolved** chemicals. (The beam of light must not be blocked by undissolved solids.) In the above reaction, the blue colour of the $Cu(NO_3)_2(aq)$ would be appropriate to measure. As the reaction proceeds, the intensity of the blue colour will increase. Plotting a graph of colour intensity versus time allows the slope of the graph to be found. But recall from exercise 6 that the RATE of the reaction is equal to the SLOPE of graph.

$$\text{Rate} = \frac{\Delta\text{colour intensity}}{\Delta\text{time}}$$

## b) Temperature change

Since the reaction is producing heat, the slope of a temperature versus time graph allows you to find the rate of the reaction.

$$\text{Rate} = \frac{\Delta\text{temperature}}{\Delta\text{time}}$$

## c) Pressure change

Since the reaction is producing a gas, $NO_2$, the reaction can be carried out in a sealed vessel attached to a gas pressure gauge. By plotting a graph of pressure versus time you can again find the slope of the graph, that is, the rate of the reaction.

$$\text{Rate} = \frac{\Delta\text{pressure}}{\Delta\text{time}}$$

## d) Mass change

Since copper metal is the only solid present in the reaction, the rate at which the copper is used up can be measured as follows. Set up several identical acid solutions and pieces of copper. The mass of the copper must be known. Put the first piece of copper in the first container of acid and let the reaction proceed for 30 s, say. Then, quickly stop the reaction by pouring the acid–copper mixture into water and washing the remaining acid off the copper. Dry and weigh the amount of copper metal left. Repeat the reaction with the second piece of copper and second container of acid, but let the reaction proceed for 60 s, say, before stopping the reaction and weighing the copper. Repeat for several other time intervals. Using the known starting masses and the masses remaining after reacting, the mass which actually reacts is found for each trial. By plotting a graph of the mass of copper which reacts versus time, the slope of the graph and therefore the rate of the reaction is found.

$$\text{Rate} = \frac{\Delta\text{mass}}{\Delta\text{time}}$$

***EXERCISES***:

7. When measuring the rate at which the mass of copper metal decreases during a reaction with nitric acid, why can't you just put the reaction vessel on a digital balance and record the decrease in mass as the copper is used up?

8. (a) Solutions of $Cu^{2+}(aq)$ are blue, while solutions of $Ag^{+}(aq)$ are colourless. Use only this information to describe how you would measure the rate of the reaction:

   $$2\,Ag^{+}(aq) + Cu(s) \longrightarrow 2\,Ag(s) + Cu^{2+}(aq) + 35\text{ kJ}.$$

   (b) Suggest two more methods that could be used to determine the rate of the reaction in part (a). For each method, state the property that you are monitoring.

9. (a) You are to measure the rate of the reaction: $H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g)$. Why is gas pressure **NOT** a good property to monitor in order to determine the reaction rate?

   (b) Calculate the reaction rate, in mol HCl/s, if 1.2 g of HCl(g) are produced in 2.0 min.

   (c) If the rate of consumption of hydrogen gas under certain conditions is 0.200 L/min, what is the rate of production of HCl(g)?

## I.3. FACTORS AFFECTING REACTION RATES

Experiments show the following relationships.

a) When two Alka Seltzer™ tablets are simultaneously "plopped" into equal volumes of hot and cold water, *THE REACTION PROCEEDS FASTER AT HIGHER TEMPERATURES.*

b) When strips of copper metal are simultaneously placed into equal volumes of concentrated nitric acid (15.4 M) and diluted nitric acid (6.0 M), *THE REACTION IS FASTER IN THE MORE CONCENTRATED SOLUTION.*

The results of such experimental work probably are exactly what you would have expected. This section will look at these and other factors which can have an effect on the rate of a reaction and come up with statements such as:

"When the ..... increases, then the rate ....".

No attempt will be made in this section to explain ***why*** these factors have an effect on the rate; explaining why an effect occurs will be left until a later section.

The factors which affect the rate of a reaction are as follows.

### a) TEMPERATURE

When temperature ***increases,*** the time required for the reaction ***decreases.*** But, a ***decrease*** in the time for the reaction is caused by an ***increase*** in the **RATE,** so that when the TEMPERATURE ***increases,*** the RATE ***increases.***

### b) CONCENTRATION

As reactant concentration ***increases,*** the time required for the reaction ***decreases.*** Hence, when REACTANT CONCENTRATION ***increases*** the RATE ***increases.***

### c) PRESSURE

When the pressure of a gaseous reactant ***increases,*** more of the reactant is compressed into a given volume (that is, the reactant concentration ***increases***). Hence, when the REACTANT PRESSURE ***increases,*** the RATE ***increases.***

***Note***: Pressure is just another way to define a concentration.

**Important:** The volume of a system is inversely proportional to the pressure applied to the system. In other words, ***when the pressure on a system is increased, the volume of the system decreases, and vice versa.***

### d) THE NATURE OF THE REACTANTS

Some reactions are naturally slow because the bonds involved are very strong and unreactive, or the electrons involved are tightly held. Other reactions are naturally fast because the reaction involves breaking weak bonds or removing loosely–held electrons. Chemists have no control over these ***fundamental*** differences in the rates of reactions.

***Definition***: The **NATURE OF THE REACTANT** is the term used to describe the chemical properties of a substance.

We say that it is simply the "**NATURE OF THE REACTANTS**" to react quickly or slowly. For example, the chemical properties of granite and nitroglycerine dictate that the "weathering" of a granite boulder by the action of sunshine and rain is naturally very slow, whereas the explosion of nitroglycerine is very fast. You can slow down or speed up the weathering of granite and the explosion of nitroglycerine TO A SMALL DEGREE, but you cannot change the fact that the weathering will ALWAYS be much slower than the explosion.

**Important:** The NATURE OF THE REACTANTS does ***not*** refer to the phase (solid, liquid, gas) of the reactants, but rather to the chemical properties of the specific molecules involved.

With respect to "the nature of the reactants", the bonding may involve more than just how strong the bonds are; the NUMBER OF BONDS being broken and made may need to be considered. For example, the following reaction is RELATIVELY SLOW because many chemical bonds have to be broken and then reformed.

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

ACTUAL SHAPES OF THE SPECIES

On the other hand, the following reaction is FAST because ***no*** bonds are broken or formed; only a single electron is transferred.

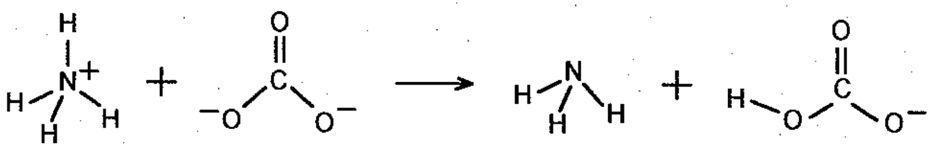
$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

***EXERCISES***:

10. Rank the following three reactions in terms of their expected reaction rates (fastest to slowest) at room temperature.

    (a) $2\,H{-}O{-}O{-}H \longrightarrow 2\,H{-}O{-}H + O{=}O$

    (b)



    (c) $2\,CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + 25\,O{=}O \longrightarrow 16\,O{=}C{=}O + 18\,H{-}O{-}H$
    [ Note that this is the combustion of octane ("gasoline") ]

11. Experimentally, it is found that at room temperature the reaction between Li(s) and water is much slower than the reaction between K(s) and water. Which of the previous four factors affecting reaction rates would best explain this observation?

## e) THE ABILITY OF REACTANTS TO MEET: SURFACE AREA AND PHASE CONSIDERATIONS

If you want to start a campfire, you start with small wood shavings rather than with a huge log. The shavings allow you to start a fire quicker because

***THE GREATER THE SURFACE AREA AVAILABLE FOR REACTION, THE GREATER THE RATE OF REACTION.***

In a sense, surface area effects are related to concentration effects. That is, if in a given volume you have more surface area exposed, then there is a greater concentration of sites at which a reaction can take place. However, surface area ***is*** a distinct effect, separate from concentration, even though surface area and concentration can be thought of in a similar manner.

Before going any further, let us consider the effect of PHASE on the SURFACE AREA.

***Definition***: A **HOMOGENEOUS REACTION** is a reaction in which all the reactants are in the same phase.

*Some examples of HOMOGENEOUS REACTIONS are reactions between:*

- two gases,
- two substances which are both dissolved in water, and
- two liquids which completely dissolve in each other (are "miscible").

***Definition***: A **HETEROGENEOUS REACTION** is a reaction in which the reactants are present in different phases.

*Some examples of HETEROGENEOUS REACTIONS are reactions between*:

- a solid and a liquid,
- a liquid and a gas,
- a solid and a gas, and
- two liquids which DO NOT dissolve in each other (are "immiscible").

Surface area is one of the factors which affect the rate of a reaction because surface area controls ***the ability of the reactants to meet***. The greater the surface area, the greater the ability of the reactants to meet, and the greater the rate of the reaction.

Another important consideration is the **PHASE** in which a reaction occurs. Reactions occurring in the solid phase are slow because the reactants cannot move freely. Reactions between gaseous species and reactions between species in the liquid phase are much faster due to the speed of the gaseous particles or the close proximity of the liquid particles. Aqueous ions have the fastest reaction rates because of their close proximity to each other in solution, their ability to move through the solvent, and their strong positive–negative attractions. In summary, the following trend in reaction rates is found.

FASTEST ⟶ SLOWEST
AQUEOUS IONS > (GASES or LIQUIDS) > SOLIDS

***EXERCISES***:

12. Will surface area have an effect on a reaction between two gases? Why? How can this conclusion be generalized to the importance of surface area in homogeneous versus heterogeneous reactions?

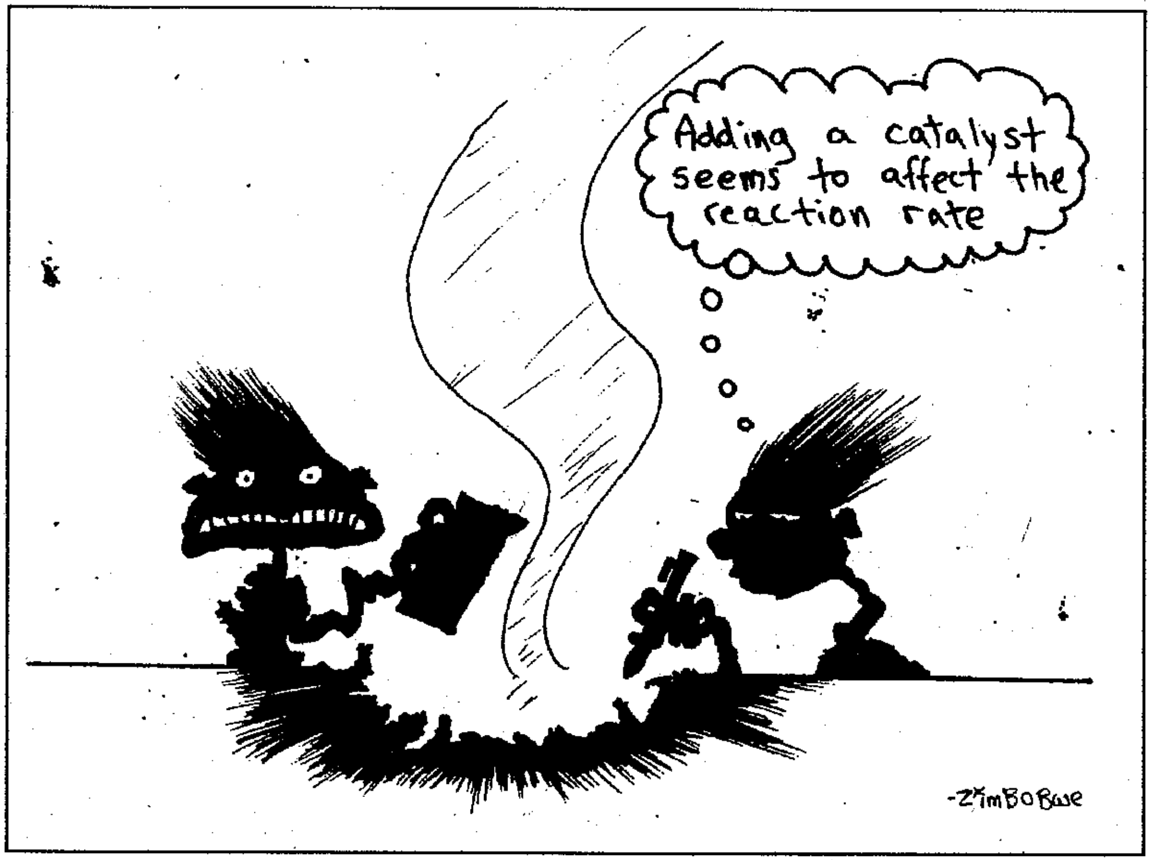
13. In each of the following pairs of reactions, which would have the faster reaction rate?
    (a) $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$ **or** $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$
    (b) $Fe(s) + 2\,H_2O(l) \longrightarrow Fe(OH)_2(s) + H_2(g)$ **or** $CH_3COOH(aq) + H_2O(l) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq)$
    (c) $Cu(s) + S(s) \longrightarrow CuS(s)$ **or** $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$
    (d) $C(s,\ powder) + O_2(g) \longrightarrow CO_2(g)$ **or** $C(s,\ chunk) + O_2(g) \longrightarrow CO_2(g)$
    (e) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ **or** $2\,H_2O_2(aq) + 2\,H^+(aq) \longrightarrow 2\,H_3O^+(aq) + O_2(g)$

14. Which of the reactions in the previous exercise are HOMOGENEOUS reactions?

## f) CATALYSTS AND INHIBITORS

A **CATALYST** is a chemical which can be added to a reaction to INCREASE the rate of the reaction. After the reaction is complete, there will be as much of the catalyst present as was originally put into the reaction.

An **INHIBITOR** is a chemical which REDUCES a reaction rate by combining with a catalyst or one of the reactants in such a way as to prevent the reaction from occurring. Examples of inhibitors are poisons and antibiotics.



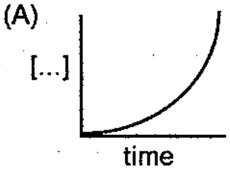
***EXERCISES***:

15. Which of the above six factors (temperature, concentration, etc.) are important in HOMOGENEOUS reactions? Which are important in HETEROGENEOUS reactions?

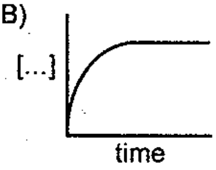
16. State 5 ways of increasing the rate of the reaction: $2\,Al(s) + 3\,F_2(g) \longrightarrow 2\,AlF_3(s)$. Assume the reaction is occurring in a closed container whose volume can be changed.

17. (a) What will happen to the concentration of the reactants as a reaction proceeds?
    (b) What will happen to the rate of a reaction as the reaction proceeds?
    (c) Which of the following graphs would best represent
        i) the ***product concentration*** versus time of a reaction? Explain your selection.
        ii) the ***reactant concentration*** versus time of a reaction? Explain your selection.

(A)

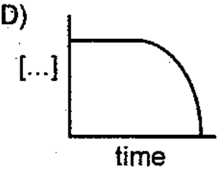


(B)



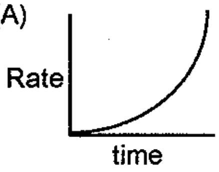
(C)

(D)

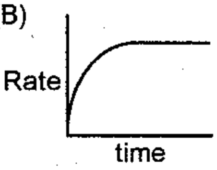


    (d) Which of the following graphs would best represent
        i) the ***RATE*** at which ***reactants*** are used versus time of a reaction? Explain.
        ii) the ***RATE*** at which ***products*** are produced versus time of a reaction? Explain.

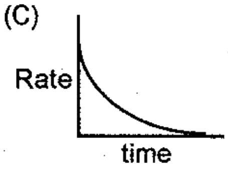
(A)



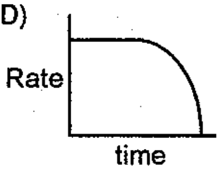
(B)



(C)



(D)



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Many everyday situations require the control of reaction rates. Some examples are given below.

a) Body chemistry requires an exact temperature to ensure that the reactions of life occur at an appropriate rate.

b) Fuels burn quickly in air and may explode in pure oxygen. As the oxygen concentration is lowered, the rate of burning drops to zero, which is why "smothering" a fire is effective.

c) Enzymes are catalysts which regulate our body chemistry.

d) Many industrial chemical reactions require precise control of the factors affecting the rate. For example, the production of compounds called "azo dyes" (used to dye wool and cotton) requires the use of low temperatures at one point so as to prevent unstable reactants from decomposing before they have a chance to react.

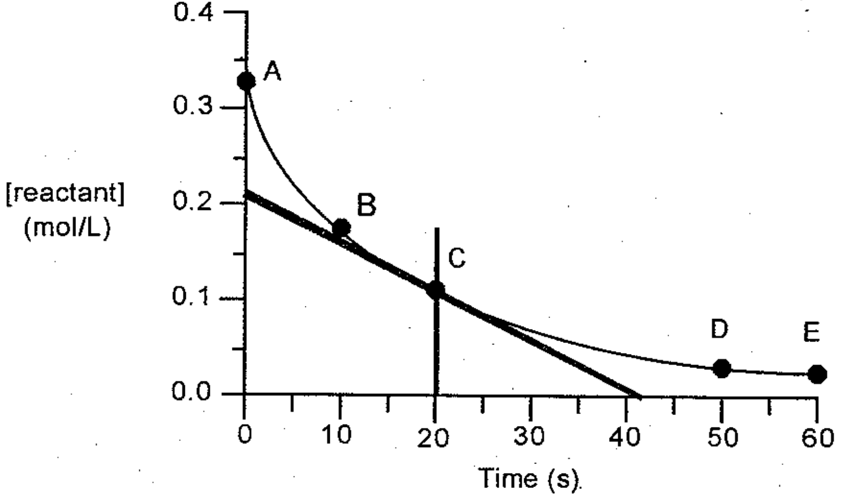
e) The metal in car bodies will quickly rust unless paint or other protection is used to prevent oxygen from reacting with the iron in the car.

f) The cooking of food requires an increase in temperature. Many of the desirable reactions in the cooking process will not occur except at high temperatures.

g) To preserve food, its temperature can be lowered in order to slow down the reactions which allow bacteria to grow.

## I.4. EXPERIMENTAL MEASUREMENT OF REACTION RATES

If the concentration of a reactant is plotted versus time, the following typical behaviour is observed.



Initially, there is a relatively high [reactant], so that the reactant is used up at a fast rate (in the first 10 s there is a large drop from A to B). Later, when most of the reactant is used up, the low [reactant] causes a slow reaction rate (in the 10 s interval from 50 – 60 s there is only a small drop in [reactant] from D to E).

The exact rate at a given time, for example at 20 s (above), is given by the slope of the line tangent to the curve at that time (see above graph).

***EXERCISES:***

18. What is the reaction rate at 20 s, according to the above graph?

19. The following data were collected for the reaction $Zn(s) + 2\,HCl(aq) \longrightarrow H_2(g) + ZnCl_2(aq)$ in which zinc metal was reacted with 0.200 M HCl(aq).

| Time (s) | Mass Zn (g) |
|---|---|
| 0 | 31.0 |
| 60 | 24.6 |
| 120 | 20.2 |
| 180 | 17.4 |

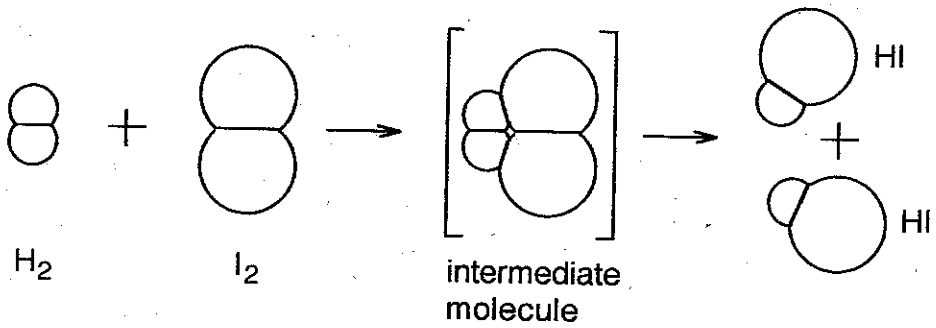
(a) Calculate the average reaction rate, in g/s, from time 0 to 60 s.
(b) Calculate the average reaction rate, in g/s, from time 120 to 180 s.
(c) Explain why the average rate in part (b) is less than that in (a).

## L5. REACTION RATES AND COLLISION THEORY

The **COLLISION THEORY** (or **Kinetic Molecular Theory**) states that molecules act as small, hard spheres which bounce off each other and transfer energy among themselves during their collisions.

Before two molecules can react, they must collide with each other. "Action at a distance" does not exist; that is, there can be no reaction without a collision.

Consider the reaction: $H_2 + I_2 \longrightarrow 2\,HI$.



Collision theory provides us with a deeper understanding of what actually causes reaction rates to change when the conditions of the reaction are altered.

a) ***The Effect of Concentration*** – if the $[H_2]$ or $[I_2]$ increases then more collisions are possible between molecules. Therefore, the rate of the reaction increases; that is, the number of collisions per second increases.

b) ***The Effect of Temperature*** – if the temperature increases then the KINETIC ENERGY (KE) of the molecules increases and the speed at which they are moving increases. Because the molecules are moving faster they collide more often ***and*** with more energy, and therefore the reaction rate increases. [NOTE: This is only PART of the reason why rate increases when the temperature increases, as will be seen in Section 7.]

***EXERCISES***:

20. How can collision theory explain the effect of surface area on reaction rate?

21. The following reaction is taking place at a very slow rate in a closed container at room temperature.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

State the effect of the following procedures on the rate of this reaction and explain the effect in terms of collision theory.

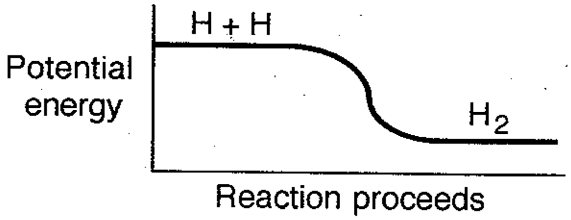
(a) The temperature is decreased.
(b) More $O_2(g)$ is added to the same volume.
(c) Some $SO_2(g)$ is removed.
(d) The sulphur is ground up into a powder.
(e) The volume of the container is increased.

22. Explain in terms of collision theory why kindling is used to start a fire, rather than a large block of wood.

# I.6. ENTHALPY CHANGES IN CHEMICAL REACTIONS

## a) Bond Energies

Consider the reaction shown on the diagram below.



As the atoms combine to form a bond, they give off energy and go to a lower, more stable level of energy. This is more clearly seen by looking at the reaction in reverse. In order to break a chemical bond, energy must be added to the molecule so that the resulting separated atoms contain more energy than before.

The negatively–charged electrons hold the positively–charged nuclei together, forming a chemical bond. Simultaneously, the electrons repel each other and the nuclei repel each other, so that the position of the atoms involved in a chemical bond is a compromise between the attractive forces and repulsive forces existing within a molecule.

The potential energy is the energy possessed by a system as a result of the position of all the particles in the system. More specifically:

> **POTENTIAL ENERGY** is the energy existing as a result of an object's position in space, as well as the sum of all the attractive and repulsive forces existing among the particles which make up the object. As a result, the potential energy (PE) of a chemical system is directly related to the energy of the electrons in the chemical bonds, as well as the number and type of atoms in the molecules.

In contrast:

> **KINETIC ENERGY** is the energy which a system possesses because of movement within the system. This energy may exist as a result of moving the entire system or moving the molecules in the system (or individual atoms within the molecules).

***Definition***: **BOND ENERGY** is the amount of energy required to break a bond between two atoms.

To break a bond, an amount of energy equal to the bond energy must be added to the bond:

$$Cl_2(g) + 243\ kJ \longrightarrow 2\ Cl(g).$$

Conversely, if two atoms form a bond, an amount of energy equal to the bond energy is released by the atoms:

$$2\ Cl(g) \longrightarrow Cl_2(g) + 243\ kJ.$$

***EXERCISE***:

23. When breaking the Br–Br bond in $Br_2$, what happens to the potential energy of the molecule?

## b) Reaction Heats

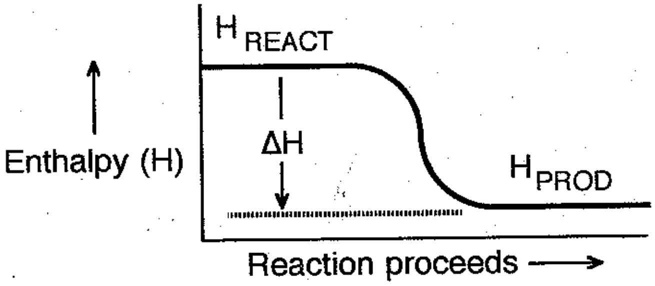
When a chemical reaction occurs, new molecules are formed as chemical bonds are broken and made, phases may change, work may be done on the system or by the system, and heat may be transferred into or out of the system. Accounting for each of these energy changes on an individual basis is complicated and beyond the level of Chemistry 12. Since many chemical reactions are carried out in open flasks or beakers, a special energy term (ENTHALPY) is defined to incorporate all the energies which exist in an open system at constant atmospheric pressure.

***Definitions***: **ENTHALPY = H** = the total kinetic and potential energy which exists in a system when at constant pressure.

**ΔH** = $H_{PROD} - H_{REACT}$ = the change in enthalpy during the course of a reaction

where: $H_{REACT}$ = the ***combined*** enthalpies of ***all*** the reactants
$H_{PROD}$ = the ***combined*** enthalpies of ***all*** the products

The relationship between ΔH, $H_{PROD}$ and $H_{REACT}$ is shown on the diagram below.



SPECIAL NOTE: In general, the individual values for $H_{REACT}$ and $H_{PROD}$ are never found and are not needed. Only ΔH, the ***difference*** between the values of $H_{PROD}$ and $H_{REACT}$, is important.

## c) The Sign of ΔH:

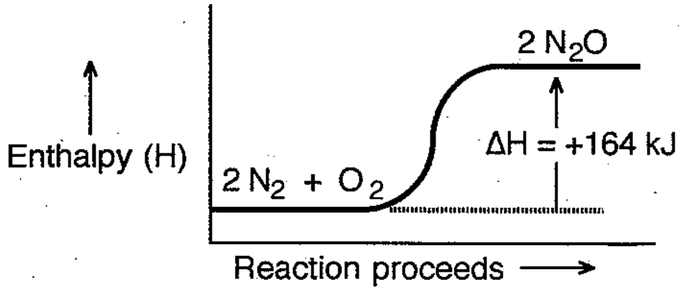
i) If a reaction is **ENDOTHERMIC** then products have MORE energy than reactants.

Substituting $H_{PROD} > H_{REACT}$ into $\Delta H = H_{PROD} - H_{REACT}$ gives $\mathbf{\Delta H > 0}$.

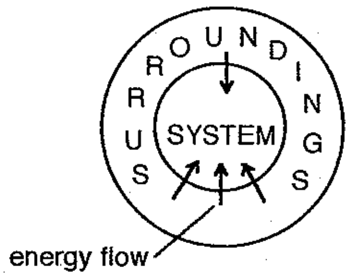
***EXAMPLE***: Two alternate ways to show an ENDOTHERMIC reaction are

$2\,N_2 + O_2 + 164\text{ kJ} \longrightarrow 2\,N_2O$
or: $2\,N_2 + O_2 \longrightarrow 2\,N_2O\ ;\ \Delta H = +164\text{ kJ}$

Examine the energy diagram below. Note that the arrow associated with ΔH always points **from** the energy level of the reactants **to** the energy level of the products. In this case, the arrow points "up" and the reactants GAIN energy to become products. Heat "**EN**ters" the system in an **EN**dothermic reaction.



The 164 kJ of heat which is absorbed by the $N_2$ and $O_2$ (the "SYSTEM") comes from the surroundings (such as the container, surrounding air, etc.), as indicated by the diagram below.



The loss of energy from the surroundings to the system ($N_2$ and $O_2$) causes the surroundings to feel cooler.

ii) If a reaction is EXOTHERMIC then products have LESS energy than reactants.

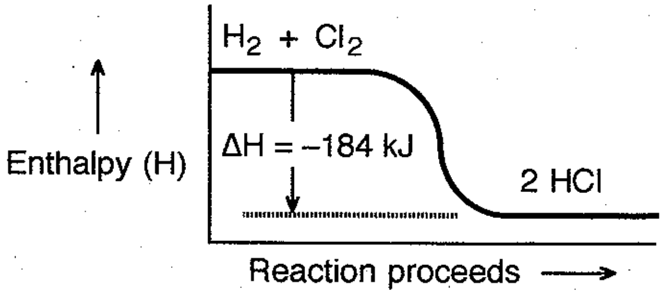
Substituting $H_{PROD} < H_{REACT}$ into $\Delta H = H_{PROD} - H_{REACT}$ gives $\mathbf{\Delta H < 0}$.

***EXAMPLE***: Two alternate ways to show an EXOTHERMIC reaction are

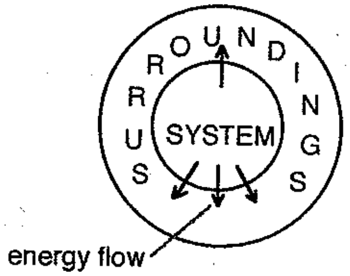
$$H_2 + Cl_2 \longrightarrow 2\,HCl + 184\text{ kJ}$$

or: $$H_2 + Cl_2 \longrightarrow 2\,HCl\,;\ \Delta H = -184\text{ kJ}$$

This situation is shown on the energy diagram below. Again, the arrow associated with ΔH points **from** the energy level of the reactants **to** the energy level of the products. In this case, the arrow points "down" and the reactants LOSE energy to become products. Heat "**EX**its" the system in an **EX**othermic reaction.



The 184 kJ of heat which is given off by the $H_2$ and $Cl_2$ (the "SYSTEM") will be absorbed by the surroundings, as indicated by the diagram below.



The loss of energy from the $H_2$ and $Cl_2$ to the surroundings causes the surroundings to feel warmer.

**MEMORY AID:** The two possible signs for a number are + and – .
(Notice that it sounds backwards to say – and +.)
In English we read from left to right, so let us put the "+" on the left side of a reaction arrow and the "–" on the right .

This gives us $+ \longrightarrow -$ which is interpreted as :

if the heat term is on the left side , then $\Delta H = +$
if the heat term is on the right side , then $\Delta H = -$

***EXERCISES:***

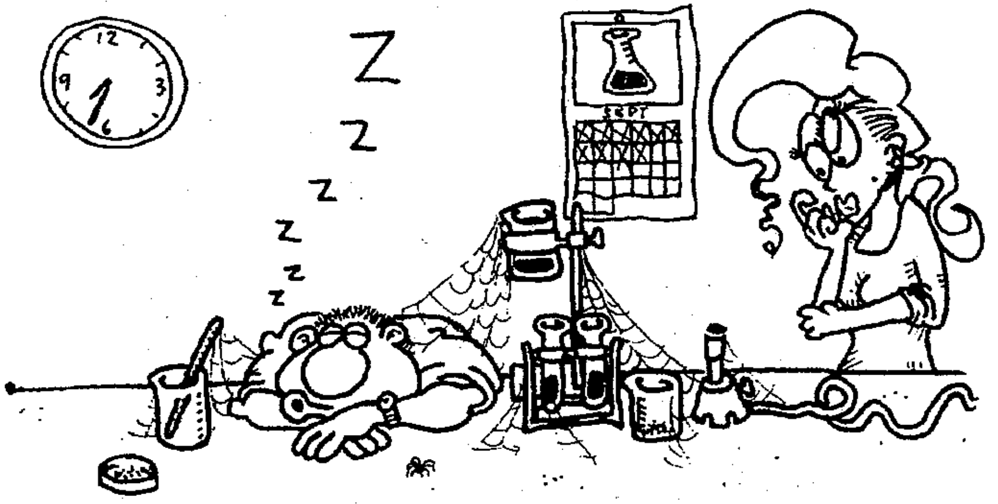
24. $\Delta H = -25$ kJ for the reaction: $A \longrightarrow B$. Re–write this equation to show the 25 kJ properly on the reactant or product side. Draw a graph of "enthalpy" versus "reaction proceeds", showing the relative enthalpies of the reactant and product, and the enthalpy change. Will the surroundings feel warmer or cooler as the reaction occurs?

25. If a reaction absorbs 40 kJ of heat, what is $\Delta H$ for the reaction?

26. What is $\Delta H$ for the reaction $A + 30\text{ kJ} \longrightarrow B$? Which have more energy, reactants or products? Draw a graph of "enthalpy" versus "reaction proceeds", showing the relative enthalpies of the reactant and product, and the enthalpy change. Will the surroundings feel warmer or cooler as the reaction occurs?

27. Draw a graph of "enthalpy" versus "reaction proceeds" for a reaction in which $R \longrightarrow P + 10\text{ kJ}$. Will the surroundings feel warmer or cooler as the reaction occurs?

28. When one mole of HCl reacts with one mole of NaOH to produce one mole of NaCl and one mole of $H_2O$, 59 kJ of heat is absorbed by the surroundings. Draw a graph of "enthalpy" versus "reaction proceeds", showing the relative enthalpies of the reactant and product, and the enthalpy change.

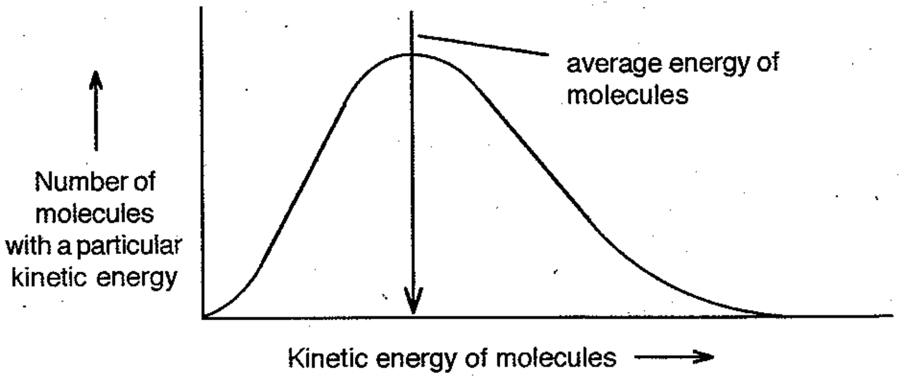


Susan was beginning to suspect that Brad had forgotten one of the reactants

## I.7. KINETIC ENERGY DISTRIBUTIONS

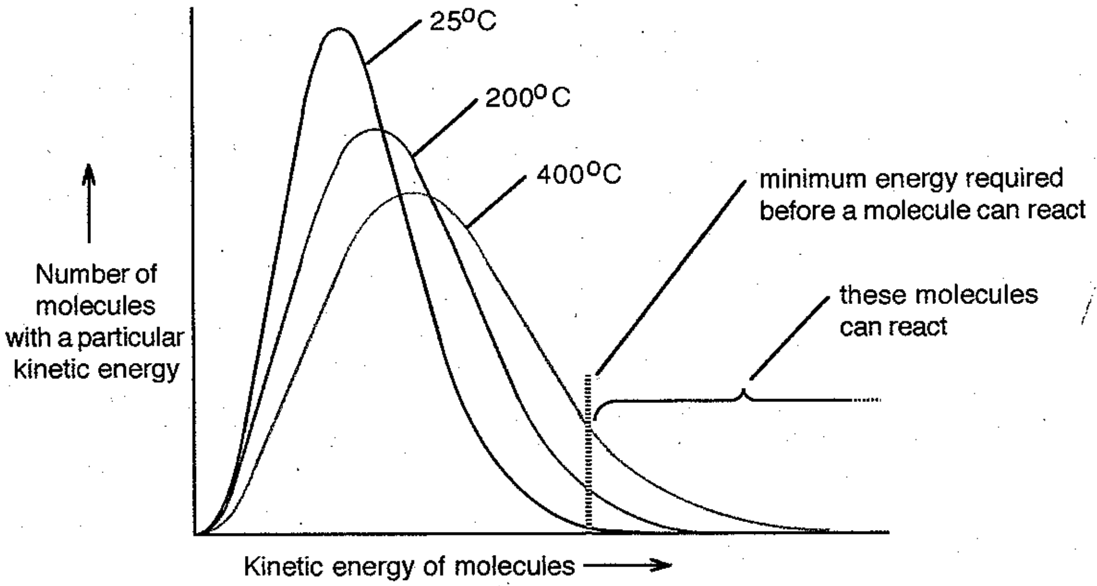
Consider the reaction: $C_2H_5OH \longrightarrow C_2H_4 + H_2O$. At room temperature the reaction rate does not occur at a detectable rate. At 200°C the rate is very slow – some molecules do react BUT only a very small amount. At 400°C the reaction is relatively rapid.

Molecules at room temperature and pressure undergo about $10^{10}$ collisions/second, so the lack of reactivity at room temperature is ***not*** due to a lack of collisions. Since high temperatures favour fast reaction rates, the energy contained in a molecule must determine whether or not a molecule will react. However, at a given temperature some molecules ***do*** react and some ***do not***, so that there MUST be a CONTINUOUS DISTRIBUTION of energies among the molecules, as shown below.



Note that some molecules have a very low kinetic energy and some have a very high kinetic energy.

As the temperature of the system is increased, the average energy of the system is increased.



***NOTE***: 1. The reaction rate is small at room temperature since only a few molecules have sufficient energy to react at a given instant. As the average energy of the molecules increases at higher temperatures, more and more molecules possess the required minimum energy to react, and hence the rate increases.

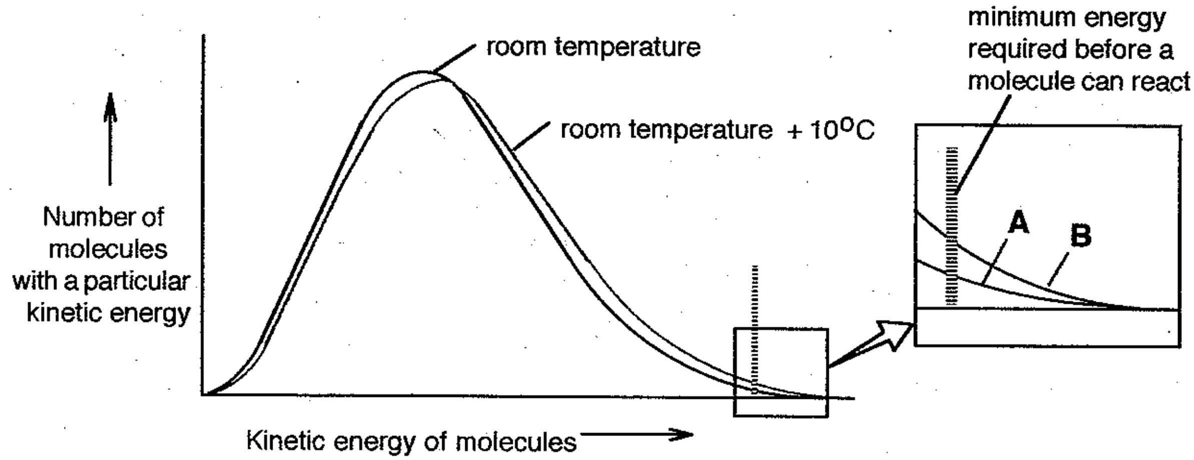
2. As the temperature increases the molecules undergo more collisions, but the increase in collisions is relatively small. (It can be shown that when going from 100°C to 110°C, the 10°C temperature increase only results in about a 1% increase in the number of collisions!)

Therefore: THE INCREASED REACTION RATE DUE TO AN INCREASE IN TEMPERATURE IS **PRIMARILY DUE** TO THE INCREASED NUMBER OF MOLECULES WITH SUFFICIENT ENERGY TO REACT, AND NOT TO THE INCREASED NUMBER OF COLLISIONS.

Chemists have a **"rule–of–thumb"** which states that

**for a SLOW reaction, a 10°C temperature increase DOUBLES the rate.**

The reason for this rule–of–thumb is that at the far right of the KE curves below, the area under curve "B" is about double the area under curve "A" (see below). Since there are twice as many molecules of B which have sufficient energy to react, the rate is doubled. ***Note***: the curves in the graph below have been deliberately distorted to help illustrate the "doubling of area" effect.



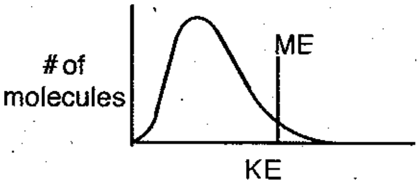
**A final comment:** The KE curves represent the number of particles with a given KE at a given temperature. The curves would look the same for a collection of reacting particles or non–reacting particles. The curves do not automatically predict whether a particle can react; such predictions can only be made if it is known from other sources how much energy a particle requires to react. The distribution tells us only that a few particles in the collection have low energy, most have an intermediate energy, and a few have very high energy.

***EXERCISES***:

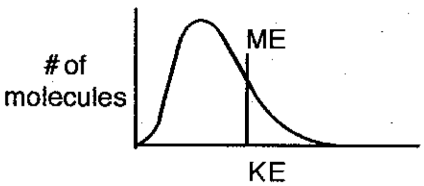
29. The reaction $C_2H_4(g) + Br_2(g) \longrightarrow C_2H_4Br_2(g)$ proceeds very fast at room temperature.

(a) Which of the following KE diagrams would best explain the rate of this reaction? ("ME" is the minimum KE required before a molecule can react.)

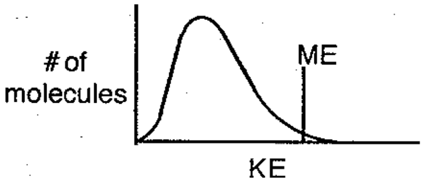
(i)



(ii)



(iii)



(b) If the temperature were increased by 10°C, would the reaction rate double? Explain.

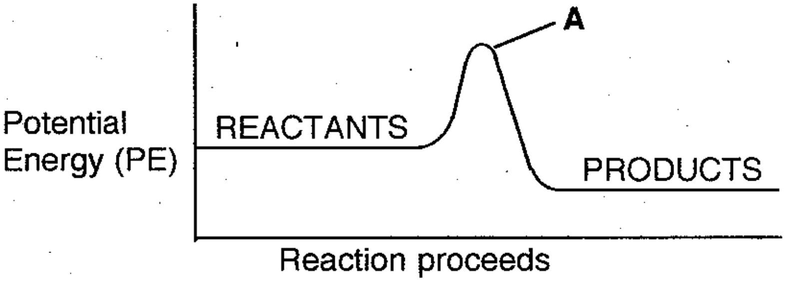
30. What happens to the shape of the KE distribution curve if the:
(a) reactant is used up at a constant temperature?
(b) temperature is decreased?
(c) reactant surface area is increased?
(d) concentration of reactants is increased?

31. The initial rate of consumption of A in the reaction A $\longrightarrow$ B is very slow: $1.0 \times 10^{-7}$ mol/s at 20°C. Estimate the rate of the reaction at 40°C.

32. If the rate of a slow reaction is $2.0 \times 10^{-4}$ mol/s at 10°C, estimate the rate at 40°C.

## I.8. ACTIVATION ENERGIES

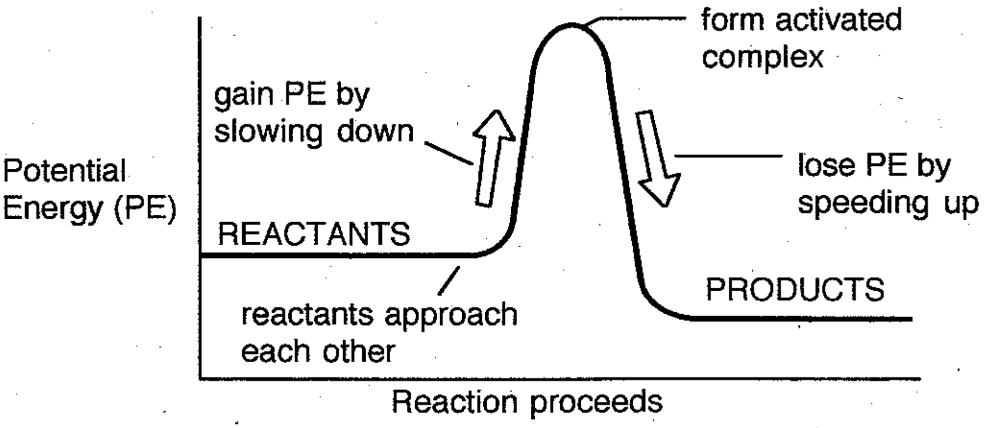
The existence of a minimum energy requirement before a molecule can react means the molecule has an energy "barrier" to overcome. Specifically:



At the peak of the hill (point A) the actual reaction occurs. If the reactants do not possess enough energy to react, they can only climb part way up the hill and don't react. Molecules with insufficient energy just bounce off each other without reacting.

As the molecules approach each other, the outer electrons on one molecule start to repel the electrons on the other, thus slowing down the molecules and converting their KE into PE. In other words, the electrons in the molecule absorb the KE lost and increase their PE. If the molecules can gain sufficient PE (by converting the KE gained into PE, and adding this extra PE to the PE they already possess), bonds can be broken and made and an **ACTIVATED COMPLEX** is formed. After the reaction, the newly–formed product molecules repel each other (their outer electrons repel) and as the molecules start to move away from each other they lose their excess PE by converting it into KE (the molecules pick up speed – "hot" molecules have a high KE).

Overall, then:



***NOTE***: The existence of the barrier is due to the mutual repulsion of the outer electrons as the reactants approach each other, as well as the energy required to cause bond breaking to begin. When the number of electrons present at the "reaction site" is increased, the repulsion between the approaching molecules is also increased. A higher energy hill results from the greater PE required to overcome this increased repulsion. In addition, the PE requirements are greater when the bond strengths involved are increased.

***Definitions*:** The **ACTIVATED COMPLEX** is the arrangement of atoms which occurs when the reactants ARE IN THE PROCESS OF REARRANGING to form products. (In other words, it is an intermediate molecule.)

**ACTIVATION ENERGY** = $E_a$ = the minimum potential energy required to change the reactants into the activated complex.

When two molecules approach each other they will start to convert their KE into PE and "climb the energy hill"; that is, they will "spend" their KE in order to "buy" PE. There are three possible cases to consider with regard to how much KE a pair of approaching molecules may possess.

***Case 1*:** The KE is less than that needed to "buy" an amount of PE equal to the activation energy.

Here, the molecules will not be able to "spend" enough KE to get to the top of the PE hill. Hence, the approaching molecules will come to a halt before a reaction can occur, then move back away from each other (rebound). This is called an **INEFFECTIVE COLLISION.**

***Case 2*:** The total KE is equal to the "minimum energy required for a reaction to occur" (see Section I.7).

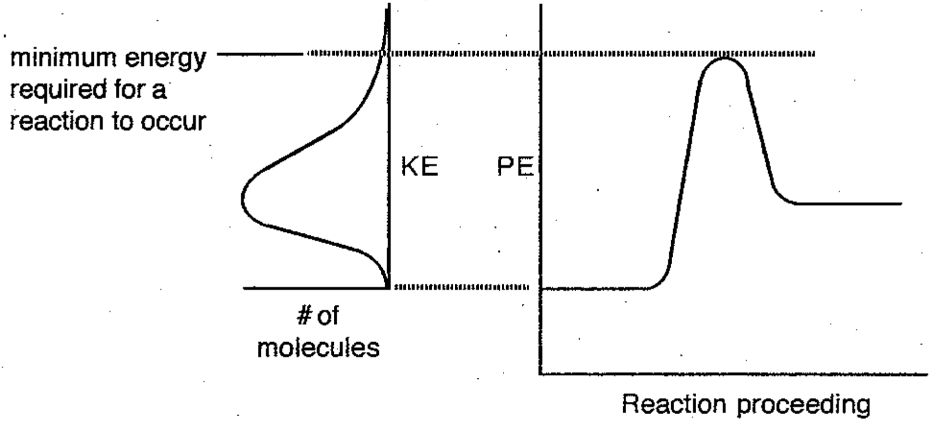
Here, the molecules "spend" just enough KE to "buy" the required activation energy. The approaching molecules will have come to standstill, but a reaction will now be possible (although a reaction is not guaranteed; the molecules may simply separate without reacting).

***Case 3*:** The total KE is more than the "minimum energy required for a reaction to occur".

Here, the molecules will be able to "spend" enough KE to be able to "buy" the required activation energy and still have some leftover KE. The reacting molecules will then be locked together while they are moving as a unit through space.

**A collision between two particles is *EFFECTIVE* if the collision results in a reaction.**

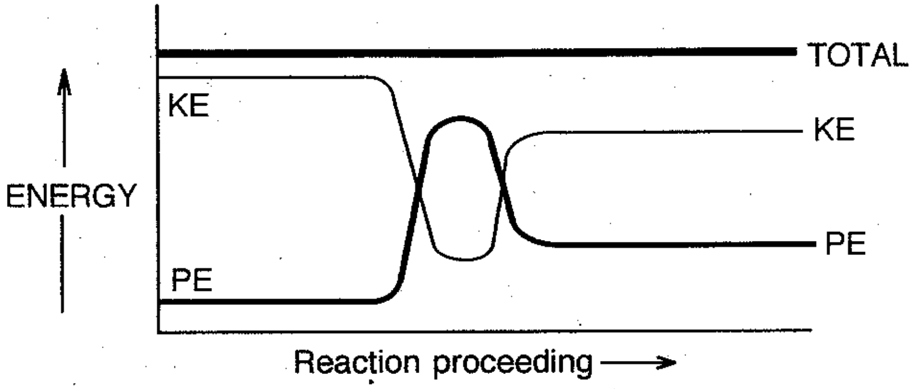
The graphs below will be used to help explain why a reaction proceeds at a fast or a slow rate.



The graph on the left is a KE distribution curve (Section I.7) tilted on its side, so that the KE is now the vertical axis. The graph on the right is a normal PE diagram. The KE diagram shows how many molecules have a

SPECIFIC AMOUNT OF KINETIC ENERGY AVAILABLE. Because the PE hill is so high, there are very few molecules which have a KE greater than or equal to the "minimum energy required for a reaction to occur". As a result, very few molecules will be able to react in a given time interval and the REACTION RATE WILL BE VERY SMALL. If the energy hill were substantially lower, then in a given time interval many more molecules would have the KE required to react and the REACTION RATE WOULD BE LARGE.

Examine the following diagram.

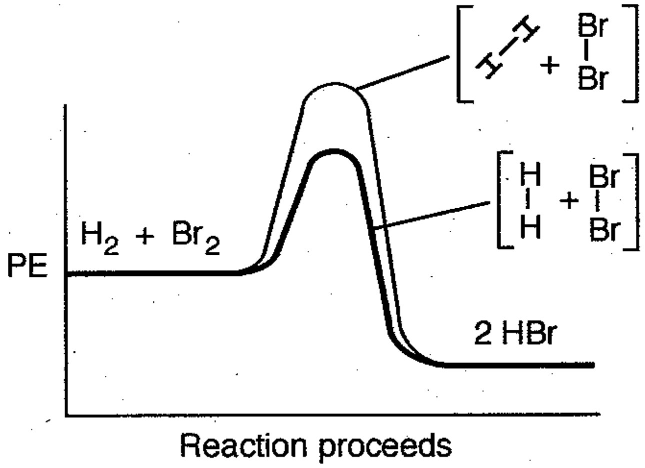


At the start of the reaction, most of the energy is stored as KE. As the molecules approach each other, the PE increases and the KE (as velocity) decreases. After the reaction, the molecules separate and pick up speed as the PE decreases. The total energy of the system never changes: PE + KE = constant.

When two species collide there are two requirements which must be met before a successful reaction can occur. The molecules must possess:

i) ***Sufficient KE*** – If insufficient KE is converted to PE then insufficient PE will be gained.

ii) ***Correct alignment*** – If the reactants are not correctly aligned, the reaction needs more energy to be completed.



As can be seen in the diagram above, if the reactants are ***not*** correctly aligned (not parallel to each other in this case) the activation energy required is increased. Therefore, experimental values given for the activation energy refer to the activation energy required when there is PERFECT ALIGNMENT of reactants. If the alignment is very poor (for example, one reactant is at right angles to its preferred orientation) the activation energy may be impossibly high.

## EXERCISES:

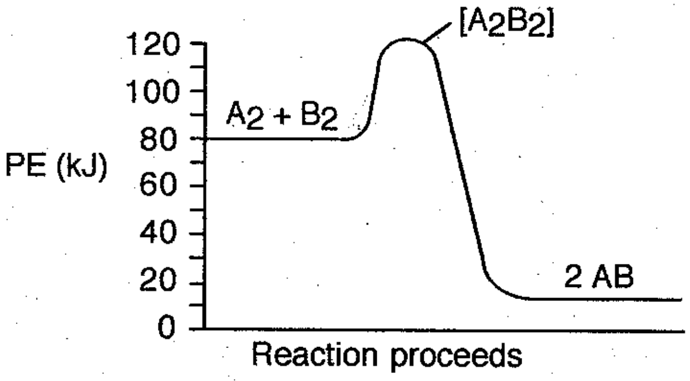
33. Why don't the oceans convert to nitric acid? (Recall that this was the problem posed at the start of this entire section.)

34. (a) Draw a PE diagram for a fast exothermic reaction.
    (b) Draw a PE diagram for a slow exothermic reaction.
    (c) Draw a PE diagram for a fast endothermic reaction.
    (d) Draw a PE diagram for a slow endothermic reaction.
    (e) How is the size of the "energy hill" related to the number of molecules which have sufficient KE to pass over the top of the hill?

35. If two reactant molecules collide with sufficient KE, are they guaranteed to have an ***effective*** collision?

36. (a) As two reactant particles approach each other, what happens to
    (i) their KE? Why? (ii) their PE? Why?
    (b) The total energy of a system is given by: $E_{TOTAL} = PE + KE$. How does the value of $E_{TOTAL}$ before a collision compare to the value of $E_{TOTAL}$ after a collision?

37. The following is a PE diagram for a collision between molecules $A_2$ and $B_2$. The molecules collide with favourable geometry.



(a) If $A_2$ and $B_2$ had collided with less favourable geometry how would the activation energy compare to that shown above?
(b) Why does PE decrease when going from the activated complex to the products, AB?
(c) Is the overall reaction exothermic or endothermic?
(d) Write a balanced equation for the reaction, including the value for the enthalpy.
(e) What is the value of the activation energy in the above reaction?

38. The bond energies of $F_2$ and of $I_2$ are almost identical. Would you expect the activation energy for

$$H_2 + F_2 \longrightarrow 2\,HF$$

to be equal to, greater than, or less than the activation energy for

$$H_2 + I_2 \longrightarrow 2\,HI\ ?$$

[Hint: why does an activation energy exist in the first place?]

39. Carbon exists in two forms, or ALLOTROPES, called graphite and diamond. The enthalpy for the reaction converting graphite to diamond is only 2 kJ, yet one can't simply heat black, opaque and inexpensive graphite and turn it into transparent and precious diamond. Suggest a reason why the reaction is so difficult to carry out.

40. After a reaction, the product molecules have less kinetic energy than the original reactant molecules. Is the reaction endothermic or exothermic? Explain your answer.

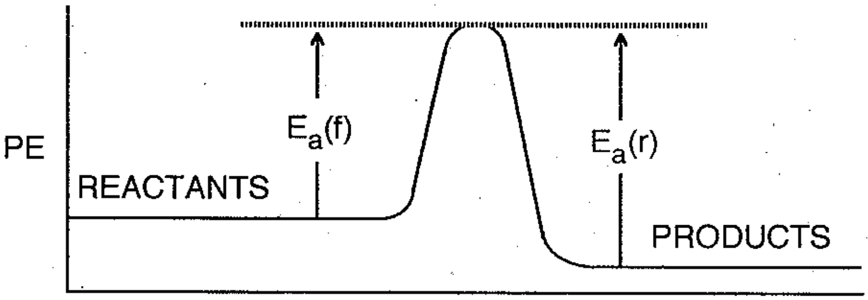
---

The concept which will now be introduced has a major impact on the rest of Chemistry 12.

If you look at any of the preceding PE diagrams showing an energy hill you should be able to see that there is no apparent reason why molecules can't go over the hill from left to right ***as well as from right to left.*** In other words, reactants can form products and products can re–form reactants.

$$\boxed{\text{REACTANTS} \rightleftharpoons \text{PRODUCTS}}$$

The possibility of going forward and backward now requires us to modify our PE diagrams so as to specify the amount of energy required to convert ***either*** the reactants ***or*** the products into an activated complex.



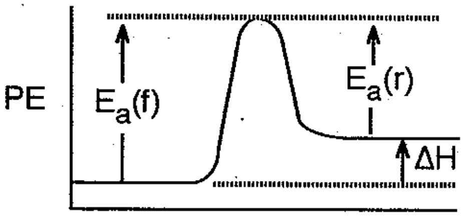
Reaction proceeds

where: $E_a(\mathbf{f})$ = the activation energy for the ***forward*** reaction
$E_a(\mathbf{r})$ = the activation energy for the ***reverse*** reaction

**IMPORTANT:** THE ACTIVATION ENERGY IS ALWAYS ***ENDOTHERMIC***; THAT IS, ENERGY MUST BE ***ADDED*** TO GET TO THE TOP OF THE ENERGY HILL.

Now to determine the relationship between $E_a(f)$ and $E_a(r)$.

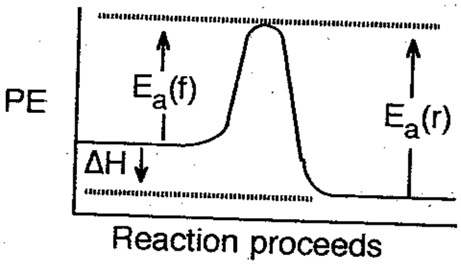
## (a) ENDOTHERMIC REACTIONS



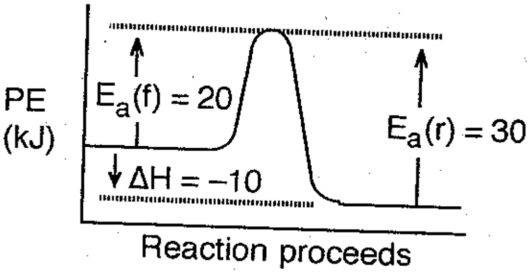
Reaction proceeds

You can see from the above diagram that: $\boxed{E_a(f) = E_a(r) + \Delta H \quad (\text{note that } \Delta H > 0)}$

### (b) EXOTHERMIC REACTIONS



At first glance, it seems that: $E_a(f) + \Delta H = E_a(r)$. However, that can't be correct because if $E_a(f) = 20$ kJ and $\Delta H = -10$ kJ (the reaction is EXOTHERMIC) then: $E_a(r) = 20 + (-10) = 10$ kJ. That is, $E_a(f) > E_a(r)$. But the above diagram for an exothermic reaction shows that $E_a(f) < E_a(r)$. Using the idea that $\Delta H$, $E_a(f)$ and $E_a(r)$ represent energy differences or "energy gaps", the diagram



shows that $E_a(f) - \Delta H = E_a(r)$ or, after rearranging: $\boxed{E_a(f) = E_a(r) + \Delta H \quad \text{(note that } \Delta H < 0)}$

which is identical to the expression found for ENDOTHERMIC reactions.

**SUGGESTION:** If you don't like having to "memorize another equation", a quick sketch of a PE diagram with labelled energy differences will help you calculate a missing value for $\Delta H$, $E_a(f)$ or $E_a(r)$.

A trick to help draw PE diagrams is to start from the "peak" and draw in the $E_a$ values. If $\Delta H$ is positive, the products are higher than the reactants – the $\Delta H$ arrow points "up" (positive direction). If $\Delta H$ is negative, the products are lower than the reactants – the $\Delta H$ arrow points "down" (negative direction).

***EXERCISES*:**

41. If $\Delta H = -15$ kJ and $E_a(f) = 40$ kJ, what is the value of $E_a(r)$?
42. A reaction has $E_a(f) = 55$ kJ and $E_a(r) = 30$ kJ. Is the reaction exothermic or endothermic?
43. Draw and label a PE diagram for the reaction: $2\,NOBr(g) \longrightarrow 2\,NO(g) + Br_2(g) + 50\text{ kJ}$, in which $E_a(f) = 30$ kJ. Indicate on your diagram the point at which the activated complex exists.
44. Draw and label a PE diagram to show the enthalpy change and activation energies for a reaction in which: $R + 25\text{ kJ} \longrightarrow P$ and $E_a(r) = 10$ kJ.
45. Draw and label a PE diagram showing the enthalpy change and activation energies for a reaction in which $E_a(f) = 20$ kJ and $E_a(r) = 45$ kJ.

## I.9. REACTION MECHANISMS

***Definition***: A **REACTION MECHANISM** is the ***actual sequence of steps*** which make up an overall reaction.

- ***Analogy***: A garment can be made using cloth, needle, thread, scissors and a pattern. Is it reasonable to expect that the garment can be made by simply throwing the cloth, etc. into a bag, shaking the contents, and pulling out a finished garment? Obviously, the process must be carried out in steps.

Assuming that a collision between two particles (a "two particle collision") is certain to occur, it can be shown that the probability of three particles simultaneously arriving at the same place at the same time (a "three particle collision") is 1000 times less likely, and a "four particle collision" is almost impossible. A little thought should convince you that in the reaction

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

the probability of **23** reactant particles coming together all at once is zero.

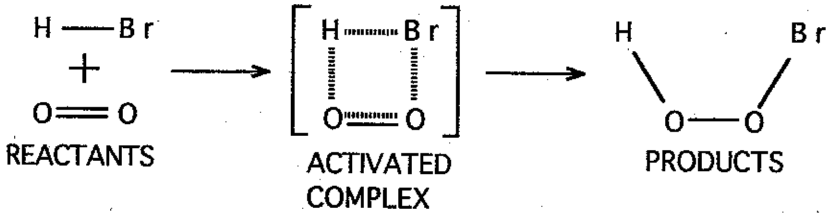
Therefore, complex reactions ***cannot*** go in a single step; there ***must*** be more than one step involved in getting from reactants to products.

Let us now examine the experimentally–determined mechanism for the reaction:

$$4\,HBr + O_2 \longrightarrow 2\,H_2O + 2\,Br_2.$$

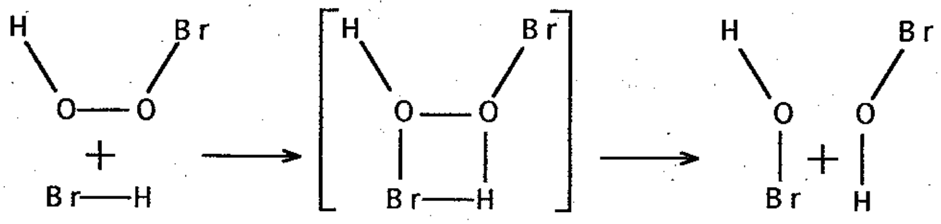
**Note:** Prediction of reaction mechanisms will ***never*** be required. Years of precise work and complex analysis may be required to determine a mechanism. You may be asked questions about a given reaction mechanism but you will not be asked to dream up a reaction mechanism on your own.

***STEP 1:*** $HBr + O_2 \longrightarrow HOOBr$ (experimentally found to be slow)

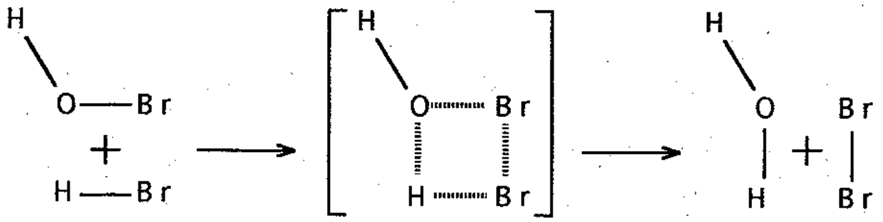


(NOTE: Dots mean the bonds are in the process of forming or breaking; going from "bond" to "no bond" and vice versa. Look at the bond between the H and Br, above. In the reactants there is a "bond". In the activated complex the bond is in the process of breaking. In the products the bond does not exist.)

***STEP 2:*** $HOOBr + HBr \longrightarrow 2\,HOBr$ (experimentally found to be very fast)



***STEP 3:*** $HOBr + HBr \longrightarrow H_2O + Br_2$ (experimentally found to be very fast)



***Definition***: An **ELEMENTARY PROCESS** is an individual step in a reaction mechanism.

Therefore, the above reaction mechanism is made up of three elementary processes.

**NOTES:**

a) The ***slowest step*** in a reaction is called the **RATE–DETERMINING STEP**, or "BOTTLE–NECK STEP". (Step 1 is the rate–determining step in the above reaction.)

b) If the reaction is instantly "frozen", very little HOOBr or HOBr will be present – they can't build up in concentration since they are made very slowly and react very fast.

c) The OVERALL RATE is unaffected by adding HOOBr or HOBr since they are not used in the rate–determining step (and are quickly eliminated from the reaction).

d) To determine the OVERALL reaction from the reaction mechanism, simply add up all the steps in the reaction equations (and cancel any species which occur on both sides of the final equation).

$$\begin{array}{rcl} HBr + O_2 & \longrightarrow & \cancel{HOOBr} \\ HBr + \cancel{HOOBr} & \longrightarrow & \cancel{2\,HOBr} \\ 2\,HBr + \cancel{2\,HOBr} & \longrightarrow & 2\,H_2O + 2\,Br_2 \\ \hline 4\,HBr + O_2 & \longrightarrow & 2\,H_2O + 2\,Br_2 \end{array}$$

e) The HOOBr and HOBr are called "reaction intermediates" or simply "intermediates." They can exist indefinitely on their own, but happen to react quickly in the above reaction mechanism.

f) The formula of an activated complex is found by simply adding up all the atoms involved in the two reacting molecules. For example, in Step 2 (above) the activated complex is $H_2O_2Br_2$ (the order of the atoms is not important).

***EXERCISES:***

46. A reaction is thought to proceed according to the following mechanism.

$$2\,NO + H_2 \longrightarrow N_2 + H_2O_2 \quad \text{(slow)}$$
$$H_2O_2 + H_2 \longrightarrow 2\,H_2O \quad \text{(fast)}$$

a) What is the overall reaction equation?
b) What is true about the $[H_2O_2]$ at any time during the reaction?
c) Which of the steps in the mechanism is the rate–determining step?
d) What would happen to the overall rate if some extra NO was injected into the reaction mixture?
e) If it were somehow possible to speed up the second step in the mechanism, what effect would this have on the overall rate of the reaction?
f) What is the formula of the activated complex in the 1st step of the reaction? In the second step?
g) How many elementary processes are involved in the reaction?

47. What is the difference between an activated complex and a reaction intermediate?

48. The reaction A ⟶ C is known to have the mechanism:

$$A \longrightarrow B \quad \text{(fast)}$$
$$B \longrightarrow C \quad \text{(slow)}$$

What would you expect to be true about the concentration of B as the reaction proceeds?

49. You have been told that phosphorous can be prepared by means of the reaction

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 + 10\,C \longrightarrow P_4 + 6\,CaSiO_3 + 10\,CO\,.$$

Why can you be certain that the reaction equation shown does not represent a reaction mechanism?

50. A two step mechanism is proposed for a reaction:

$$ClO^- + ClO^- \longrightarrow ClO_2^- + Cl^-$$
$$ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^-$$

(a) What is the overall reaction which occurs?
(b) Is $ClO_2^-$ a reaction intermediate or an activated complex?
(c) What is the chemical formula for the activated complex in the second step?

51. The decomposition of acetone, $(CH_3)_2CO$, proceeds according to

$$2\,(CH_3)_2CO \longrightarrow C_2H_4 + 2\,CO + 2\,CH_4\,.$$

If the decomposition is a two–step reaction, and the second step is

$$2\,CH_2CO \longrightarrow C_2H_4 + 2\,CO\,,$$

(a) what is the first step?
(b) what is the formula for the activated complex in the first step? The second step?

52. A chemist suggested that the reaction: $2\,NO + O_2 \longrightarrow 2\,NO_2$ has a three–step mechanism. If the proposed first and third steps are:

$$2\,NO \longrightarrow N_2O_2 \quad \text{(first)}$$
$$N_2O_4 \longrightarrow 2\,NO_2 \quad \text{(third)}\,,$$

(a) what is the second step in the proposed reaction?
(b) what is the formula of the activated complex in the second step?

53. The reaction between gaseous hydrogen and chlorine proceeds as follows.

$$Cl_2 + \text{light} \longrightarrow 2\,Cl \quad \text{.... (1)}$$
$$Cl + H_2 \longrightarrow HCl + H \quad \text{.... (2)}$$
$$H + Cl_2 \longrightarrow HCl + Cl \quad \text{.... (3)}$$

(a) Suggest what step might occur after step 3? [Hint: Steps 2 and 3 show what happens when an ***individual*** pair of Cl and $H_2$ react; not all the Cl's and $H_2$'s react at once.]
(b) What function is served by the light?
(c) Suggest why this reaction is called a "chain reaction".

## I.10. ENERGY DIAGRAM OF A REACTION MECHANISM

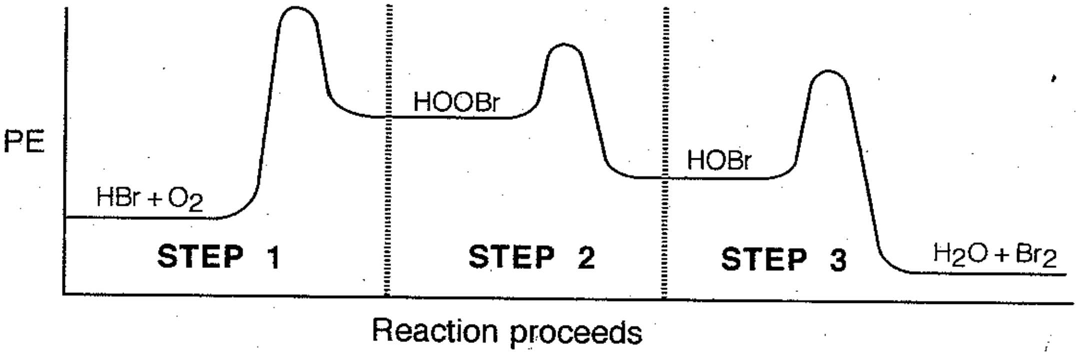
Recall the reaction mechanism:

$HBr + O_2 \longrightarrow HOOBr$ (slow)
$HBr + HOOBr \longrightarrow 2\,HOBr$ (fast)
$2\,HBr + 2\,HOBr \longrightarrow 2\,H_2O + 2\,Br_2$ (fast).

Each step involves an individual activated complex and activation energy. Since there are three steps, there are three "humps" in the PE diagram. The overall PE diagram for the reaction

$$4\,HBr + O_2 \longrightarrow 2\,H_2O + 2\,Br_2$$

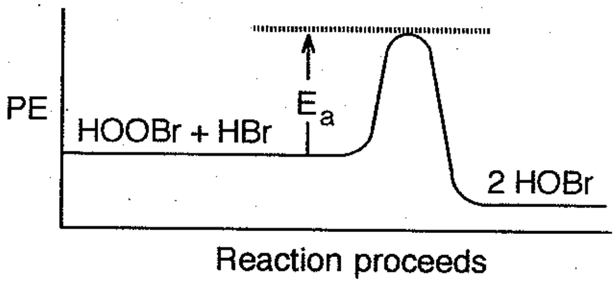
has been experimentally determined to have the following form.



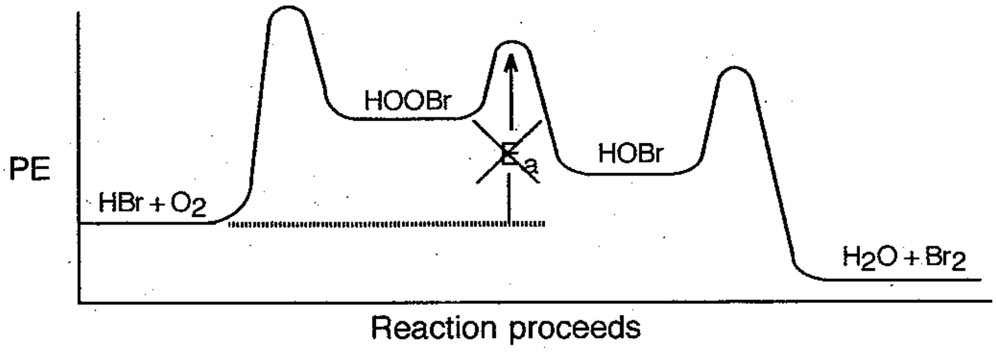
The activation energy, $E_a$, for a particular step in a reaction can be defined as

$$E_a = \text{PE(activated complex)} - \text{PE(reactants for the step)}\ .$$

For step 2 of the reaction $4\,HBr + O_2 \longrightarrow 2\,H_2O + 2\,Br_2$, the activation energy is the PE difference between the activated complex for the 2nd step and the reactants involved in the 2nd step.



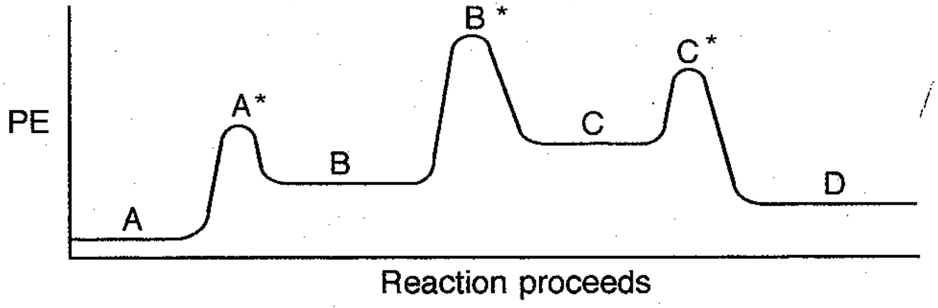
It is ***NOT*** correct to show the activation energy for step 2 as the difference between the PE possessed by the original reactants and the PE possessed by the 2nd activated complex, as shown below.



***EXERCISES***:

54. Which of the steps in the reaction $4\ HBr + O_2 \longrightarrow 2\ H_2O + 2\ Br_2$ has the greatest activation energy? Which has the least?

55. In the following PE diagram:



(a) How many steps does this reaction have?
(b) Is the second step (B $\longrightarrow$ C) exothermic or endothermic?
(c) Is the overall reaction exothermic or endothermic?

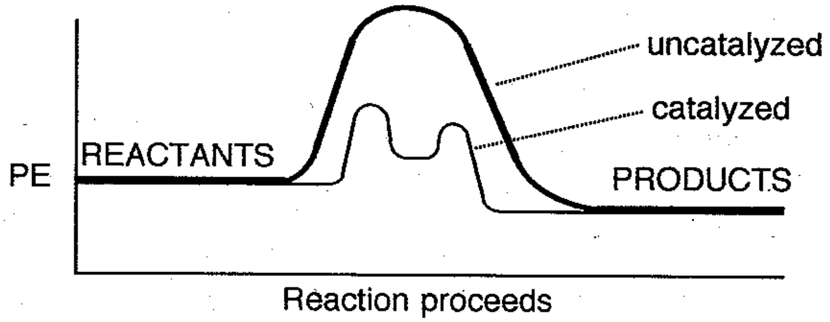
## I.11. THE EFFECT OF CATALYSTS ON THE ACTIVATION ENERGY

You know that a catalyst can speed up a reaction. The problem is: how does this increase in rate occur? The research that has been done on catalysts gives us the answer. Rather than simply saying "a catalyst is a substance which speeds up a reaction", the following definition is now favoured.

***Definition***: A **CATALYST** is a substance which provides an overall reaction with an alternative mechanism having a lower activation energy.

As shown in the diagram below, the energy difference between the reactants and products, ΔH, is not changed but the height of the energy hump is lowered.

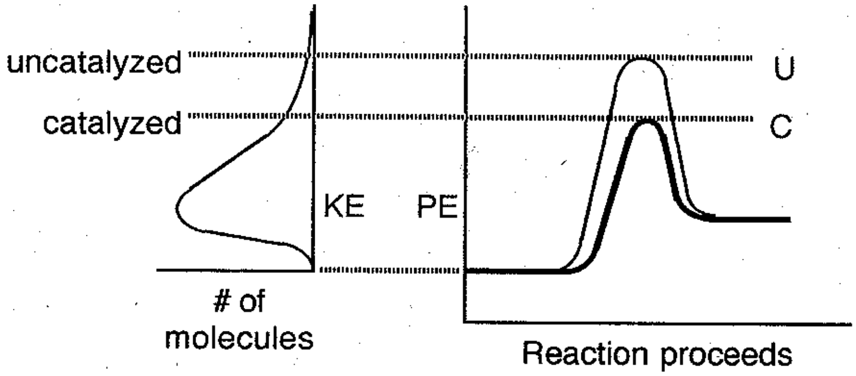
***EXAMPLE:***



If the activation energy is lowered by adding a catalyst, more reactant molecules will possess the minimum KE required to form the activated complex. Therefore, in a given time interval more molecules can react; that is, the ***forward reaction rate increases***. However, by lowering the height of the "energy hump" not only is the forward activation energy lowered, but the reverse activation energy is also lowered. Therefore, more product molecules possess the kinetic energy required to form the activated complex, more PRODUCT molecules react in a given time, and the ***reverse reaction rate increases.***

It can be shown that **if the forward reaction rate doubles, the reverse reaction rate also doubles.**

**NOTE:**

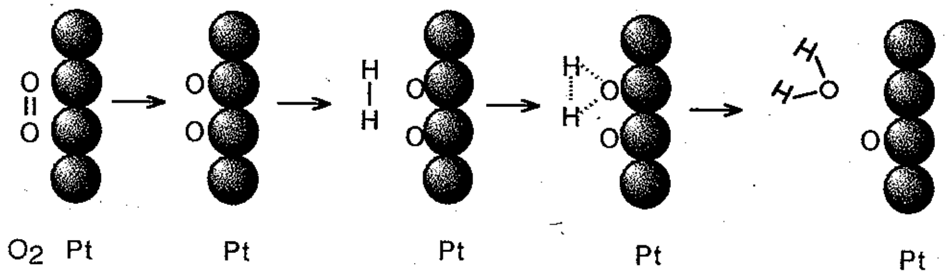


As was seen in Section I.8, those particles which have a critical amount of KE will be able to convert the KE into PE and obtain the critical amount of PE required to reach the peak of the energy hill.

Those particles which go by the uncatalyzed reaction route require more PE (labelled U, above) than those particles which go by the catalyzed route (labelled C, above). The lower PE required in the catalyzed reaction translates as a lower KE requirement for the catalyzed reaction. Since more particles have this lower KE requirement, the reaction rate is faster for the catalyzed reaction. It must be kept in mind that the uncatalyzed pathway is still available, but very few reactants will go over the higher "hump", relative to the numbers that go over the lower, catalyzed hump.

**EXAMPLE**: The uncatalyzed reaction between $H_2$ and $O_2$ to form water is quite complex, having numerous steps in the mechanism. In addition, the reaction requires a substantial activation energy in order to proceed. If a platinum catalyst is used, the reaction proceeds quickly and easily at room temperature in a two–step mechanism.

$$2H_2(g) + O_2(g) \xrightarrow{\text{Pt catalyst}} 2H_2O(g)$$



$O_2$ molecule sticks on the Pt, which supplies enough energy to break the $O_2$ bond

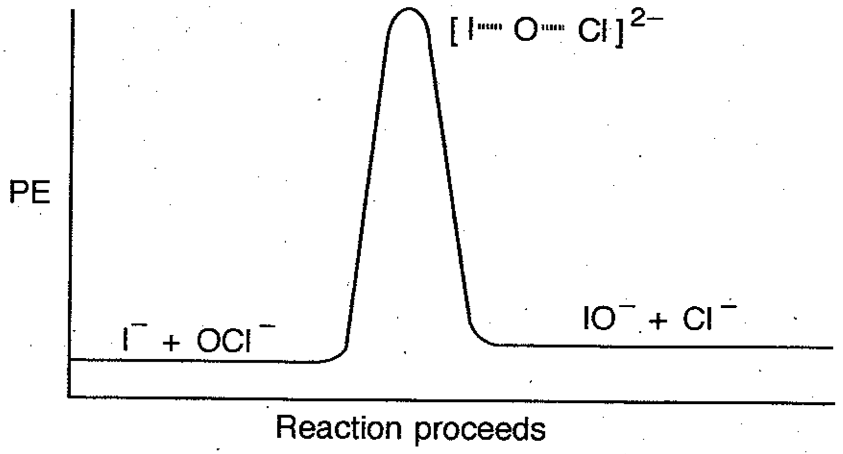
$H_2$ attacks the O atoms

The energy given off by the formation of $H_2O$ is absorbed by the Pt

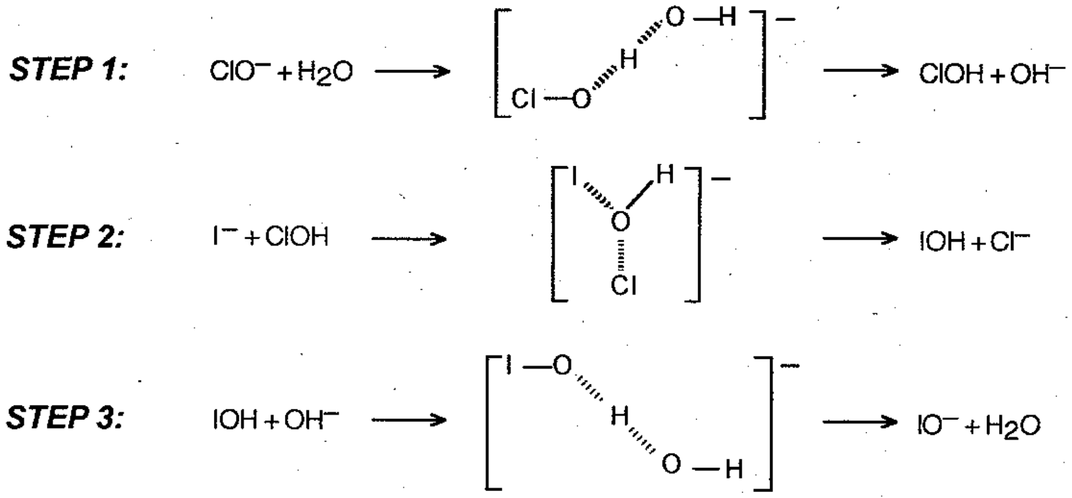
The high energy atoms of platinum metal "loan" some of their energy in order to break the bonds in $O_2$. The highly reactive individual oxygen atoms form bonds with hydrogen to make water. The overall reaction is highly exothermic (242 kJ/mol $H_2O$) and the energy given off is received by the platinum, thereby repaying the energy "loaned" by the platinum. As a result, the platinum gets very hot. This additional heat makes it even easier for the platinum to catalyze subsequent reactions between hydrogen and oxygen.

## I.12. THE EFFECT OF A CATALYST ON THE REACTION MECHANISM

Let us examine the reaction: $OCl^- + I^- \longrightarrow OI^- + Cl^-$. The uncatalyzed reaction has a very high activation energy because it demands that two negatively charged species approach each other and react. This requires a substantial energy input. Therefore, the uncatalyzed reaction shown in the diagram below is very unlikely to occur.



On the other hand, water acting as a catalyst for this reaction ***provides an alternate mechanism with a lower overall activation energy.***



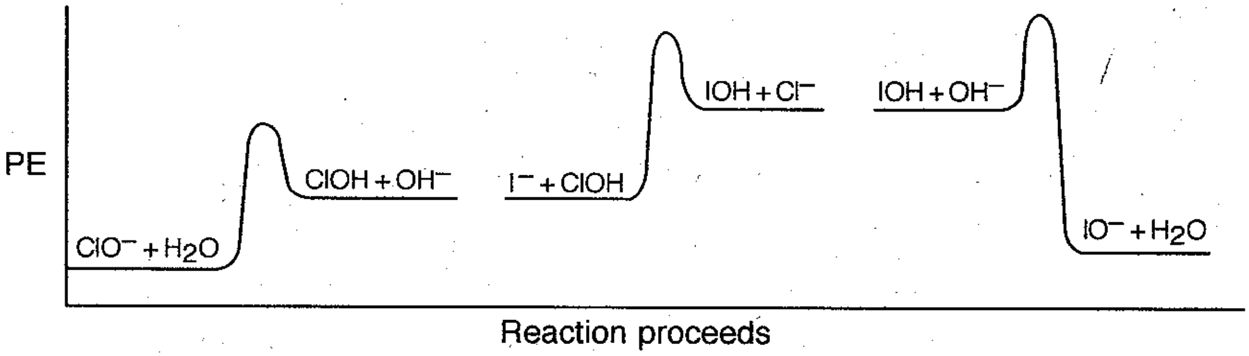
***STEP 1:*** $ClO^- + H_2O \longrightarrow$ $\longrightarrow ClOH + OH^-$

***STEP 2:*** $I^- + ClOH \longrightarrow$ $\longrightarrow IOH + Cl^-$

***STEP 3:*** $IOH + OH^- \longrightarrow$ $\longrightarrow IO^- + H_2O$

***OVERALL:*** $OCl^- + I^- \longrightarrow OI^- + Cl^-$.

The PE diagram below represents the situation which exists when a catalyst is added.



**NOTES:**

a) The essential nature of a catalyst is shown in the above mechanism. A catalyst is NOT a substance which "takes no part in a reaction" (as you may have heard previously); rather, ***the catalyst is an active participant which is REGENERATED in a later step of the reaction mechanism.*** At the end there is as much of the catalyst ($H_2O$) as there was at the beginning. The catalyst will be used up in some specific step (not necessarily the first) and regenerated at some later step (not necessarily the last).

b) It should be noted that ΔH for the overall reaction is the same for both the catalyzed and uncatalyzed reaction. The initial and final PE remain the same; only the intermediate reaction details differ.

c) Both intermediate species and catalysts cancel out when the individual steps in a mechanism are added to get the overall reaction. For example, look carefully at the 3 steps in the above mechanism. **Intermediate species ($ClOH$, $IOH$ and $OH^-$) do not appear in the overall reaction because they are first produced and then used up as reactants in subsequent steps. On the other hand, the catalyst ($H_2O$) is initially used up as a reactant and then subsequently produced again.**

***EXERCISES:***

56. In the following reaction mechanisms identify
    (i) the catalyst (ii) the reaction intermediate(s) (iii) the overall reaction

    (a) $CH_2{=}CH_2 + H^+ \longrightarrow CH_3{-}CH_2^+$
    $CH_3{-}CH_2^+ + H_2O \longrightarrow CH_3{-}CH_2{-}OH + H^+$

    (b) $A + B \longrightarrow C$
    $C + D \longrightarrow E + F$
    $E + B \longrightarrow D + F$

    (c) $NH_2NO_2 + CH_3COO^- \longrightarrow CH_3COOH + NHNO_2^-$
    $NHNO_2^- \longrightarrow N_2O + OH^-$
    $OH^- + CH_3COOH \longrightarrow H_2O + CH_3COO^-$

    (d) $Pt + C_2H_2 \longrightarrow PtC_2H_2$
    $PtC_2H_2 + H_2 \longrightarrow PtC_2H_4$
    $PtC_2H_4 + H_2 \longrightarrow Pt + C_2H_6$

    (e) $A \longrightarrow 2B$
    $B + C \longrightarrow D + E$
    $D + F \longrightarrow C + G$
    $B + G \longrightarrow H$

57. "All catalyzed reaction mechanisms have more than one step." Why must this statement be true?

58. Suppose a catalyzed reaction is occurring in a reaction container. If the catalyst is removed, will the reaction stop completely? Explain your answer.

59. Can a catalyst cause an exothermic reaction to become endothermic, or vice versa? Explain.

60. Consider the following reaction mechanism: $X + Y \longrightarrow Z$ (very fast)
    $Z + Y \longrightarrow P$ (very fast)
    $P + Y \longrightarrow Q$ (slow)

    Suppose there was a catalyst that worked on step 1, and another catalyst that worked on step 3. Which catalyst would be **ineffective** in increasing the rate of the overall reaction?

61. If you have a slow reaction and add a substance that provides an alternate reaction mechanism having a higher activation energy, what will happen to the reaction rate? Why does this occur?

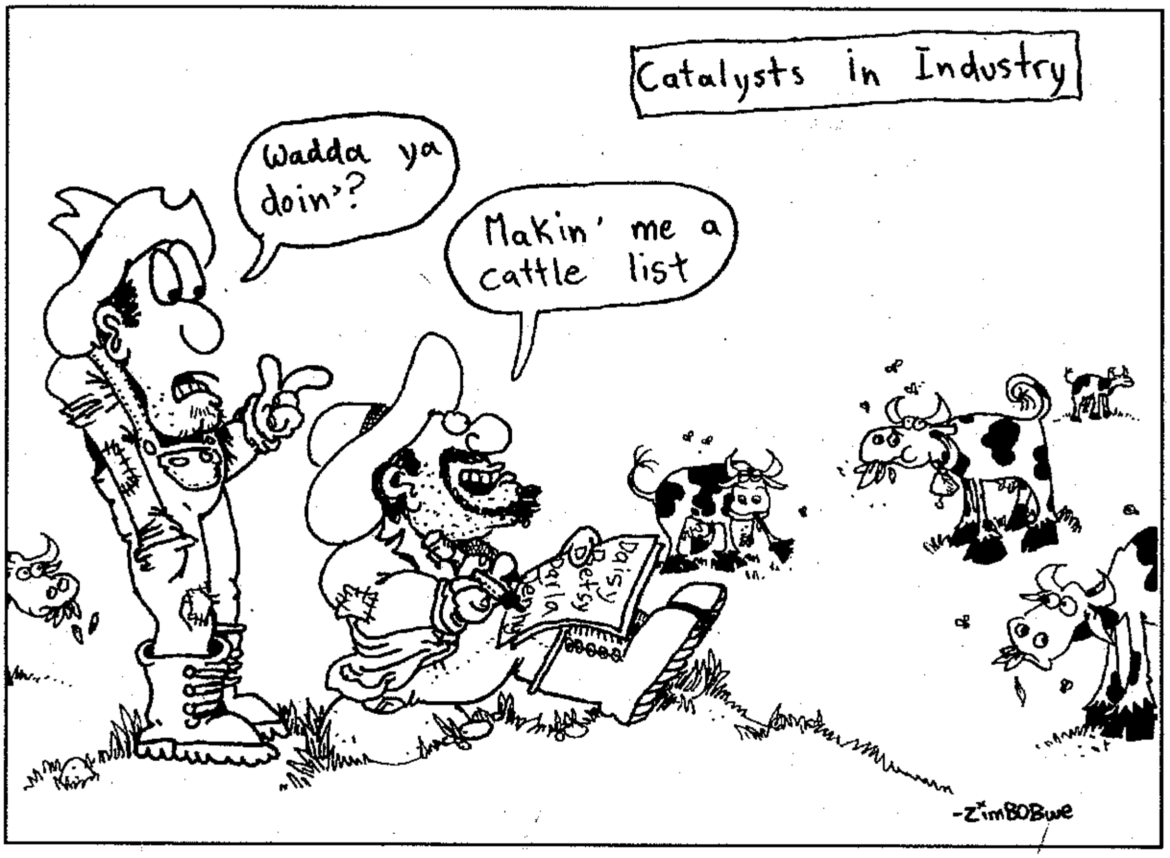
## I.13. SOME USES OF CATALYSTS

Modern chemistry and chemical technology rely extensively on the use of catalysts, but biological systems mastered the use of catalysts long before chemists learned to recognize that catalysts existed. This section will briefly examine some important catalysts and their uses.

(a) Most biological reactions are initiated or aided by catalysts called ENZYMES. Enzymes are protein molecules, each of which depends on its composition and shape to catalyze a specific reaction of a specific molecule. The particular molecule upon which an enzyme acts is called its "substrate". Frequently, a particular reaction may involve several enzymes working together, and even simple cells contain thousands of different enzymes.

For example the enzyme "maltase" breaks down the sugar "maltose" into the simpler sugar "glucose", but has no effect on other sugars.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2\,C_6H_{12}O_6}$$



(b) The industrial process for making $H_2SO_4$ involves several steps. First, sulphur is burned to make $SO_2$:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

Next, the $SO_2$ is passed over a catalyst consisting of finely divided particles of platinum (Pt) or vanadium pentoxide ($V_2O_5$) to form $SO_3$.

$$2\,SO_2(g) + O_2(g) \xrightarrow{V_2O_5\text{ catalyst}} 2\,SO_3(g)$$

The resulting $SO_3$ is then added to water to make sulphuric acid:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l).$$

(c) A series of upper atmosphere reactions produces a more or less constant ozone concentration. Initially, ultraviolet (UV) light breaks apart oxygen molecules to form highly reactive oxygen atoms:

$$O_2 + h\nu \longrightarrow 2\,O \quad \text{(where } h\nu \text{ represents UV light energy)}. \qquad \ldots(1)$$

The oxygen atoms then combine with oxygen molecules to form ozone:

$$O + O_2 \longrightarrow O_3. \qquad \ldots(2)$$

The ozone molecules absorb ultraviolet light, reforming atomic oxygen and an oxygen molecule:

$$O_3 + h\nu \longrightarrow O + O_2. \qquad \ldots(3)$$

In addition, some of the atomic oxygen combines with ozone molecules to reform oxygen molecules:

$$O_3 + O \longrightarrow 2\,O_2. \qquad \ldots(4)$$

(d) Automobile engines operate at sufficiently high temperatures to allow nitrogen and oxygen from the air to combine and form nitric oxide, NO:

$$N_2 + O_2 \longrightarrow 2\,NO.$$

The NO coming out of the exhaust then reacts with more oxygen to form $NO_2$, a harmful pollutant:

$$2\,NO + O_2 \longrightarrow 2\,NO_2.$$

Carbon monoxide, CO, and unburned hydrocarbons are also emitted from the exhaust.

Many modern automobiles have a catalytic converter which treats the exhaust fumes so as to lessen the amount of harmful pollutants. Most of these catalytic converters have two reaction chambers.

- The first chamber contains particles of finely divided metals, such as platinum, palladium and rhodium, which convert the CO and unburned hydrocarbons to $CO_2$ and $H_2O$.
- The second chamber contains a transition metal or transition metal oxide which converts the NO back to $N_2$ and $O_2$.

(e) One of the most commonly used catalysts in chemistry is $H^+(aq)$, found in solutions of acids.

***EXERCISES:***

62. Chlorine atoms are present in the upper atmosphere as a result of emissions from volcanoes and man–made pollutants. The reaction between chlorine atoms and ozone is thought to proceed by a 2–step mechanism:

$$\begin{aligned} O_3 + Cl &\longrightarrow ClO + O_2 \\ O + ClO &\longrightarrow O_2 + Cl. \end{aligned}$$

(a) What is the overall reaction?
(b) Identify any reaction intermediates or catalysts present.
(c) Suggest a reason why chlorine atoms in the upper atmosphere are a threat to the environment.
(d) Why does the presence of chlorine atoms in the upper atmosphere allow more UV light to reach the earth's surface? [Hint: look at reaction (3) on the previous page.]

63. The catalyzed reaction between $CH_3OH$ (an alcohol) and $CH_3COOH$ (an organic acid) to make $CH_3COOCH_3$ (an ester) proceeds as follows.

$$\begin{aligned} &CH_3OH + H^+ \longrightarrow CH_3OH_2^+ \\ &CH_3OH_2^+ \longrightarrow CH_3^+ + H_2O \\ &CH_3^+ + CH_3COOH \longrightarrow CH_3COOHCH_3^+ \\ &CH_3COOHCH_3^+ \longrightarrow CH_3COOCH_3 + H^+ \end{aligned}$$

(a) What is the overall reaction?
(b) Why is the reaction said to be "acid catalyzed"?
(c) If the $H^+$ used in the first step was radioactive, would the $CH_3COOCH_3$ produced in the 4th step contain a radioactive hydrogen atom? Why?