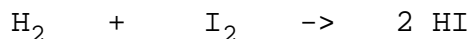


Reaction Rates

The rate of a reaction is the change in concentration of reactants or products in unit time e.g.



Say we mix together 1 mole of H_2 and 1 mole of I_2 and measure the changes in concentrations of H_2 , I_2 and HI with time. The results are given in the table below.

Time (s)	[H_2] mol	[I_2] mol	[HI] mol
0	1	1	0
10	0.9	0.9	0.2
20	0.8	0.8	0.4
30	0.7	0.7	0.6

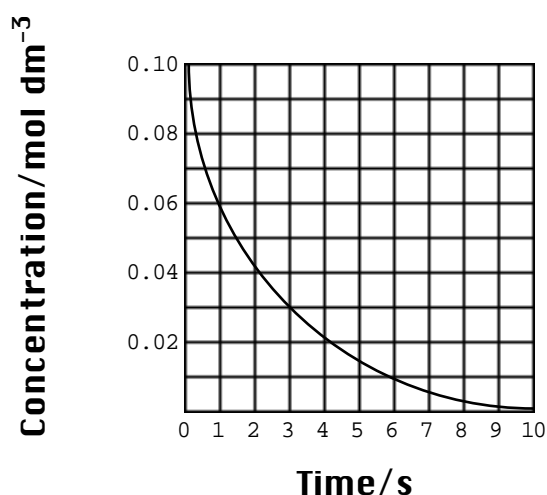
$$\text{Rate of disappearance of } \text{H}_2 = \frac{1 - 0.9}{10} = 0.01 \text{ mol s}^{-1}$$

$$\text{Rate of disappearance of } \text{I}_2 = \frac{1 - 0.9}{10} = 0.01 \text{ mol s}^{-1}$$

$$\text{Rate of appearance of } \text{HI} = \frac{0.2 - 0}{10} = 0.02 \text{ mol s}^{-1}$$

Question

The graph shows the variation of concentration of a reactant with time as the reaction proceeds.



What is the average reaction rate during the first 3 s of the reaction?

Answer

$$\text{Rate} = \frac{0.10 - 0.03}{3} = \frac{0.07}{3} = 0.023 \text{ mol l}^{-1} \text{ s}^{-1}$$

Factors affecting reaction rate

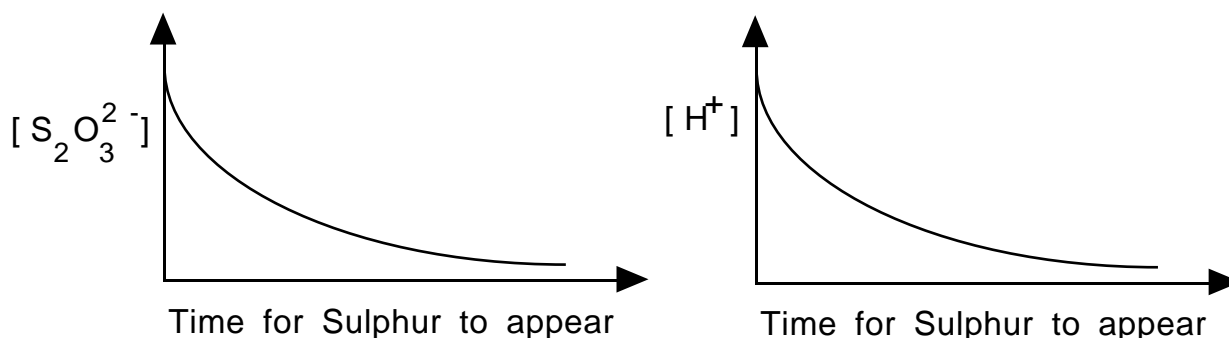
1. Concentration

Chemical reactions are the result of collisions between the reacting particles resulting in the rearrangement of bonds. The more crowded together the reactants the better the chance of collision.

Example : the rate of production of Sulphur by the reaction :

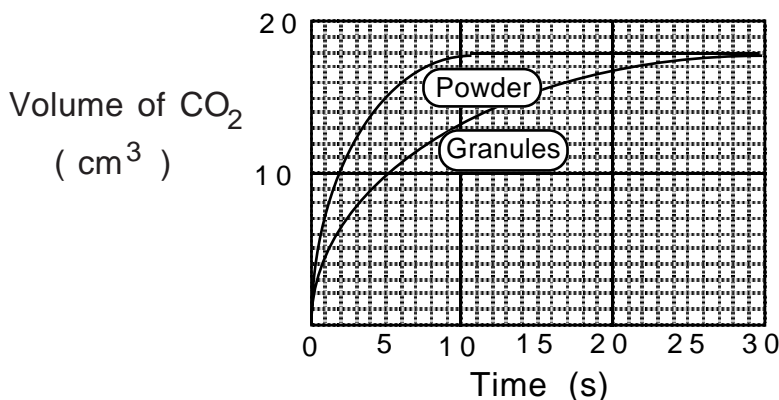
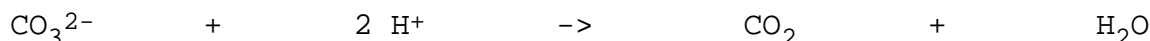


increases when either $[\text{S}_2\text{O}_3^{2-}]$ or $[\text{H}^+]$ are increased.



2. Small particle size

1g powdered Calcium carbonate reacts faster with acid than 1g Calcium carbonate granules since the surface area exposed to acid is greater in the powder leading to more collisions :



We can compare the initial rates of the above two reactions by measuring the time taken (t) for each reaction to produce a fixed volume (say 10 cm^3) of Carbon dioxide. The longer the time the slower the reaction i.e. rate $\propto 1/t$

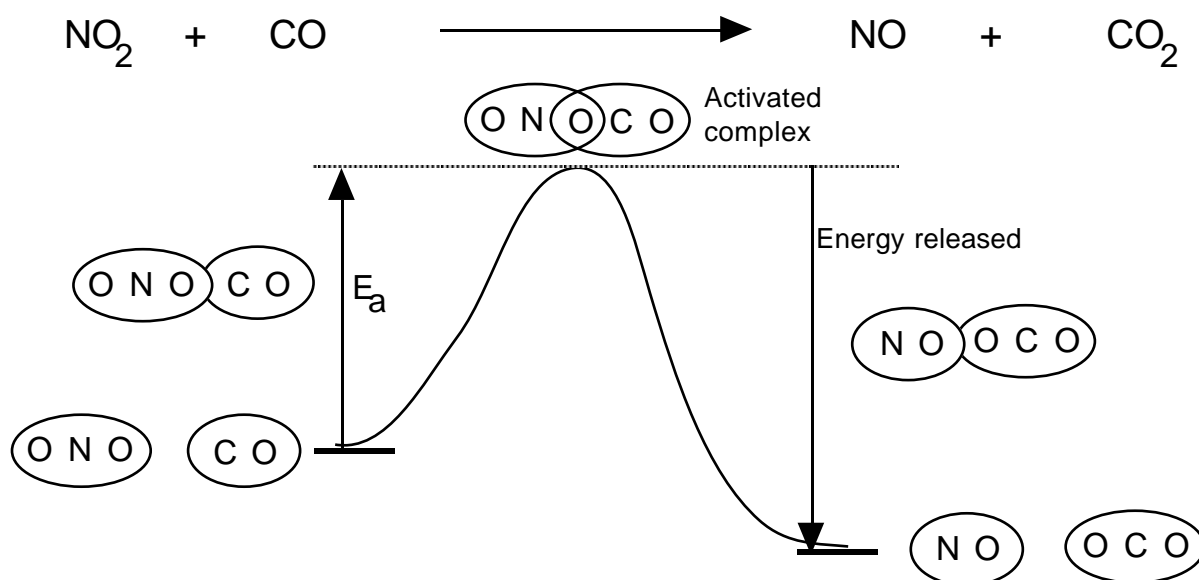
Reaction	t (s)	$1/t$ (s^{-1})
Powder	2	0.5
Granules	5	0.2

From the above table we can see that the powder reacts 2.5 times faster than the granules.

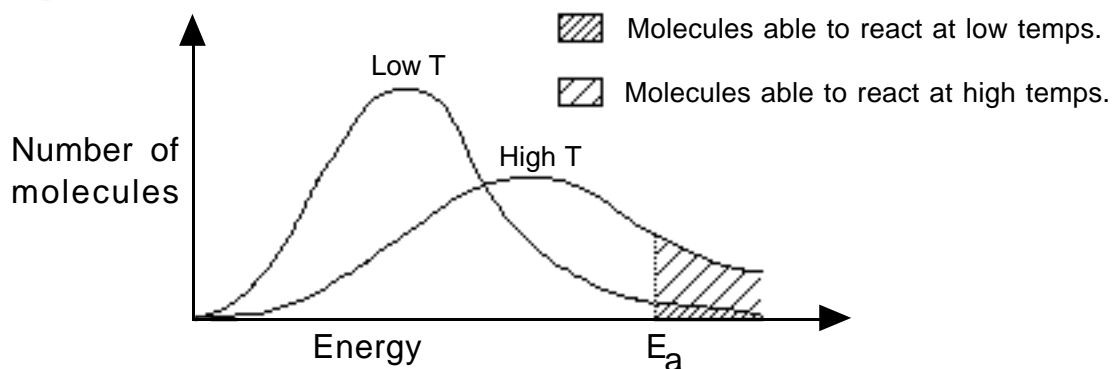
3. High temperature

Not every collision leads to a reaction. When molecules collide, repulsion between their similarly charged electron clouds will cause them to bounce apart. If they collide with sufficient energy to overcome this initial repulsion an activated complex, a highly unstable arrangement of atoms, is formed. The electrons of one molecule or atom are then attracted by the nucleus of the other. Sharing or transfer of electrons may then occur releasing energy. The minimum kinetic energy required to overcome the initial repulsion is called the Energy of Activation, E_a .

e.g. reaction of NO_2 and CO

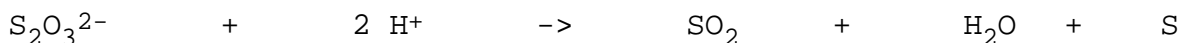


Only a few molecules have the required energy at low temperatures so reaction is slow. Heating makes the molecules move faster (increases their kinetic energy) and thus increases the proportion with energy greater than E_a able to overcome the energy barrier.

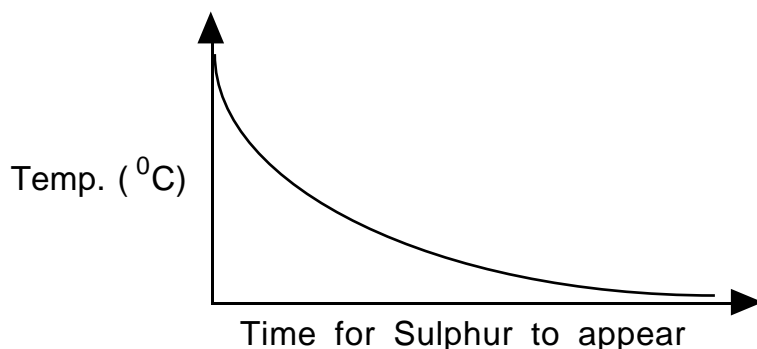


The rate therefore increases. A small rise in temperature can result in a large increase in rate.

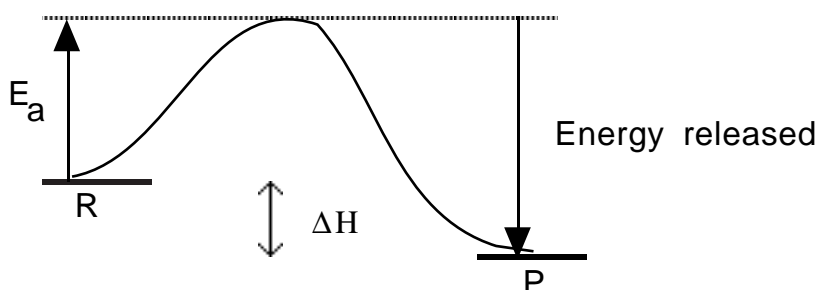
Example : The rate of production of Sulphur by the reaction :



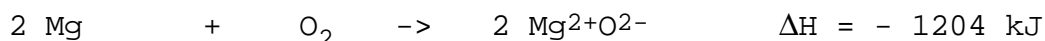
increases as temperature increases.



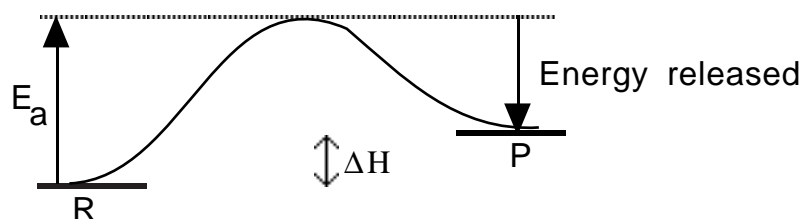
Exothermic reactions : Energy released $>$ E_a



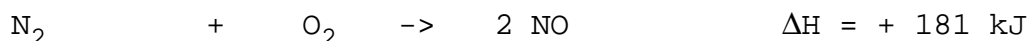
It is necessary only to trigger the reaction. Thereafter it supplies its own E_a . Excess energy is given out, ΔH e.g.



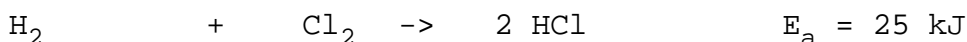
Endothermic reactions : Energy released $<$ E_a



Energy released is insufficient to supply E_a so additional energy, ΔH , must be supplied to keep the reaction going e.g.

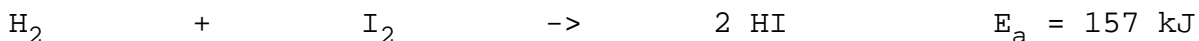


N.B. Reactions with a low E_a proceed rapidly at room temperature since, then, a high proportion of the molecules will have an energy $>$ E_a e.g.



For this particular reaction, the activation energy may be provided by UV light.

Reactions with a high E_a proceed slowly at room temperature since very few of the molecules will have energy $> E_a$ e.g.



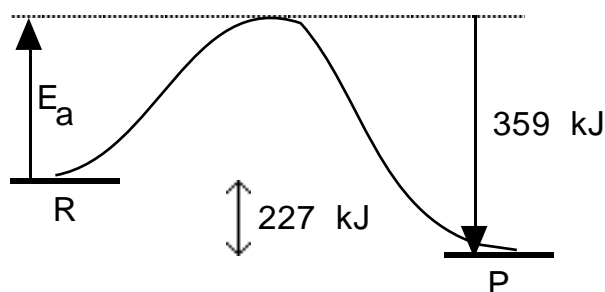
Note that E_a can be calculated from the above energy diagrams if the values of ΔH and energy released are known.

Problem : For the reaction



$\Delta H = -227 \text{ kJ}$ and the energy released is 359 kJ . Calculate the value of the activation energy.

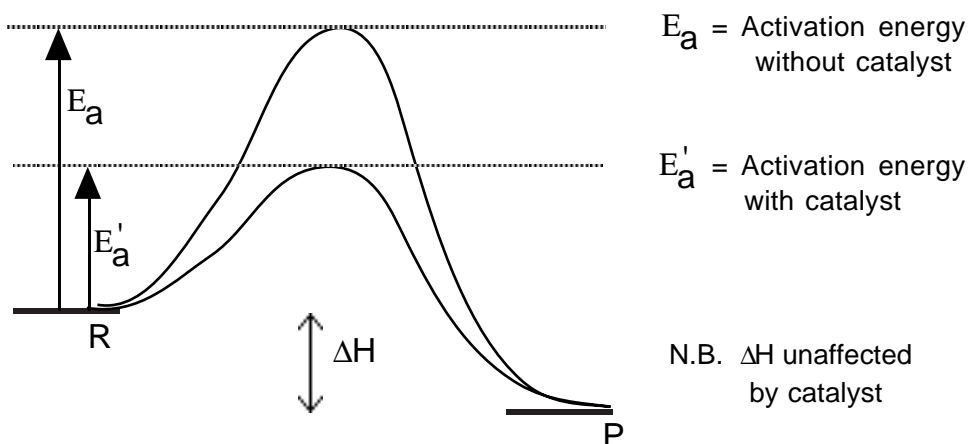
Answer :



$$E_a = 359 - 227 = \underline{132 \text{ kJ}}$$

4. Catalysts

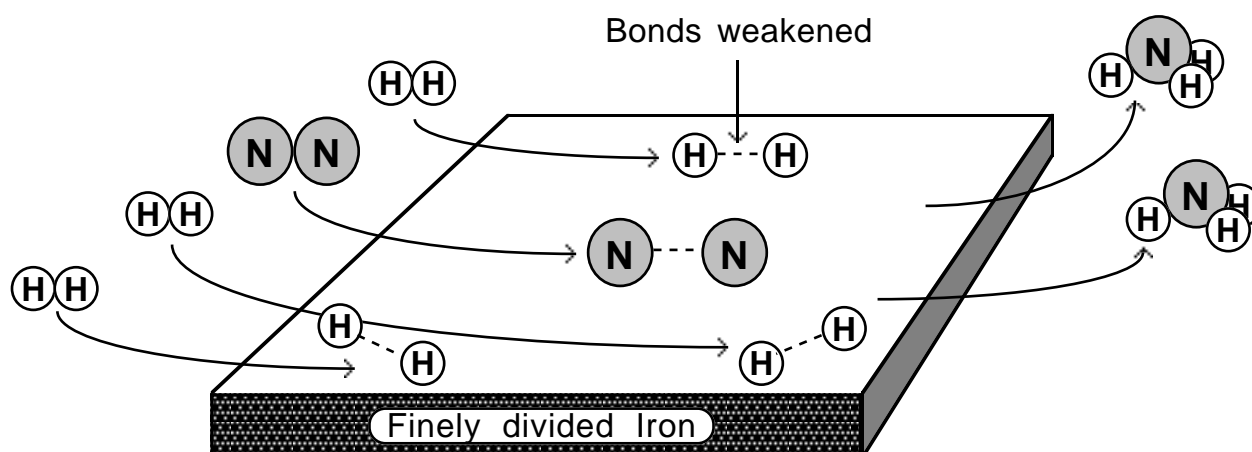
The function of a catalyst is to lower the energy of activation so that the reaction can proceed rapidly at a lower temperature. It lowers E_a by permitting the reaction to occur by an easier mechanism. It remains unchanged at the end of the reaction.



There are TWO types of catalyst : Heterogeneous and homogeneous.

1. Heterogeneous Catalysts

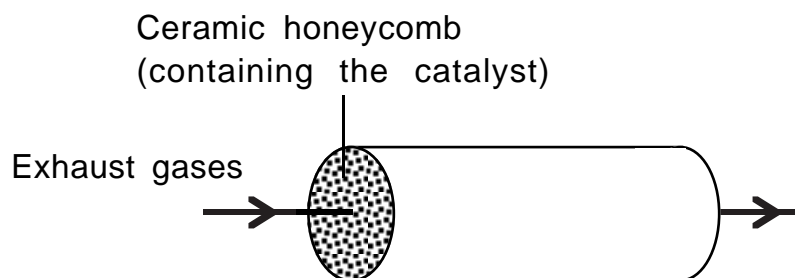
These are surface catalysts. They are in a different phase from the reactants. Reactants become adsorbed on the catalyst surface which must, therefore, have a large surface area. This crowds the molecules together in a favourable orientation for reaction. New bonds form with the catalyst weakening the original bonds thus lowering E_a . Reaction occurs on the catalyst and the products are desorbed leaving the site vacant for further reaction.
e.g. Haber process :



Surface catalysts are often highly specific e.g. Platinum cannot be used in the Haber process since adsorption of Nitrogen is too weak.

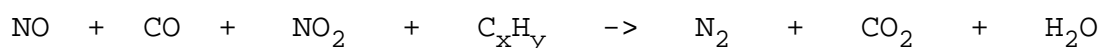
When a heterogeneous catalyst is used the reactants must be carefully purified since certain impurities become, themselves, adsorbed on the catalyst surface. This blocks, or poisons, the active sites on the catalyst and prevents access of reactant molecules. The catalyst ceases to function properly. Iron in the Haber process is easily poisoned by Sulphur, Arsenic, Water, Carbon monoxide and Carbon dioxide. Poisoned catalysts must be either regenerated or renewed.

Catalytic Convertors in Cars



The catalyst is 1.5 - 2.0g of a Platinum/Rhodium alloy (sometimes Palladium is used) sprayed on to a ceramic honeycomb. The honeycomb structure spreads the catalyst out and provides a larger surface area.

The reactions catalysed may be summarised as :



Drawbacks :

- Can only be used with 'lead-free' petrol since Lead poisons the surface of the catalyst.
- Poisoning (by other substances) shortens the life of the catalyst. It must be replaced every 50,000 miles.
- Increases the price of the car by about £500.
- Does not remove but actually increases, by 15%, the amount of Carbon dioxide in car exhaust [Carbon dioxide is a 'greenhouse' gas]
- The catalyst only works efficiently when the exhaust gases are in the correct ratio. This requires a 15% increase in fuel consumption.

