Chem Factsheet

January 2001 Number 10

Kinetics I - Rates of Reaction

To succeed in this topic you need to:-
- Understand how particles are arranged in solids, liquids and gases (kinetic theory)
- Be familiar with energy level diagrams.
- Understand the terms exothermic and endothermic reactions and the use of energy level diagrams.

After working through this Factsheet you will be able to:-
- Understand what the rate of a reaction is.
- Recall the factors affecting the rate of reaction.
- Explain how reaction rate is affected using collision theory.
- Understand activation energies.
- Draw and understand reaction profiles.
- Understand the role of catalysts.

Exam Hint: *At AS Level, the treatment of reaction rates is qualitative, in that candidates are required to understand the theory but calculations are not necessary. Good candidates will use diagrams and graphs in their answers (similar to those used in this Factsheet).*

Rates of Reaction

The rate of reaction describes the **speed** at which reactants are converted to products for a particular reaction.

Some reactions are slow and therefore have a low rate e.g. the corrosion of iron. Other reactions are fast, and therefore have a high rate e.g. the detonation of T.N.T.

To measure the progress of a chemical reaction, we find the reaction rate. This is the change in concentration of either the reactants or products with time.

Rate of reaction $= \dfrac{\textit{change in concentration (mol dm}^{-3}\textit{)}}{\textit{change in time (s)}}$

Units of rate are mol dm^{-3}s^{-1}

eg 1. The concentration of product P increases by 1.0 mol dm^{-3} every second. What it the rate of reaction with respect to P?

$$\text{Rate of reaction} = \frac{\Delta(\text{Concentration})}{\Delta(\text{time})} = \frac{1.0}{1} = 1.0\ \text{moldm}^{-3}\text{s}^{-1}$$

eg 2. Concentration of reactant R decreases by 0.5 moldm^{-3} every 10 seconds. What is the rate of reaction with respect to R?

$$\text{Rate of reaction} = \frac{\Delta(\text{Concentration})}{\Delta(\text{time})} = \frac{0.5}{10} = 0.05\ \text{moldm}^{-3}\text{s}^{-1}$$

Two key facts about rates that must be learnt:

- *Chemical equations (also called the stochiometric equation) tell us **nothing** about the rate of a reaction*
- *The rate of a reaction has to be discovered by **experiment.***

Collision Theory

Collision theory examines what happens on a molecular scale during reactions. We will see how this works by looking at a particular reaction:

Consider the reaction between hydrogen and fluorine gases.

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

Before molecules of hydrogen fluoride can be produced:-
- A collision must occur between a hydrogen molecule and a fluorine molecule, i.e. they have to meet each other.
- There must be enough energy in that collision to break the H-H bond and the F-F bond, before the H-F bonds can be formed.

More details on the "enough energy" required - the **activation energy** of the reaction - will be found below.

Collision theory criteria for a reaction:
- *A collision takes place*
- *The collision has sufficient energy to overcome the activation energy of the reaction.*

Therefore if there are no collisions of reacting particles, or the reacting particles only collide with little energy, no reaction occurs. The energy of the collision depends on the speed with which the particles were moving - the higher the speed, the greater the energy.

To increase the rate of reaction the number of high energy collisions per second must be increased. This tells us how various factors affect rates of reaction (see Table 1 overleaf).

Activation Energy, E_A

Consider again the reaction:-

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

This can also be represented as follows:-

$$\text{H—H} \quad \text{F—F} \xrightarrow[\text{(energy required)}]{\text{bonds broken}} \text{H} \quad \text{H} \quad \text{F} \quad \text{F} \xrightarrow[\text{(energy released)}]{\text{bonds formed}} \text{H—F} \quad \text{H—F}$$

During a chemical reaction, bonds are first broken, and then others formed. Consequently, energy is required to break bonds and start this process whether the overall reaction is exothermic (giving out energy) or endothermic (taking in energy). (See Factsheet 8 - Energetics 1 for more on exothermic and endothermic reactions). It is therefore reasonable to assume that particles do not always react when they collide since they may not have sufficient energy for the necessary bonds to be broken.

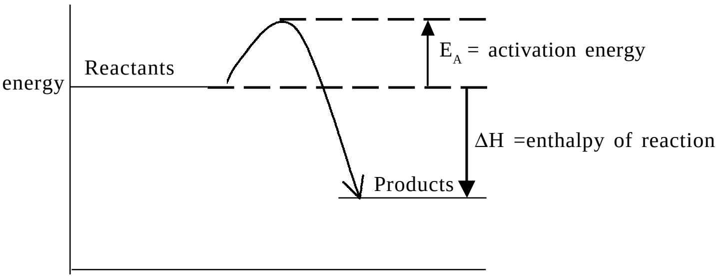
Table 1. Factors affecting reaction rate

Factor	How it affects rate	Explanation
Concentration (solutions) Pressure (gases)	Increased concentration/ pressure increases the rate	An increase in the concentration of a solution or the pressure of a gas, results in the particles being more crowded, and therefore colliding more times per second.
Surface Area (solids)	Increased surface area increases the rate	The smaller the size of the reacting particles, the greater their total surface area. The greater surface area means that a larger area is exposed for reaction, allowing more collisions per second
Temperature	Increased temperature increases the rate	As temperature is increased, the average speed of the reaching particles increases. This results in more collisions per second.
Catalyst	Catalysts generally speed up reactions, but some (called inhibitors) slow it down	Not only are there more collisions per second, but as particles have a higher energy, or greater percentage of the collisions will involve enough energy for a reaction to occur (see activation energy later). A catalyst alters the rate of reaction without itself being used up or undergoing any permanent chemical change. It alters the rate by lowering the **activation energy** by providing an alternative **reaction pathway**
Light	Increased light intensity increases the rate of some reactions. Some reactions do not proceed without UV light.	Light transfers energy to the particles, so the collisions are more energetic.

A reaction only occurs as the result of a collision between particles, which possess more than the minimum amount of energy required, the Activation Energy, E_A.

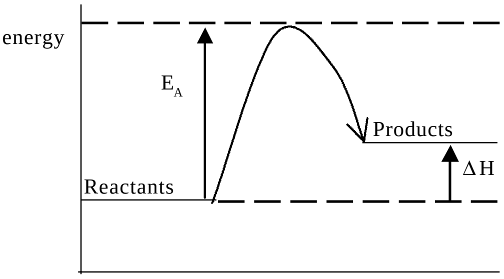
Activation energies can be used to add more detail to energy level diagrams (see Factsheet 8 – Energetics 1) to produce Reaction Profiles.

For an exothermic reaction:-



The reaction profile clearly shows how a minimum amount of energy (E_A) is required before the reaction can proceed, but in this **exothermic** reaction, we have: **Energy released > Energy absorbed**.

For an endothermic reaction:-



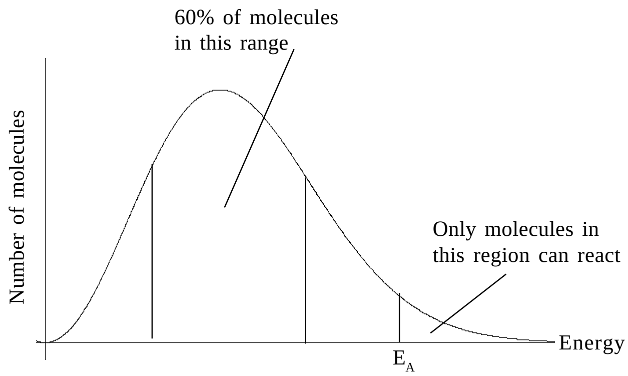
Here the reaction profile shows that a large amount of energy (E_A) is required to start the reaction and only a fraction of this energy is released as the products are formed. **In an endothermic reaction, we have: Energy released > Energy absorbed**.

It is important to relate Activation Energy, E_A, to rate of reaction.

- *If E_A is large, only a small proportion of particles have enough energy to react on collision , so rate is low.*
- *If E_A is small, a greater fraction of particles possess enough energy to react on collision, so rate is high.*

The Maxwell-Boltzmann Distribution

This shows the distribution of molecular energies (in a gas) at a constant temperature.



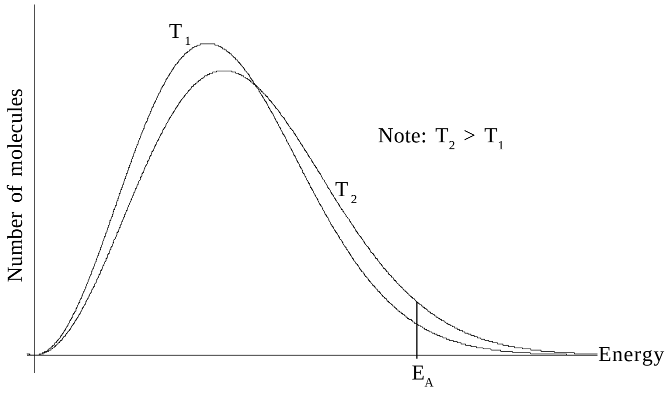
Points to note about this distribution curve:-

- The total number of gas molecules is equal to the area under the curve.
- No molecules have zero energy.
- Most of the molecules have energies within a relatively narrow range.

Notice that the activation energy is marked on the curve – only the molecules with energy higher than this can react.

Exam Hint: *Questions on this area are popular. You need to learn:*
- *the shape of the curve*
- *how it alters with temperature*
- *how this explains the effect of temperature on rate.*

Now consider the effect on the distribution curve of increasing the temperature.



The shape of the distribution curve changes with temperature, as shown above. As the temperature increases:

- the height of the "peak" decreases
- the position of the peak moves to the right
- the number of molecules having energy greater than E_A increases, whatever the value of E_A.

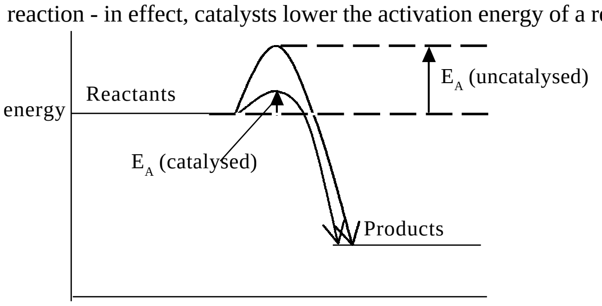
The **total** area under the curve - which gives the **total** number of molecules - remains the same.

> *Temperature increases rate because:*
> - *particles move faster, increasing the number of collisions*
> - *more particles have energy greater than E_A, so more collisions produce a reaction*

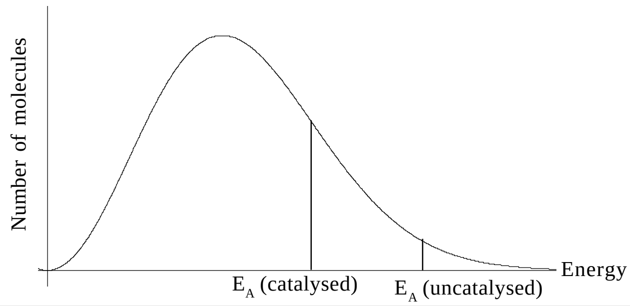
> ***Exam Hint:*** *Many candidates lose marks by suggesting that **all** the particles will be moving at a high speed if the temperature is high - although the **average** speed increases, there will still be some particles with low speeds.*

The Role of Catalysts

As mentioned before, catalysts alter the rate of a reaction (usually speeding it up) without being chemically charged themselves. Catalysts are able to increase reaction rate because they provide a lower energy route for the reaction - in effect, catalysts lower the activation energy of a reaction.



This can be linked with the Maxwell-Boltzmann distribution curve - with the activation energy lowered, a greater number of molecules passes enough energy to react on collision, so the rate of reaction is increased.



Thermodynamic / Kinetic Stability

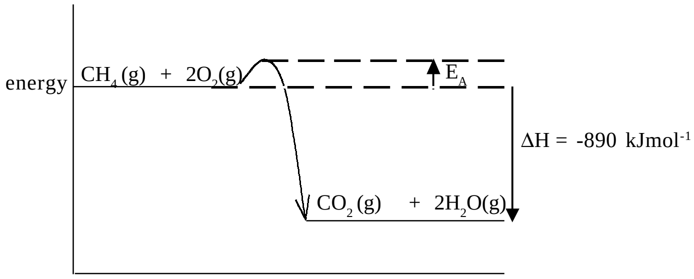
The fact that a certain minimum energy (the activation energy, E_A) is required to initiate most reactions is well illustrated by the fact that fuels and explosives usually require a small input of energy before a very exothermic reaction takes place.

Consider the combination of methane:-

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H_c = -890\ kJmol^{-1}$$

The reaction is very exothermic – therefore the products are for more **thermodynamically stable** than the reactants. Despite this, combustion is not **spontaneous** – heat is required (i.e. supplying the activation energy) before the reaction takes place. The reactants are therefore **kinetically stable.**

The reaction profile can be represented by this diagram.



It is worth noting that the activation energy for this reaction is low, and once started the temperature at which the reaction occurs is quite high, due to the heat energy released. Due to these factors, the **rate** at which this reaction proceeds is **high**.

Questions

1. 50cm^3 of 4M hydrochloric acid is added to 10g of large marble (calcium carbonate) chips. The reactants are at room temperature.

$$2HCl_{(aq)} + CaCO_{3\,(s)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

a) If the concentration of the acid halved in the first minute, what was the average rate of reaction during this minute?

b) What would happen to the rate of reaction if the temperature of the acid were increased to 50^{o}C? Use collision theory to explain.

c) What would happen to the rate of reaction if 10g of small marble chips were used instead of large marble chips? Use collision theory to explain.

d) What information about the rate of reaction do we gain from the given stoichiometric equation?

2. Define the following terms:-
   a) Catalyst
   b) Activation energy.

3. Draw the reaction profile of the reaction.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92$ kJ mol^{-1}

   Assume the reaction is not spontaneous.

4. The graph below requests the Maxwell-Bolzmann distribution of molecular energies in a gas at a temperature T_1.

a) (i) Copy the graph, and on the same axes stretch the curve which shows the distribution of molecular energies at a lower temperature T_2. Assume T_2 is around 30^{o}C higher than T_1.

(ii) Use the graphs to explain how the rate of a gas phase reaction is changed when temperature is decreased.

b) For a reaction in the gas phase, explain the effect of a catalyst on:-
(i) The energy distribution of the gas molecules.

(ii) The activation energy for the reaction.

(iii) The rate of reaction.

Answers

1. a) 0.0333 moldm^{-3}s^{-1}
   b) Reaction rate would increase.
   - Molecules moving faster, therefore more collisions per second.
   - More molecules colliding with energies greater that the activation energy.

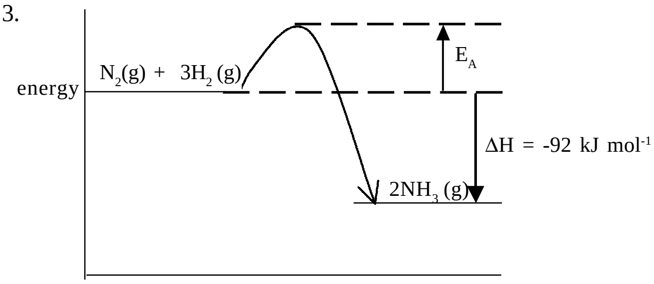
   c) Reaction rate would increase.
   - Smaller chips have greater surface area exposed for reaction, leading to more collisions per second with acid particles.

   d) Stoichiometric equations tell us nothing about the rate of a reaction.

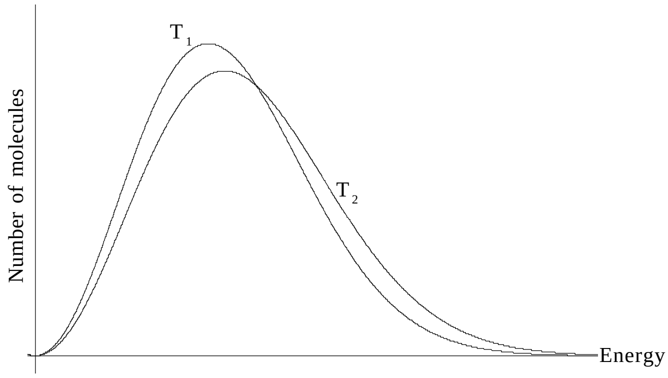
2. a) A catalyst is a substance which alters the rate of a reaction, but remains chemically unchanged at the end of the process.

   b) Activation energy is the minimum amount of energy required before colliding reactant particles react.

3.



4. a) (i)



(ii) It should be pointed out that he area under the distribution curve is equal to the number of molecules present. At a lower temperature, the average energy of the molecules is lower, and a smaller fraction of the gas molecules have energy in excess of the activation energy. The rate of the gas phase reaction will decrease with decreasing temperature because:-
- Molecules move slower, they collide less frequently.
- Fewer molecules passes the activation energy.

b) (i) A catalyst does not effect the energy distribution of the gas molecules.
(ii) A catalyst lowers the activation energy for the reaction, as it provides as lower energy route for the reaction.
(iii) A catalyst will increase the rate of reaction, as a greater fraction of the molecules will possess the new (lower) activation energy, so there will be more reactive collisions per second.

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