## Chemical kinetics

It is a branch of chemistry that deals with the measurement of reaction velocities/rates and determination of mechanisms by which reactants are converted into products.

The knowledge of chemical kinetics is useful when altering the rates of chemical reaction is needed. For instance, manufacturers of fertilizers aim at speeding up the formation of ammonia from nitrogen and hydrogen whereas a car manufacturer wishes to slow down the rate at which iron rust.

## Rates of reaction

**Reaction rate** is the speed at which a chemical **reaction** proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product that is formed in a unit of time or the concentration of a reactant that is consumed in a unit of time.

Consider the reaction

A → product (p) ………………………………………… (I)

The rate of the reaction or reaction velocity may be defined as the rate of disappearance of the reactant (A) or the rate of appearance or formation of the product (P) with respect to time.

Thus rate $= -\dfrac{dA}{dt} = \dfrac{dP}{dt} = K[A]$

Where, K, is the rate constant.

In general for a reaction

aA + bB → cC + dD …………………………………….(II)

The rate of reaction is given as

Rate $= -\dfrac{1}{a}\dfrac{dA}{dt} = -\dfrac{1}{b}\dfrac{dB}{dt} = +\dfrac{1}{c}\dfrac{dC}{dt} = +\dfrac{1}{d}\dfrac{dD}{dt}$

Since the reaction depends on the concentration of the reactants, the rate equation for the reaction in (II) can be expressed in a rate equation represented as

Rate $= K[A]^x[B]^y$.

Definitions terms in a rate law
 (i)  [A] is molar concentration of reactant A
 (ii)  $x$ is the order of reaction with respect to A
 (iii)   $y$ is the order of reaction with respect to B.
 (iv) The algebraic sum $(x+y)$ is the overall order of the reaction. i.e. order of reaction is the sum  power dependence of the rate on the concentration of each reactant.

(v) K is the rate constant of the reaction is a proportionality factor in the **rate** law of **chemical** kinetics that relates the molar concentration of reactants to reaction **rate**.

(vi)**Stoichiometry of a reaction** is the quantitative relationships of the amount of products and reactants in a given reaction

The values of x and y are often 1 or 2 and rarely 0, 3, fraction or negative number. These values x and y are experimentally determined values and cannot be predicted until one has carried out the experiment. The order of the reaction has nothing to do with stoichiometry of the equation for the reaction.

For example, a simple reaction between bromated (V) ions, bromide ions and hydrogen ions to give bromine is represented by the equation:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$
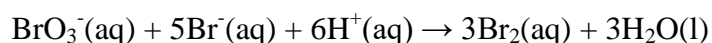
This has a complex rate equation from kinetic measurements as expressed below:

$$-\frac{d[BrO_3^-]}{dt} = K[BrO_3^-][Br^-][H^+]^2$$

Determining the order of reaction

The order of a reaction can be found by comparing the initial rates of two more or reactions at known initial concentrations.

**Example 1**

The following results obtained for a reaction between A and B; can be used to determine the order of reaction with respect to A and with respect to B and the rate constant.

| Run | Concentration $(moldm^{-3})$ | | Initial rate $(moldm^{-3})$ |
|-----|-----|-----|-----|
| | A | B | |
| (a) | 0.50 | 1.0 | 2.0 |
| (b) | 0.50 | 2.0 | 8.0 |
| (c) | 0.50 | 3.0 | 18.0 |
| (d) | 1.0 | 3.0 | 36.0 |
| (e) | 2.0 | 3.0 | 72.0 |

Method
Rate equation = $K[A]^x[B]^y$

To obtain x, which compare reactions in which the concentrations of B are constant but those of A vary such as (d) and (e):

$$\frac{Rate\ (e)}{Rate\ (d)} = \frac{72}{36} = \frac{\cancel{K}[2.0]^x\cancel{[0.3]^y}}{\cancel{K}[1.0]^x\cancel{[0.3]^y}}$$

$$2 = 2^x$$
$$x = 1$$

To obtain y, which compare reactions in which the concentrations of A are constant but those of B vary such as (b) and (a):

$$\frac{Rate\ (b)}{Rate\ (a)} = \frac{8.0}{32.06} = \frac{\cancel{K[0.50]^x}[2.0]^y}{\cancel{K[0.50]^x}[1.0]^y}$$

$$4 = 2^y \implies y = 2$$

**Calculating the rate constant, K,**

We substitute for x and y in any of the experiment above e.g. (a)
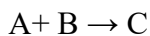
$$2 = K[0.5]^1 \times [1.0]^2$$
$$K = 4.0 dm^6 mol^{-2} s^{-1}$$

### Trial 1

(a) Explain terms:
   (i) Rate of reaction
   (ii) Order of reaction
   (i) Stoichiometry of reaction
   (ii) Rate constant

(b) For the reaction
   $$A + B \rightarrow C$$
   The following results were obtained for kinetic runs at the same temperature.

| $[A]_0$ (moldm$^{-3}$) | $[B]_0$ (moldm$^{-3}$) | Initial rate (moldm$^{-3}$s$^{-1}$) |
|---|---|---|
| 0.20 | 0.10 | 0.20 |
| 0.40 | 0.10 | 0.80 |
| 0.40 | 0.20 | 0.80 |

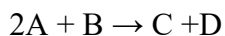   Why do kinetic experiments carried out at constant temperature
(c) Find
   (i) the rate equation for the reaction,
   (ii) the rate constant,
   (iii) the initial rate of reaction, when $[A]_0 = 0.60$moldm$^{-3}$ and $[B]_0 = 0.3$moldm-$^3$.

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## Trial 2

Tabulated are values of initial rates for the reaction

$2A + B \rightarrow C + D$

| Experiment | $[A]_0$ (moldm$^{-3}$) | $[B]_0$ (moldm$^{-3}$) | Initial rate (moldm$^{-3}$ min$^{-1}$) |
|---|---|---|---|
| 1 | 0.150 | 0.25 | $1.4 \times 10^{-5}$ |
| 2 | 0.150 | 0.50 | $5.6 \times 10^{-5}$ |
| 3 | 0.075 | 0.50 | $2.8 \times 10^{-5}$ |
| 4 | 0.075 | 0.25 | $7.8 \times 10^{-5}$ |

(a) Find the order of reaction with respect to A, the order of reaction with respect to B and overall order of the reaction.

(b) Find the value of the rate constant

(c) Find the initial rate of the reaction when $[A]_0 = 0.120$ moldm$^{-3}$ and $[B]_0 = 0.22$ moldm-$^3$.

## Trial 3

The reaction between nitrous oxide and ozone is given by the equation

$NO\ (g) + O_3(g) \rightarrow NO_2 + O_2$
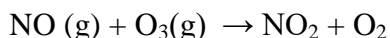
Was studied in the lab at $25^0C$ and the following results were obtained.

| Exp. 21No. | $[NO]$moll$^{-1}$ | $[O_3]$moll$^{-1}$ | Rate (moll$^{-1}$s$^{-1}$) |
|---|---|---|---|
| 1 | $1.00 \times 10^{-6}$ | $3.00 \times 10^{-6}$ | $0.66 \times 10^{-4}$ |
| 2 | $2.00 \times 10^{-6}$ | $3.00 \times 10^{-6}$ | $1.32 \times 10^{-4}$ |
| 3 | $1.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | $1.98 \times 10^{-4}$ |
| 4 | $2.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | $3.96 \times 10^{-4}$ |
| 5 | $3.00 \times 10^{-6}$ | $9.00 \times 10^{-6}$ | $5.9 \times 10^{-4}$ |

(a) Write an expression for the rate equation for the reaction above.

(b) Determine the order of reaction with respect to NO and $O_3$.

(c) Write the true rate equation for the reaction.

(d) Calculate the value of rate constant.

## Trial 4

The kinetic data for the reaction between X and Y are shown in the table below

| Expt. | [X]<br>mol dm$^{-3}$ | [X]<br>mol dm$^{-3}$ | Rate<br>Mol dm$^{-3}$s$^{-1}$ |
|---|---|---|---|
| 1 | 0.30 | 0.15 | 1.5 x 10$^{-2}$ |
| 2 | 0.30 | 0.30 | 3.0 x 10$^{-2}$ |
| 3 | 0.60 | 0.30 | 6.0 x 10$^{-2}$ |
| 4 | 0.60 | 0.60 | 12.0 x 10$^{-2}$ |

(a) Determine the order of reaction with respect to
   (i) X
   (ii) Y
(b) Determine the overall order
(c) Calculate the rate constant for the reaction and indicate its units.

## Trial 5

The rate equation for a certain reaction is:

Rate = K[P][Q}$^2$[R]

(a) State what would happen to the rate of reaction if
(i) the concentration of P and Q are kept constant, but that of R is doubled.
(ii) the concentration of all species are halved
(iii) the concentration of all species are doubled
(b) the following were obtained in a study of reaction between peroxodisulphate and iodide ions

| Expt.<br>No. | [S$_2$O$_8$)$^{2-}$]<br>Moldm$^{-3}$ | [I$^-$]<br>Moldm$^{-3}$ | Rate<br>Moldm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.024 | 0.024 | 9.60 x 10$^{-6}$ |
| 2 | 0.048 | 0.024 | 1.92 x 10$^{-6}$ |
| 3 | 0.048 | 0.012 | 9.60 x 10$^{-6}$ |

 (i) Write the rate equation
 (ii) Calculate the rate constant for the reaction and state its units

### Reactions of various orders

### 1.  First order reaction

A reaction is said to be order if the rate is proportional to the first power of concentration of reactants on which the reaction kinetics depends. That is, the rate law for the first order reaction is given by
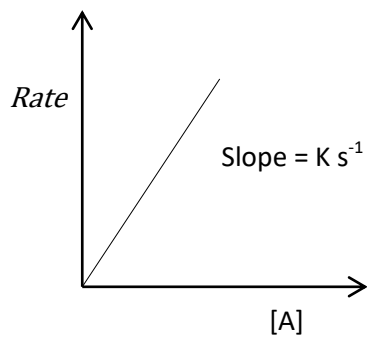
Rate = K[A] or K[$A$]$^{\frac{1}{2}}$[$B$]$^{\frac{1}{2}}$

<span style="color:red">Identification of a first order reaction</span>

First order reaction can be identified by the shapes of the following graphs.

All these graphs that show that the rate of reaction is proportional to the concentration of the reactant in the chemical reaction.

(i)     Rate of reaction against concentration



*Rate*

Slope = K s$^{-1}$

[A]

A straight line with positive gradient shows that the rate is proportional concentration of the reactant and that the reaction is thus first order.

(ii)    Concentration of the reactant against time.



[A]

t
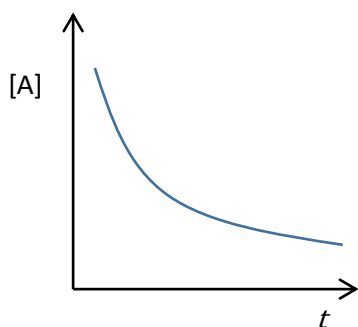
Hyperbola shows that the rate of reaction is proportional to concentration of the reactant and thus a first order reaction

(iii)   For a first order reaction, a plot logarithm of concentration against time gives a straight line with negative gradient.



Log[A]

Slope = -K

t
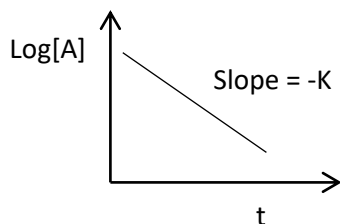
A typical example of a reaction that follows a first order reaction mechanism is a radioactive disintegration process.

**Definition**

Radioactive decay (also known as nuclear decay, radioactivity, radioactive disintegration or nuclear disintegration) is the process by which an unstable atomic nucleus loses energy by radiation.

**Integrated rate law for first order reaction**

Consider a first order reaction

$A \rightarrow P$

If the initial concentration [A] of reactant (A) at time, t=0, is a moldm$^{-3}$ and the concentration of product, P, after time t is x moldm$^{-3}$; then concentration of A at time, t, will be (a-x) moldm$^{-3}$.

Then, the rate of reaction as the rate of formation of the product is represented as

$$\frac{dx}{dt} = K[a - x]$$

Or, separating variables;

$$\frac{dx}{(a-x)} = kdt$$

To get relationship between concentration and time, integrate both sides. i.e.

$$\int \frac{dx}{(a-x)} = \int Kdt$$

$-ln(a-x) = Kt + C$

At time, t = 0, x = 0, thus, C= $-lna$

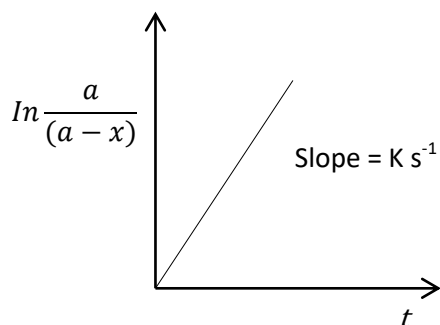Substituting for C we derive the relationship:

$lna-ln(a-x) = Kt$

Or

$$In\frac{a}{(a-x)} = Kt$$

The plot of $In\frac{a}{(a-x)}$ against time gives a straight line and the slope of this graph is equal to K s$^{-1}$.



## Half-life of the first order reactions

Half-life $(t_{\frac{1}{2}})$ of the reaction is the time taken by the reactant to reduce to half of its initial concentration.

The expression for half-life of a first order reaction is obtained from the integrated rate law: i.e.

$$In\frac{a}{(a-x)} = Kt$$

At $t = t_{\frac{1}{2}}$, $(a-x) = \frac{a}{2}$ where $t_{\frac{1}{2}}$ if half life

Then
$$In\frac{a}{\frac{a}{2}} = Kt_{\frac{1}{2}}$$
and thus, $t_{\frac{1}{2}} = \frac{ln2}{K}$
not that, In x = 2.303log x

This shows that in first order reaction, half-life is independent of the initial concentration of the reactants. The time necessary for the reactants to decrease to any other given fraction can be derived in the similar manner.

**Trial 6**

(a) The rate of a chemical reaction is given by the relationship:

$Rate = K[A]^a[B]^b$

State

(i) What each of the following stands for

  [A] ……………………………………………

   a …………………………………………….

   b ……………………………………………

(ii) One factor that can affect the constant K.

(b) Write an equation for the decomposition of dinitrogen oxide

(c) At 858K, the half-life of dinitrogen oxide is 75.09hours

   Calculate

   (i) The rate constant for the decomposition of

      dinitrogen oxide

   (ii) the total pressure after 75.09hours at 858K, if the initial pressure was one atmosphere.

**Trial 7**

(a) Derive the expression for the half-life for a first order reaction:

   $2303\log\left[\frac{a_0}{a_0-x}\right]$ = kt: Where $a_0$ is the initial concentration of the reactant and $(a_0 - x)$ is the

   concentration at time, t.
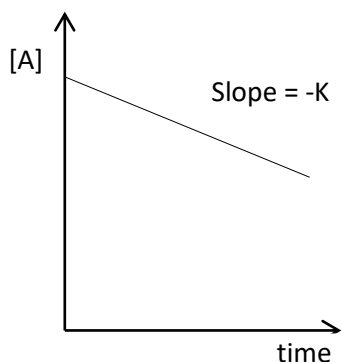
(b) The half-life of a first order reaction is 100s

   (i) calculate the rate constant.

   (ii) Determine the percentage of the reactant that has reacted after 250s.

## 2. Zero order reactions

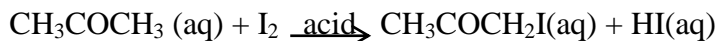In a zero order reaction, the rate is independent of the concentration of the reactants.

A plot of the concentration [A] of the reactant against time has the form below:



The rate equation for a zero order reaction:

   $Rate = K[A]^0$ or $Rate = K\ s^{-1}$

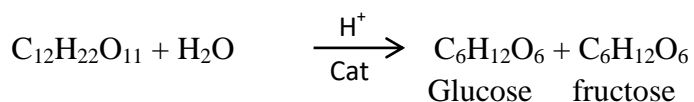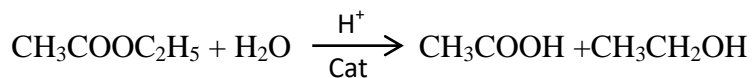Example, the reaction between iodine and propanone is a zero order with respect to iodine.

$$CH_3COCH_3 \text{ (aq)} + I_2 \xrightarrow{\text{acid}} CH_3COCH_2I(aq) + HI(aq)$$

## Pseudo-order reaction

A **pseudo order reaction** is a reaction that is truly **higher order** but can be approximated to a **lower order** under special circumstances.

For instance, an elementary reaction between two reactants A and B is normally expected to be a second order; for example, hydrolysis of an ester and inversion of sucrose.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{Cat}]{H^+} CH_3COOH + CH_3CH_2OH$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Cat}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

However, if one of the reactant B is present at a very much greater concentration than that of A or else only acts as catalyst, then concentration of B is considered constant ad the rate law become

Rate = K'[A]

Such a reaction is said to be pseudo first order since the rate is proportional to concentration of A raised to the first power. Nevertheless, it must be remembered that the new constant (K') in not a true constant because it also depends on the concentration of B. Since water is usually found in excess, the reactions given above are in practice found to be pseudo first order.

Note that:
(1) For a zero order reaction, any change in concentration of the reactant does not affect the rate of reaction.
(2) For a first order reaction increasing the concentration of the reactant two or three times also increases the rate two or three times.

### Trial 8
(a) State what is meant by the term order of a reaction
(b) Methylethanoate is hydrolyzed by water in presence of an acid according to the following reaction:
   $$CH_3COOCH_3 + H_2O \text{ (l)} \leftrightarrow CH_3CH_2OH + C H_3OH$$
   (i) State the molecularity of the reaction
   (ii) State the conditions under which the reaction can be overall first order

(c) The table below shows some kinetic data for the following reaction:

| Expt. No. | [A] Moldm$^{-3}$ | [B] Moldm$^{-3}$ | Rate Moldm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.20 | 0.20 | 1.2 x 10$^{-8}$ |
| 2 | 0.20 | 0.60 | 1.2 x 10$^{-8}$ |
| 3 | 0.40 | 0.60 | 4.8x 10$^{-8}$ |

(i) Write the overall order of reaction

(ii) Calculate the rate constant and give its units.

**Measuring the rates of reactions**

The rate of a chemical reaction can be obtained by following some property which alters with the extent of the reaction. By analyzing the reaction mixture at suitable intervals, it's possible to determine the concentration of both the reactant and/or the product at different times and hence obtaining the rate (i.e. the rate at which the concentration of a particular substance changes with time).

In practice, the rates may be measured by observing the rate of change of physical properties such as refractive index, volume, color, and if the reaction is sufficiently slow, its rate may be found by frequent withdrawal of small portion of the reacting mixture and analyze then chemically at intervals.

Examples,

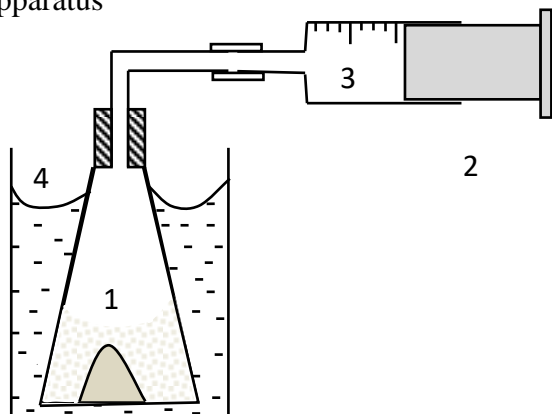1. An experiment to measure the rate of chemical reaction in which a gas is produced such as

$Mg (s) + 2HCl (aq) \rightarrow MgCl_2 (g) + H_2 (g)$

Or $\qquad 2H_2O_2 (aq) \rightarrow 2H_2O (l) + O_2 (g)$
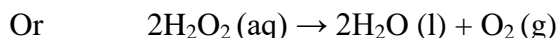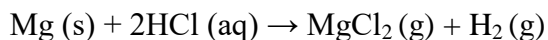
The volume of a gas is recorded at intervals
Apparatus

(a) $H_2O_2$ solution and catalyst.
(b) Plunger of syringe moves outwards.
(c) Oxygen: Volume is recorded at certain times after the start of the reaction
(d) Thermostat bath maintains temperature.

(e) The rate of reaction is given by $\frac{dV}{dt}$ where V is the volume of the gas.

2. An experiment to determine the order reaction with respect to iodine in the reaction of iodine with propanone in presence of acid catalyst.

a.   Fixed volume of standard Iodine solution is added to an excess of propanone solution in a flask.

b.   To this mixture is added a fixed volume of dilute sulphuric acid and a stop clock started immediately.

c.   At intervals of time say (every 10 minutes for 50minutes) a specified portion is pipetted from the mixture and into a flask containing sodium hydrogen carbonate which stops the reaction.

d.   The resultant mixture is titrated with standard sodium thiosulphate using starch indicator.

e.   The volume ($V_t$) of thiosulphate used on the portion of mixture after a specified time (t) is proportional to the amount of iodine remaining in the mixture.

f.   The initial amount of iodine ($V_0$) is obtained by titrating a similar portion of the original mixture with sodium thiosulphate solution.

g.   A plot of the graph of $V_t$ against time gives a straight line as shown below showing that the order of reaction with respect to iodine is zero.
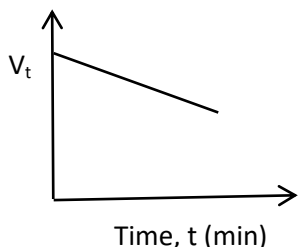


NB. The gradient gives the rate constant whose units is $molcm^{-3} s^{-1}$.

**Activated complex**
With exception of radioactive disintegration all elementary reaction occurs via a transition state, for example, substitution reaction is expected to proceed as below

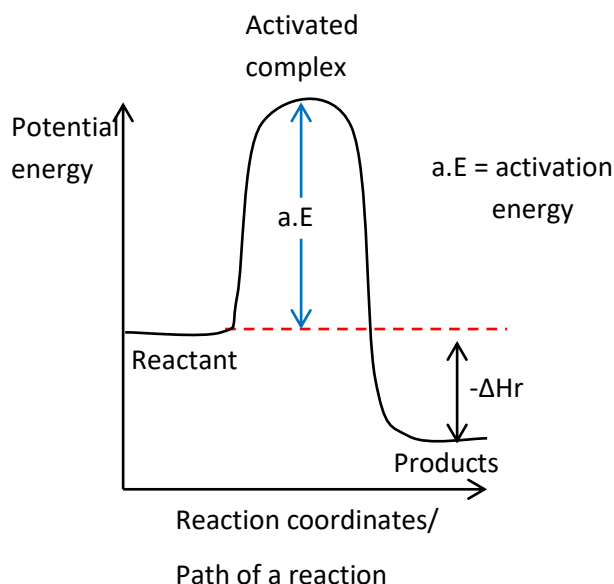$A + BC \leftrightarrow [A....B.....C] \leftrightarrow AB + C$
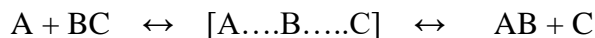
In order to form the transition state, the reactants must first acquire activation energy i.e. This is the minimum energy required for the reaction to take place. Being energy rich, the transition species is unstable one and cannot be isolated and is usually referred to as activation complex. This may decompose either to give the product or original reactants. The energy variation during the above process may be represented by the figures below:

Definition
An **activated complex** is the structure that results in the maximum **energy** point along the reaction path.

The energy diagram for the reaction for exothermic reaction

Activated
complex

Potential
energy

a.E = activation
energy

a.E

Reactant

-ΔHr

Products

Reaction coordinates/

Path of a reaction

The energy diagram for the reaction for endothermic reaction

Activated
complex

Ea. = activation
energy

Potential
energy

Products

Ea.

+ΔHr

Reactant

Reaction coordinates/

Path of a reaction
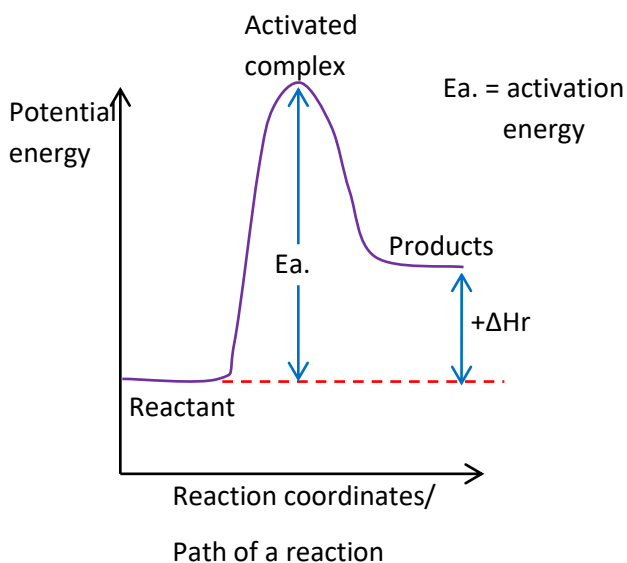
The difference between the energy of the reactants and the product is the enthalpy of the reaction ($\Delta$Hr) which is negative for exothermic reaction (i.e. energy given out during the reaction and the reaction mixture heats up) or positive for endothermic reaction (i.e. energy is required for the reaction to take place.)

**Definition**
The **molecularity** of a reaction is defined as the number of molecules or ions that participate in the rate determining step.

The **activation energy** of a **chemical** reaction is the difference between the energy of the **activated complex** and the **energy** of the reactants.

Factors that affect the rate of reaction
The main factor which influence reaction rate are
(i) concentration of the reactant
(ii) temperature
(iii) Pressure
(iv) presence of light
(v) the size of the particles for solid reactants.
(vi) Catalyst

**1. Particle size**
The smaller the particle sizes the faster the reaction in solid state because of increase surface area for contact. e.g.

$CaCO_3(s) + 2HCl (aq) \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)$

The reaction is faster when $CaCO_3$ is in powder form than big chips.

**2. Concentration**
The higher the concentration of reactants; the faster is the rate of reaction due to increase in the rate of collision among the reacting molecules.

**3. Pressure**
Pressure increases the rate of reaction when the reactants are in gaseous phase because it increases the proximity and the rate of collision of the reacting molecules.
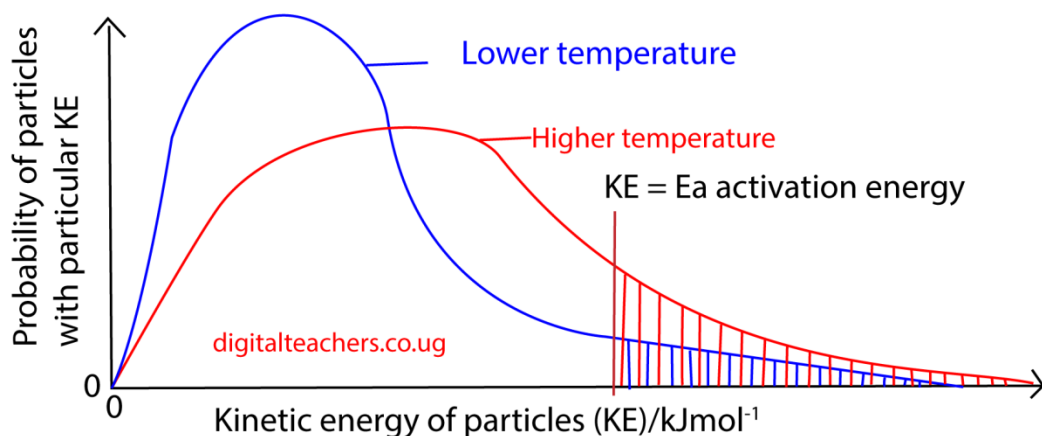
**4. Temperature**
Temperature increases the rate of reaction because
    (i)      Particles gain kinetic energy which increases the rate collision

(ii)      it increases the fraction of molecules with energy equal or higher than the activation energy that enables the reaction to take place in case collision take place between molecules.

The graph below shows the distribution of kinetic energies of molecules of a gas at temperatures $T_1$ and $T_2$; $T_2$ being higher than $T_1$.

Distribution of molecular kinetic energies at different temperatures



The number of molecules with energy equal to or greater then Ea increases rapidly with temperature as shown by the shaded area under graph above

## 5. Light

Some reactions are catalyzed by light such as photosynthesis and formation of silver from silver salts that take place when a photographic film is exposed to light. The higher the light intensity, the higher the rate of reaction will be.
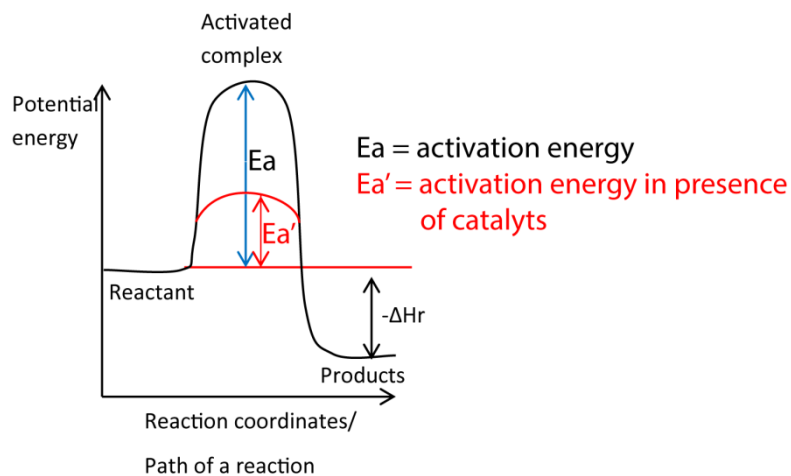
## Surface area

Increasing surface area of the reactant increase the rate of reaction because it brings the reacting substances into more intimate contact to facilitate their interaction.
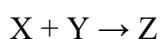
## Catalyst

Increase the rate of reaction by lowering the activation energy

The energy diagram for the reaction for exothermic reaction in absence and presence of a catalyst

Activated
complex

Potential
energy

Ea

Ea = activation energy
Ea' = activation energy in presence
of catalyts

Ea'

Reactant

-ΔHr

Products

Reaction coordinates/
Path of a reaction

## Trial 9

The tale below shows the initial rate of the reaction.

$$X + Y \rightarrow Z$$

Varies with different starting concentrations of X and Y.

| [X] mol | [Y] mol | Initial rate mol s$^{-1}$ |
|---------|---------|---------------------------|
| 0.200   | 0.200   | $4.0 \times 10^{-5}$      |
| 0.200   | 0.400   | $4.0 \times 10^{-5}$      |
| 0.400   | 0.200   | $16.0 \times 10^{-5}$     |

(a) Determine the order of the reaction with respect to
   (i) X
   (ii) Y
(b) Write the rate equation for the reaction
(c) Calculate
   (i) the rate constant
   (ii) the rate of the reaction when $[X] = 0.100M$ and $[Y] = 0.200M$.

## Trial 10

The table below shows the rate of the reaction between substances A ad B at different concentration

| EXpt. | Initial concentration Mol dm$^{-3}$ of | | Initial rate of reaction Mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| | A | B | |
| 1 | 0.50 | 0.50 | 2.0 x 10$^{-2}$ |
| 2 | 1.00 | 0.50 | 8.0 x 10$^{-2}$ |
| 3 | 1.00 | 1.00 | 16.0 x 10$^{-2}$ |

(a) Determine

(i) The order of reaction with respect to A and B

(ii) Overall order of the reaction

(b)(i) Write the expression for the rate of the reaction.

(ii) Calculate the rate constant for the reaction and state the units.

## Trial 11

(a) Differentiate between order and molecularity of reaction (5marks)

(b) The table below shows some data for the reaction

A + 2B →C ΔH = +Q kJ mol$^{-1}$:

| EXpt. | Initial concentration Mol dm$^{-3}$ of | | Initial rate of reaction Mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| | A | B | |
| I | 1.00 x 10$^{-2}$ | 2.80 x 10$^{-3}$ | 2.1 |
| II | 5.00 x 10$^{-3}$ | 2.80 x 10$^{-3}$ | 1.1 |
| III | 1.00 x 10$^{-2}$ | 5.60 x 10$^{-3}$ | 4.3 |

(i) determine the order of the reaction with respect to A and B

(ii) Write the rate equation for the reaction

(iii)Calculate the rate constant for the reaction and give its units

(iv)Calculate the rate of reaction when the concentration of A and B are 8.50 x 10$^{-3}$ mol dm$^{-3}$ and 3.83 x 10$^{-3}$ mol dm$^{-3}$ respectively.

(v) State what would happen to the order of the reaction in (b) if B was present in larger excess. Explain your answer.

(vi) draw a fully labeled energy diagram for the reaction I (b) (4marks)

## Trial 12

The data in the table below was obtained foe the reaction

2A → Product

| Time (hr) | 0 | 1.3 | 2.0 | 4.0 | 5.3 |
|---|---|---|---|---|---|
| Log$_{10}$[A] | -0.07 | -0.24 | -0.33 | -0.57 | -0.74 |

(a) Plot a graph of $Log_{10}[A]$ against time.
(b) From the graph, determine the order of reaction.
(c) Calculate
    (i) the rate constant for the reaction.
   (ii) the half-life of the reaction.

## Trial 13

Propanone reacts with iodine in the presence of an acid catalyst according to the equation.

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + I_2 \dashrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH + HI$$

The reaction is first order with respect to propanone and independent of the concentration of iodine.
(a) Explain the term order of reaction
(b) Write the expression for the rate law for the reaction
(c) Describe briefly how the order of the reaction with respect to iodine can be determined (8marks)

## Trial 14

   (a) Figure below shows the energy diagram for the reaction between nitrogen monoxide and oxygen



Reaction co-ordinate
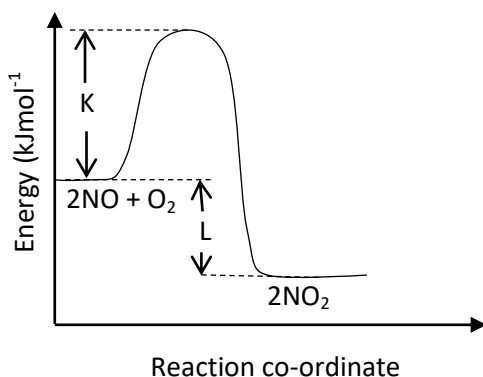
   (i) Identify K and L (½ each)
   (ii) State whether the reaction is endothermic or exothermic (½ mark)
  (iii) Give a reason for your answer (a)(ii)
   (b) The experiment results in the table below were obtained for the reaction (a)

| Initial concentrations (moldm$^{-3}$) | | Rates of reaction (moldm$^{-3}$s$^{-1}$) |
|---|---|---|
| NO | O$_2$ | |
| 0.03 | 0.03 | 2.7 x 10$^{-5}$ |
| 0.03 | 0.06 | 5.4 x 10$^{-5}$ |
| 0.06 | 0.03 | 10.8 x 10$^{-5}$ |

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(i) deduce the order of the reaction with respect to

    Nitrogen monoxide                         (1mark)

    Oxygen                              (1mark)

  (ii)   Write the rate equation for the reaction
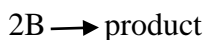                                  (½ mark)
  (c)  Calculate the overall
       (i)  overall order of reaction ( ½ mark)
       (ii) rate constant (K) for the reaction and state its units          (1½ marks)


## Trial 15

    (a) State what is meant by the following terms 'order of reaction' and 'Half-life' of a reaction
    (b) A compound B decompose according to the following equation
       $2B \longrightarrow$ product

The table below shows the concentration of B at various times

| Time (minute) | 2.0 | 4.0 | 7.0 | 10.0 | 14.0 | 20.0 |
|---|---|---|---|---|---|---|
| [B] $(moll^{-1})$ | 0.820 | 0.670 | 0.490 | 0.372 | 0.240 | 0.141 |

Draw a graph of $\log_{10}[B]$ against time.      (05marks)

    (c) Using the graph, determine the:
       (i)      Original concentration of B
       (ii)     Order of the reaction
       (iii)    Rate constant for the reaction
       (iv)    Half-life for the reaction
    (d) (i)  Using the same axes, draw a labelled diagram for energy-reaction coordinate for a catalyzed and uncatalyzed reaction
                      (3½marks)
       (ii) State the difference in your diagrams (1mark)
       (iii)State how a catalyst increases the rate of reaction (2marks)

## Trial 16

(a) Describe an experiment that can be carried out to show that the catalytic decomposition of hydrogen peroxide is a first order reaction. (09marks)

(b) The rate of a certain reaction is

Rate $=K[A][B]^2[C]$

Where [ ] is the concentration in moles per litre and K is the rate constant

Show how the rate of reaction would change if:

(i) [B] and [C] were kept constant and [A] was doubled. (1mark)

(ii) [A] and [C] were kept constant and [B] was halved. (1mark)

(iii) [A] and [C] were kept constant and [B] was doubled. (1mark)

(iv) [A], [B] and [C] were doubled.

## Trial 17

(a) (i) Define the term **radioactivity**.

(i) Name three types of radiations emitted during radioactivity and state how they affect the nucleus of radioisotope. (04marks)

(b) The table below shows how the mass of radioactive protactinium, $^{234}_{91}Pa$ varies with time

| Mass of $^{234}_{91}Pa$ g | 60.0 | 38.5 | 26.0 | 17.2 | 11.1 |
|---|---|---|---|---|---|
| Time (minute) | 0 | 40 | 80 | 120 | 160 |

(i) Plot a graph of mass of protactinium against time (03marks)

(ii) Use your graph to determine half-life of protactinium. (2marks)

(iii)Calculate the radioactive decay of protactinium (2marks)

(iv)Determine the time taken for 8g of protactinium to decay to 1g (2marks)

(c) Briefly describe how

(i) Carbon-14 can be used to determine the age of archeological objects (3marks)

(ii) Oxygen-18 can be used to determine the mechanism for esterification of a mon carboxylic acid with a primary alcohol (4marks)

## Trial 18

(a) Differentiate between **order of reaction** and **molecularity**. (2marks)

(b) The table below shows kinetic data for the following reaction.

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O$ (l)
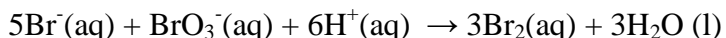
| Volume of $BrO_3^-$/cm$^3$ | 3.0 | 4.0 | 5.0 | 6.0 | 8.0 | 10.0 |
|---|---|---|---|---|---|---|
| Time (t)/s | 69.0 | 45.0 | 35.0 | 31.0 | 24.0 | 18.5 |

(i)  Plot a graph of 1/t against volume of bromate (V), $BrO_3^-$.
(ii) Determine the order of reaction with respect to bromate (V) and give a reason for your answer. (1mark)
(iii)Determine the rate constant for the reaction and state its units. (1mark)
(iv)Write equation for the rate of reaction in terms concentration of $BrO_3^-$ (1mark).of


## Suggested answers

Trial 1

(a)   (i) **Reaction rate** is the speed at which a chemical **reaction** proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product that is formed in a unit of time or the concentration of a reactant that is consumed in a unit of time.
   (ii) Order of reaction is the sum power dependence of the rate on the concentration of each reactant.
   (iii) **Stoichiometry  of a reaction** is the quantitative relationships of the amount of products and reactants in a given reaction
   (iv) The rate constant of the reaction is a proportionality factor in the **rate** law of **chemical** kinetics that relates the molar concentration of reactants to reaction **rate**
   (b) The experiment were carried out at constant temperature in order to eliminates changes in the rate of reaction due to changes in temperature
   (c) (i) the order of reaction with respect to A is derived using values of experiments 1 and 2
      i.e, $\left(\frac{0.40}{0.20}\right)^x = 2^x = \frac{0.80}{0.20} = 4 = 2^2 => x = 2$
      the order of reaction with respect to is derived by using values of experiment 2 and 3
      i.e, $\left(\frac{0.20}{0.10}\right)^x = 2^x = \frac{0.80}{0.80} = 1 = 2^0 => x = 2$
      Rate equation: rate = $K[A]^2$.
      (ii) Substituting values of experiment 1
            $0.2 = K(0.2)^2$
            $K = 5mol^{-1}dm^3s^{-1}$
      (iii) Substitution in rate equation
            Rate = $5 (0.6)^2 = 18moldm^{-3}s^{-1}$

Trial 2

(a) Rate equation: rate = $K[A][B]^2$
(b) $K = 1.49 \times 10^{-3} \, mol^{-2}dm6s^{-1}$
(c) Rate = $8.67 \times 10^{-6} moldm^{-3}s^{-1}$

Trial3

(a) Rate = $K[NO]^x[O3]^y$
(b) Order of reaction with respect to NO = 1
    Order of reaction with respect to O3 = 1
(c) Rate = $K[NO][O_3]$
(d) $K = 2.2 \times 10^{-7} mol^{-1}s^{-1}$

Trial 4

(a) Order of reaction with respect to X  = 1
    Order of reaction with respect to Y  = 1
(b) Overall order  = 1+ 1          = 2
(c) $K = 0.3 mol^{-1}dm^3s^{-1}$

Trial 5

(a) (i) the rate doubles

    (ii) The rate is multiplied by $\left(\frac{1}{2}\right)^4$      $= \frac{1}{16}$
    (iii)The rate is multiplied by $2^4$      = 16
(b) (i) Order of reaction with respect to $(S_2O_8^{2-})$  = 1
    Order of reaction with respect  to $I^-$          = 1
    Rate equation:
    Rate = $K[S_2O_8^{2-}][I^-]$
    (ii) Rate constant $K = \frac{Rate}{[S_2O_8^{2-}][I^-]} = \frac{9.6 \times 10^{-6}}{0.024 \times 0.024} = 0.017 mol^{-1}dm^3s^{-1}$

Trial 6

(a) [A]  = concentration of a
    a = order of reaction with respect to concentration of A
    b = order of reaction with respect to concentration of B
(b) Temperature
(c) (i) rate constant $K = \frac{In2}{t_{\frac{1}{2}}} = \frac{In2}{75.09} = 0.0092 hr^{-1}$

    (ii) $N_2O(g) \rightarrow N_2(g) + \frac{1}{2} O_2(g)$
    Moles of gas after halt-life  = moles of $N_2O$ + Moles  of $N_2$ + moles of $O_2$
                                  = 0.5 + 0.5 + 0.25
                                  = 1.25

Since pressure is proportional to the number of moles of gases
The final pressure = 1 x 1.25 = 1.25 atmospheres

Trial 7

(a) Time = half-life; => $a_0 - x = \dfrac{a_0}{2}$

It implies that; $2.3031\log\left[\dfrac{a_0}{\frac{a_0}{2}}\right] = Kt_{\frac{1}{2}}$

$$2.3031\log 2 = Kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \dfrac{0.691}{K}$$

(b) $K = \dfrac{0.691}{100} = 6.93 \times 10^{-3}s^{-1}$

(iii) $2.3031\log\left[\dfrac{a_0}{(a_0-x)}\right] = 6.93 \times 10^{-3} \times 250$

$\dfrac{a_0-x}{a_0} = 0.177$ or 17.7%

Trial 8

(b) (i) 2
(ii) when water is in excess
(c) Order of reaction with respect to A = 2
Order of reaction with respect to B = 0
Overall order = 2 + 0 = 2

Rate constant $K = \dfrac{1.2 \times 10^{-8}}{0.2 \times 0.2} = 3 \times 10^{-7}mol^{-1}dm^{3}s^{-1}$

Trial 9

(a) X = 2
    Y = 0
(b) Rate = $K[X]^2$
(c) (i) K = 1 x $10^{-3}mol^{-1}dm^{3}s^{-1}$
(iii) 1 x $10^{-5}moldm^{-3}s^{-1}$

Trial 10

(a) (i) order of reaction with respect to A = 2
    Order of reaction with respect to B = 1
    (ii) overall order = 1 + 2 = 3
(b) (i) Rate = $K[A]^2[B]$
    (ii) K = $0.16mol^{-2}dm^{6}s^{-1}$

Trial 11

(a) Order of reaction is the sum power dependence of the rate on the concentration of each reactant while molecularity is the number of molecules or ions that participate in the rate determining step.

(b) (i) order of reaction with respect to A = 1

Order oof reaction with respect to B = 1
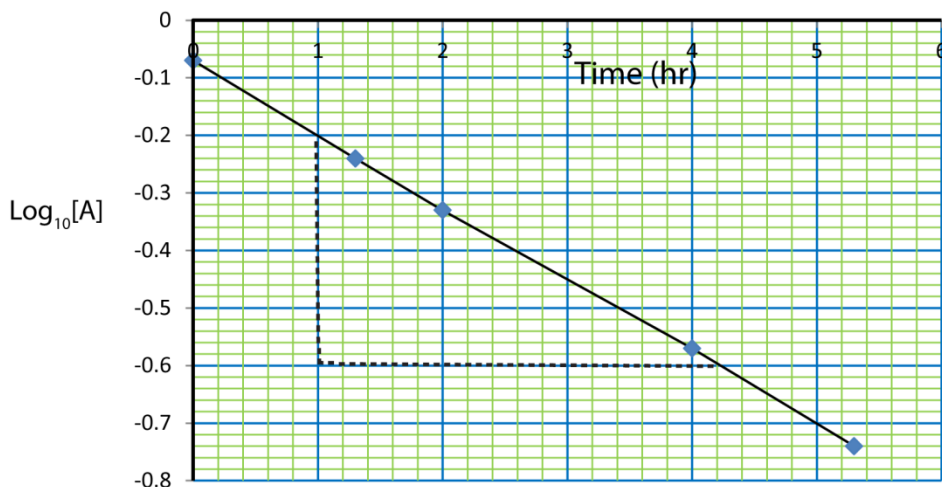(ii) Rate = K[A][B]
(iii) K = 7.5 x $10^5$ mol$^{-1}$dm3s$^{-1}$
(iv) 24
(v) Becomes pseudo order 1

Trial 12

(a)

A graph of $Log_{10}[A]$ against time



(b) The reaction is first order since the shape of the graph suggests that the rate is proportional to concentration of the reactant.
(c) (i) Rate constant K = negative slope
$$= - \left( \frac{-2 - \,^-6}{1 - 4.1} \right)$$
$$= 1.29 \text{hr}^{-1}$$
(iii) Half-life, $t_{\frac{1}{2}} = \frac{In2}{K} = \frac{In2}{1.29} = 0.537hr$

Trial 13

(a) Order of reaction is the sum power dependence of the rate on the concentration of each reactant.
(b) Rate = K[$CH_3COCH_3$]
(c) An experiment to determine the order reaction with respect to iodine in the reaction of iodine with propanone in presence of acid catalyst.

(i) Fixed volume of standard Iodine solution is added to an excess of propanone solution in a flask.

(ii) To this mixture is added a fixed volume of dilute sulphuric acid and a stop clock started immediately.

(iii)At intervals of time say (every 10 minutes for 50minutes) a specified portion is pipetted from the mixture and into a flask containing sodium hydrogen carbonate which stops the reaction.

(iv)The resultant mixture is titrated with standard sodium thiosulphate using starch indicator.

(v) The volume $(V_t)$ of thiosulphate used on the portion of mixture after a specified time (t) is proportional to the amount of iodine remaining in the mixture.

(vi)The initial amount of iodine $(V_0)$ is obtained by titrating a similar portion of the original mixture with sodium thiosulphate solution.

(vii) A plot of the graph of $V_t$ against time gives a straight line as shown below showing that the order of reaction with respect to iodine is zero.
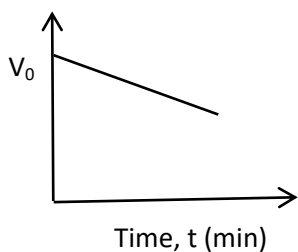


NB. The gradient gives the rate constant whose units are molcm$^{-3}$ s$^{-1}$.

Trial 14

(a)  (i) K = activation energy
      L = enthalpy of reaction
    (ii) exothermic
    (iii) Products have less energy than reactants

(b)  (i) $\left(\frac{0.06}{0.03}\right)^x = 2^x = \frac{10.8 \; x \; 10^{-5}}{2.7 \; x \; 10^{-5}} = 4 = 2^2 \gg x = 2$
    The order of reaction with respect to [NO] = 2

    $\left(\frac{0.06}{0.03}\right)^y = 2^{xy} = \frac{5.4 \; x \; 10^{-5}}{2.7 \; x \; 10^{-5}} = 2 = 2^1 \gg y = 1$
    Order of reaction with respect to [Y] = 1
    (ii) Rat = $K[NO]^2[O_2]$

(c)  (i) Overall order = 2 + 1 = 3
    (ii) K = 1mol$^{-2}$dm$^6$s$^{-1}$

Trial 15

(a) Order of reaction is the sum power dependence of the rate on the concentration of each reactant

(b) Half-life $(t_{\frac{1}{2}})$ of the reaction is the time taken by the reactant to reduce to half of their initial concentration.

| Time (minute) | 2.0 | 4.0 | 7.0 | 10.0 | 14.0 | 20.0 |
|---|---|---|---|---|---|---|
| [B] $(moll^{-1})$ | 0.820 | 0.670 | 0.490 | 0.372 | 0.240 | 0.141 |
| Log [B] | -0.086 | -0.173 | -0.309 | -0.429 | -0.619 | -0.850 |

(b)



A graph of log B against time
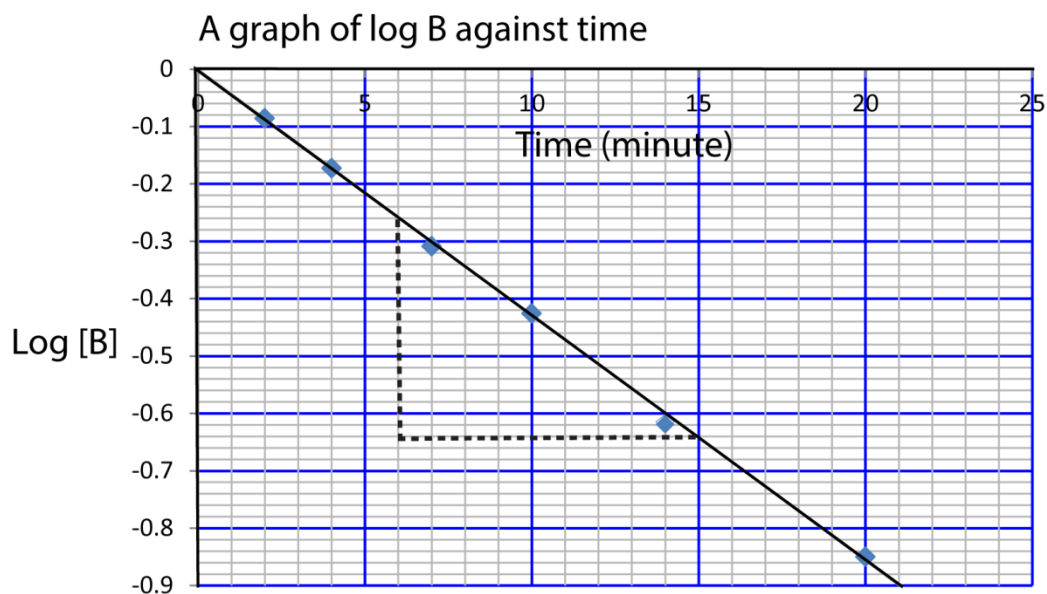
(c)(i) Log B = 0

$$B = 10^0 = 1$$

(ii) Order of reaction is first order since the rate is proportional to concentration
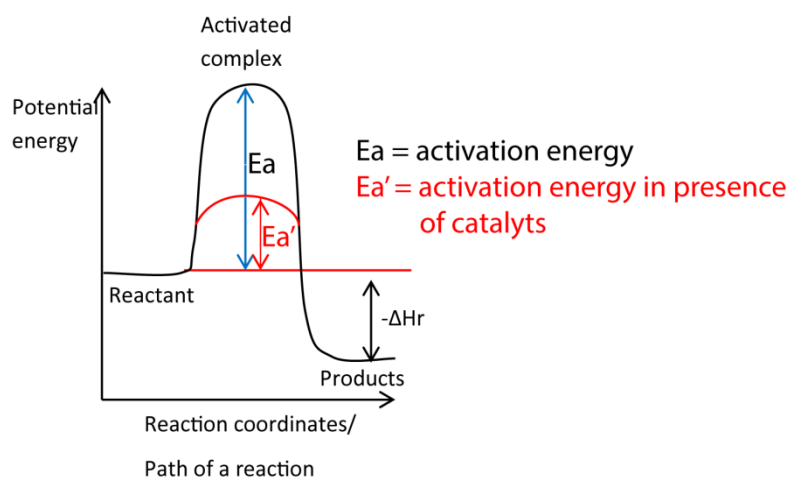
(iii) Rate constant K = negative slope

$$= -\left(\frac{-0.26 - \ ^-0.64-}{6-15}\right)$$

$$= 0.04 \text{min}^{-1}$$

(iv) Half-life, $t_{\frac{1}{2}} = \frac{In2}{K} = \frac{In2}{0.04} = 17.3 minutes$

(d)(i)



Potential energy diagram showing: Activated complex at the peak, Ea = activation energy, Ea' = activation energy in presence of catalyts, Reactant, Products, -ΔHr, with axis labels Reaction coordinates/ Path of a reaction

Ea = activation energy
Ea' = activation energy in presence of catalyts

(ii) the catalyzed reaction has lower activation energy

(iii) A catalyst increase the rate of reaction by lowering activation energy.