PART THREE
CHEMICAL KINETICS

Chapter 9

INTRODUCTION TO CHEMICAL KINETICS

Not all possible reactions are detectable. Many reactions are very slow at room temperature and some reactions may take even many years to be observable. Reactions like conversion of diamond to graphite or hydrogen and oxygen (to give water) are all possible at normal conditions but are not detectable because are so slow that no reasonable change can be observed.

In real life, the reactions must occur at fairly high rate to be useful. If we want to produce ammonia for producing fertilizer for example, we cannot just mix nitrogen and hydrogen at room temperature and pressure and waiting for them to react; we will wait for years and years and nothing significant we will be obtained! To get the ammonia, we must understand and apply factors governing the rate of reaction between nitrogen and hydrogen, and this is what chemical kinetics is all about!

Chemical kinetics *is the branch of physical chemistry which is concerned about the study of determination of rates of chemical reactions and factors affecting it.* The study of chemical kinetics deals with the qualitative and quantitative study of:

- The rates of reactions
- The factors affecting rate of reactions and
- The mechanism of reactions

RATE OF REACTION

Rate of reaction *is the quantity of reactant consumed or the quantity of a product formed in unit time.* It is the change of concentration of reactants or products per unit time in the course of a chemical reaction.

$$\text{Rate of the reaction} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

The rate of reaction is expressed in unit of $(\text{concentration})(\text{time})^{-1}$ like: Ms^{-1}(or $\text{moldm}^{-3}\text{s}^{-1}$), Mmin^{-1} (or $\text{moldm}^{-3}\text{min}^{-1}$) etc.

- For gases, it can be expressed in terms of partial pressure like atms^{-1} or atmmin^{-1}.

As the reaction proceeds, the concentration of products increases while that of reactants decreases. Thus the change of concentration of products is positive while that of reactants is negative.

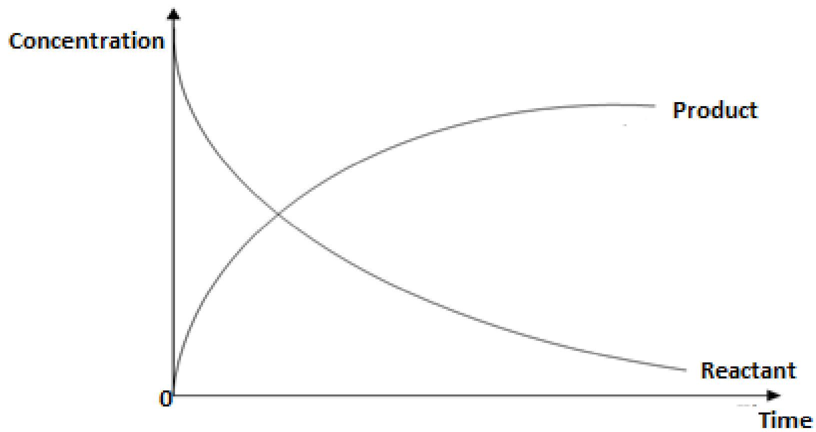


Figure 9.1 Variation of concentration of products and reactants in the reaction

- Reaction rate is the amount of reaction which occurs in unit time and the therefore, if we wish to measure the rate of a chemical reaction we must choose some property of the reaction which will indicate how far the reaction has changed, and observe the way in which the magnitude of that property varies with time.

- It is advantageous to choose a property of the reaction which can be observed without disturbing the reaction itself. Thus, in a reaction where a colourless substance is changing to a coloured one, the rate at which the intensity of the colour increases would give the rate of reaction. In a similar way, for a reaction in which a gas is liberated from solution it may be, it may be possible to collect that gas and measure the way which the volume of gas increasing with time.

Reaction rate as an average rate

When the reaction rate is represented as the change in concentration divided by change in time, the result is known as **average rate** of the reaction.

That is: Average rate $= \frac{\text{change in concentration}}{\text{time taken}} = \frac{C_{t_2} - C_{t_1}}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$

Where C_{t_1} and C_{t_2} are molar concentration at time t_1 and t_2 respectively.

Reaction rate as an instantaneous rate

As the reaction proceeds, concentration of reactants decreases and whence the rate of reaction decreases.

- Thus the rate of reaction is maximum at $t = 0$ (at the beginning of the chemical reaction) and continues to decrease as the time for the reaction increases until the reaction is complete where the rate is zero.
- So the graph of concentration against time for the common reaction whose rate of reaction decreases with decrease in concentration of reactants will look as follows;

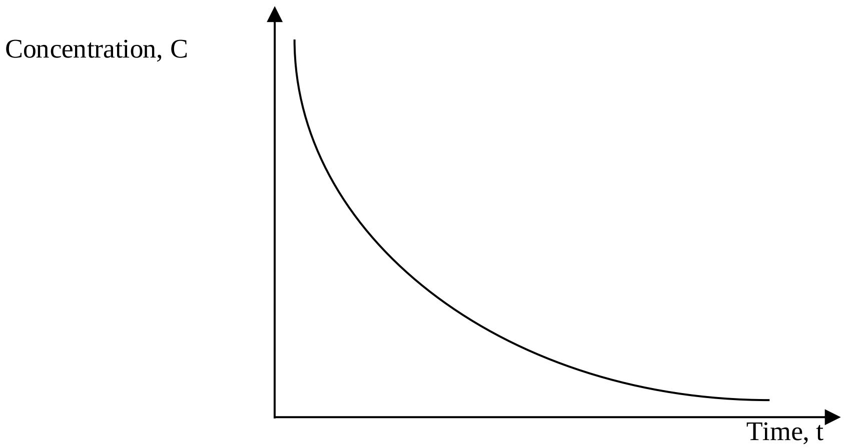


Figure 9.2 Variation of reactants concentration versus time of the reaction

Things to note from the graph:

- Slope of the curve $\left(\frac{\Delta C}{\Delta t}\right)$ represents the rate of reaction.
- When t approaches zero (at the beginning of the reaction) the curve is very steep (the curve has large slope) indicating high rate of the reaction when concentration of the reactant is still large.
- As the reaction proceed (t increases) the curve becomes less steep (the slope becomes small) indicating low rate of the reaction as the concentration of the reactant decreases. When the reaction is about to reach completion, (where the concentration of the reactant approaches zero) the curve is almost horizontal meaning the slope and hence the rate of reaction approaches zero.
- Like any curve, the slope of the above curve is not constant. It varies as t varies. This means that the rate of reaction also varies as t varies. This provides very important conclusion that:
- We can only find rate of reaction at particular **instant** time hence the term **instantaneous rate of reaction**.

The average rate of reaction defined earlier is just an estimation of the rate of reaction over given time interval. It is the mean of several instantaneous rates of reaction taken over period of time.

- When the change in time $(t_2 - t_1)$ approaches zero (that is $t_1 \approx t_2$), the average rate of reaction provides good approximation to the instantaneous rate of the reaction.

Thus; **instantaneous rate of reaction**$= \frac{\Delta C}{\Delta t}$ **as** $\Delta t \to 0$

- This is formally shortened as $\frac{dC}{dt}$ (derivative of C with respect to t).
  That is $\frac{dC}{dt}$ stands for $\frac{\Delta C}{\Delta t}$ as $\Delta t \to 0$

Thus in the formal mathematical language; **instantaneous rate of reaction** $= \frac{dC}{dt}$

Because reactions slow down over time, instantaneous rate of reaction is the better way of expressing the rate of reaction. In chemistry we are usually interested in the instantaneous reaction rate at the very beginning of the reaction. So whenever we talk about just rate of reaction (without any extra information), the implication will be the instantaneous rate of reaction at the very beginning of the reaction.

- The instantaneous rate of reaction is also known as **reaction velocity** (or **reaction speed**).

Reaction rates and stoichiometry

Consider the following reaction:

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

In this reaction the mole ratio of all species is 1:1. For any one mole of C_4H_9Cl (or H_2O) which disappear, there is one mole of C_4H_9OH or (or HCl) which is formed.

- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH

Hence in this case:

$$\text{Rate} = \frac{-d[C_4H_9Cl]}{dt} = \frac{-d[H_2O]}{dt} = \frac{d[C_4H_9OH]}{dt} = \frac{d[HCl]}{dt}$$

(Note: the negative sign appears in species of reactants side because their concentrations are decreasing during the reaction)

Now consider another reaction:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Hence we **cannot** say that $\frac{-d[O_2]}{dt} = \frac{-d[NO]}{dt}$ or $\frac{-d[O_2]}{dt} = \frac{d[NO_2]}{dt}$

Because from the reaction stoichiometry, it is clearly seen that for every **one** mole of O_2 which react, there must be also **two** moles of NO which reacts at the same time. Or for any **one** mole of O_2 which disappears, there are must be **two** moles of NO_2 which are produced at the same time.

- This means that the rate of disappearance of NO must be twice that of O_2

That is: $\frac{-d[[NO]]}{dt} = \frac{-2d[O_2]}{dt}$ or $\frac{-1}{2}\frac{d[NO]}{dt} = \frac{-d[O_2]}{dt}$ … … … … … (i)

- And the rate of appearance of NO_2 must be twice the rate of disappearance of O_2

That is: $\frac{d[NO_2]}{dt} = \frac{-2d[O_2]}{dt}$ or $\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{-d[O_2]}{dt}$ … … … … (ii)

Combining (i) and (ii) gives appropriate equation of rate in terms of rate of individual species appearing in the reaction which is;

Rate $= \frac{-1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$ (Have you noticed how stoichiometric coefficient appears in this equation?)

Generally, for the reaction: $\mathbf{a}A + \mathbf{b}B \longrightarrow \mathbf{c}C + \mathbf{d}D$

The reaction rate can be written in a number of different but equivalent ways as follows:

$$R = \frac{-1}{\mathbf{a}}\frac{d[A]}{dt} = \frac{-1}{\mathbf{b}}\frac{d[B]}{dt} = \frac{1}{\mathbf{c}}\frac{d[C]}{dt} = \frac{1}{\mathbf{d}}\frac{d[D]}{dt}$$

Example 1

(a) How the rate at which ozone disappears is related to the rate at which oxygen appears in the reaction: $2O_3(g) \longrightarrow 3O_3(g)$?

(b) If the rate of which O_2 appears is $6.0 \times 10^{-5} M/s$ at particular instant, at what rate is O_3 disappearing at the same time?

Solution

(a) $\frac{-1}{2}\frac{d[O_3]}{dt} = \frac{1}{3}\frac{d[O_2]}{dt}$

(b) Given that $\frac{d[O_2]}{dt} = 6.0 \times 10^{-5} M/s$

Then substituting $\frac{-1}{2}\frac{d[O_3]}{dt} = \frac{1}{3} \times 6.0 \times 10^{-5} M/s$

Or $\frac{-d[O_3]}{dt} = \frac{2}{3} \times 6.0 \times 10^{-5} M/s = 4\times 10^{5} M/s$

Hence the rate of disappearing O_3 is $4\times 10^{5} M/s$

Example 2

Consider the reaction: $2H_3PO_4 \longrightarrow P_2O_5 + 3H_2O$

Using the information in the following table, calculate

(a) The average rate of formation of P_2O_5 between 10.0s and 40.0s

(b) The average rate of decomposition of H_3PO_4 between 10s and 40s

Time (s)	0	10.0	20.0	30.0	40.0	50.0
$[P_2O_5]/M$	0	1.5×10^{-3}	4.5×10^{-3}	6.3×10^{-3}	7.5×10^{-3}	8.1×10^{-3}

Solution

Using;

Average rate of formation of product= $\frac{\text{Change in concentration over certain time interval}}{\text{the time interval}}$

Thus the average of formation of $P_2O_5 = \frac{\Delta[P_2O_5]}{\Delta t} = \frac{[P_2O_5]_{t=40} - [P_2O_5]_{t=10}}{\Delta t} = \frac{(7.5\times10^{-3} - 1.5\times10^{-3})}{(40-10)s}$

$$= 2 \times 10^{-4} Ms^{-1}$$

(a) Hence the average rate of formation of P_2O_5 is $2 \times 10^{-4} Ms^{-1}$

Average rate of decomposition of H_3PO_4 is related to the average rate of formation of P_2O_5 by following $\frac{-1\Delta}{2}\frac{[H_3PO_4]}{\Delta t} = \frac{\Delta[P_2O_5]}{\Delta t}$

Where the negative sign$(-)$ indicate that the concentration of H_3PO_4 is decreasing in the reaction

Thus $-\frac{\Delta[H_3PO_4]}{\Delta t} = \frac{2\Delta[P_2O_5]}{\Delta t} = 2 \times 2 \times 10^{-4} Ms^{-1} = 4 \times 10^{-4} Ms^{-1}$

(b) Hence the rate of decomposition of H_3PO_4 is $4 \times 10^{-4} Ms^{-1}$

Example 3

Consider the following reaction: $\mathrm{Fe(s) + 2AgNO_3(aq) \longrightarrow 2Ag(s) + Fe(NO_3)_2(aq)}$

In an experiment, an iron nail placed into a solution of $\mathrm{AgNO_3}$ and the following data is collected:

Time (hour)	Mass (g) of Fe
0.0h	2.95g
2.0h	1.87g
4.0h	0.98g

Calculate the overall rate of this reaction in grams of Ag produced per hour. (Atomic masses: $\mathrm{Fe = 55.8, Ag = 107.9}$).

Solution

Mass of iron reacted in $\mathrm{4h = (2.95 - 0.98)g = 1.97g}$

Using $\mathrm{n = {}^{m}/_{M_r}}$

Number of moles of iron reacted in $\mathrm{4h = \frac{1.97g}{55.8g/mol} = 0.0353mol}$

Rate of $\mathrm{Fe = \frac{0.0353mol}{4h} = 8.825 \times 10^{-3} mol/h}$

Rate of Fe and Ag are related by the following equation:

Rate of $\mathrm{Ag = 2 \times 8.825 \times 10^{-3} mol/h = 0.01765 mol/h}$

Using $\mathrm{m = nM_r}$;

Rate of Ag in $\mathrm{g/h = 0.01765 mol/h \times 107.9 g/mol = 1.9 g/h}$

Hence the overall rate of production of silver is $\mathrm{1.9g/h}$

Collision theory and rate of reaction

Collision theory attempts to explain the results of kinetic experiments in terms of the individual atoms and molecules that are undergoing chemical reactions.

- Specifically, collision theory explains the temperature dependence of reaction rates, as well as some aspects of the behaviour of catalyst. Generally, most of factors affecting reaction rate can be explained by the collision theory.

Collision theory recognises that, for a reaction to take place, at least three conditions must be met:

First condition: A collision between reacting particles must take place

- For a chemical reaction to take place the molecules must collide. Even if the reaction involves the decomposition of single molecule, that molecule must have collided with something to give it the energy necessary to decompose.
- *The number of collisions between particles per second* is known as **collision frequency**.
- So it is reasonable to expect that the reaction rate will depend on collision frequency; the greater the number of collision per second (collision frequency), the faster the rate of reaction. The increase in collision frequency explains why **stirring** increase the rate reaction.

Second condition: The colliding particles must be properly oriented in such a way that a reaction takes place.

- Not every collision will result into reaction. Only collisions of properly oriented molecules may result into reaction.
- For example, if hypothetical molecules, A_2 and B_2 react according to the equation, $A_2 + B_2 \longrightarrow 2AB$, then according to the **first condition**; for the reaction to take place A_2 and B_2 (**not** A_2 and A_2 or B_2 and B_2) must collide. The second condition say that not every collision between A_2 and B_2 results into collision unless the two molecules are properly oriented.

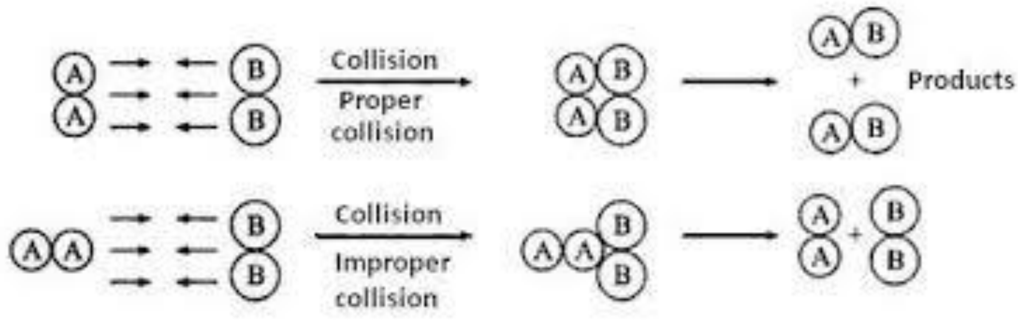


Figure 9.3 Proper and improper collisions

Third condition: The collision must be sufficiently energetic for it to result in a chemical reaction.

- The reaction may not occur even after collision between properly oriented reacting molecules. For the reaction to take place, the **collision energy** of the molecules must be large enough to overcome **activation energy** ($\mathbf{E_a}$).
- This means that collision must occur with **enough energy** to overcome the electron-electron repulsion of the valence shell electrons of the reacting species and must have enough energy to transform translational energy into vibration energy in order to penetrate into each other so that electrons can rearrange and form new bonds. Such collisions are termed to be **effective collisions**.
- If the collision energy is above the activation energy, the **activated complex** (*the unstable intermediate which is formed when the two molecules collide*) disintegrates into products and therefore the reaction occurs but if the energy is below the activation energy the activated complex disintegrates into reactants and therefore the reaction does not occur.

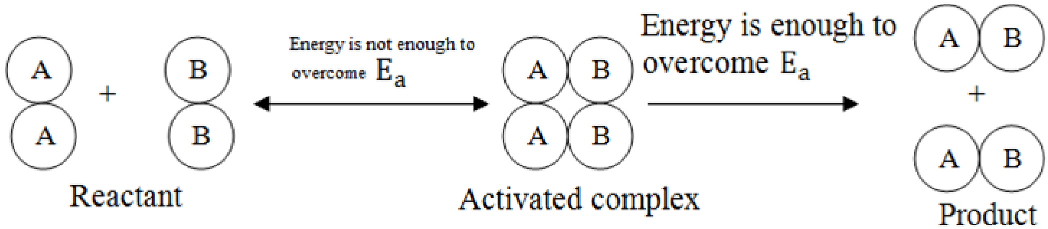


Figure 9.4 Formation of activated complex

- Lower activation energy means more collisions will result into reaction and hence greater the reaction rate.

Definition of terms:

Collision energy *is the combined energy of colliding particles.*

So in terms of collision energy, **activation energy** may be defined as *the minimum collision energy required for a collision to be successful.*

Activated complex *is the unstable chemical specie that results upon successful collision (collision between reacting particles with activation energy) that momentarily exists with partially formed and broken bonds.* It is the intermediate product which is formed when reactants have just attained activation energy

Activated complex is also known as transition state, why?

This is because the activated complex is the maximum energy value between two energy states (reactant energy and product energy). The transition state is higher energy than the product so it moves from that 'transition' state to the product.

- In one sentence the activated complex **transit** from the reactant to the product and hence the term transition state. (See figure below).

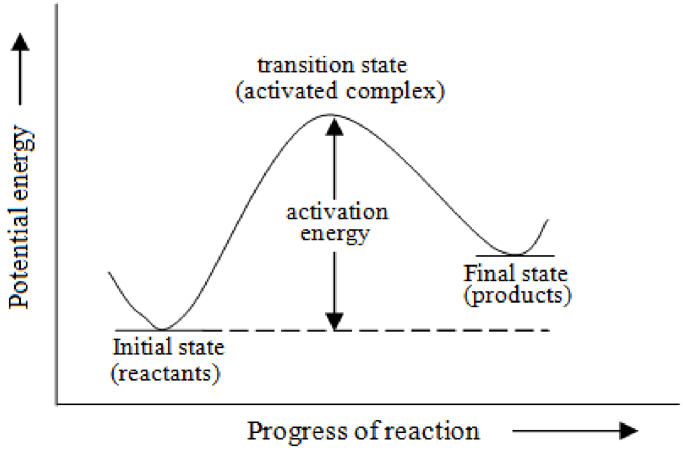


Figure 9.5 Energy profile diagram to show formation of activated complex

Activation energy and reaction rate

At room temperature, reactant particles have some potential energy. This potential energy is usually less than the **threshold energy** which is the minimum energy required for reactants to change into products. However, if energy is supplied in the form of heat, light etc., the reactant molecules absorb this energy so that their potential energy becomes equal to or greater than the threshold value. Hence, they start to change into products. In other words, the reactants need to be **activated** so as to change into products and hence the energy needed to do such activation is known as **activation energy**.

By definition:

Activation energy *is the minimum amount of energy required to activate atoms or molecules to a state in which they can undergo a chemical reaction.*

If reactant particles possess energy equal to or greater than the activation energy, they can cross the 'energy barrier' and the reaction occur.

- Conversely, if the reactant particles do not possess the activation energy required for a reaction, this reaction will not occur.

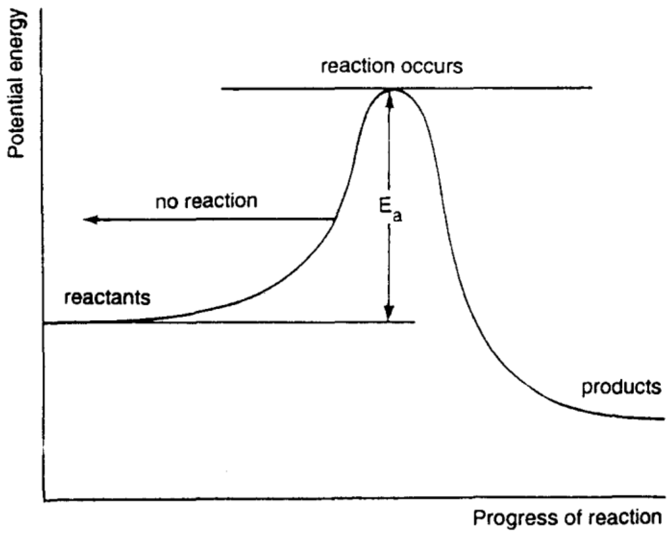


Figure 9.6 Potential energy diagram for a reaction

Some molecules will get energy equal to or greater than activation energy during collusion and are called **activated molecules**.

- The collisions taking place between activated molecules are called **activated collisions** (or **effective collisions** or **fruitful collisions).**
- The products are formed only during the activated collisions.

Activated molecules constitute a small fraction of total molecules. Therefore, the effective (activated) collisions constitute a small fraction of total collisions and hence all the chemical reactions do not occur as fast as one could expect if all collision would be effective.

- If activation energy for the reaction is low, means that greater number of reactant particles may have that energy and hence the reaction rate will be high and vice-versa.

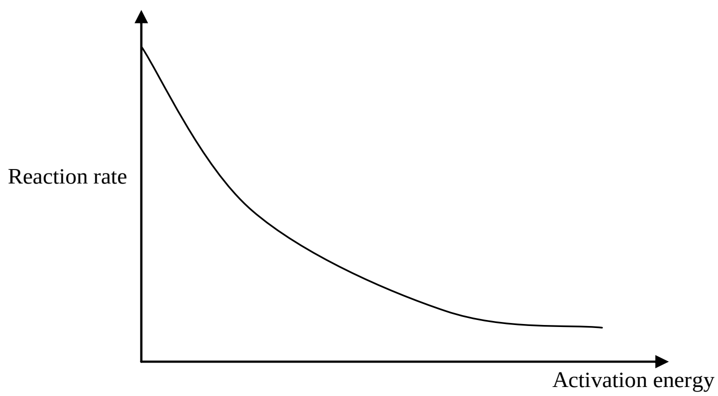


Figure 9.7 Graph to show relation between activation energy and reaction rate

The activation energy depends on the nature of chemical bonds, which are breaking during the reaction. Stronger the bond, greater the activation energy. However, it does not depend on the enthalpy of reaction.

- **The reaction may be highly exothermic, which in turn means that it is thermodynamically favoured but still can be very slow if the activation energy is very high**. A good example of this is **the rusting of iron** which is very slow exothermic reaction. In other words, rusting of ion is **thermodynamically favoured** (it is exothermic) but it is **kinetically unfavoured** (it is slow) due to high activation energy for the rusting process.

- Or **the reaction may be highly exothermic, (thermodynamically favoured), but still need to be initiated by applying suitable conditions** due to presence of the activation energy. A clear example of this is burning of wood. The wood burning is highly exothermic but wood cannot burn itself. It starts burning only after igniting it.

The facts that:

- Exothermic reactions may be slow and
- Exothermic reactions may not start if there are no suitable initiating conditions, are evidences of presence of activation energy for reactions.

Threshold energy versus activation energy

Although the two terms are commonly used interchangeably, there is a subtle difference between the two.

- **Threshold energy** *is the minimum amount of energy required by colliding reactant particles to yield products.*

Now because at standard conditions (or any other conditions), reactants are already having some **average energy** (*The potential energy possessed by normal reactant particles under standard conditions)* which is lower than the threshold energy; there is some energy which must be subjected to the reactant particles so as to attain the threshold energy. This energy is known as **activation energy.** So the activation energy is difference between threshold energy and average energy.

That is; $\textbf{Activation energy} = \textbf{threshold energy} - \textbf{average energy}$

However, the two terms are very close related; high threshold energy implies that high activation energy is required for the reaction to take place. Or if the reactants have gained enough activation, automatically implies that the reactants have attained threshold energy and hence they can be used interchangeably despite the difference in their actual meaning.

Factors affecting rate of reaction

The rate of a chemical reaction is affected by several factors including:

- Concentration of reactants
- Pressure
- Temperature
- Catalyst
- Nature of reactants
- Surface area
- Intensity of light
- Nature of solvent

Concentration

Rate of a reaction is directly proportional to the concentration of reactants.

Explanation

The frequency of collisions and hence the effective collisions between reactant particles increases with increase in concentration. Therefore, according to the collision theory, the rate of a reaction should increase with increase in the concentration since the rate is directly proportional to the collision frequency.

Pressure

The partial pressure is another way of expressing concentration of gases.

- The partial pressure of the gas can be increased in two ways.

1) By increasing amount of a particular gas

When mass and therefore number of moles of particular gas in the given volume of reacting mixture is increased at constant temperature, partial pressure (concentration) of the gas $\left(P = \frac{nRT}{V}\right)$ increases. This increases the frequency of collision of reacting particles and hence the rate of reaction is increased too.

2) By increasing total pressure of the system

When total pressure of the system is increased, the partial pressure of each gas $\left(P_{gas} = X_{gas}P_{total}\right)$ in the given amount of reactant mixture increases and whence collision frequency increases too leading to higher reaction rate.

Another way of explaining this is that: the increase in the total pressure of the system (compression) decreases volume (which automatically increases concentration) of the gases, making them more compact and hence greater collision frequency which in turn means faster reaction rate.

You should keep in mind that:

- Since the partial pressure of gases do not change by adding total pressure through addition of inert gas or any other gas which has no reaction with the present reaction mixture, rate of reaction is not affected when noble gases or non – reacting gases are added to the reaction mixture.
- Since liquid and solid are incompressible, changing in total pressure of the system has no effect on the rate of chemical reactions with liquid and solid reactants.

Temperature

Generally, the rate of chemical reaction increases with rise in temperature due to the following reasons:

- Rise in temperature increases average kinetic energy of colliding particles and therefore makes the collisions more energetic which in turn increase numbers of reacting particles which attains activation energy.
- Rise in temperature, increases the frequency of collision of reacting particles by increasing speed of the particles.
- In other words, increase in temperature increases the rate of reaction by increasing collision energy and collision frequency. However, the second factor of increasing collision frequency as result of temperature increase is the minor factor compared to the first factor.

Generally, the rate of normal chemical reactions (with positive activation energy) doubles for every increase in temperature of 10^{o}C (or 10K).

- *The ratio of rate constants of reaction of two different temperatures which differ by 10°C* is called **temperature coefficient**.

However, it is not always true that the rate of a reaction increases with increase in **temperature.**

- Certain reactions like biological reaction which are catalysed by enzyme may be slowed down with increase in temperature since the enzyme (biological catalyst) may lose their activity at high temperature.

Catalyst

Catalyst increases the rate of reaction by giving alternative mechanism (route) of the reaction which has lower activation energy.

- Lower activation energy, means more colliding particle will have that energy and hence greater rate of reaction.

Catalyst are not consumed during the course of the reaction (at the end of the reaction, both identity and amount of the catalyst is conserved).

Nature of reactants

This can further be sub-divided into:

- Physical state of reactants and

- Chemical identity of reactants

The physical state:

Solids will react much more slowly than liquid (or aqueous solutions) and gases for example;

$K_2SO_4(s) + BaNO_3(s) \rightarrow$ No reaction while the reaction is very fast in aqueous solution.

Generally, the order of reaction rate of the three common states of matter is as follows:

$$\xrightarrow[\text{Decrease in rate of reaction}]{\text{Gas>liquid>solid}}$$

The chemical identity:

Rate of a reaction depends on the nature of bonding in the reactants.

Usually the ionic compounds (consist of ions) react faster than covalent compounds (consist of molecules).

Explanation

The reaction between ionic compounds in water occurs very fast they involve only exchange of ions, which were already separated in aqueous solutions during their dissolution. For example: AgCl is precipitated out immediately when $AgNO_3$ solution is added to NaCl.

That is:

$$\left.\begin{array}{r} AgNO_3(aq) \xrightarrow{\text{dissolve}} Ag^+(aq) + NO_3^-(aq) \\ NaCl(aq) \xrightarrow{\text{dissolve}} Na^+(aq) + Cl^-(aq) \end{array}\right\} \text{ions already present in the solution}$$

Then:

$$\underbrace{Ag^+(aq) + Cl^-(aq)}_{\text{Form } AgCl(s)} + \underbrace{Na^+(aq) + NO_3^-(aq)}_{\text{Form } NaNO_3} \rightarrow AgCl + NaNO_3(\text{ion exchange})$$

Whereas, the reaction between covalent compounds take place slowly because they require energy for the breaking the existing covalent bonds. For example, the esterification of ethanoic (acetic) acid occurs slowly since the breaking of covalent bonds present in the reactants requires energy.

Also the more bonds between reacting atoms in a molecule, the slower the reaction rate because more energy is required to break bonds in the molecule. In other words, these reactants with more bonds to break are said to have higher activation energy and hence slower rate of reaction.

Surface area

The rate of a reaction increases with increase in the surface area of solid reactant. The greater surface area exposed, the greater chance of collisions between reacting particles, hence, the reaction should proceed at a much faster rate due to the increase of the collision frequency.

- The surface area of a solid can be increased by grinding it to a fine powder. For example, the reaction between zinc and hydrochloric acid occurs within second if the zinc metal is finely powdered while the reaction will be slower when a zinc wire is used.
- This is also true with solid catalysts, which are usually employed in finely powdered form, while carrying out a chemical reaction. For example, finely powdered nickel is used during hydrogenation of alkenes.

In most cases, effect of surface area is greater than the effect of concentration and this explain why the rate of reaction between magnesium and dilute hydrochloric acid is increased more by changing magnesium from ribbon to powder than by increasing the concentration of the acid.

- The increase in surface area increases more collision frequency between reacting particles than the increase in concentration.

Intensity of light

Reactions which occur in presence of light are known as **photochemical reactions**.

- The rate photochemical reactions, increase with increase in the intensity of suitable light used. With increase in the intensity, the number of photons in light also increases. Hence more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change. For example, the rate of photosynthesis is greater on brighter (sun) days.
- However, some photochemical reactions involving the free radicals, generated in chain process are not greatly affected by the intensity of the light. Just one photon is sufficient to cause the formation of a free radial which in turn initiate a chain process in which more free radicals are formed repeatedly in each step without the need of extra photons.

Nature solvents

The solvents are used to dissolve the reactants and while doing so they help in providing more interactive surface between reactant particles which may be otherwise different phases or strongly bonded in solid phase.

- The polar molecules and ionic compound tend to dissolve more in polar solvents while non – polar molecules tend to dissolve in polar solvent.

So the reaction involving polar or ionic reactants is faster in polar solvent and slower in non – polar solvent while the reaction involving non – polar reactants is faster in non – polar solvent and slower in polar solvent.

Example 4

For each of the following statement, say whether you **agree** or **disagree** with the given argument and give brief explanation to defend your response:

(i) Every chemical reaction involving gaseous reactants is favoured by high pressure.
(ii) Exothermic reactions are always fast reactions.

Solution

(i) Agree

Explanation

High pressure means high collision frequency and hence high reaction rate.

(ii) Disagree

Even exothermic reaction may have high **activation energy** leading to slow reaction.

Example 5

For each of the following reactions, list three ways in which the rate of the reaction could be increased.

(a) $\mathrm{CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)}$
(b) $\mathrm{H_2(g) + I_2(g) \longrightarrow 2HI(g)}$
(c) $\mathrm{2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)}$

Solution

(a)

1) Using high temperature
2) Reducing particle size of $CaCO_3$ (increasing surface area of $CaCO_3$)
3) Using high concentration of $HCl(aq)$

(b)

1) Using high pressure
2) Using high temperature
3) Using high concentration of H_2(or I_2)

(c)

1) Using high temperature
2) Using high concentration of H_2O_2
3) Addition of catalyst

DIGGING DEEPER EXERCISE 9

EXERCISE 9A: BINDER QUESTIONS

Question 1

Identify two quantities that must be measured to establish the rate of a chemical reaction.

Question 2

Average rate of reaction does not give the true picture of the reaction. Explain.

Question 3

(a) What is meant by the terms;
  (i) Collision frequency
  (ii) Collision energy
  (iii) Activation energy (in terms of collision energy)
(b) How can these be changed in a chemical system?

Question 4

How the following are related to the rate of chemical reaction?

  (i) Collision frequency
  (ii) Collision energy
  (iii) Activation energy

Question 5

Describe how temperature, concentration, light, pressure and surface area can affect the rate of a chemical reaction.

Question 6

Why the rate of reaction does not remain constant throughout?

Question 7

For the reaction given below, what is the instantaneous rate for each of the reactant and product?

$3A + 2B \longrightarrow 4C$

Question 8

Explain why the rate of disappearance of NO and the rate of formation of N_2 are not the same in the reaction,

$2CO\,(g) + 2NO(g) \rightarrow 2CO_2\,(g) + N_2\,(g)$.

Question 9

For a chemical reaction $A \longrightarrow B$, it was found that concentration of B increases by $0.2\ \text{molL}^{-1}$ in half an hour. What is the average rate of reaction?

Question 10

Consider the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$

The average rate consumption of Br^- is $1.06 \times 10^{-4}\text{M/s}$ over the first two minutes, what is the average rate of formation of Br_2 during the same time interval?

Question 11

The decomposition of N_2O_5 proceeds according to the following equation;

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

If the rate of decomposing of N_2O_5 at particular instant in a reaction vessel is $4.2 \times 10^{-7}\text{M/s}$, what is the rate of appearance of: (a) NO_2 (b) O_2?

EXERCISE 9B: REAL QUESTIONS

Question 12

Why keeping foods in the fridge, prevent them from spoiling?

Question 13

It takes many days for rusting of iron to be observable although the process is highly exothermic; why?

Question 14

Dropping a light stick into hot water makes it glow more intensely. Explain.

Question 15

Oxygen is available in plenty in air, yet woods do not burn by themselves at room temperature. Explain.

Question 16

A lump of coal burns at moderate rate in air while coal dust burns explosively. Explain.

Question 17

Why does coal not burn itself in air, but once initiated by flame continues to burn. Explain.

Question 18

Akilikubwa is a laboratory technician. In an effort to find the proper way of completing the reaction between magnesium and dilute hydrochloric acid quicker, he found that the time consumed for the reaction completion becomes shorter by changing magnesium from ribbon to powder than by doubling the concentration of the acid. Explain why.

Question 19

Another day, our laboratory technician, **Akilikubwa**, was doing an experiment that involved the reaction between manganate (VII) ions, MnO_4^-, and ethanedioate ions, $C_2O_4^{2-}$, in acid solution as per the following equation:

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

He observed that the reaction starts slowly, the rate of reaction then increases, before it decreases again. Unfortunately, **Akilikubwa** was unable to make sense of this sequence. Offer the desired help to our technician!

EXERCISE 9C: HOT QUESTIONS

Question 20

Although the reaction between H_2 (g) and O_2 (g) is highly feasible, leaving the gases in the same vessel at room temperature does not result in the creation of water. Explain.

Question 21

Consider a hypothetical reaction; P ⟶ Q;

Average rates for the reaction was determined after 30min and 60min and found to be 0.08M/min and 0.03M/min respectively. Account for the difference of the average rates.

Question 22

Even a reaction with large number of colliding reactant molecules which have attained activation energy may be slow. Explain.

Question 23

The activation energy for forward and backward reactions for a hypothetical reaction, P ⟶ Q; are 15 kJ/mol and 9 kJ/mol respectively. Potential energy of P is 10 kJ/mol. Predict:

(a) Threshold energy of the forward reaction.
(b) Potential energy of Q.
(c) Heat of reaction.

Question 24

Potassium superoxide(KO_2) is used to produce oxygen according to the following equation

$4KO_2(s) + 2H_2O\ (l) \longrightarrow 4KOH(aq) + 3O_2(g)$

When a sample of KO_2 was placed in water in an open flask, the following data was collected

Time in s	Mass of flask and content in g
0.0	150.00
30.0	145.50

Calculate;

(a) The rate of O_2 production in grams of O_2 per second
(b) The mass of KO_2 that reacted.(Atomic masses:$O = 16, K = 39.1$)

Question 25

Consider the following reaction: $2Al(s) + 3CuCl_2(aq) \longrightarrow 2AlCl_3(aq) + 3Cu(s)$

If the rate of consumption of Al is 0.46g/min, how many minutes will it take to produce 0.89g of Cu?

Chapter 10

ORDER OF CHEMICAL REACTIONS

GULDBERG AND WAAGE'S RATE LAW

In the previous chapter, we have seen that, commonly reaction rate increases as the concentration of reactants increases. However experimentally it has been found that the relationship between reaction rate and concentration is not always linear; doubling the concentration may increase reaction rate, two times (linear relationship) our four times or even eight times! The **rate law** (also known as **Guldberg and waage's rate law** in honour of people who discovered it) help us to understand specific *relationship between reaction rate and concentration of reactants*.

Guldberg and waage's rate law or simply **rate law** gives mathematical relationship between rates of reactions and concentrations of reactants and the law state that, *''the rate of reaction is directly proportional to the concentration of reactants each raised to its respective order."*

To understand the law, consider the reaction between reactants A and B such that: $\mathrm{A + B \rightarrow\ P}$

From the rate law: $\mathrm{R \propto [A]^m[B]^n}$

Introducing the constant of proportionality, the relationship become: $\mathrm{R = k[A]^m[B]^n}$

And the result is known as the **rate law (**or **differential rate equation** or simply **rate equation** or **expression)** for the reaction between A and B to form P.

Where:

R $=$ **Rate of the reaction**

k $=$ **Rate constant or velocity constant or rate coefficient.**

m $=$ **Order of the reaction with respect to A**

n $=$ **Order of the reaction with suspect to B**

And $\mathrm{m + n}$ is the **overall order of the reaction** (it results from **partial orders of reaction** which are m and n).

The rate law may or may not include concentration of all the reactants. Sometimes, the rate law may include the concentration of species like catalysts, which do not appear in their stoichiometric equations.

By definition:

Rate law *is the differential equation that describes the mathematical dependence of rate of reaction on the concentration terms of the reactants.*

Order of the reaction *is powers (exponents) of concentration of reactants in the rate law.*

Order of the reaction describes the extent of which the concentration of particular reactant affects the rate of chemical reaction.

- If the order of the reaction with respect to a reactant is greater than that of another reactant, then the rate of chemical reaction is affected more by changing of the concentration of the reactant than that of another.
- That is if rate law is $\mathrm{R = k[A]^m[B]^n}$ and m > n then changing concentration of A has more effect on the rate of the reaction (value of R) than changing concentration of B.
- If the order of the reaction with respect to the particular reactant is zero, then changing concentration of the reactant has no effect on the rate of the reaction.

Overall order of the reaction is the sum of powers (exponents) of concentration of reactants in the rate law.

Overall order of the reaction expresses the extent to which the rate of the chemical reaction is affected by changing of concentration of reactants.

- If the overall order of one reaction is greater than that of another, then the rate of the reaction is affected more by changing concentration of its reactants than another reaction does.

That is if the rate law of first reaction is:$R_1 = k_1[A_1]^m[B_1]^n$

Where overall order of the reaction is m + n

And the rate law of second reaction is: $R_2 = k_2[A_2]^x[B_2]^y$

Where overall order of the reaction is $x + y$

Then if: $(m + n) > (x + y)$, the rate of first reaction has more dependence on concentration of reactants than the second reaction does.

- If the overall order of a reaction is zero, then the rate of the chemical reaction is not affected by changing in concentration of the reactants. For example, **when the reactant presents in excess, further increase in concentration of the reactant has no effect on the rate of the reaction and hence the reaction is always of zero order with respect to the excess reactant.**

The order of reaction may have positive, negative or zero values.

- The order with respect to an individual reactant may be sometimes fractional. However, the order of the overall reaction is usually an integer.

If the overall order of chemical reaction is:

- **Zero** then the reaction is termed as **zero order chemical reaction**.
- **One** then the reaction is termed as **first order chemical reaction**.
- **Two** then the reaction is termed as **second order chemical** reaction etc.

Very important to understand that:

For most chemical reactions order of the reaction can never be predicted from their balanced chemical equations. Determination of order of the reaction is experimental work.

Rate constant or **velocity constant** or **rate coefficient** *is a temperature dependent fixed factor which gives the relationship between rate of the reaction and concentration of reactants.* This is the qualitative definition of the constant.

Quantitatively, rate constant may be defined as:

The temperature dependent fixed factor which is given as a ratio of the rate of the reaction to concentration of reactants raised to their respective order.

That is if; $R = k[A]^m[B]^n$; then $k = \frac{R}{[A]^m[B]^n}$ where k is rate constant

So **rate constant** *is the **specific rate** of a reaction at the unit concentration of all the reactants of the reaction* and hence the term **specific rate** for the rate constant.

That is, if the rate law is, $R = k[A]^m[B]^n$

It clearly understand that, when $[A] = [B] = 1M$ (unit concentration)

$$R = k \times 1^m \times 1^n = k$$

And hence R = k for unit concentration of all the reactants.

Units of rate constant

Consider **nth** order chemical reaction with the following rate law:

$$R = k[A]^n$$

If follows that:

Units of R = units of k $\times$ (units of [A])^n

From which, units of k = $\frac{\text{units of R}}{(\text{units of [A]})^n}$

Substituting units of k = $\frac{\text{moldm}^{-3}\text{s}^{-1}}{(\text{moldm}^{-3})^n} = (\text{moldm}^{-3})^{1-n}\text{s}^{-1}$

Hence unit of rate constant for the reaction is $(\mathbf{moldm^{-3}})^{\mathbf{1-n}}\mathbf{s^{-1}}$ where n is the overall order for the reaction.

Example 1

The rate constant for certain reaction is $0.01282\text{Lmol}^{-1}\text{sec}^{-1}$. What is the order of the reaction?

Solution

The unit of rate constant for the reaction of nth order is given by $(\text{molL}^{-1})^{1-n}\text{s}^{-1}$

Thus, $\text{Lmol}^{-1}\text{s}^{-1} = (\text{molL}^{-1})^{1-n}\text{s}^{-1}$ or $\text{Lmol}^{-1} = (\text{molL}^{-1})^{1-n}$

It follows that $(\text{molL}^{-1})^{-1} = (\text{molL}^{-1})^{1-n}$ or $-1 = 1 - n$ or $n = 2$

Hence the reaction is of the second order.

CHEMICAL REACTIONS OF ZERO ORDER

Most reactions involving a single reactant show either first order or second order kinetics. However, sometimes such a reaction can be a zero order reaction. Chemical reactions of zero order are not common reactions; are rare, but they exist. Example of zero order reaction is the decomposition of ammonia (NH_3) or hydrogen iodide (HI) on metal surface such as gold.

In zero-order reaction, the rate of reaction is not affected by the change of concentration of reactant and thus the reaction rate remain constant throughout the reaction process in contradiction to what we had studied in the introduction of the previous chapter. The graph of rate against time is horizontal while that of concentration of reactant against time is the straight line (not a curve!) with negative slope as illustrated below.

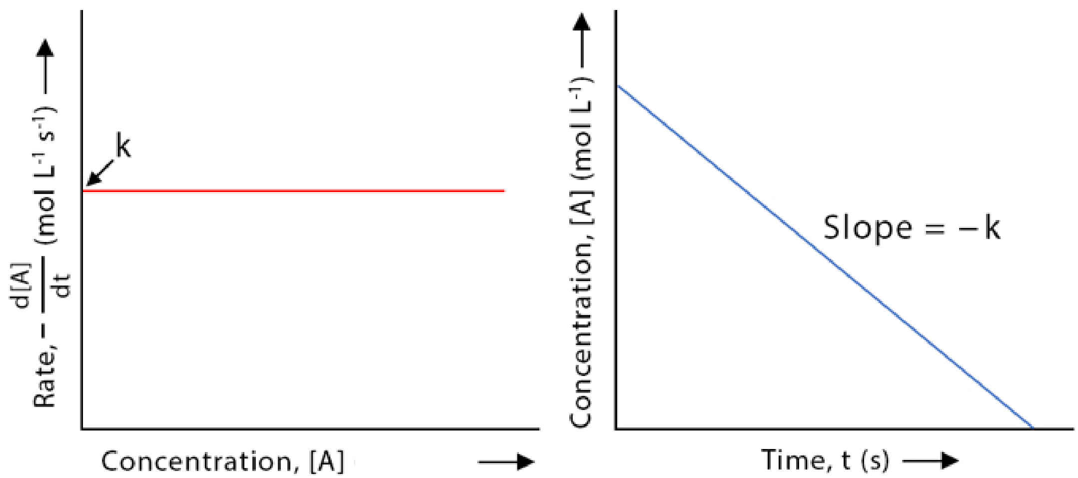


Figure 10.1: Graphs for zero order reaction

Integral equation for zero order chemical reaction

Consider the following zero order chemical reaction in which a reactant, A, reacts to give a product, P.

That is: A → P

a	0	Initial concentration at $t = 0$
$a - x$	x	Concentration after time, t

From the rate law: $R = k[A]^n$ (Where [ ] stands for molar concentration in mol/dm^3)

But for the zero order chemical reaction, $n = 0$

Thus the rate law (differential rate equation) of the reaction becomes: $R = k$

$$\text{Using Rate, } R = \frac{\text{change in concentration}}{\text{change in time}} = \frac{-d[A]}{dt}$$

(The negative sign indicate that the concentration is continuously decreasing as the reaction proceed)

But $-\frac{d[A]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$

Substituting $\frac{dx}{dt}$ for R in $R = k$, gives $\frac{dx}{dt} = k$

Then $\frac{dx}{dt} = k$ or $dx = kdt$ ……………………………………… (i)

Integrating throughout the equation (i) $\int dx = \int kdt$ or $x = kt + c$

When $t = 0$ and $x = 0$

Hence $\mathbf{x = kt}$……………………………………………………(ii)

Now let:

$a - x = [A]_t$ (concentration of A present after anytime, t.

And $a = [A]_o$ (Initial concentration of A at the reaction beginning)

Then $[A]_t = [A]_o - x$ or $x = [A]_o - [A]_t$……………………..(iii)

Substituting (iii) into (ii) gives;

$$[A]_o - [A]_t = kt \text{ or } [A]_t = -kt + [A]_o$$

Hence integral equation for zero order chemical reaction is $\mathbf{[A]_t = -kt + [A]_o}$

Where:

$[A]_o$ is the initial concentration of the reactant.

$[A]_t$ is the concentration of the reactant remained after any time, t.

k is the rate constant (or velocity constant).

Units of rate constant for zero order reactions

Consider the first order chemical reaction with the following rate law: $R = k$

It follows that: Units of R = units of k

But units of R= $\text{moldm}^{-3}\text{s}^{-1}$

Hence units of rate constant for zero order reactions is $\text{moldm}^{-3}\text{s}^{-1}$

Half-life of zero order chemical reactions

The half-life of a reaction, $t_{½}$ *is the time required for the concentration of the reactant(s) to be reduced to a half of its initial concentration of the reactant (s) to react.*

For zero order chemical reaction, it has been shown that; $\mathbf{x = kt}$

But when $t = t_{1/2}$, $x = a/2$ (where a is initial concentration of reactant and $t_{1/2}$ is the half-life)

Thus $a/2 = kt_{1/2}$ or $t_{1/2} = \frac{a}{2k}$

Hence for zero order chemical reaction: $\mathbf{t_{1/2}} = \frac{\mathbf{a}}{\mathbf{2k}}$

Thus the half-life for the zero order reaction increases at exact proportional as an increase in initial concentration of the reactant. For example, if the initial concentration is doubled, the half-life will double too or if the concentration is increased by a factor of 5, the half-life will increase by the same factor.

Time for completion of zero order chemical reaction

From the integral rate equation of zero order reaction: $[A]_t = -kt + [A]_o$

Upon reaction completion, the reactant is entirely consumed and therefore $[A]_t = 0$

Substituting $0 = -kt + [A]_o$ or $t = \frac{[A]_o}{k}$

Hence **the zero order reaction can reach completion** and the time required to have zero concentration of reactant is given by;

$$\mathbf{t} = \frac{\mathbf{[A]_o}}{\mathbf{k}}$$

Example 2

In the reaction, A → products, with the initial concentration, $[A]_o = 1.512\ M$, [A] is found to be 1.496M at t = 30s. With the initial concentration $[A]_o = 2.584M$, [A] is found to be 2.552M at t = 1min. What is the order of this reaction?

Using; average rate $= \frac{\text{change in concentration}}{\text{time taken}} = \frac{C_{t_2} - C_{t_1}}{t_2 - t_1}$

Then using first set of values; average rate, $R_1 = \frac{(1.512-1.496)M}{(30-0)S} = 5.33 \times 10^{-4} M/s$

And from second set of values; average rate, $R_2 = \frac{(2.584-2.552)M}{(60-0)s} = 5.33 \times 10^{-4} M/s$

Since the reaction rate remained the same even after changing initial concentration, the order of the reaction is zero order.

Example 3

The decomposition of hydrogen iodide on gold at 323K is zero order reaction and the rate constant is $1.2 \times 10^{-4} Ms^{-1}$.

(a) If the initial concentration of hydrogen iodide is 0.5M, calculate its concentration after 3×10^3s.

(b) How long will it take for all of the hydrogen iodide to decompose?

Solution

(a) Using integral rate equation for zero order reaction; $[A]_t = -kt + [A]_o$

Substituting $[A]_t = (-1.2 \times 10^{-4} Ms^{-1} \times 3 \times 10^3 s) + 0.5M = 0.14M$

The concentration is 0.14M

(b) The time required is given by; $\mathbf{t} = \frac{\mathbf{[A]_o}}{\mathbf{k}}$

Substituting $t = \frac{0.5M}{1.2 \times 10^{-4} Ms^{-1}} = 4.17 \times 10^3 s$

The time required is 4.17×10^3s.

CHEMICAL REACTIONS OF FIRST ORDER

First order chemical reaction *is the reaction whose summation of powers (exponents) in the rate law is one.* Thus in the chemical reaction of the first order, the rate of chemical reaction increases at equal times as the increase in the concentration e.g. if the concentration of the reactant is doubled the rate of chemical reaction is also doubled. Most of first order chemical reactions are **decomposition reactions** e.g. decomposition of hydrogen peroxide (H_2O_2) into water and oxygen gas. All radioactive disintegrations are first order reactions.

Relationship between the initial concentration of the reactant and time for forming given amount of product in the first order chemical reaction

The rate of first order reaction varies directly proportional to the concentration of the reactant (raised to one).

Thus if: R is the rate of the reaction and C is the original concentration of the reactant.

Then $R \propto C$

Introducing constant of proportionality: $R = kC$

From which: $\frac{R}{C} = k$

Therefore $\frac{R_1}{C_1} = \frac{R_2}{C_2} = k$ or (by rearranging the equation) $\frac{R_1}{R_2} = \frac{C_1}{C_2}$

But the rate of the chemical varies inversely to the time taken for the reaction to take place.

Thus if *t* is the time taken for the reaction to form given amount of product:

$$R \propto \frac{1}{t} \quad \text{or } R = \frac{k}{t}; \quad \text{then } \frac{R_1}{R_2} = \frac{k/t_1}{k/t_2} = \frac{t_2}{t_1}$$

Substituting $\frac{R_1}{R_2} = \frac{t_2}{t_1}$ in $\frac{R_1}{R_2} = \frac{C_1}{C_2}$ gives $\frac{t_2}{t_1} = \frac{C_1}{C_2}$ From which $C_1t_1 = C_2t_2$

Hence for first order chemical reaction; $\mathbf{Ct = constant}$

i.e. $C_1t_1 = C_2t_2 = C_3t_3 = \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. = C_nt_n$

Where C is the initial concentration of the reactant

t is the time taken for the reaction to form given amount of product.

Integral equation for first order chemical reaction

Most of the first order chemical reactions have single reactants.

So they in the form of: A → P

a	0	Initial concentration at $t = 0$
$a - x$	x	Concentration after time, t

From the rate law: $R = k\,[A]^n$

But for the first order chemical reaction, $n = 1$

Thus the rate law (differential rate equation) of the reaction becomes: $R = k\,[A]$

Where [ ] stands for molar concentration in mol/dm^3

$$\text{Using Rate, } R = \frac{\text{change in concentration}}{\text{change in time}} = \frac{-d[A]}{dt}$$

(The negative sign indicate that the concentration is continuously decreasing as the reaction proceed)

But $-\frac{d[A]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$

Substituting $\frac{dx}{dt}$ for R in $R = k[A]$ gives $\frac{dx}{dt} = k[A]$

But [A] after any time, t is $(a-x)$

Then $\frac{dx}{dt} = k(a-x)$ or $\frac{dx}{(a-x)} = kdt$ ……………………………………………… (i)

Integrating throughout the equation (i) $\int \frac{dx}{(a-x)} = \int kdt$ or $-\ln(a-x) = kt + c$

When $t = 0$ and $x = 0$; then $-\ln(a-x) = k \times 0 + c$; from which $c = -\ln a$

Thus $-\ln(a-x) = kt - \ln a$ or $\ln a - \ln(a-x) = kt$

Then $\ln\left(\frac{a}{a-x}\right) = kt$

And by changing natural logarithm to common logarithm the equation become;

$2.303\log\left(\frac{a}{a-x}\right) = kt$

Hence for first order chemical reaction: $\mathbf{\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}}$

Where:

a is the initial concentration of the reactant

x is the concentration of the reactant decreased (reacted) after any time, t

$(a-x)$ is the concentration of the reactant remained after any time, t

k is the rate constant (or velocity constant)

You should understand that:

The ratio; $\left(\frac{a}{a-x}\right)$ in the above first order equation allows to substitute partial pressure (for gas phase reaction) of the reactant instead of its concentration. This can be clearly shown as follows:

From an ideal gas equation: $PV = nRT$ or $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V}$ = Molar concentration, [ ]

Thus $P = [\ \ ]RT$, from which; $[\ \ ] = \frac{P}{RT}$ then $a = \frac{P_o}{RT}$ and $(a-x) = \frac{P_o - P}{RT}$

Thus $\frac{a}{a-x} = \frac{P_o}{RT} \div \frac{P_o - P}{RT} = \frac{P_o}{P_o - P}$

Substituting $\frac{P_o}{P_o - P}$ for $\frac{a}{a-x}$ in the obtained first order equation gives:

$\mathbf{\log\left(\frac{P_o}{P_o - P}\right) = \frac{kt}{2.303}}$ in terms of partial pressure of the reactant

Where: P_o is the initial pressure of the reactant before the reaction starts,

P is the decrease in pressure after any time, t of the reaction,

$P_o - P$ is the recoded pressure after any time, t of the reaction (pressure of the reactant which remains after any time, t).

Units of rate constant for first order reactions

Consider the first order chemical reaction with the following rate law: $R = k[A]$

It follows that: Units of R = units of k × units of [A]

From which, unit of k = $\frac{\text{unit of R}}{\text{unit of [A]}}$

Then substituting units of k = $\frac{\mathrm{moldm^{-3}s^{-1}}}{\mathrm{moldm^{-3}}} = \mathrm{s^{-1}}$

Hence units of rate constant for first order reaction is $\mathrm{s^{-1}}$ (or $\mathrm{min^{-1}}$, $\mathrm{hr^{-1}}$etc., depending on unit used for measuring time).

Half-life of first order chemical reactions

The half-life equation for fist order reaction can be derived from the first order equation as follows: From $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$; $t = \frac{2.303}{k}\log\left(\frac{a}{a-x}\right)$: When $t = t_{1/2}, x = a/2$

Thus $t_{1/2} = \frac{2.303}{k}\log\left(\frac{a}{a-a/2}\right) = \frac{2.303}{k}\log 2 = \frac{0.693}{k}$

Hence the half life for the first order chemical reactions is given by: $\mathbf{t_{1/2} = \frac{0.693}{k}}$

Thus the half-life for the first order reaction is always constant and does not depend on initial concentration of the reactants.

Understand this interesting fact!

Not only the time required for a half of reactant to react (or to remain) which is constant but the rule holds for any fraction amount, whether it is $t_{1/4}, t_{3/4}, t_{2/3}$ etc. To understand this, consider the following general scenario;

Let us assume **f** represents fraction of initial concentration of reactant that remains after anytime, t.

Then $f = \frac{a-x}{a}$ or $a - x = af$

Then the equation $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ becomes;

$\log\left(\frac{a}{af}\right) = \frac{kt}{2.303}$ or $\log\left(\frac{1}{f}\right) = \frac{kt}{2.303}$

From which; $t = \frac{2.303}{k}\log\frac{1}{f}$ or $\frac{-2.303}{k}\log f$

Hence the time required (t) for any fraction of reactant (f) to remain is given by;

$$\mathbf{t = \frac{-2.303}{k}\log f}$$

From the above equation, there is no term for initial concentration and thus it is clearly understood that the time required for the given fraction amount of reactant to remain (or react) is constant at given temperature.

Also from the above equation, the equation of half-life can be easily deduced as follows:

If $t = t_{1/2}, f = \frac{1}{2}$

Then our bolded equation becomes;

$t_{1/2} = \frac{-2.303}{k}\log\frac{1}{2} = \frac{0.693}{k}$ (As we have seen earlier)

Time for completion of first order chemical reaction

From the integral rate equation of first order reaction: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

Upon reaction completion, the reactant is entirely consumed and therefore $x = a$ and $a - x = 0$

Substituting $\log\left(\frac{a}{0}\right) = \frac{kt}{2.303}$ or $t = \frac{2.303}{k}\log^{-1}\left(\frac{a}{0}\right)$

Since $\log^{-1}\left(\frac{a}{0}\right)$ is undefined , the value of t is undefined (cannot be found) too and hence **the first order reaction can never reach completion by 100% and the concentration of reactant cannot be exactly zero (will be zero at infinite time)!**

Example 4

Consider a first order reaction: A $\rightarrow$ P

The rate constant at 298K is $2 \times 10^{-3}\ \text{sec}^{-1}$. If the initial concentration of A is 0.8M, calculate:

(i) Amount of A present after 9 minutes of the reaction
(ii) The percentage of A which has reacted after 100 seconds
(iii) The time required for 60% to react.

Solution

Using the equation

$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ where $k = 2 \times 10^{-3}$, $t = 9\text{minutes} = 9 \times 60\text{sec} = 540\text{sec}$

Then $\log\left(\frac{a}{a-x}\right) = \frac{2 \times 10^{-3} \times 540}{2.303} = 0.47;\ \frac{a}{a-x} = \log^{-1}(0.47) = 2.95$

Then $(a-x) = \frac{a}{2.95} = \frac{0.8}{2.95} = 0.27\text{M}$

(i) Amount of A after 9 minutes of the reaction is 0.27M

Using: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

When $\mathbf{t = 100sec}$

$\log\left(\frac{a}{a-x}\right) = \frac{2 \times 10^{-3} \times 100}{2.303} = 0.0868;\ \frac{a}{a-x} = \log^{-1}(0.0868) = 1.2212$

Then $\frac{a-x}{a} = \frac{1}{1.2212} = 0.8189$

Thus the percentage of A remained after 100s is $0.8189 \times 100\% = 81.89\%$

(ii) Hence the percentage of A reacted is $(100 - 81.89)\% = 18.11\%$

From $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

$\log\left(\frac{a-x}{a}\right)^{-1} = \frac{kt}{2.303}$

Then $-\log\left(\frac{a-x}{a}\right) = \frac{kt}{2.303}$ or $\log\left(\frac{a-x}{a}\right) = \frac{-kt}{2.303}$

But it is given that: 60% of A reacted

Thus $\frac{a-x}{a} \times 100\% = 40\%$ (Amount of A remained $= 100\% - 60\% = 40\%$)

Then substituting $\frac{a-x}{a} = 0.4$ and $k = 2 \times 10^{-3}\text{sec}^{-1}$ to $\log\left(\frac{a-x}{a}\right) = \frac{-kt}{2.303}$;

It gives: $\log 0.4 = \frac{-2 \times 10^{-3}t}{2.303}$ or $t = 458\text{sec}$

(iii) Hence the time required for 60% to react is 458seconds.

Example 5

A certain first order reaction has a half – life of 20 minutes:

(i) What is the rate constant for the reaction?
(ii) How long will it take for this reaction to be 75% complete?

Solution

For first order reaction, the half life $\left(t_{1/2}\right)$ is given by: $t_{1/2} = \frac{0.693}{k}$

From which $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20\text{min}} = 0.03465\text{min}^{-1}$

(i) Thus the rate constant is 0.03465min^{-1}

Using $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

Where:

$a = 100$

$a - x = 25$ ((100 − 75) as the reaction is 75% complete)

t = time taken for the reaction to be 75%complete

k = Rate constant = $0.03465\ \text{min}^{-1}$

Substituting $\log\left(\frac{100}{25}\right) = \frac{0.03465t}{2.303}$; from which $t = 40$

(ii) Thus it will take 40 minutes for the reaction to be 75% complete.

Example 6

The first-order rate constant for the decomposition of N_2O_5 sat 67°C is $5.2 \times 10^{-3}s^{-1}$.

(a) Calculate the time required for the concentration of N_2O_5 to fall to 50% of its initial concentration
(b) Without doing any further calculation, determine the time required for the concentration of N_2O_5 to decrease to one-fourth of its initial value.

Solution

(a) The time required for the reactant to fall to 50% is the half-life.

The half life $\left(t_{1/2}\right)$ is given by: $t_{1/2} = \frac{0.693}{k}$

Substituting $t_{1/2} = \frac{0.693}{5.2\times10^{-3}s^{-1}} = 133s$

The time required is 133s

(b) Since for the first order reaction, half-life is independent to initial concentration, the time required for the concentration to decrease to one-half (50%) is the same as the time required to decrease the concentration from one-half to one-fourth (25%). Hence the time required for the decrease in the concentration of N_2O_5 to 25% of its initial value is twice the half-life, that is 266s.

Question 7

After five half-life periods for a first order reaction, calculate fraction of reactant that remains?

Solution

Single period half-life of first order reaction is given by: $t_{1/2} = \frac{0.693}{k}$

But for first order reaction, half-life is the same irrespective to initial concentration.

Thus total time after five periods, $t = 5t_{1/2} = \frac{5\times0.693}{k} = \frac{3.465}{k}$

Then using; $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$;

$\log\left(\frac{a}{a-x}\right) = \frac{k \times 3.465}{2.303 \times k} = 1.5046$

From which; $\frac{a}{a-x} = \log^{-1}(1.5046) = 32$

Fraction that remains $= \frac{a-x}{a} = \frac{1}{\frac{a}{a-x}} = \frac{1}{32}$

Hence the fraction is $\frac{1}{32}$

CHEMICAL REACTIONS OF SECOND ORDER

Second order chemical reaction is the reaction whose summation of powers (exponents) in the rate law is two. A good example of second order reaction is the decomposition of nitrogen dioxide(NO_2) to nitrogen monoxide (NO) and oxygen (O_2).

Most of the second order reactions have two reactants of the following form: $A + B \rightarrow P$

Relationship between the initial concentration of the reactant and time for forming given amount of product in the second order reaction

The rate of second order reaction varies directly proportional to the square of concentration of the reactant.

Thus if: R is the rate of the reaction and C is the original concentration of the reactant.

Then $R \propto C^2$

Introducing constant of proportionality: $R = kC^2$

From which: $\frac{R}{C^2} = k$

Therefore $\frac{R_1}{(C_1)^2} = \frac{R_2}{(C_2)^2} = k$ or (by rearranging the equation) $\frac{R_1}{R_2} = \frac{(C_1)^2}{(C_2)^2}$

But the rate of the chemical varies inversely to the time taken for the reaction to take place.

Thus if t is the time taken for the reaction to form given amount of product:

$R \propto \frac{1}{t}$ or $R = \frac{k}{t}$; then $\frac{R_1}{R_2} = \frac{k/t_1}{k/t_2} = \frac{t_2}{t_1}$

Substituting $\frac{R_1}{R_2} = \frac{t_2}{t_1}$ in $\frac{R_1}{R_2} = \frac{(C_1)^2}{(C_2)^2}$ gives $\frac{t_2}{t_1} = \frac{(C_1)^2}{(C_2)^2}$

From which $(C_1)^2 t_1 = (C_2)^2 t_2$

Hence for second order chemical reaction; $\mathbf{C^2 t = constant}$

Where C is the initial concentration of the reactant

t is the time taken for the reaction to form given amount of product.

Integral equation for second order chemical reaction

Consider A and B with the same concentration say "a" react together to form P according to the following equation:

	A	+	B	→	P
Initially (At t = 0)	a		a		0

After any time, t $\qquad a - x \quad a - x \qquad x$

From the rate law: $R = k[A][B]$
Let $m = n = 1$ Such that $m + n = 2$ (for the second order chemical reaction)

Then the rate law of the reaction becomes: $R = k[A][B]$

But $R = -\frac{d}{dt}[A] = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$

But from the rate law: $R = k[A](B) = k(a - x)(a - x) = k(a - x)^2$

Thus $\frac{dx}{dt} = k(a - x)^2$ or $\frac{dx}{(a-x)^2} = k dt$

Then $\int \frac{dx}{(a-x)^2} = \int kdt$ or $(a - x)^{-1} = kt + c$ or $\frac{1}{(a-x)} = kt + c$

When $t = 0, x = 0$ then $c = \frac{1}{a}$

Thus $\frac{1}{(a-x)} = kt + \frac{1}{a}$ or $\frac{1}{(a-x)} - \frac{1}{a} = kt$

$$\frac{a - (a - x)}{a(a - x)} = kt$$

Hence for second order chemical reaction: $\frac{x}{a(a-x)} = kt$

Where:

a is the initial concentration of the reactant

x is the decrease in concentration of the reactant at any time, *t*

$(a - x)$ is the concentration of the reactant at any time, *t*

k is the rate constant of chemical reaction.

Note:

The above formula holds for second order reaction with single reactant only or for mixed reactants of the type $aA + bB \longrightarrow$ product, if and only if $a[A]_o = b[B]_o$ or $[A]_o = [B]_o$ if $a = b$.

The discussion of the integral rate equation of the type $aA + bB \longrightarrow$ product where $a[A]_o \neq b[B]_o$ is beyond the scope of this book.

Units of rate constant for second order chemical reaction

Consider the second order chemical reaction with the following rate law: $R = k[A]^2$

It follows that: Unit of R = unit of $k \times (\text{unit of }[A])^2$

From which, unit of k = $\frac{\text{unit of R}}{(\text{unit of }[A])^2}$

Then substituting units of k = $\frac{moldm^{-3}s^{-1}}{(moldm^{-3})^2} = (moldm^{-3})^{-1}s^{-1}$ or $dm^3mol^{-1}s^{-1}$

Hence units of rate constant for first order reaction is $(moldm^{-3})^{-1}s^{-1}$ or $dm^3mol^{-1}s^{-1}$

(In place for s^{-1}, min^{-1}, hr^{-1}etc., may be used depending on unit used for measuring time).

Half-life for second order chemical reaction

If the time taken for the reaction to proceed is the half life $t_{1/2}$ then $x = \frac{a}{2}$

So from $kt = \frac{x}{a(a-x)}$

$t_{1/2} = \frac{a/2}{a(a-a/2)} = 1/a$

$t_{1/2} = \frac{1}{ak}$

Hence the half-life for the second order chemical reaction is given by $t_{1/2} = \frac{1}{ak}$

Where 'a' is the initial concentration of the reactant and *k* is the rate constant

Thus unlike the first order chemical reaction whose half-life is independent to initial concentration, *the half-life of the second order chemical reaction depends on the initial concentration of the reactant and it is inversely proportional to the initial concentration. For example, when concentration is halved, half-life will be doubled.*

Again!

The rule holds for any fraction amount. For better understanding, consider the following general scenario;

Again, let **f** represents fraction of initial concentration of reactant that remains after anytime, t.

Then $f = \frac{a-x}{a}$ or $a - x = af$

Then the equation $kt = \frac{x}{a(a-x)}$ becomes;

$kt = \frac{x}{a\times af}$ or $kt = \frac{x}{a^2f}$ or $t = \frac{x}{a^2kf}$

But from $a - x = af; x = a - af = a(1 - f)$

Then $t = \frac{a(1-f)}{a^2kf} = \frac{(1-f)}{akf}$

Hence the time required (t) for any fraction of reactant (f) to remain is given by;

$$\mathbf{t = \frac{(1-f)}{akf}}$$

From the above equation, there is a term for initial concentration and thus it is clearly understood that the time required for the given fraction amount of reactant to remain (or react) depends on the initial concentration of the reactant and it is inversely proportional to the initial concentration.

Also from the above equation, the equation of half-life can be easily deduced as follows:

If $t = t_{1/2}, f = \frac{1}{2}$

Then the above equation becomes;

$t_{1/2} = \frac{(1-\frac{1}{2})}{ak\times\frac{1}{2}} = \frac{1}{ak}$ (As we have seen earlier)

Time for completion of second order chemical reaction

From the integral rate equation of second order reaction: $kt = \frac{x}{a(a-x)}$

Upon reaction completion, the reactant is entirely consumed and therefore $x = a$ and $a - x = 0$

Substituting $kt = \frac{x}{a\times 0}$ or $t = \frac{x}{0}$

Since $\frac{x}{0}$ is undefined, the value of t is undefined (cannot be found) too and hence like first order reaction, **the second order reaction can never reach completion by 100% and the concentration of reactant cannot be exactly zero!**

Pseudo first order reactions

When a reaction is known to follow a rate of higher order than 1, concentration can often be adjusted to make the kinetics appear first order. To understand these, consider the reaction,

$$2A + B \longrightarrow C;$$

with the rate law: $R = \frac{-1}{2}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = k[A][B]$

This rate law is second order in overall and is rate constant unit is $M^{-1}s^{-1}$.

But if we run the reaction with a very large excess of B, say $[B]_o = 100[A]_o$ (where $[B]_o$ and $[A]_o$ stands for initial concentration of B and A respectively), then $[B]$ will change very little during the reaction; it will be nearly equal to $[B]_o$ the whole time.
That is if B present in excess;

$$[B] = \text{constant}$$

Then the equation $R = k[A][B]$ becomes;

$$R = k[A] \times \text{constant}$$

Where $k \times$ constant gives another constant, say k'

Hence we can write: (if B present in excess)

$$R = k'[A] \text{ (Where } k' = k[B])$$

Where $\mathbf{R = k'[A]}$ is known as **pseudo first order rate law**, (**Pseudo** comes from Greek meaning *pretended* or *fake*)

$\mathbf{k'}$ is the **pseudo rate constant** with unit, s^{-1}.

And the reaction $2A + B \longrightarrow C$ is now said to be **pseudo first order reaction**.

By definition

A pseudo first order reaction *is the reaction that is truly second order but can be approximated to be the first order when one the reactant present so much in excess.*

Most of hydrolysis reactions like hydrolysis of ester are pseudo first order reactions because in these reactions water presents in so large amount that its change in concentration can be ignored.

Example 8

The rate constant for the second order chemical reaction: $2NOBr \rightarrow 2NO + Br_2$ is $0.8\ mol^{-1}\ dm^3\ sec^{-1}$ at 283K starting with initial concentration of 0.088 $mol\ dm^{-3}$ in NOBr. Calculate concentration of NOBr after 20 seconds of the reaction

Solution

From the second order equation: $\frac{x}{a(a-x)} = kt$

Substituting given values: $\frac{x}{0.088(0.088-x)} = 0.8 \times 20$ or $x = 0.0515$

The concentration of NOBr remained

$= a - x = (0.088 - 0.0515)moldm^{-3} = 0.0365moldm^{-3}$

Hence concentration of NOBr after 20seconds is $0.0365moldm^{-3}$

METHODS OF DETERMINING ORDER OF CHEMICAL REACTION

Generally, the order of the reaction can be determined from experimental data by various methods. Important methods which we are going to discuss in this book are four, namely:

- Graphical method
- Half-life method
- Integral rate equation method (calculation of the rate constant method).
- Initial rate method

Among the four methods, the graphical method and the integral method are done by trial and error and hence the two methods are collectively known as trial and error method.

Graphical method

For reactions which involve only one reactant, we can determine the reaction order by checking whether a graph of the data fits in one of the integral rate equations.

For the first order reaction

From the first order integral equation: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

The equation can be rearranged as follows: $\log a - \log(a - x) = \frac{kt}{2.303}$

From which, $\mathbf{\log(a - x) = \frac{-kt}{2.303} + \log a}$

The final equation corresponds to the equation of the straight line graph of the form of;

$\mathbf{y = mx + c}$

With:

y corresponds to $\mathbf{\log(a - x)}$

x corresponds to **t**

m (slope) corresponds to $\frac{-\mathbf{k}}{2.303}$ (The graph has negative slope)

y-intercept corresponds to **log a**

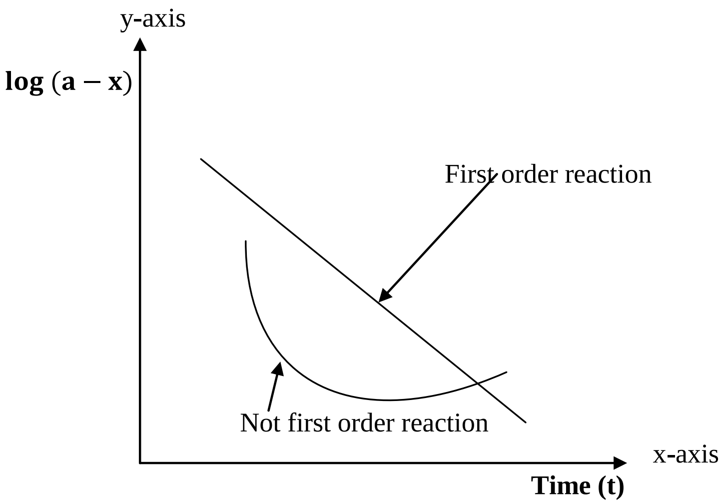


Figure 10.2 Graph of logarithm of concentration of reactant against time of the reaction

For the second order reaction

Here we are going to use this form of the second order integral equation; $\frac{1}{(a-x)} = kt + \frac{1}{a}$

Thus the graph of $\frac{1}{(a-x)}$ against t has the following characteristics (for the second order chemical reaction).

- The graph is straight line
- The slope of the graph, m is equal to the rate constant, k
  That is $m = k$
- The y- intercept, *c* is equal to reciprocal of the original concentration
  That is: $c = \frac{1}{a}$

The reader should be aware with the fact that:

The graph can also be plotted by applying rate law. For the first order reaction, the rate law; $\mathbf{R = k[A]}$ will be used and the rate equation corresponds to the equation of straight line of the form of $\mathbf{y = mx}$ with positive slope which corresponds to the rate constant (**k**) of the reaction when the graph of **Rate (y)** is plotted against **concentration (x)**. The graph also passes through the origin as illustrated below:

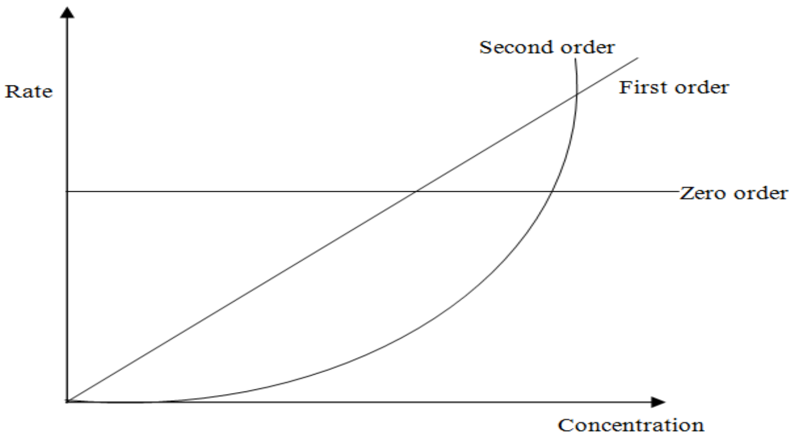


Figure 10.3 Graph of rate against concentration for different reaction orders

Summary on features of the graph

- The graph is straight line
- The graph passes through the origin
  That is: $x -$ intercept $= 0$ and $y -$ intercept $= 0$
- The graph has positive slope such that: Slope of the graph $=$ Rate constant.

For the second order reaction, the rate law is $\mathbf{R = k[A]^2}$ and hence the graph of **rate (y)** against **square of concentration (x)** will be plotted to give the straight line of the form of **y=mx**.

Also the reader should understand that:

- Since rate of chemical reaction varies inversely proportional to time taken for the reaction to take place. **In most cases the reciprocal of the time (1/t) is used instead of the rate and the graph has the same features.**
- The rate of the reaction is equal to the slope of the graph of concentration plotted against time (slope of tangent lines drawn at each point of the graph).

Example 9

For the reaction: $N_2O_4(g) \rightarrow 2NO_2\ (g)$

Following data was collected:

Time (sec)	0	200	400	600	800
$[N_2O_4]$	1.64	1.45	1.28	1.13	1.00

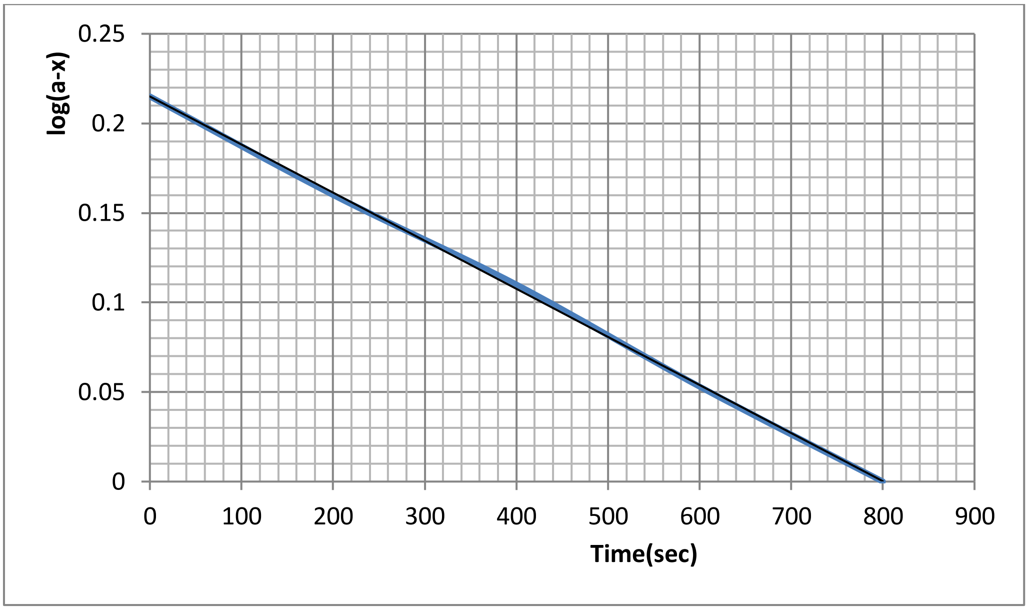
(i) Determine the order of the reaction graphically.
(ii) What is the rate constant of the reaction?

Solution

A table for data analysis

Time (t)/ sec	0	200	400	600	800
(a − x)	1.64	1.45	1.28	1.13	1
log (a − x)	0.215	0.16	0.11	0.053	0.00

GRAPH OF $\log(a-x)$ AGAINST TIME (t)



(i) Thus the reaction is of the first order since the nature of the graph agrees with the first order equation which is $\log(a-x) = \frac{-kt}{2.303} + \log a$

Comparing the equation: $\log(a-x) = \frac{-kt}{2.303} + \log a$ with the equation: $y = mx + c$

The slope, $m = \dfrac{-k}{2.303}$

But $m = \frac{\Delta y}{\Delta x} = \frac{\Delta \log(a-x)}{\Delta t}$

Taking any two points from the graph gives the slope, m of -0.000265

So from $m = \dfrac{-k}{2.303}$; $\quad -0.000265 = \dfrac{-k}{2.303}$

or $k = 2.303 \times 0.000265 sec^{-1} = 6.1 \times 10^{-4} sec^{-1}$

(ii) Hence the rate constant of the reaction is 6×10^{-4} sec^{-1}.

Half-life method

This method is used when there is only one concentration term in the rate law.

Consider half-life equations for various order chemical reactions as given below:

For first order chemical reaction: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{a^0 k}$

For second order chemical reaction: $t_{1/2} = \frac{1}{ak} = \frac{1}{a^1 k}$

For third order chemical reaction: $t_{1/2} = \frac{1}{a^2 k}$

For fourth order chemical reaction: $t_{1/2} = \frac{1}{a^3 k}$

Thus from the half-life equations of various order chemical rectums , it appears that : *Half-life is inversely proportional to initial concentration, c, of the reactants raised to the order of the reaction decreased by one.*

That is: $t_{1/2} \propto \frac{1}{C^{n-1}}$

Where:

c $=$ is the initial concentration of the reactant

n $=$ is the order of the reaction with respect to the reactant

For two deferent initial concentrations, C_1 and C_2 with respective half-lives of t_1 and t_2

$t_1 \propto \frac{1}{{C_1}^{n-1}}$ or $t_1 = \frac{1}{k{C_1}^{n-1}}$ ……………………………………….. (i)

$t_2 \propto \frac{1}{{C_2}^{n-1}}$ or $t_2 = \frac{1}{k{C_2}^{n-1}}$……………………...……………… (ii)

Taking (i) $\div$ (ii) gives: $\frac{t_1}{t_2} = \frac{{C_2}^{n-1}}{{C_1}^{n-1}}$ or $\frac{t_1}{t_2} = \left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_1}{C_2}\right)^{1-n}$

Hence; $\mathbf{\frac{t_1}{t_2} = \left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_1}{C_2}\right)^{1-n}}$

Where t_1 is the half life when the initial concentration is C_1

t_2 is the half life when the initial concentration is C_2

n is the order of the reaction

The reader should understand that:

First order of chemical reaction can also be spotted by studying half-lives of the reaction at different concentration. In this case graph of concentration against time is plotted. From the graph, several half-lives at different concentration are determined and compared. The graph of concentration plotted against time has always the nature given below: **(Except for zero order chemical reaction where the graph is straight line with negative slope which is equal to the rate constant).**

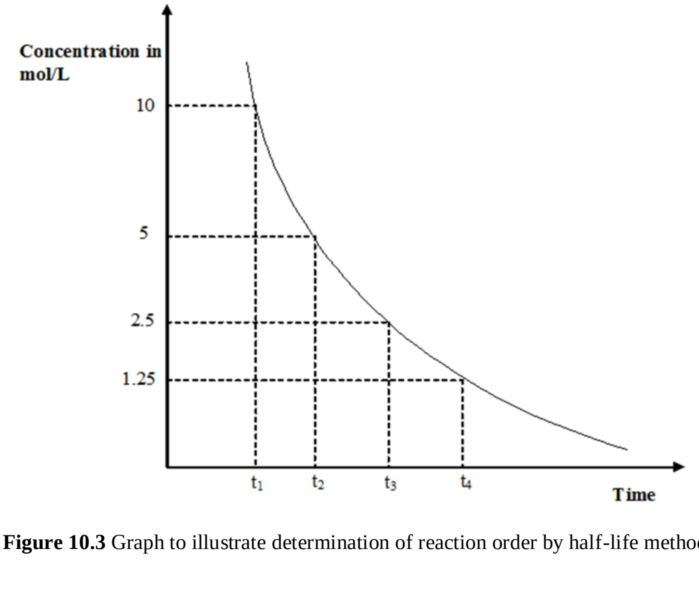


Figure 10.3 Graph to illustrate determination of reaction order by half-life method

Where:

$t_2 - t_1$ is the half life at concentration of $10 mol/dm^3$ (The time taken for concentration to decrease from 10 to 5 mol/dm^3 in the reaction)

Similarly:

$t_3 - t_2$ is the half at concentration of 5 mol/dm^3 (The time taken for the concentration to decrease from 5 to 2.5 mol/dm^3) And $t_4 - t_3$ is the half life at concentration of 2.5 mol/dm^3 (The time taken for the concentration to decrease from 2.5 to 1.25 mol/dm^3)

Then from the graph, if the reaction is the first order the half-lives determined at different concentration will almost be equal. If the half-lives varies greatly the reaction is not of the first order.

Thus: If $t_2 - t_1 = t_3 - t_2 = t_4 - t_3$ then the reaction is of the first order.

But if $t_2 - t_1 \# t_3 - t_2 \# t_4 - t_3$ then the reaction is not of the first order.

Example 10

Decomposition of hydrogen peroxide obey first order reaction when started with 1.33M of H_2O_2; its half life was found to be 90sec .What would be the half life if one started with 0.57M of H_2O_2 under the same conditions.

Solution

Since the half-life of the first order chemical reaction does not depend on the initial concentration of the reactants, the half-life remains constant (unchanged).

Hence the half-life if one started with 0.57M of H_2O_2 is 90sec.

Alternative solution:

Using: $\frac{\mathbf{t_1}}{\mathbf{t_2}} = \left(\frac{\mathbf{C_2}}{\mathbf{C_1}}\right)^{\mathbf{n-1}}$ Where $\mathbf{t_1} = 90\text{sec}, \mathbf{C_1} = 1.33\text{M}, \mathbf{C_2} = 0.57\text{M}, \text{n} = 1$

Then: $\frac{\mathbf{90}}{\mathbf{t_2}} = \left(\frac{\mathbf{1.33}}{\mathbf{0.57}}\right)^{\mathbf{1-1}} = \mathbf{1 \text{ or } t_2 = 90 \text{ sec}}$

Hence the half-life if one started with 0.57M of H_2O_2 is 90sec.

Example 11

In a simple conversion reaction: G $\rightarrow$ P when concentration of G was changed from 0.52M to 1.03M, the half life dropped from 150sec to 75sec

(a) What is the order of this reaction?
(b) Calculate the rate constant of this reaction

Solution

(a) Using $\frac{\mathbf{t_1}}{\mathbf{t_2}} = \left(\frac{\mathbf{C_1}}{\mathbf{C_2}}\right)^{\mathbf{1-n}}$

Where $t_1 = 150\text{sec}, t_2 = 75\text{sec}, C_1 = 0.52\text{M}, C_2 = 1.03\text{M}$

$\frac{150}{75} = \left(\frac{0.52}{1.03}\right)^{1-n}$ or $n - 1 = 1$ or $n = 2$

Hence the reaction is of the second order

(b) Using $t_{1/2} = \frac{1}{ak}$ (for second order reaction)

Then: $t_1 = \frac{1}{kC_1}$ or $k = \frac{1}{t_1C_1}$

So $k = \frac{1}{150\times0.52}M^{-1}sec^{-1} = 0.01282M^{-1}sec^{-1}$

Hence the rate constant for the reaction is $0.01282M^{-1}sec^{-1}$

Integral rate equation method

This method is also known as simply **integral method**. It is suitable when there is only one reactant. In this case, the integral rate equation of is used to calculate rate constant and hence the method is also known as **calculation of rate constant method**. This is done by taking different initial concentrations of the reactant **(a)** and noting the concentration **(a – x)** after regular time intervals **(t)**. The experimental values of a, (a – x) and t are then substituted into the integral rate equations for the first, second and third order reactions to check whether the equation will give uniform value of k or not. **The rate equation which yields a constant value of k corresponds to the correct order of the reaction**.

As an example, for first order reaction; several rate constants are calculated at different concentrations by using first order equation.

That is; $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

From which**;** $\mathbf{k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)}$

If the rate constants obtained (by using the above final rearranged equation) at different concentrations are equal, then the reaction is of the first order but if are different (vary greatly), the reaction is not of the first order.

Example 12

Experimental studies on the rearrangement of methyline nitrite to cotonitrite at 20°C yielded the following results:

Time	0	1000	2000	5000	10000	15000
Pressure of methyline nitrite in mmHg	150	142	135	115	88.8	68.2

Use the data above to determine the order of the reaction by calculation of the rate constant method. What is the rate constant of this reaction?

Solution

From $\log\left(\frac{P_o}{P_o - P}\right) = \frac{kt}{2.303}$ which is first order equation in terms of pressures

$k = \frac{2.303}{t}\log\left(\frac{P_o}{P_o - P}\right)$ where $P_o = 150\text{mmHg (when t} = 0)$

When $\mathbf{t = 1000sec, P_o - P = 142mmHg}$

$$\mathbf{k_1} = \frac{2.303}{1000}\log\left(\frac{150}{142}\right) = 5.48 \times 10^{-5}\text{sec}^{-1}$$

When $\mathbf{t = 2000sec, P_o - P = 135mmHg}$

$$\mathbf{k_2} = \frac{2.303}{2000}\log\left(\frac{150}{135}\right) = 5.27 \times 10^{-5}\text{sec}^{-1}$$

When $\mathbf{t = 5000sec, P_o - P = 115mmHg}$

$$\mathbf{k_3} = \frac{2.303}{5000}\log\left(\frac{150}{115}\right) = 5.32 \times 10^{-5}\text{sec}^{-1}$$

When t = 10000, $\mathbf{P_o - P}$ **= 88.8mmHg**

$$\mathbf{k_4} = \frac{2.303}{10000}\log\left(\frac{150}{88.8}\right) = 5.24 \times 10^{-5}\text{sec}^{-1}$$

When $\mathbf{t = 15000, P_o - P = 68.2mmHg}$

$$\mathbf{k_5} = \frac{2.303}{15000}\log\left(\frac{150}{68.2}\right) = 5.26 \times 10^{-5}\text{sec}^{-1}$$

Since rate constants for given reaction do not differ much, the reaction is of the first order.

$$\text{Rate constant}, \mathbf{k} = \frac{\mathbf{k_1} + \mathbf{k_2} + \mathbf{k_3} + \mathbf{k_4} + \mathbf{k_5}}{5} = \frac{(5.48 + 5.27 + 5.32 + 5.24 + 5.26) \times 10^{-5}}{5}$$

$$= 5.31 \times 10^{-5}\text{sec}^{-1}$$

Hence the rate constant for the reaction is $5.31 \times 10^{-5}\text{sec}^{-1}$

Initial rate method

This method suits reactions with more than one reactant. In this case, initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant.

If A reacts with B to give P the order of reaction with respect of each reactant can be determined as follows:

- Firstly the rate of chemical reaction is determined with given concentration of A and B say A_1 and B_1

  Then $R_1 = k\,[A_1]^x[B_1]^y$................................ (i)

- To determine the order of the reaction with respect to A, the concentration of A is varied to A_2 while that of B is kept constant and then the new rate of chemical reacting , R_2 is measured

  So $R_2 = k\,[A_2]^x[B_1]^y$... ....(ii)

  Then taking $R_2 \div R_1$; gives: $\frac{R_2}{R_1} = \frac{[A_2]^x[B_1]^y}{[A_1]^x[B_1]^y} = \left(\frac{[A_2]}{[A_1]}\right)^x$

- To determine the order of the reactions with respect to B the concentration of B is varied to B_2 while that of A is kept constant

  That is $R_3 = k\,[A_1]^x[B_2]^y$ .... (iii)

  Then taking $R_3 \div R_1$ gives; $\frac{R_3}{R_1} = \frac{[A_1]^x[B_2]^y}{[A_1]^x[B_1]^y} = \left(\frac{[B_2]}{[B_1]}\right)^y$

Example 13

Consider the following reaction: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O$

The following data collected:

[NO]/M	$[H_2]$/M	Rate /Msec^{-1}
0.6	0.37	0.18
1.2	0.37	0.72
1.2	0.74	0.72

Determine the order of the reaction with respect to each reactant.

Solution

$R = k\,[NO]^x[H_2]^y$ (From the rate law)

When $R = 0.18\text{Msec}^{-1}, [NO] = 0.6$ and $[H_2] = 0.37$

Thus $R_1 = k\,[0.6]^x[0.37]^y$... (i)

When $R = 0.72Msec^{-1}$ $[NO] = 1.2M$ and $[H_2] = 0.37$

Thus $R_2 = k\,[1.2]^x[0.37]^y$ …………………………………………….. (ii)

When $R = 0.72Msec^{-1}$ $[NO] = 1.2M$ and $[H_2] = 0.74M$

Thus $R_3 = k\,[1.2]^x[0.74]^y$ …………………………………………….(iii)

To find the order of the reaction with respect to NO, $[H_2]$ must be constant while [NO] is changed. So taking (ii) ÷ (i) $\frac{R_2}{R_1} = \frac{[1.2]^x}{[0.6]^x}$

But $R_2 = 0.72M\,sec^{-1}$ and $R_1 = 0.18M\,sec^{-1}$

Then $\frac{0.72}{0.18} = \left(\frac{1.2}{0.6}\right)^x$

$4 = 2^x$ or 2^x or $x = 2$

Hence the order of the reaction with respect to NO is 2

To find the order of the reaction with respect to H_2, concentration of NO must be kept constant while $[H_2]$ is changed .So taking (iii) ÷ (ii) gives $\frac{R_3}{R_2} = \frac{[0.74]^y}{[0.37]^y}$

$1 = 2^y$ or $2^0 = 2^y$ or $y = 0$

Hence the order of the reaction with respect to H_2 is zero

It should be understood that:

The zero order reaction with respect to H_2 means that the change in concentration of hydrogen gas has no effect on the rate of the reaction e.g. in given data of above question when the $[H_2]$ is doubled from 0.37M to 0.74M (while [NO] is kept constant the rate of the reaction remains unchanged with value of $0.72\ M\,sec^{-1}$)

Example 14

For the reaction: $PCl_3 + Cl_2 \rightarrow PCl_5$

The following experimental data were obtained

Experiment	$[PCl_3]$/**M**	$[Cl_2]$**M**	**Rate /M** $\mathbf{min^{-1}}$
1	0.36	1.26	0.036
2	0.36	0.63	0.009
3	0.72	0.63	0.018

(a) Determine the rate law of the reaction
(b) Calculate the value of rate constant and give its units
(c) Calculate the rate with which $[PCl_3] = 0.04M$ and $[Cl_2] = 0.02M$

Solution

$R = k\,[PCl_3]^x[Cl_2]^y$

$R_1 = k\,[0.36]^x[1.26]^y$

$R_2 = k\,[0.36]^x[0.63]^y$

$R_3 = k\,[0.72]^x[0.63]^y$

(a) Taking (i) ÷ (ii);

$$\frac{R_1}{R_2} = \frac{[1.26]^y}{[0.63]^y} = \left(\frac{1.26}{0.63}\right)^y = 2^y$$

But $\frac{R_1}{R_2} = \frac{0.036}{0.009} = 4 = 2^2$

Then $2^2 = 2^y$ or $y = 2$

Taking (iii) ÷ (ii);

$$\frac{R_3}{R_2} = \left(\frac{0.72}{0.36}\right)^x = 2^x$$

But $\frac{R_3}{R_2} = \frac{0.018}{0.009} = 2^1$

Then $2^1 = 2^x$ or $x = 1$

Thus the reaction is of the second order with respect to Cl_2 and is the first order with respect to PCl_3

Hence the rate law of the reaction is $R = k[PCl_3][Cl_2]$

(b) From the above rate law $k = \frac{R}{[PCl_3][Cl_2]^2}$

Substituting values of **experiment I** (You may choose any set of value from respective experiment).

$$k = \frac{0.036\text{Msec}^{-1}}{(0.36)(1.26\text{M})^2} = 6.2988 \times 10^{-2}\text{M}^{-2}\text{sec}^{-1}$$

Hence the rate constant is $6.2988 \times 10^{-2}\text{M}^{-2}\text{sec}^{-1}$

(c) $R = k[PCl_3][Cl_2]^2$

Where $k = 6.2988 \times 10^{-2}\text{M}^{-2}\text{sec}^{-1}$

And it is given that $[PCl_3] = 0.04\text{M}$ and $[Cl_2] = 0.02\text{M}$

$R = 6.2988 \times 10^{-2} \times 0.04 \times (0.02)^2\text{Msec}^{-1}$

$R = 1.007808 \times 10^{-6}$ Msec^{-1}

Hence the rate will be 1.007808×10^{-6} Msec^{-1}

DIGGING DEEPER EXERCISE 10

EXERCISE 10A: BINDER QUESTIONS

Question 1

Comment on half-life of a zero order, first order and second order reaction.

Question 2

In the reaction A → products, we find that when [A] has fallen to half of its initial value, the reaction proceeds at the same rate as its initial rate. Is the reaction zero order, first order, or second order? Explain.

Question 3

What is wrong with the following statement; *"Zero-order reactions are independent of concentration of reactants."*

Question 4

Give at least two examples in each of the following:

(i) Zero order reaction
(ii) First order reaction
(iii) Second order reaction
(iv) Pseudo first order reaction

Question 5

A first order reaction has a rate constant $1.15 \times 10^{-3}\,\mathrm{s^{-1}}$. How long will 5g of this reactant take to reduce to 3g?

Question 6

The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2.

(i) What is the overall reaction order?
(ii) What is the effect of doubling the concentration of each reagent on the reaction rate?

Question 7

The rate constant of a reaction is $1.2 \times 10^{-2}\,\mathrm{s^{-1}}$; what is the order of the reaction?

Question 8

A reaction is 20% complete in 20 minutes. Calculate the time required for 80% completion of reaction, if the reaction is of the first order.

Question 9

The half –life of radioisotope is found to be 4.55 minutes. If the decay follows first order kinetics what percentage of isotope will remain after 2hours?

Question 10

The rate constant of a zero order reaction in A is 0.003M/s. How long will it take for the initial concentration of A to fall from 0.10M to 0.075M?

Question 11

From the following data for a chemical reaction between A and B at 25℃.

$[\mathbf{A}]$	$[\mathbf{B}]$	**Initial rate in** $\mathbf{molL^{-1}sec^{-1}}$
2.5×10^{-4}	3×10^{-5}	5×10^{-4}
2.5×10^{-4}	6×10^{-5}	4×10^{-3}
1×10^{-3}	6×10^{-5}	1.6×10^{-2}

Calculate:

(i) The order of reaction with respect to each reactant.
(ii) The rate constant at 25°C.

Question 12

A first order reaction, A → products, has a rate of reaction of 0.00250 M s^{-1} when [A] = 0.484 M.

(a) What is the rate constant, *k*, for this reaction?
(b) Does $t_{3/4}$ depend on the initial concentration? Explain.

Question 13

The reaction between bromate ions and bromide ions in acidic aqueous solution is

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$

Using the data from four experiment shown below determine the orders of the rate of reaction for all the three reactants the overall reaction order, and the value of the rate constant, k.

Experiment	$[BrO_3^-]/M$	$[Br^-]/M$	$[H^+]/M$	$Rate/Ms^{-1}$
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Question 14

When N_2O_4 decompose; it forms NO_2

$N_2O_4 \longrightarrow 2NO_2$

If the half –life of this reaction is 1836seconds, how much of a 10g sample would be left after 1500seconds? State any assumption made on your calculation.

EXERCISE 10B: REAL QUESTIONS

Question 15

According to Tanzania chemistry syllabus, you are supposed to study order of chemical reactions up to second order. As a chemistry student who understand how chemical reaction occurs, suggest a possible reason of excluding reactions of higher order in the syllabus.

Question 16

You were having a discussion about chemical kinetics with your friend **Kipute.** *"It is impossible for the rate of reaction to remain constant throughout."* Explain to her whether you agree or disagree with her statement.

Question 17

Kipute was studying one of the book in Ngaiza book series titled physical chemistry. In the chapter of chemical kinetics, she read the following phrase; *"Example of zero order reaction is the decomposition of ammonia* (NH_3) *or hydrogen iodide (HI) on metal surface such as gold."* Unfortunately, **Kipute** was unable to make sense of how the decomposition on metal surface turns the reaction to be zero order. Since you are a good friend of **Kipute**, you decided to help her. What explanation you would give her?

Question 28

In the nuclear industry, workers use a rule of thumb that the radioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period.

Question 19

Ngaiza Gauging Examination (NGE) is the examination conducted under Hopegen Company Limited for the aim of improving academic performance in Tanzania. In order to ensure good performance in NGE chemistry examination, student is advised to learn through reading books tilted Ngaiza's series of advanced chemistry which are under Hopegen Book Project. Assuming that the loss of ability to recall learned material in Ngaiza's series of chemistry books is a first order process with a half –life of 35days.Compute the number of days requires to forget 90% of the material that the student learned through studying Ngaiza's book series in the preparation of NGE chemistry examination.

Question 20

Your best friend, **Kipute**, was assigned to solve the following question:

At 700K, the rate constant for the reaction, $2HI(g) \longrightarrow H_2(g) + I_2(g)$*, is* $1.83 \times 10^{-3} M^{-1} s^{-1}$*. Calculate the time taken for* $1 \times 10^{-2} MHCl$ *to fall to one-eighth of its initial concentration.*

Kipute blamed that the question is incomplete because it did not state whether the reaction is zero, first or second order. Do you agree with **Kipute**? If you agree, explain why and if you don't agree, help **Kipute** to solve the question.

EXERCISE 10C: HOT QUESTIONS

Question 21

Many reactions involving heterogeneous catalysis are zero order; that is, rate = k. An example is the decomposition of phosphine (PH_3) over tungsten (W):

$$4PH_3\ (g) \rightarrow P_4\ (g) + 6H_2\ (g)$$

The rate for this reaction is independent of $[PH_3]$ as long as phosphine's pressure is sufficiently high (>= 1 atm). Explain.

Question 22

Three-fourth of a reaction is completed in 32minutes. What is the half-life period of this reaction?

Question 23

The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Question 24

For the reaction in a closed vessel: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; Rate = k $[NO]^2[O_2]$

If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction?

Question 25

A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?

Question 26

First order reaction takes 69.3min for 50% completion. What is the time needed for 80% completion?

Question 27

The rate of decomposition of a gas was 7.25M/hr when 5% had reacted and it was 5.14M/hr in the same unit when 20% had undergone decomposition. What is the order of the reaction?

Question 28

Compounds A and B both decay by first-order kinetics. The half-life of A is 20 minutes and the half-life of B is 48 minutes. If a container initially contains equal concentrations of compounds A and B, after how long will the concentration of B be twice that of A?

Question 29

The rate of the reaction between substance A and substance B was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of A and B. These results were used to deduce the order of reaction with respect to A and the order of reaction with respect to B.

(a) When the concentrations of A and B were both doubled, the initial rate was quadrupled. Deduce the overall order of the reaction.
(b) In another experiment, the concentration of A was increased by factor of three and the concentration of B was halved. This caused the initial rate to increase by a factor of nine.
 (i) Deduce the order of reaction with respect to A and the order with respect to B.
 (ii) Using your answer from part (i), (ii), write a rate equation for the reaction and suggest suitable units for the rate constant.

Question 30

Consider the following reaction equation:

$2HgCl_2(aq) + C_2O_4^{2-}(aq) \longrightarrow 2Cl^- + 2CO_2(g) + Hg_2Cl_2(aq)$

The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above.

The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table.

Experiment	Initial $[HgCl_2]$	Initial $[C_2O_4^{2-}]$	Initial rate of formation of Cl^- in $molL^{-1}min^{-1}$
1	0.0836M	0.202M	0.52×10^{-4}
2	0.0836M	0.404M	2.08×10^{-4}
3	0.0418M	0.404M	1.06×10^{-4}
4	0.0316M	?	1.27×10^{-4}

(a) According to the data shown, what is the rate law for the reaction above?
(b) On the basis of the rate law determined in part (a), calculate the specific rate constant specify the units.
(c) What is the numerical value for the initial rate of disappearance of $C_2O_4^{2-}$ for experiment 1?
(d) Calculate the initial oxalate ion concentration for experiment 4.

Question 31

(a) The initial rate of reaction between ester A and aqueous sodium hydroxide was measured in a series of experiments at constant temperature. The data obtained are shown below.

Experiment	Initial [NaOH]	Initial [A]	Initial rate in $molL^{-1}s^{-1}$
1	0.040M	0.030M	4.0×10^{-4}
2	0.040M	0.045M	6.0×10^{-4}
3	0.060M	0.045M	9.0×10^{-4}
4	0.120M	0.060M	To be calculated

Use the date in the table to deduce the order of reaction with respect to A and the order of the reaction with respect to NaOH.Hence calculate the initial rate of reaction in experiment 4.

(b) In a further experiment at different temperature the initial rate of reaction was found to be 9.0×10^{-3} $moldm^{-3}s^{-1}$ when the initial concentration of A was $0.02moldm^{-3}$ and the initial concentration of NaOH was $2.00moldm^{-3}$.
 (i) Write a rate equation for the reaction under these new conditions
 (ii) Calculate a value for the rate constant under these new conditions and state its units
 (iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

Chapter 11

TEMPERATURE AND CATALYST ON RATE OF REACTION

TEMPERATURE ON RATE OF REACTION

Without any doubt, you know that papers which have been used to make a book which you are reading right now, are highly combustible material. But you are using this wonderful book comfortably without any worry, why? This is simply because, the activation energy for the reaction is too high to be achieved by temperature of the room. Most of collisions between oxygen molecules in the room and papers of your book are ineffective. However, when those papers are heated (temperature is raised) by flame from a match, it reaches a point where the molecules attain heat energy which is enough to overcome the activation energy and therefore they react. The reaction is highly exothermic, so the heat released in the initial stages of reaction will provide further energy to allow reaction to continue until your book turns to ashes! That is how temperature is involved in reaction rate; it affects number of collisions with activation energy and remember that only collisions with at least activation energy have possibility to react.

Generally, the rate of chemical reaction increases with rise in temperature because rise in temperature, increases the frequency of collision of reacting particles and makes the collisions more energetic (by increasing speed of reacting particles) thus increasing numbers of reacting particles which attains activation energy.

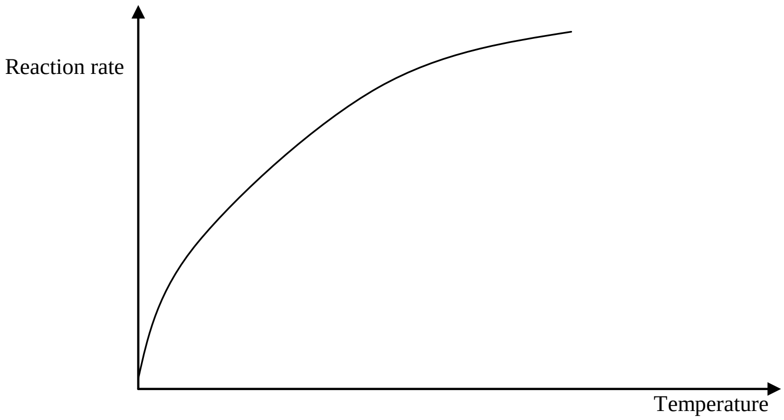


Figure 11.1 Graph to show relation between temperature and reaction rate

The effect of temperature on the reaction rate can well be illustrated by using **Maxwell Boltzmann's distribution curve**.

Understanding the Maxwell Boltzmann's curve

In any system, the particles present will have a wide range of energies. For gases, this can be shown on a graph called the **Maxwell-Boltzmann distribution curve** which *is a plot of the number of particles having each particular energy.*

The following is the sketch of the Boltzmann distribution curve.

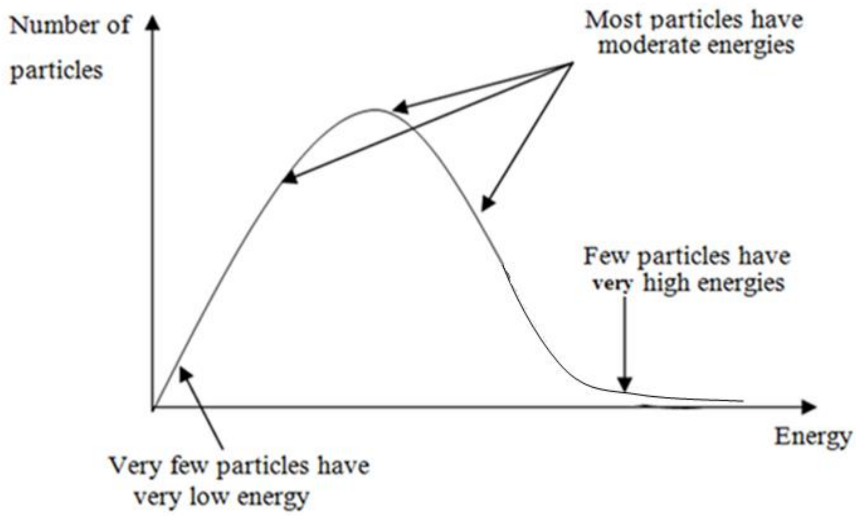


Figure 11.2 Maxwell Boltzmann's distribution curve

The area under the curve is a measure of the total number of particles present.

The reader should understand that:

Although the Maxwell-Boltzmann distribution curve applies to gases, the conclusions that we can make from it can also be applied to reactions involving liquids.

The Boltzmann distribution curve and activation energy:

Remember that for a reaction to happen, particles must collide with energies equal to or greater than activation energy for the reaction. We can mark the activation energy on the Maxwell-Boltzmann distribution curve as follows:

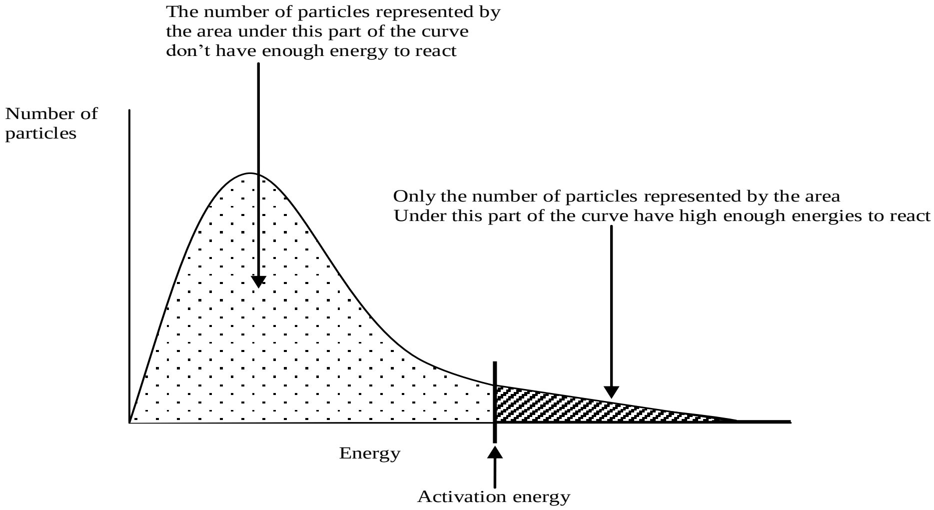


Figure 11.3 Activation energy on the Boltzmann distribution curve

Things to note from the above Maxwell-Boltzmann distribution curve:

- Most of particles have lower energy than E_a (the area under the curve which represents total number of particles is larger at the left of E_a than at the right of it).
- This means that most of collisions between particles are ineffective. They do not lead to the reaction.

- Only few particles have kinetic energy greater than E_a, (at the right of E_a mark). This means that only few collisions are effective.

Only those particles represented by the area to the right of the activation energy mark will react when they collide. The majority of particles does not have enough energy, and will simply bounce apart.

- If we increase the temperature from T_1 to T_2, more molecules are energetic enough to achieve the activation energy, thus more molecules react and overall reaction rate increases. This is illustrated in the Maxwell-Boltzmann distribution diagram below.

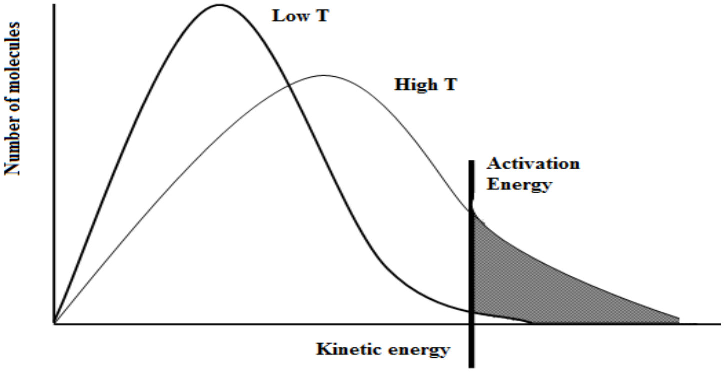


Figure 11.4 Boltzmann distribution curve to show effect of temperature on the reaction rate

Things to note from the Maxwell-Boltzmann distribution curve

- At higher temperature(T_2), fewer particles will have lower energy (at the left side of E_a mark).
- At higher temperature (T_2), greater number of particles will have higher energy than E_a. This is justified by the area under curve of T_2 at the right hand side of E_a mark which is greater than the area under curve of T_1.

Conclusion

Since more particles have energy greater than E_a at T_2, the increase in temperature (from T_1 to T_2) increases the rate of reaction.

Arrhenius equation

Arrhenius equation gives mathematical relationship between temperature and rate constant. It expresses quantitatively how the rate constant is affected by the change in the temperature

According to Arrhenius: $k \propto e^{-\frac{Ea}{RT}}$ or $k = Ae^{-\frac{Ea}{RT}}$

Where:

k is the rate constant

E_a is the activation energy

R is the molar gas constant

T is the absolute temperature

e is the natural number = 2.71828

A is the Arrhenius constant or pre exponential factor or simply pre factor. Its units are identical to those of the rate constant and will vary depending on the order of reaction, e.g. if the reaction is of the first order its unit will be sec^{-1} which is also the unit of frequency hence the name *frequency factor or attempt frequency* of the reaction for A. $e^{-E_a/RT}$ is the Boltzmann's constant

Significance of Arrhenius Constant (A)

It gives the total number of proper oriented collisions that result in a reaction (leading to reaction or not) per unit time.

Significance of Boltzmann's constant, $e^{-E_a/RT}$

It gives the probability that any given collision will result will result to reaction. That it is gives a fraction of number of collisions which have attained activation energy.

Generally $e^{-E/RT}$ is the fraction of molecules with at least energy, E (equal or greater than E and not necessary to be E_a) at temperature T.

Significance of rate constant (k or $Ae^{-E_a/RT}$)

It gives the number of collisions that result to reaction per second; that is, it gives number of proper oriented collisions which attain activation energy per unit time.

Understanding Arrhenius constant (A)

From $k = Ae^{-E_a/RT}$;

$\mathbf{A = pz}$

Where; **p** is a **probability factor** or **steric factor** or **orientation factor**. *It represents the probability that the collision will have good orientation.* **Steric factor** can be defined as *the fraction of all collisions which have proper orientation for the reaction to take place*.

z is a total number of binary collisions per unit time. *It represents total number of collisions whether they have proper orientation or not or whether they have activation energy or not.*

So **A** will *represent total number of binary collisions with proper orientation.*

Thus in words Arrhenius equation may be written as:

$$\textbf{Number of binary collisions with with energy equal to or greater than activation energy} = \textbf{Total number of proper oriented collisions} \times \mathbf{e^{-Ea/RT}}$$

If it is assumed that all collisions are proper oriented, $\mathbf{p = 1}$ and therefore $\mathbf{A = z}$ and in this case the *Arrhenius constant will represent total number of binary collisions occurred per unit time.*

Simplified Arrhenius equation

Also from the Arrhenius equation: $\mathbf{k = Ae^{-E_a/RT}}$

Introducing natural logarithm both sides: $\ln k = \ln Ae^{-E_a/RT}$

$\ln k = \ln A + \ln e^{-E_a/RT}$;

$$\ln k = \ln A + \frac{-E_a}{RT}\ln e$$

But $\ln e = 1$

$$\text{Then } \ln k = \ln A + \frac{-E_a}{RT}$$

Changing natural logarithms to common logarithm:

Using $\ln x = 2.303\log x$

Then the above equation become $2.303\log k = \dfrac{-E_a}{RT} + 2.303\log A$

$$\text{Hence, } \mathbf{\log k = \frac{-E_a}{2.303RT} + \log A}$$

So the simplified linear equation is in the form of $y = mx + c$ with $y = \log k$ and $= 1/T$

Hence the graph of logk against 1/T has the following characteristics:

- The graph is straight line
- The slope of the graph, $m = \frac{-E_a}{2.303R}$

From which $E_a = -2.303mR$ where $R = 8.314 Jmol^{-1}K^{-1}$

It should be noted that:

The value of logA should b equal to the y – intercept of the graph and hence the value of Arrhenius constant could be found directly from the graph. However y- intercept is found when $x = 0$ and in the equation $x = 1/T$ which can never be zero .Therefore to find the value of Arrhenius constant we must take any one point from the graph and then substituting its corresponding coordinates which are logk and $1/T$ in the equation after calculating the value of activation energy (E_a) from the slope of the graph

The reader should understand that:

Practically it is difficult to determine the rate constant directly. Alternatively the rate constant is always expressed in terms of time by using the fact that the rate constant varies directly proportional to the rate of the reaction which also varies inversely proportional to the time (t) and hence the rate constant varies inversely proportional to the time (t); so the graph of $\log {}^1/t$ against $^1/_T$ has the same characters as the graph of logk against $1/T$.

Also from the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

If the rate constant changes from k_1 to k_2 when the temperature changes from T_1 to T_2 respectively

Then $\log k_1 = -\frac{E_a}{2.303RT_1} + \log A$………..…………………………………… (i)

And $\log k_2 = -\frac{E_a}{2.303RT_2} + \log A$ …………………………………………… (ii)

Taking (i) – (ii)

$$\log k_1 - \log k_2 = \frac{E_a}{2.303RT_2} - \frac{E_a}{2.303RT_1}$$

$$\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Hence, $\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$

If time is used instead of rate constant the equations become:

$$\log\left(\frac{t_2}{t_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$$

Example 1

The rate constant of a simple conversion reaction A → P at 27°C is $2 \times 10^{-3}\ Sec^{-1}$. Activation energy of the reaction is $15.2 kJ/mol$. Calculate the rate constant of this reaction at 127°C.

Solution

Using: $\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\log\left(\frac{k_1}{k_2}\right) = \frac{15200}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{400}\right)$$

$\frac{k_1}{k_2} = \log^{-1}(-0.66) = 0.22$

$$k_2 = \frac{k_1}{0.22} = \frac{2 \times 10^{-3}}{0.22} \text{sec}^{-1} = 9.1 \times 10^{-3} \text{sec}^{-1}$$

Hence the rate constant for the reaction at 127°C is $9.1 \times 10^{-3}\ \text{sec}^{-1}$

Example 2

Boiling an egg denatures protein the process which has activation energy of $5.11 \times 10^2 \text{kJmol}^{-1}$. At sea level and 100°C a favoured boiling time is 3 minutes. How long it is required for the same stage to be reached at the top of the mountain of 2440m high where the boiling point of water is 95°C?

Solution

Using: $\log\left(\frac{t_2}{t_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Then $\log\left(\frac{t_2}{t_1}\right) = \frac{5.11 \times 10^5}{2.303 \times 8.314}\left(\frac{1}{368} - \frac{1}{373}\right) = 0.972$

$\frac{t_2}{t_1} = \log^{-1}(0.972)$

Or $t_2 = 9.37562 t_1$

But $t_1 = 3\text{minutes}$

So $t_2 = 9.37562 \times 3\text{minutes} = 28.1\text{minutes}$

Hence it will consume 28.1minutes

Example 3

(a) Under acidic conditions sucrose (table sugar) can be broken down into its individual sugars, glucose and fructose. At 27°C,it takes 54.5 minutes to convert half the sucrose to glucose and fructose and at 37°C it takes 13.7minutes. Estimate the activation energy for the breakdown of sucrose.

(b) The above reaction is known to be second order which means that the half-life is dependent on the initial concentration. Will this affect your calculation of the activation energy above? Why or why not?

Solution

(a) Using $\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.30R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$

Since half-life varies inversely to the rate constant; $\frac{k_1}{k_2} = \frac{t_2}{t_1}$ where t_1 and t_2 are half lives at T_1 and T_2 respectively

Then $\log\left(\frac{t_2}{t_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$

Substituting $\log\left(\frac{13.7}{54.5}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{300 - 310}{300 \times 310}\right)$

From which $E_a = 106783\text{J/mol}$ or 106.783kJ/mol

(b) No; it makes no difference.

Half-life for the first order reaction is given by $t_{1/2} = \frac{0.693}{k}$

From which it clearly understood that, $\frac{1}{k}$ can be substituted by $t_{1/2}$, that is $\frac{t_2}{t_1} = \frac{0.693}{K_2} \div \frac{0.693}{K_1} = \frac{K_1}{K_2}$

Half-life for the second order reaction is given by: $t_{1/2} = \frac{1}{[A]K}$ Where [A] is the initial concentration?

From which you can also substitute $\frac{1}{k}$ by $t_{1/2}$ as long as [A] is the same for all runs;

That is $\frac{t_2}{t_1} = \frac{1}{[A]K_2} \div \frac{1}{[A]K_1} = \frac{K_1}{K_2}$

Hence in both cases (Whether the reaction is first order or second order); $\frac{t_2}{t_1} = \frac{k_1}{k_2}$ giving the same result for activation energy with the given data.

Example 4

A particular reaction in the gas phase has activation energy of 8kJ/mol. For 1 mole of gas, calculate the number of molecules which exceed activation energy at:

(a) 300K
(b) 400K

Solution

Fraction of number of molecules which have been attained activation energy is given by $e^{-E_a/RT}$ (from the Arrhenius equation).

Thus total number of molecules with energy greater than activation energy =Total number of molecules $\times\, e^{-E_a/RT}$ (under assumption that all collisions have proper orientation).
But with given number of moles, total number of molecules $= nN_A$ where n is the number of moles of gas and N_A is the Avogadro's constant.

Thus number of molecules with energy greater than E_a

$$= nN_A \times e^{-\frac{E_a}{RT}} = 1 \times 6.02 \times 10^{23} \times e^{\frac{-8000}{8.314T}}$$

(a) When T=300K

The number of molecules $= 6.02 \times 10^{23} \times e^{\frac{-8000}{8.314\times300}} = 2.4 \times 10^{22}$ molecules
Hence number of molecules with energy greater than Ea at 300K is 2.4×10^{22} molecules

(b) When $T = 400K$

The number of molecules $= 6.02 \times 10^{23} \times e^{\frac{-800}{8.314\times400}} = 5.43 \times 10^{22}$molecules

Hence number of molecules with energy greater than E_a at 400K is 5.43×10^{22} molecules

The answer is convincing! Number of molecules with energy greater than E_a increases as the temperature increases (from 2.4×10^{22} molecules 300T to 5.43×10^{22} molecules at 400K).

Example 5

At 250K, the activation energy for a gas phase reaction was determined to be $6.5kJ/mol$. what percentage of gaseous molecules would be expected to have less than this energy at 250K.

Solution

Fraction of molecules with energy equal or greater than $E_a(6.5kJ/mol)$

$$= e^{-E_a/RT} = e^{\frac{-6500}{8.314\times250}} = 0.0438 \text{ or } 4.38\%$$

Thus the percentage of molecules with energy less than $E_a = (100 - 4.38)\% = 95.62\%$

CATALYST ON RATE OF REACTION

Catalysis *is the change in rate of a chemical reaction due to the participation of a substance called a* ***catalyst****.* While the **catalyst** *is a substance which alters the rate of reaction and itself remains unchanged at the end of the reaction.*

According to physical states of catalysts and those of reactants; catalysts can be classified into

- Homogeneous catalyst
- Heterogeneous catalyst

Homogenous catalyst is the catalyst which functions in the same phase as the reactants. One example of homogeneous catalyst involves the influence of *acidic medium on esterification.*

Homogeneous catalyst actually appears in the rate law because their concentration affects the rate of reaction.
Heterogeneous catalyst is the catalyst which functions in different phase to the reactants. Example in *Haber process*, finely divided reduced iron which is solid serves as a catalyst for the synthesis of ammonia from nitrogen gas and hydrogen gas. Another place where a heterogeneous catalyst is applied is in *contact process.*

Heterogeneous catalyst has the following advantages:

- Product are easily separated from the heterogeneous catalyst
- Heterogeneous catalysts are often more stable and degrade much slower than homogeneous catalyst.

Heterogeneous catalyst usually involves gaseous reactants **adsorbed** (not **absorbed!**) on the surface of a solid catalyst.

Don't confuse the use of absorption and adsorption!

Adsorption *refers to the collection of one substance on the surface of another.*

Absorption *refers to the penetration of one substance into another.* (For example, water is absorbed by sponge).

Positive and negative catalysts

Depending on whether the catalyst speed up or slow down the rate of chemical reaction; catalysts can be classified into

- Positive catalyst
- Negative catalyst

Positive catalysts are those which speed up the rate of the reaction. Positive catalysts increase the rate of chemical reaction by providing alternative route of the reaction which has lower activation energy. In some cases, the chemical structure of the catalyst may enhance proper orientation of reactants in a manner conducive to reaction and whence the steric factor is increased.

So positive catalysts can increase the rate of reactions in two ways:

1) They can lower the activation energy by providing the alternative mechanism (route) for the reaction with smaller activation energy.
2) They can properly orient reactants, thereby increasing the steric factor.

Generally, activation energy of catalysed (positive catalysis) is lower than that of uncatalysed reaction as verified in the energy profile graph shown below.

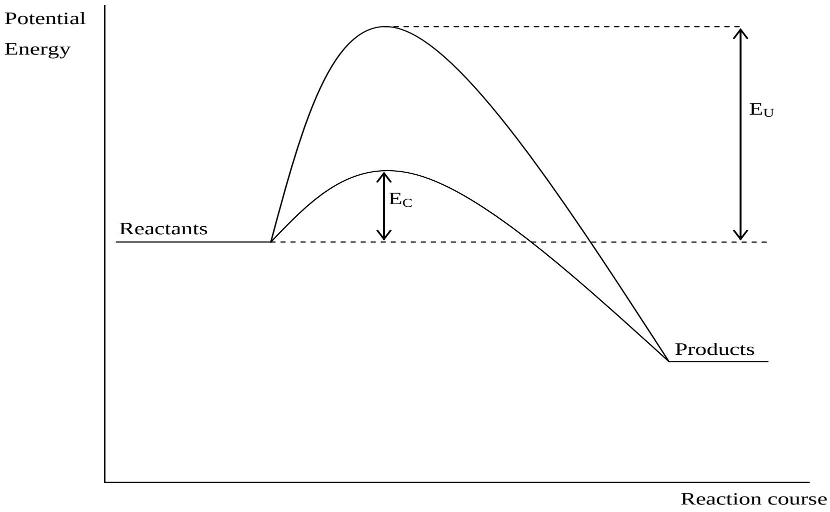


Figure 11.5 Energy profile diagram for catalysed and uncatalysed reaction

Where: E_C is the activation energy of catalysed reaction

E_C is the activation energy of uncatalysed reaction

And it is clearly seen that $E_U > E_C$

So due to the decrease in the activation energy, the addition of catalyst increases number of reactant particles with kinetic energy equal to or greater than activation energy as illustrated in the Boltzmann distribution curve below.

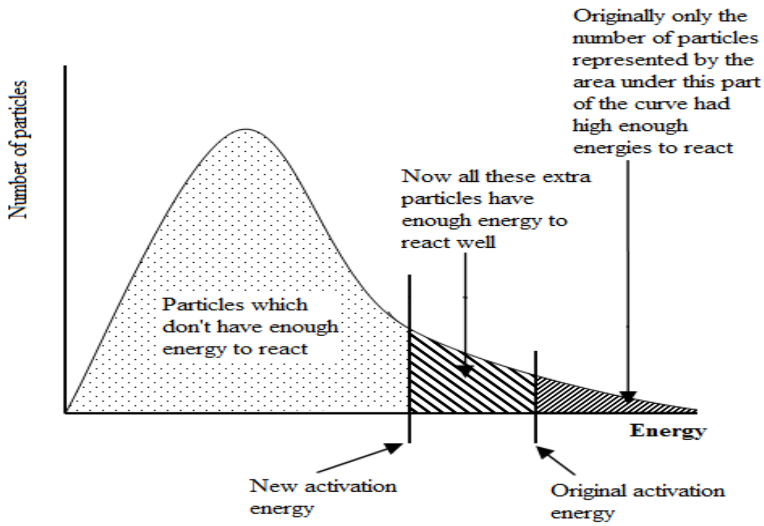


Figure 11.6 Boltzmann distribution curve to show effect of catalyst on the reaction rate

From the curve above it is clearly seen that due to decrease of activation energy, area under the curve to the right hand side of the lower activation energy mark is greater than that of higher activation energy mark (before introduction of catalyst). This means that number of molecules with kinetic energy equal to or greater than activation energy is greater than that obtained before the introduction of the catalyst.

Substances that increase the activity of positive catalysts are called **promoters**.

On another hand, substances that deactivate (decrease the activity of) the catalysts are called **catalytic poisons**.

Negative catalysts are those which slow down the rate of reaction. Negative catalysts are also known as **inhibitors**

The reader should understand that: in most cases positive catalysts are used thus *the term catalyst is commonly used to mean positive catalyst.*

Autocatalysis

A single chemical reaction is said to have undergone **autocatalysis,** or to be **autocatalytic** if the reaction product itself is the catalyst for that reaction.

So **autocatalyst** *is the catalyst of a certain reaction which is automatically produced as the product of the same reaction.*

Understanding factors affecting rate constant

We have seen that rate constant represents total number of **proper oriented** binary collisions which have attained **activation energy**. With this understanding we can deduce the following useful facts:

- If the collision energy is increased, number of collisions which have attained activation energy will also increase and thus the value of rate constant will increase as well.
- If the activation is lowered, number of collisions which have attained activation energy will also increase and thus the value of rate constant will increase as well.
- If orientation of reactants has been improved, number of collisions with proper orientation will also increase and thus the value of rate constant will increase as well.

The three facts are better understood if we return to our Arrhenius equation.

From the equation; $k = Ae^{-E_a/RT}$

But $A = pz$;

So the Arrhenius equation may be re-written as;

$$k = pz \times e^{-E_a/RT}$$

From which it is clearly understood that, the value of k will be affected by two probabilities:

- The probability of having proper orientation (orientation factor, p) whereby greater value of p, means greater value of k. You are not supposed to forget the fact that *catalyst may increase the chance of having proper orientation and therefore increasing the value of orientation factor.*
- The probability of attaining activation energy $\left(e^{-E_a/RT}\right)$ which in turn depends on temperature (T) and activation energy (E_a) of which, greater value of T or smaller value of E_a means greater value of $e^{-E_a/RT}$ and hence greater value of k. In this case, you have to remember that catalyst *makes the activation energy smaller.*

After this discussion, we may conclude that, *the value of rate constant is affected by catalyst and temperature.*

- The use of catalyst, increases the value of rate constant by reducing activation energy and enabling reactants to have proper orientation.
- The increase in temperature, increases the value of rate constant by increasing collision energy of reactants and therefore increasing number of reactants particles with activation energy.

Application of catalysis

Catalysis is significant in various ways including the following:

1. **Energy processing**: Petroleum refining makes intensive use of catalysis for *alkylation*, *catalytic cracking, naphtha reforming* and *steam reforming* (conversion of hydrocarbon into synthesis gas)
2. **Bulk chemicals:** Some of the largest – scale are produced via catalytic oxidation, often using oxygen. Example, manufacture of sulphuric acid (from SO_2 to SO_3) in *contact process.* Many other chemical products are generated by large scale reduction; often via hydrogenation. The largest scale example is the manufacture of ammonia in *Haber process* from nitrogen.
3. **Fine chemicals:** Many fine chemicals are prepared via catalysis methods include those heavy industry as well as more specialized process that could be prohibitively expensive on large scale. Examples include *olefin metathesis* using *Grubb's catalyst*
4. **Food processing:** One of the most obvious applications of catalysis is *hydrogenation* of *fats* using *nickel catalyst* to produce *margarine*.
5. **Biology:** In nature *enzymes* are catalysts in *metabolism* and *catabolism.* Enzymes are also known as **biocatalysts**.
6. **In the environment:** Catalysis impacts the environment by increasing the efficiency of industrial processes. But catalysis also plays a direct role in the environment. A notable example is the catalytic role of chlorine free radicals in the breakdown of **ozone** (These radicals are formed by the action of ultraviolet radiation on chlorofluorocarbons

   That is
   $Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$ (Cl which is catalyst is initially participated in braking O_3 to O_2)
   Then
   $ClO^{\bullet} + O^{\bullet} \rightarrow Cl^{\bullet} + O_2$ (Finally the catalyst, $Cl^{\bullet}$, is regenerated)

Example 6

The energy of activation for a chemical reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on the rate of reaction at 20°C, if other factors remains unaltered?

Solution

From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

If the rate constant changes from k_1 to k_2 when the activation energy changes (due to the application of catalyst) from E_1 to E_2 respectively at temperature, T.

Then $\log k_1 = -\frac{E_1}{2.303RT} + \log A$……….……………………………………. (i)

And $\log k_2 = -\frac{E_2}{2.303RT} + \log A$ ……………………………………..-…… (ii)

Taking (ii) – (i)

$$\log k_2 - \log k_1 = \frac{E_1}{2.303RT} - \frac{E_2}{2.303RT}$$

$$\mathbf{\log\left(\frac{k_2}{k_1}\right) = \frac{E_1 - E_2}{2.303RT}}$$

Where: $E_1 - E_2 = \frac{75}{100} \times 100\text{kJ/mol} = 75\text{kJ/mol} = 75000\text{J/mol}$ (E_a decreased by 75%)

And $T = 20°C = (20 + 273)K = 293K, R = 8.314Jmol^{-1}K^{-1}$

Substituting $\log\left(\frac{k_2}{k_1}\right) = \frac{75000Jmol^{-1}}{2.303 \times 8.314Jmol^{-1}K^{-1} \times 293K} = 13.3687$

From which;

$\frac{k_2}{k_1} = \log^{-1}(13.3687) = 2.34 \times 10^{13} = \frac{R_2}{R_1}$ (Reaction rate is directly proportional to rate constant).

Hence the reaction rate will increase by a factor of 2.34×10^{13} after application of catalyst.

Example 7

A hydrogenation reaction is carried out at 550K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20kJ/mol.

Solution

From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

If the temperature changes from T_1 to T_2 when the activation energy changes (due to the application of catalyst) from E_1 to E_2 respectively with rate constant, k (the same reaction rate means the same rate constant).

Then $\log k = -\frac{E_1}{2.303RT_1} + \log A$.........……………………………………. (i)

And $\log k = -\frac{E_2}{2.303RT_2} + \log A$ ……………………………………-…… (ii)

Taking (ii) – (i)

$$0 = \frac{E_1}{2.303RT_1} - \frac{E_2}{2.303RT_2} \text{ or } \frac{\mathbf{E_2}}{\mathbf{T_2}} = \frac{\mathbf{E_1}}{\mathbf{T_1}}$$

But $E_1 - E_2 = 20\text{kJ/mol}$ or $E_2 = E_1 - 20$

Substituting $\frac{E_1 - 20}{T_2} = \frac{E_1}{T_1}$ or $\frac{E_1 - 20}{400} = \frac{E_1}{550}$

Solving the above equation gives $E_1 = 73.33\text{kJ/mol}$ (Actual activation energy without catalyst).

The activation energy is 73.33kJ/mol

DIGGING DEEPER EXERCISE 11

EXERCISE 11A: BINDER QUESTIONS

Question 1

Write down factor (s) which affects both rate of chemical reaction and rate constant.

Question 2

The rate constant of a reaction is given by the expression;

$$k = Ae^{-E_a/RT}$$

Which factor in this expression should register a decrease so that the reaction proceeds rapidly?

Question 3

Suggest an appropriate reason for the observation: *"On increasing temperature of the reacting system by 10 degrees, the rate of reaction almost doubles or even some times becomes five folds."*

Question 4

If the activation energy for reaction is zero; what does this tell about the effect of temperature on the reaction rate and rate constant?

Question 5

Which parameters in the Arrhenius equation are affected by nature of reactants?

Question 6

The gas-phase reaction between hydrogen and chlorine is very slow at room temperature.

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(a) Give one reason why the reaction between hydrogen and chlorine is very slow at room temperature
(b) Explain why an increase in pressure, at constant temperature, increases the rate of reaction between hydrogen and chlorine.
(c) Explain why a small increase in temperature can lead to a large increase in the rate of reaction between hydrogen and chlorine.
(d) Suggest one reason why a solid catalyst for a gas-phase reaction is often in the form of powder

Question 7

Changing the temperature and no other conditions changes the rates of most chemical reactions. Two factors are commonly cited as accounting for the increased rate of chemical reaction as the temperature is increased.

(i) State and briefly discuss the two factors
(ii) Which of the two is more important?

Question 8

The gas reaction: $N_2O_5 \longrightarrow 2NO_2 + {}^1/_2\,O_2$;

Follows the Arrhenius question, $K = Ae^{-Ea/RT}$ where $R = 8.314JK^{-1}mol^{-1}$ and $1\ calorie = 4.18KJ$. At the temperature $T = 273K,\ k = 3.46 \times 10^{-5}s^{-1}$, whereas at $T = 298K,\ k = 8.87 \times 10^{-3}s^{-1}$. What is the value of the activation energy in $kcal/mol$.

Question 9

For the reaction; $(A + B \rightarrow C)$, the rate constant at 215°C is 5×10^{-3} and the rate constant at 452°C is 1.2×10^{-1}

(a) What is the activation energy in kJ/mol
(b) What is the rate constant at 100°C

Question 10

What will be the temperature at which the rate constant is $15M^{-1}s^{-1}$ while temperature $389K$ the rate constant is $7M^{-1}s^{-1}$, the activation energy is $600kJ/mol$.

Question 11

The activation energy of reaction is 94.14kJ/mol and the rate constant at 313K is

$1.8 \times 10^{-1}\ \text{sec}^{-1}$, calculate the Arrhenius constant for given reaction.

Question 12

Given that the rate constant is $11\text{M}^{-1}\text{s}^{-1}$at 345K and the pre-exponential factor is $20\text{M}^{-1}\text{s}^{-1}$. Calculate the activation energy.

EXERCISE 11B: REAL QUESTIONS

Question 13

Give at least two examples of catalysts which are common in daily life. In each case, give its main use.

Question 14

"Rate of a chemical reaction increases as temperature increases." Just this statement by using two examples which are common in daily life.

Question 15

You were discussing about Arrhenius equation with your dearest friend, **Kipute**. **Kipute** wrote down the following equation:

$$\boldsymbol{k = Ae^{-E_a/RT}}$$

"From this equation, it is clear that the value of rate constant varies when activation energy and temperature changes. So, I think two reactions having identical values of activation energy will have the same rate constant if they run at the same temperature." She said.

Did you agree or disagree with her? Explain.

Question 16

Kipute was asked the following question in the examination:

The rate constant of a simple conversion reaction $A \rightarrow P$ at 27°C is $2\ \times\ 10^{-3}\ sec^{-1}$. Activation energy of the reaction is $15.2kJ/mol$. Calculate the rate constant of this reaction at 127°C.

After solving, she found the rate constant to be $8\ \times\ 10^{-4}\ sec^{-1}$.

Without doing any calculation, explain to Kipute that the answer she got, it is **not** correct.

Question 17

Your friend, **Kipute**, was given the following problem:

The rate of a reaction triples when the temperature changes from 20°C to 50°C. Calculate the activation energy of the reaction.

After solving, she found the activation energy to be 284.24J/mol. How could help your friend to show that she got the wrong answer without re-working the problem?

Question 18

The wrong answer **Kipute** got in question 4 above was due to the fact that she used the value of universal gas constant (**R**) as 0.082 instead of 8.314. Without re-working the problem, help your friend to get the correct value of activation energy.

EXERCISE 11C: HOT QUESTIONS

Question 19

An increase of 10°C in temperature rarely doubles the kinetic energy of particles but doubles the rate of reaction, why.

Question 20

The diagram below shows the Maxwell − Boltzman distribution of molecular energies in a sample of a gas;

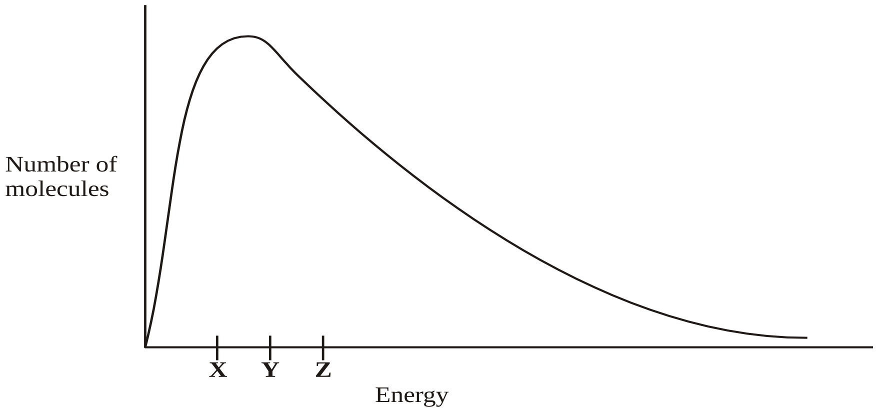


Figure 11.7 Maxwell-Boltzmann distribution for question 20

(a) Explain the process of that causes some molecules in this sample to have very low energies.
(b) On the diagram above, sketch a curve to show distribution of molecular energies in the same sample of gas at higher temperature.
(c)
  (i) Explain why, even in a fast reaction, a very small percentage of collisions lead to a reaction.
  (ii) Other than by changing the temperature, state how the proportion of successful collisions between molecular can be increased. Explain why this method causes an increase in the proportion of successful collisions.

Question 21

For the reaction: $2NH_3(g) \longrightarrow 3H_2(g) + N_2(g)$

The rate constant is measured at two different temperatures.

$T_1 = 500K, K = 9.51 \times 10^{-9} Lmol^{-1}s^{-1}$ and $T_2 = 600K, K = 1.1 \times 10^{-5} Lmol^{-1}s^{-1}$

Using the above information, calculate;

(a) The activation energy and
(b) The value of the pre-exponential Arrhenius factor

Question 22

A certain reaction is 50% complete in 20min at 27°C and the same reaction is again 50% complete in 5min at 77°C. Calculate the activation energy if it is a first order reaction.

Question 23

The experimental rate constant for the reaction of iodide ion with methyl bromide is $7.7 \times 10^{-3} dm^3mol^{-1}s^{-1}$ at 100°C and $4.25 \times 10^{-5} dm^3mol^{-1}s^{-1}$ at 0°C.Calculate the frequency factor and activation energy.

Question 24

According to the Farmer's Almanac, one can tell the temperature according to how fast crickets chirp. It has been scientifically proven that cricket chirp is directly related to the temperature. At 10°C, the average rate of chirping is 20chirps/min. When the temperature rises to 20°C, the average rate of chirping is 120chirps/min. Based on this data, what is the activation energy for crickets to chirps?

Question 25

A cook finds that it takes 30minutes to boil potatoes at 100°C in an open sauce pan and only 12minutes to boil them in a pressure cooker at 110°C. Estimate the activation energy for cooking potatoes, which involves the conversion of cellulose into starch.

Chapter 12

MECHANISM OF CHEMICAL REACTIONS

One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the reaction mechanism. Understanding the mechanism allows us to find ways to facilitate the reaction. Below are terms associated with reaction mechanism whose understanding is crucial in mastering reaction mechanism.

Reaction mechanism *is steps involved in the chemical reaction. It shows the path followed by the reaction course in forming products.*

Elementary reaction *is the reaction of particular step in the reaction mechanism.* So the reaction mechanism is the combination of various elementary reactions involved in the reactions.

Intermediate product (reaction intermediate or simply intermediate) *is the product of a particular step of reaction mechanism*, i.e. it is the product of elementary reaction.

- Reactions intermediate are always unstable and therefore they undergo further change (chemical reaction) to give final products.

MOLECULARITY

Molecularity is the total number of reactant molecules which take part in a particular elementary reaction. Example if the elementary reaction is $NO_3 + CO \rightarrow NO_2 + CO_2$, then its molecularity is 2 because **one** molecule of NO_3 and **one** molecule of CO react making a total of **two** molecules which react. *So unlike the **reaction order** (which is determined experimentally) the molecularity can be deduced from be balanced chemical equation and it must be whole number while order of chemical reaction may take fraction.*

- The molecularity of elementary reaction may be **unimolecular**, **bimolecular** or **termolecular**.

Unimolecular involves one reactant molecule that collides with a solvent or background molecule thereby becoming collisionally activated.

- In this state, the reactant molecule is thermodynamically favourable for converting into product.

Bimolecular involves collision between two reactant particles.

- Bimolecular reaction may become **pseudo-unimolecular** if one of the reactant is present so much in excess.

Termolecular involves simultaneous collision between three reactant particles.

- Since it is very difficult for three molecules to collide at the same time, termolecular is very rare. For similar reason, it is practically impossible to have molecularity of greater than three.

DEDUCING ORDER OF REACTION FROM REACTION MECHANISM

In a multistep reaction each step will have its own rate constant (and of course its activation energy).

For example if the mechanism for the reaction $2A + B \longrightarrow C$ is thought to be;

Step 1; $A + B \longrightarrow I$ (slow)

Step 2; $I + A \longrightarrow C$ (fast)

Then the rate law for each step will be:

$$R_1 = k_1[A][B] \quad \text{(for step 1)}$$

$$R_2 = k_2[I][A] \quad \text{(for step 2)}$$

Where k_1 and k_2 are rate constants for step 1 and step 2 respectively.

In the multistep process, one of the steps will be slower than all others.

- The overall reaction cannot occur faster than this slowest step and hence *the slowest step in the reaction mechanism* is the **rate-determining step** or the **rate limiting step** because it limits the rate of the overall reaction.

Thus from the above mechanism, because step1 is the slowest one, the rate law of the overall reaction will be equal to the rate law of step 1.

- That is the rate law of the overall reaction will be: $\mathrm{R = k[A][B]}$.

The trick of deducing rate law depends whether the slowest step contains an intermediate as its reactant or not.

If the slowest step does not contain an intermediate as reactant:

The rate law of the overall reaction must contain species which appears in the overall reaction equation.

- So if all reactants of the slowest step appear in the overall reaction (which in turn means there is no any intermediate in the reactants side of the step) there is no any special trick in deducing the required rate law! **The rate law of the slowest step will be the rate law of the overall reaction without any modification.**

For example, if the reaction $\mathrm{2A + B \longrightarrow C}$ is supposed to take place under the following mechanism:

$\mathrm{A + A \longrightarrow I}$ (slow)

$\mathrm{I + B \longrightarrow C}$ (fast)

Then the rate law of the overall reaction will simply be:

$$\mathrm{R = k[A][A] = k[A]^2}$$

If the slowest step does not contain an intermediate as reactant:

Now consider the same reaction, $\mathrm{2A + B \longrightarrow C}$ is now supposed to take place under the following mechanism:

$\mathrm{A + B \longrightarrow I}$ (fast)

$\mathrm{I + A \longrightarrow C}$ (slow)

Considering the slowest step (rate determining step), one may suggest the rate low of the overall reaction to be:

$$\mathrm{R = [I][A]}$$

However, there is one problem, with the above rate law. The intermediate, I, do not appear in the overall reaction, so in reality its concentration does not affect the rate of overall reaction. *How can we get more correct rate law?*

To get correct rate law, one must assume the first step forms the rapid (very fast) equilibrium.
That is, $\mathrm{A + B \rightleftharpoons I}$

Then we can use the above rapid equilibrium to eliminate, I, in the suggested rate law as follows:

- If the first step is considered to form the rapid equilibrium.

$\mathrm{R_f = R_b}$ (At equilibrium of the first step rates of forward and backward reactions are equal)
But $\mathrm{R_f = k_f[A][B]}$ and $\mathrm{R_b = k_b[I]}$

Then $\mathrm{k_f[A][B] = k_b[I]}$ (At equilibrium)

From which; $\mathrm{[I] = \frac{k_f}{k_b}[A][B]}$

Substituting $\mathrm{[I] = \frac{k_f}{k_b}[A][B]}$ to the suggested rate law ($\mathrm{R = [I][A]}$) gives;

$$R = \frac{k \times k_f}{k_b}[A][B][A] = \frac{k \times k_f}{k_b}[A]^2[B]$$

But $\frac{k \times k_f}{k_b}$ gives another constant, sayk'

Thus $R = k'[A]^2[B]$

Hence the correct rate law of the overall reaction from the above mechanism will be:

$$R = k[A]^2[B]$$

The situation where the slowest step contains the intermediate as the reactant occurs when the slowest step is not the first step. Since the intermediate must be formed in the elementary reaction (the intermediate can never be present at the beginning of the reaction as the initial reactant) there is no possibility of meeting with this situation when the slowest step is the first step.

To insist, if the slowest step is the first step in the reaction mechanism, no need of any special treatment of its obtained rate law; its rate law will automatically be the rate law of the overall reaction.

The reader should note that:

Even if it is not stated whether the elementary step is fast or not, as long as there is a sign of reversible reaction in the step, that step must be fast.
For example; if you are given with the following mechanism:

$$\text{Step 1: } A + A \rightleftharpoons I$$

$$\text{Step 2: } I + B \longrightarrow C$$

Even if it is not stated, there is no way the step 1 will be slower than step 2. This is because the intermediate formed in the step 1 is one required as reactant for step 2 to occur. The only way to make this possible is for step 1 to form very fast (rapid) equilibrium while step 2 occurs very slowly. Hence the step 2 will be the rate –determining step.

However, the reader should know that the rate law (and hence order of chemical reaction) cannot be deduced from the reaction mechanism when one of the following conditions occurs:

- If there is no slowest step.
- If all molecules appearing in the slowest step do not appear in the overall reaction.

Understand this fact!

For the reaction which takes place in single step, the rate law may be deduced from the balanced chemical equation where:

Molecularity of the reaction = order of the reaction
Stoichiometric coefficients of the reaction equation are powers of the concentration in the rate law.
For example; if the hypothetical reaction $A + B \longrightarrow C$ is found to undergo in the single step, then the rate law of the reaction will be: $R = k[A][B]$

DEDUCING REACTION MECHANISM FROM RATE LAW

With given experimental rate law of a given chemical reaction, the mechanism from the reaction can be deduced. For the reaction mechanism to be plausible, it must agree with the two conditions as explained below.

First condition: the summation if all steps in the reaction mechanism must agree with the stoichiometry of the overall reaction.

This means that the sum of all elementary reaction equations must give the correct balanced equation of the overall reaction.
For example, if the overall reaction equation is 2A + B → C, and one suggest the mechanism for the reaction to be:

Step 1: $A + B \rightarrow I$ (slow)

Step 2: $I + A \rightarrow C$ (fast)

This mechanism satisfy the **first condition** because step 1 + step 2 gives;

$$A + B + I + A \rightarrow I + C$$

Or $2A + B + \cancel{I} \rightarrow \cancel{I} + C$

Or $2A + B \rightarrow C$ which is exactly the same as the given overall reaction equation.

Second condition: the suggested mechanism must agree with the experimental rate law of the overall reaction.

This means that if one follows the procedures of deducing the rate law from the suggested mechanism, the deduced rate law must be the same as the experimental rate law of the reaction.
To have better understanding of this, consider again our hypothetical reaction, $2A + B \rightarrow C$; then assume we have $R = k[A][B]$ as the experimental rate law of the reaction.

And also assume we have two suggestions of the mechanism for the reaction.
First suggestion:

$A + B \rightarrow I$ (Slow)

$I + A \rightarrow C$ (Fast)

Second suggestion:

$A + A \rightarrow I$ (Slow)

$I + B \rightarrow C$ (Fast)

Now consider the following analysis of the suggested mechanisms.

- Both of the two suggested mechanisms satisfy the first condition because the summation of steps in either mechanism gives $2A + B \rightarrow C$ which is the overall reaction equation.
- However the rate determining step of the second suggestion gives the rate law of $R = k\,[A]^2$ which is different to the given experimental rate law while that of first suggestion gives $R = k[A][B]$ which is equal to the given experimental rate law. Thus the first suggestion has satisfied second condition while the second suggestion has not.

Conclusion from the analysis

The first suggested mechanism is the plausible mechanism for the reaction $2A + B \rightarrow C$ because:

- Summation of its steps gives $2A + B \rightarrow C$ which is equal to the given overall reaction equation, and
- Rate law of the overall reaction deduced from it ($R = k[A][B]$) is the same as the given experimental rate law of the reaction.

Don't overlook this point!
In predicting reaction mechanism, no steps can have more than molecularity of 3 (even molecularity of 3 itself is not common).

Energy profile diagram for multistep reaction mechanism

In a multistep reaction, each step will have its own activation energy and therefore its own transition state (activated complex); where the step with highest activation energy will be the slowest one and hence the rate determining step for the reaction.

For the reaction, with three steps in the reaction mechanism, its energy profile diagram will look as follows:

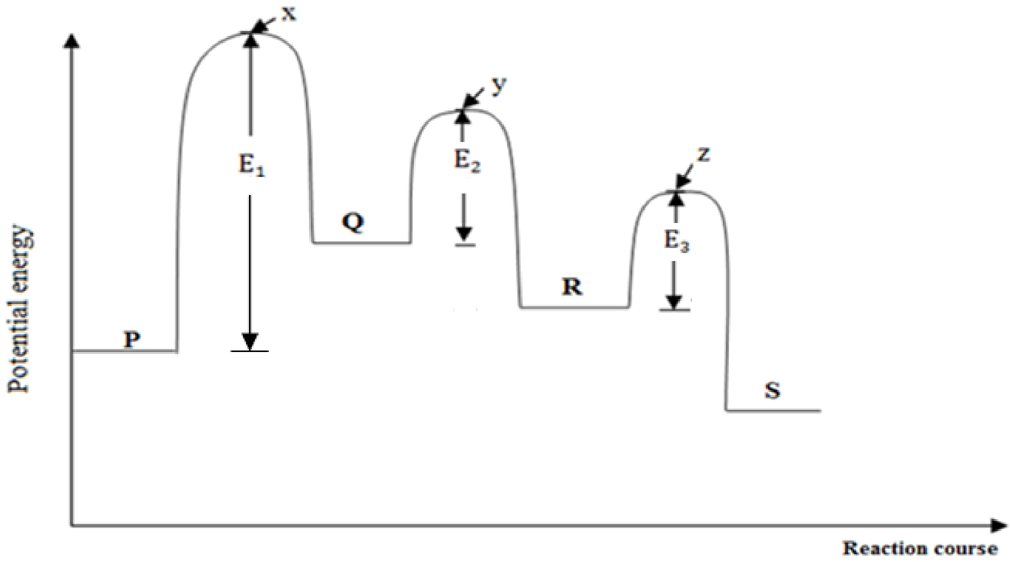


Figure 12.1 Energy profile diagram for multi-step reaction mechanism

Where: E_1, E_2 and E_3 are activation energy for first, second and third step respectively

Q and R are reaction intermediates for first and second step respectively

X, Y and Z are transition states for first, second and third step respectively

P is the reactant for first step

S is the product for the third step

Differences between order and molecularity of reaction

Differences between order and molecularity of reaction are summarised in the table below.

Table 12.1 Differences between order and molecularity of reaction

	ORDER		MOLECULARITY
01	Is the sum of the powers of concentrations in the rate law	01	Is the total number of atoms, molecules or ions taking part in an elementary reaction
02	Order corresponds to the overall reaction.	02	Molecularity is defined for elementary reactions.
03	Order of a reaction can change with the conditions such as pressure, concentration etc.	03	Molecularity is invariant for a chemical equation.
04	It may be zero, positive or negative integers	04	It may be only positive integers (1, 2 or 3)
05	It may be fraction	05	It must be whole number
06	It is determined experimentally	06	It is deduced theoretically from the mechanism of the reaction

Example 1

Ozone reacts with NO_2 to give dinitrogen pentoxide and oxygen:

$$O_3(g) + 2NO_2(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction occurs in the following two steps:

Step 1: $O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$

Step 2: $NO_3(g) + NO_2(g) \longrightarrow N_2O_5\ (g)$

The experimental rate law is Rate $= K[O_3][NO_2]$

What can you say about the relative rate of the two steps of the mechanism?

Solution

Step 1 is slower than step 2 (because rate law of step 1 is the same as experimental rate law of overall reaction and hence it must the rate –determining step).

Example 2

Propose a mechanism for the reaction: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ and show that the chosen mechanism is consisted with the rate law; $R = k[NO]^2[O_2]$

Solution

Mechanism

Step 1: $2NO + NO \rightleftharpoons N_2O_2$ (fast)

Step: 2 $N_2O_2 + O_2 \longrightarrow 2NO_2$ (slow)

Showing that mechanism is consistent with the given rate law:

From step 2 (rate determining step)

$R = k[N_2O_2]\ [O_2]$

Eliminating $[N_2O_2]$ by using the fact that:

$k_f[NO]^2 = K_b[N_2O_2]$ ($R_f = R_b$ For rapid equilibrium in step 1)

From which $[N_2O_2] = \frac{k_f}{k_b}[NO]^2$

Thus $R = \frac{k \times k_f}{k_b}\ [NO]^2[O_2]$

But $R = \frac{k \times k_f}{k_b}$ gives another modified rate constant k say k'

Hence $R = k[NO]^2[O_2]$ and the given mechanism is consistent with the given rate law.

Example 3

The reaction between NO and H_2 is believed to occur in the following three-step process.

$$NO + NO \rightleftharpoons NO_2O_2 \text{ (fast)}$$

$$NO_2O_2 + H_2 \longrightarrow N_2O + H_2O \text{ (slow)}$$

$$N_2O + H_2 \longrightarrow N_2 + H_2O \qquad \text{(fast)}$$

(a) Write a balanced equation for the overall reaction
(b) Identify the intermediates in the reaction. Explain your reasoning
(c) From the mechanism represented above, a student correctly deduced that the rate law for the reaction is; Rate= $K[NO]^2[H_2]$. The student then concluded that:

1. The reaction is third order, and

2. The mechanism involves the simultaneous collision of two NO molecules and a H_2 molecule. Are conclusions **1** and **2** correct? Explain.

(d) Explain why an increase in temperature increases the rate constant, k, given the rate law in (c).

Solution

(a) Given that:

$$NO + NO \rightleftharpoons N_2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(i)$$

$$N_2O_2 + H_2 \longrightarrow H_2O + N_2O \ldots\ldots\ldots\ (ii)$$

$$N_2O + H_2 \longrightarrow N_2 + H_2O \ \ldots\ldots\ldots\ldots\ (iii)$$

Taking (i) + (ii) + (iii);

$$NO + NO + NO_2O_2 + H_2 + N_2O + H_2 \longrightarrow NO_2O_2 + N_2O + H_2O + N_2 + H_2O$$

Cancelling like terms which appears in opposite sides;

$$NO + NO + \cancel{NO_2O_2} + H_2 + \cancel{N_2O} + H_2 \longrightarrow \cancel{NO_2O_2} + \cancel{N_2O} + H_2O + N_2 + H_2O$$

Combining like terms which appears in the same side gives overall reaction equation which is;

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ (overall reaction)

(b) N_2O_2 and N_2O

Reason

They appear in the elementary reactions of the mechanism but not in the overall products or reactants of the overall reaction

(c) Conclusion **1** is correct.

Explanation:

The sum of the powers (exponents) in the rate law is 2+1=3, showing the overall third order

(d) Conclusion **2** is not correct.

Explanation:

No elementary reaction (step) in the mechanism involves two NO molecules and one H_2 molecules

Increase in temperature, increase the rate of reaction. So from the rate law, $\text{rate} = K[NO]^2[H_2]$ as the concentration does not change with temperature the value of K must change to explain the change in the rate of reaction

DIGGING DEEPER EXERCISE 12

EXERCISE 12A: BINDER QUESTIONS

Question 1

For the elementary step of a chemical reaction:

$$A + H_2O \longrightarrow B; \text{ Rate} \propto [A]$$

What is the (i) Molecularity and (ii) Order of the reaction?

Question 2

Reactions of high molecularity are less in number. Explain.

Question 3

Why can't molecularity of any reaction be equal to zero or negative?

Question 4

In a reaction mechanism:

(a) What is the difference between an **activated complex** and an **intermediate**?
(b) What is meant by the rate-determining step?
(c) Which elementary reaction in a reaction mechanism is often the rate-determining step?

Question 5

(i) What are the chief requirements that must be met by a plausible reaction mechanism?
(ii) Why do we say "plausible" mechanism rather than "correct" mechanism?

Question 6

The mechanism of reaction is shown below.

(a) What is the overall reaction?
(b) Which compounds are intermediates?
(c) Predict the rate law based on this mechanism
(d) What is the overall order of reaction?

$$HOOH + I^- \longrightarrow HOI + OH^- \text{ (Slow)}$$

$$HOI + I^- \longrightarrow I_2 + OH^- \text{ (Fast)}$$

$$2OH^- + 2H_3O^+ \longrightarrow 4H_2O \text{ (Fast)}$$

Question 7

Consider the following hypothetical reaction: $2XY \longrightarrow X_2 + Y_2$

For the hypothetical reaction above:

(a) Give a rate law that shows that the reaction is first order in the reactant XY
(b) Give the units for the specific rate constant for this rate law
(c) Propose a possible mechanism for the reaction.

Question 8

When we find a reaction mechanism, according to the rate law, that perfectly works to solve a complex reaction, why can we not say that the reaction mechanism proves that the rate law is right?

EXERCISE 12B: REAL QUESTIONS

Question 9

"Understanding reaction mechanism is crucial in everyday life." Justify this statement by outlining at least three points.

Question 10

Most of your fellow students fail to make sense of reaction mechanism. Fortunately, you are one of few students who have mastered well the concept. Your chemistry teacher, assigned you to help your classmates to understand the concept by using a process of making tea as analogy to chemical reaction. Starting with a cup of hot water, a tea bag and sugar;

(i) Give one possible mechanism for making tea.
(ii) Deduce overall equation for the process.
(iii) Identify intermediate (s).

Question 11

One of real reactions occurring in the atmosphere is a catalysed decomposition of ozone (O_3) which occurs in a series of steps as illustrated below;

Step 1: $O_3 + \text{sunlight} \longrightarrow O_2 + O$

Step 2: $O_3 + NO \longrightarrow NO_2 + O_2$

Step 3: $NO_2 + O \longrightarrow NO + O_2$

Write the equation for the overall reaction and then identify the catalyst.

Question 12

An environment concern is the depletion of ozone O_3, in the Earth's upper atmosphere, where O_3 is normally in equilibrium with $O_2$and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

Step1: $O_3 + Cl \longrightarrow O_2 + ClO$

Step2: $ClO + O \longrightarrow Cl + O_2$

(a) Write balance equation for the overall reaction represented by step 1 step 2 above.
(b) Clearly identify the catalyst in the mechanism above. Justify your answer.
(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

Question 13

You were arguing with your friend, **Kipute** about the effect of temperature on the reaction rate. **Kipute** gave a statement that was completely against your understanding. *"Temperature does not increase the rate of all reactions. There are several enzymatic reactions and even inorganic reactions whose rate tend to decrease as the temperature increases."* She said with a tone reflecting her confidence for what she is saying. *"What?! Are you kidding me? Even inorganic reactions?"* You responded with a voice of disbelief. *"I know enzymes may become inactive at high temperature; so for those biological reactions which depend on enzymes as their catalyst, their rates are lowered at high temperature; that's absolutely true. But for inorganic reactions! I don't agree at all."* Now with a tone of calmness, you added, *"Please, can you show me how this can happen? I want to make sense of it if such thing exists!" "Okay, I'm going to show it to you."* **Kipute** replied, she took a piece of paper and wrote the following mechanism for hypothetical reaction of A to give products:

Step 1: $A \rightleftharpoons B$ (Fast, exothermic).

Step 2: $B \longrightarrow \text{Products}$ (Slow)

Now, after studying above mechanism, explain how the mechanism supports **Kipute's** argument.

EXERCISE 12C: HOT QUESTIONS

Question 14

Consider the reaction: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

(a) If the reaction would follow a one elementary step mechanism, what would be the rate law?
(b) However, the experimentally determined rate law was found to be; Rate = $k[NO_2]^2$. This suggests that the reaction must involve at least two elementary steps. Propose one mechanism which agrees with the experimental rate law.

Question 15

Consider the following reaction: $A(g) + B(g) \longrightarrow C(g) + D(g)$ ΔH^{θ} reactiion $= -10kJ/mol$

(a) Describe the two factors that determine whether a collision between molecules A and B results in a reaction
(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
(c) Write the rate law equation that would result in the reaction proceeded by the mechanism shown below

$$A + B \rightleftharpoons AB \text{ (fast)}$$
$$AB + B \longrightarrow C + D \text{ (slow)}$$

(d) Explain why a catalyst increases the rate of reaction?

Question 16

$2A + 2B \longrightarrow C + D$

The following data about the reaction above were obtained from three experiments:

Experiment	[A]	[B]	Initial rate of formation of C in $molL^{-1}\ min^{-1}$
1	0.60	0.15	6.3×10^{-3}
2	0.20	0.60	2.8×10^{-3}
3	0.20	0.15	7.0×10^{-4}

(a) What is the rate equation for the reaction?
(b) What is the numerical value of the rate constant? What are its dimensions?
(c) Propose a reaction mechanism for this reaction

Question 17

NO reacts with H_2 according to the following equation: $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

The reaction has rate law of $R = k[H_2][NO]^2$ and its proposed mechanism is as follows:

Step 1: $NO + NO \longrightarrow N_2O_2$

Step2: $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$

Step 3: $N_2O + H_2 \longrightarrow H_2O + N_2$

(a) Based on the data presented, which of the step is the rate determining step?
(b) Show that the mechanism is consistent with;
    (i) The observed rate law for the reaction, and
    (ii) The overall stoichiometry of the reaction

Question 18

The decomposition of hydrogen peroxide is catalysed by iodide ion;

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

Find a possible mechanism and identify the intermediate

Question 19

Consider the following diagram:

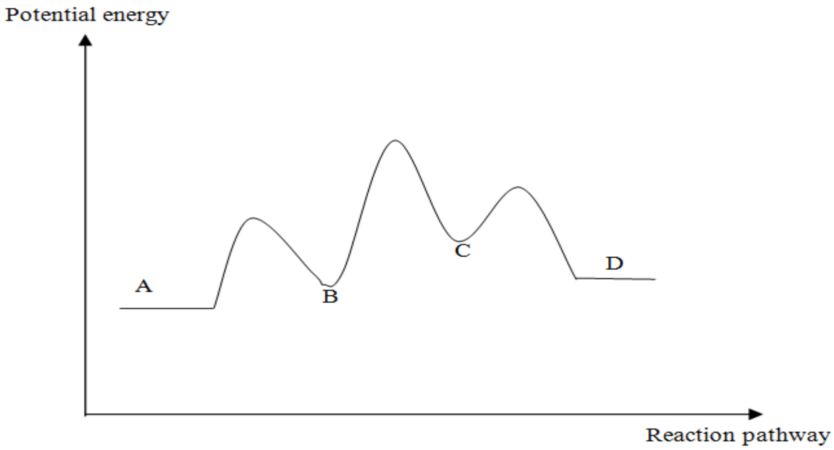


Figure 12.2 Energy profile diagram for question 12

(i) How many elementary reactions are there in the mechanism?
(ii) How many intermediates?
(iii) Which step is rate limiting?
(iv) Which is the fastest step?
(v) Is the reaction exothermic or endothermic?

EXAMINATION QUESTIONS FOR PART THREE

Question 1

(a) Why termolecular elementary reactions are very rare?
(b) At 298K the following data was obtained from the following reaction $A + B \rightarrow C + D$

[A]/M	[B]/M	Rate /Ms^{-1}
0.1	0.1	5.02×10^{-4}
0.1	0.05	2.51×10^{-4}
0.05	0.05	1.251×10^{-4}

(i) What is the order of reaction with respect to each other?
(ii) What is the rate constant at 298K?
(iii) If at 342K the rate constant for the reaction was $6.71\ M^{-1}\ sec^{-1}$, what was the activation energy of the reaction?
(iv) What was the rate constant at 310K?

Question 2

(a) Give one reason to support or oppose each of the following:
(i) The rate of every common reaction is favoured by increasing temperature
(ii) Catalysed reaction has higher activation energy than uncatalysed reaction
(iii) Rate of reaction increase with concentration in a zero order reaction
(b) The rate constant for thermal decomposition of first order reaction:

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$ at 593K is $2.2 \times 10^{-5}\ sec^{-1}$. What percentage of the sample will decompose after heating the sample at this temperature for 1hour?

Question 3

(a) *An elementary reaction is characterized by its molecularity, which is the number of particles or molecules involved in the formation of transition-state complex.* Based on this statement, state types of elementary reactions.
(b) Given the reaction between A and B;

Experiment	[A] / M	[B] / M	Rate
1	0.1	1.0	5.02×10^{-4}
2	0.2	1.0	1.004×10^{-3}
3	0.2	2.0	2.008×10^{-3}

Find the overall order of reaction.

Question 4

(a) State the meaning of **activation energy** in terms of **threshold energy** and hence give the mathematical equation that relates the two terms.
(b) Mercury (II) Chloride, $HgCl_2$ reacts with oxalate $C_2O_4^{2-}$ to give precipitate of Hg_2Cl_2

$2HgCl_2 + C_2O_4^{2-} \rightarrow Hg_2Cl_2 + 2Cl^- + 2CO_2$

Initial rates at 373K and concentration expressed as $moldm^{-3}min^{-1}$ and $moldm^{-3}$ respectively are shown in the following table:

Experiment	[$HgCl_2$]	[$C_2O_4^{2-}$]	Rate $\times 10^{-4}$
1	0.0836	0.202	0.52
2	0.0836	0.404	2.08
3	0.0418	0.404	1.06

(i) Deduce the order of reaction with respect to each reactant
(ii) Write down the rate law expression for this reaction
(iii) Calculate the value of rate constant and its correct units if any
(iv) Determine the overall order of reaction

Question 5

(a) Why stirring reacting mixture increases the rate of reaction?
(b) In experimental studies on the hydrolysis of sucrose to glucose and fructose at 25℃

$$C_{12}H_{22}O_{11} \rightarrow \text{Glucose} + \text{fructose}$$

Time /Min	$[C_{12}H_{22}O_{11}]/M$
0.00	1.0023
30.00	0.9022
60.00	0.8077
90.00	0.7253
130.00	0.6300
160.00	0.5750
200.00	0.5010

(i) Determine the half-life and order of reaction
(ii) What would be the $[C_{12}H_{22}O_{11}]$ after 4 hours of reaction

Question 6

(a) Many coalmine disasters have resulted when a spark ignites coal dust in the air. Explain using the collision theory.
(b) The half-life of radium is 1590 years. How long will it take for a sample of radium to decay to 25% of its original radioactivity? Assume this reaction to be first order.

Question 7

(a) Why a lump of coal does not react with oxygen at room temperature and pressure?
(b) If the half-life of a radioactive element is 300sec, what percentage of the isotope will remain after 1200 seconds? Assume this reaction to be first order reaction

Question 8

(a) State two reasons why some collisions may not result in a chemical reaction.
(b) Calculate the activation energy, E_a, for the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + {}^1/_2\, O_2(g)$, from the following information:

k at 20℃ is $4.46 \times 10^{-5}/s$

k at 55℃ is $1.5 \times 10^{-3}/s$

Question 9

(a) *"In one reaction 2g of aluminium was formed after every 5 minutes while 2g of iron was formed after the same time by another reaction."* Does this mean the rate of formation of aluminium is equal to that of iron? Explain.

(b) The table below gives the value of varying terms of the reaction rate constant for given reaction:

$$NH_3 \rightarrow {}^1/_2 N_2 + {}^3/_2 H_2$$

Temperature (K)	$k(sec^{-1})$
273	7.9×10^{-7}
298	3.5×10^{-5}
303	1.4×10^{-4}
312	5.0×10^{-4}
318	1.5×10^{-3}
320	4.9×10^{-3}

(i) Determine the activation energy
(ii) Arrhenius factor

Question 10

(a) What is the difference between half-life of a zero order reaction and that of second order reaction?

(b) Consider the following reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$
If the rate constant, k at 317°C and 427°C is $1.4 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$ and $6.4 \times 10^{-2}\ dm^3\ mol^{-1}s^{-1}$ respectively; what is the activation energy E_a for the reaction?

Question 11

(a) *"There is more than one method which can be employed in determining order of chemical reaction from kinetic data."* Justify this statement.

(b) The reaction between compound Y and Z represented as $Z(g) + 3Y(g) \rightarrow ZY_3(g)$
The reaction produced the following experimental results show in the following table:

Experiments	Initial concentration of Z ($mol\ dm^{-3}$)	Initial concentration of Y($mol\ dm^{-3}$)	Initial rate of formation of ZY_3 ($mol\ dm^{-3}min^{-1}$)
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.100	0.300	0.01805
4	0.200	0.100	0.00399
5	0.300	0.100	0.00601

(i) Using the results in the table calculate the order with respect to: Z, Y, and overall reaction.
(ii) Find the rate constant for the reaction and its units.

Question 12

(a) For each of the following reactions suggest any two properties which can be followed in measuring the rate of its reaction.
(i) $2KMnO_4(aq) + 5H_2C_2O_4(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l) + 10CO_2(g)$
(ii) $CuCl_2(aq) + 2AgNO_3(aq) \rightarrow CuNO_3(aq) + 2AgCl(s)$

(b) For first order reaction at 27°C, the concentration of the reactant is reduced to half of its initial value after 5000seconds. At 37°C the concentration is halved after 1000seconds Calculate:
(i) The rate constant at 27°C and 37°C
(ii) The activation energy of the reaction

Question 13

(a) It is known that an increase in concentration of reactant(s) tend to increase rate of chemical reactions.
  (i) How the increase in concentration increases the rate?
  (ii) Doubling the concentration of reactant always doubles the reaction rate. Is this true? Explain.

(b) The rate of decomposition of hydrogen peroxide was studied by titrating known volumes of the reaction mixture with potassium permanganate at different time intervals and the results obtained were tabulated as follows:

Volume of $KMnO_4$ used (cm^3)	75	47	30	13	7.20
Time (minutes)	00	06	09	20	29

  (i) Show that the reaction is first order.
  (ii) Find the rate constant.

Question 14

(a) Activation energy plays crucial role in determining rate of chemical reactions.
  (i) What is the relationship between activation energy and the reaction rate?
  (ii) Explain factors affecting activation energy.

(b) A gaseous reaction: $2A + B \rightarrow A_2B$ take place in two steps;

$A + B \rightarrow AB$ ………………………………………… (1)

$AB + A \rightarrow A_2B$ …………………………………… (2)

It was observed that when concentration of B was kept constant while that of A doubled, the rate of reaction doubled. When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled.

  (i) Out of the two steps of reaction (1) and (2) above, which one is the rate determining step?
  (ii) Write an expression representing the rate law for this gaseous reaction.

Question 15

(a) When helium gas is added to a reaction vessel containing nitrogen and hydrogen gas under suitable condition to allow the formation of ammonia, total pressure in the vessel increases; however, the rate of formation ammonia remains the same. Explain why the rate remains constant?

(b) For the reaction between G and F the following initial rates were measured at 25°C

S/N	Initial rates($moldm^{-3}\ s^{-1}$)	G ($moldm^{-3}$)	F($moldm^{-3}$)
1	3.10×10^{-3}	2.0	3.0
2	7.75×10^{-4}	1.0	1.5

Calculate the overall order of reaction between G and F if the rate constant is $3.44 \times 10^{-4}\ dm^3\ mol^{-1}\ sec^{-1}$

Question 16

(a) Is it possible to alter activation energy of given reaction? Explain.

(b) One of the dozens of reactions that may occur in is a single ridden area is the linked oxidation of carbon monoxide and nitric oxide: $CO + NO + O_2 \rightarrow CO_2 + NO_2$

One suggested mechanism for this reaction involves the unstable molecular fragment HO as a catalyst

  (i) Verify that these steps add to give the correct net reaction.
  (ii) Identify the intermediates in the mechanism.
  (iii) Tell why HO is considered to be a catalyst in this reaction path way.

Question 17

(a) In performing experiment which involves the reaction between zinc and hydrochloric acid, zinc powder is preferred to zinc wire; why?

(b) The half-life for the disintegration of an is tope $X - 210$ is 3days .Calculated the:

(i) Rate constant in sec^{-1}

(ii) Time in days needed for 0.031mg of $x - 210$ to disintegrate to 0.001mg

Question 18

(a) Reaction rate is also known as reaction speed or reaction velocity. Why do you think it is more appropriate to use reaction velocity than reaction speed?

(b) A gaseous reaction:

$2Z(g) + W(g) \rightarrow Z_2W(g)$, takes place in two steps:

$Z(g) + W(g) \rightarrow ZW$……………………………….I **(slow)**

$Z + ZW \rightarrow Z_2W$…………………………………..II **(fast)**

Deduce the following:

(i) The rate equation of the overall reaction.

(ii) The molecularity of slow step.

Question 19

(a) How does a catalyst increase the rate of a chemical reaction?

(b) The data analysis of the results of the experiment of certain reaction indicated that the graph of $\log_{10}$ k against $\frac{1}{T}$ gave a slope of -9.8×10^3K.

(i) What is the value of activation energy?

(ii) Calculate the factor by which the rate decreased when the rate temperature was lowered from $409K$ to $389K$

Question 20

For a reversible reaction shown below $\Delta H^\theta = +50kJ$ and the activation energy, $E_a = 200kJ$ for the forward reaction: $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

The following data was obtained experimentally on the rates of reaction under different conditions at 300K

[A] / M	[B] M	Rate / $Msec^{-1}$
$2 \times 10^{-2}M$	$1 \times 10^{-2}M$	1×10^2
$2 \times 10^{-2}M$	$2 \times 10^{-2}M$	2×10^2
$4 \times 10^{-2}M$	$1 \times 10^{-2}M$	2×10^2

(i) Write down the expression for the experimental rate equation using this data and show your reasoning.

(ii) Calculate the rate constant at 300K and give its units.

(iii) What is the activation energy of backward reaction?

Question 21

(a) If a particular reactant in a chemical reaction has negative order; what does this mean?

(b) X and Y reacts together. For a three –fold increase in the concentration of X there is a nine-fold increase in the rate of reaction. What is the order of reaction with respect to X?

Question 22

(a) If a reactant has an order of -1, what happens to the initial reaction rate when the concentration of that reactant is tripled?

(b) The initial rate of a second– order reaction is 8.0×10^{-3} $moldm^{-3}$. The initial concentrations of the two reactants, A and B are 0.2 $moldm^{-3}$. What is the rate constant in $dm^3mol^{-1}s^{-1}$?

Question 23

(a) With an example in each case, give two evidences of presence of activation energy.
(b) The following data was collected from the mode on position of acetaldehyde: $CH_3CHO \rightarrow CH_4 + CO$

Initial pressure of CH_3CHO/atm	Initial rate atm / sec
0.46	1.04
0.20	2.05×10^{-4}

Calculate the rate constant for this reaction.

Question 24

(a) A large excess of zinc was added to $100cm^3$ of 0.2M hydrochloric acid. After the reaction had ended, $240cm^3$ of hydrogen been formed. In three further experiments, extra substances were added to the original mixture as shown in the table below. Fill in the table to show the total volume of hydrogen formed in each experiment and the qualitative effect of these additions on the initial rate of reaction compared to the original experiment.

Substances added to an excess of zinc and $100cm^3$ of 0.2M hydrochloric acid	**Volume of hydrogen/cm^3**	**Effect on initial rate of reaction**
$100cm^3$ water		
10g zinc		
$50cm^3$ 0.2M hydrochloric acid		

(b) The rate of reaction between compounds A and B was studied at a fixed temperature and some results obtained are shown in the table below.

Experiment	**Initial concentration of A/$moldm^{-3}$**	**Initial concentration of B/$moldm^{-3}$**	**Initial rate/ $moldm^{-3}s^{-1}$**
1	0.16	0.20	5.0×10^{-5}
2	0.24	0.20	7.5×10^{-5}
3	0.32	0.10	5.0×10^{-5}
4	0.12	0.15	To be calculated

Use the data in the table to deduced the order of reaction with respect to compound A and the order of reaction with respect to compound B. Hence calculate the initial rate of reaction in experiment 4.

Question 25

(a) How can you distinguish between an intermediate and a catalyst in the reaction mechanism?
(b) The rate equation for the decomposition of a compound N has a rate constant with the units s^{-1}. The rate constant is $4.31 \times 10^3 s^{-1}$ at 700K and $1.78 \times 10^4 s^{-1}$at a temperature T. Use this information to deduce the overall order of reaction and whether temperature T is greater or smaller than 700K.

Question 26

(a) When you are performing titration experiment in the laboratory, how pressure affects the time taken to observe end-point? Explain.
(b) For 1 mole of a particular gas, the average molecular energy is found to be $1.3kJ/mol$ at 298K. Approximately how many molecules have at least five times the average molecular kinetic energy.

Question 27

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

For the exothermic reaction represented above, carried out at $298K$, the rate law is as follows;

$$\text{Rate } = K[H_2][I_2]$$

Predict the effect of each of the following changes on the initial rate of reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume
(b) Increase in volume of the reaction vessel at constant temperature
(c) Addition of catalyst. In your explanation, include diagram of potential energy versus reaction coordinate.
(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

Question 28

An initial- rate study was performed on the reaction system. Data for the experiment are given in the table below

Trial	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of disappearance of Mno_4^- in Ms^{-1}
1	0.0104	0.0040	3.00	2.25×10^{-8}
2	0.0312	0.0040	3.00	2.03×10^{-7}
3	0.0312	0.0020	3.00	1.02×10^{-7}

(a) Using the information in the table, determine the order of the reaction with respect to each of the following; justify your answer.
  (i) Cl^-
  (ii) MnO_4^-
(b) The reaction is known is to be third order with respect to H^+. Use this information and your answers to part (a) above, complete both of the following.
  (i) Write the rate law for the reaction
  (ii) Calculate the value of the rate constant, k, for the reaction, including appropriate units
(c) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

Question 29

Some alkyl halides, such as $(CH_3)_3CCl$, $(CH_3)_2CBr$ and $(CH_3)_3CI$, represented by RX are believed to react with water according to the following sequence of reactions to produce alcohols

$$RX \longrightarrow R^+ + X^- \text{ (Slow reaction)}$$

$$R^+ + H_2O \longrightarrow ROH + H^+ \text{ (Fast reaction)}$$

(a) For the hydrolysis of RX,write a rate expression constant with the reaction sequence above
(b) When the alkyl halides RCl,RBr and RI are added to water under the same experimental conditions, the rates are in the order RI > RBr > RCl. Construct properly labelled potential energy diagrams that are consistent with the information on the rates of hydrolysis of the three alkyl halides. Assume that the reactions are exothermic.

Question 30

Consider the following reaction: $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$; $\Delta H^\theta = -137kJ/mol$

Account for the following observations regarding the exothermic reaction represented by the equation above.

(a) An increase in the pressure of the reactants causes an increase in the reaction rate.
(b) A small increase in temperature causes a large increase in the reaction rate.
(c) The presence of metallic nickel causes an increase in the reaction rate
(d) The presence of powdered nickel causes a larger increase in reaction rate than does the presence of a single piece of nickel of the same mass.

ANSWERS TO DIGGING DEEPER EXERCISES

EXERCISE 9

1. The rate of a reaction is defined as the change in concentration as a function of time. Thus, the two quantities that must be measured are:

1) Molarity of either a reactant or product and
2) Time.

2. As the reaction proceeds, concentration of reactants decreases and whence the rate of reaction decreases. So the reaction rate is unique in each particular instant of time. This makes the average rate which is taken over certain range of time less useful. To get true picture of the reaction, instantaneous rate of reaction is used.

3.(a)

(i) Number of collisions between particles per second.
(ii) Combined energy of the colliding particles.
(iii) Minimum collision energy required for a collision to be successful.

(b) **Collision frequency can be changed by;**

- Changing pressure (greater pressure means more collision frequency and vice-versa)
- Changing concentration (greater concentration of reactant means more collision frequency vice-versa)
- Changing temperature (Higher temperature means more collision frequency and vice-versa)
- Changing surface area (Greater surface area of reactant means more collision frequency and vice-versa)

Collision energy can be changed by changing temperature (Higher temperature means greater collision energy and vice-versa)
Activation energy can be changed by adding or removing catalyst (in most cases, addition of catalyst, lowers activation energy and vice-versa).

4.

(i) Greater collision frequency means greater rate of chemical reaction and vice-versa
(ii) Greater collision energy means greater rate of chemical reaction and vice-versa.
(iii) Greater activation energy means lower rate of reaction and vice-versa.

5.

Temperature

The increase in temperature increases both collision frequency and collision energy of reacting particles and hence the rate of chemical reaction increases with rise in temperature.

Concentration

The increase in concentration of reactants increases collision frequency and hence the reaction rate will increase as the reactants concentration increases.

Light

The increase in the light intensity increases the number of photons in light and therefore more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change. Consequently, the rate of photochemical reactions, increase with increase in the intensity of suitable light used.

Pressure

The increase in partial pressure of gaseous reactants increases collision frequency and hence the reaction rate will increase as the pressure increases.

Surface area

The greater surface area exposed, the greater chance of collisions between reacting particles leading to higher collision frequency and hence the rate of a reaction increases with increase in the surface area of solid reactant.

6. Usually the reaction rate depends on concentration of reactants. As the reaction proceed, concentration of reactants is progressively decreasing leading to the progressive decrease in the reaction rate as well.

7.

$$-\frac{1}{3}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$$

8. Because of the 2:1 stoichiometric ratio between NO and N_2, the NO must use 2 moles for each mole of N_2 produced. This means that the rate of consumption of NO is twice as fast as the rate of production of N_2.

9. $0.4 \text{molL}^{-1}\text{hr}^{-1}$ **10.** $6.36 \times 10^{-5} \text{M/s}$ **11.** (a) $8.4 \times 10^{-7} \text{M/s}$ (b) $2.1 \times 10^{-7} \text{M/s}$

12. Food spoilage is the chemical reaction. So low temperature of the fridge decreases the rate of the spoilage process.

13. Because the iron rusting reaction has very high activation energy which makes the reaction slow.

14. Higher temperature in hot water increases the rate of reaction that makes the light sticks to produce light.

15. For the combustion reaction to occur between woods and air, the potential energy of the reactants must be large enough to overcome activation energy. Since the activation energy for the reaction is too high to be achieved at room temperature, woods do not burn themselves unless they are ignited.

16. Coal dust has larger surface area than the coal lump. Larger surface area means more frequent collision between coal particles and oxygen molecules in air and hence higher reaction rate.

17. The activation energy of combustion of coal is so high that cannot be attained at normal temperature. When the flame is applied, part of coal and air in contact with the flame absorb heat energy from the flame and the heat is enough to overcome activation energy making the combustion to begin. The heat generated in the initial stage of combustion, liberates more heat to overcome activation energy and the combustion continues.

18. Changing magnesium from ribbon to powder increase surface area for the magnesium. The increase in the surface area increases more frequency of collisions than the increase in concentration and hence the reaction rate is increased more by changing the magnesium to powder than doubling the acid concentration.

19. Initially, the reaction rate is low because both reactants are negatively charged making to repel each other and hence high activation energy for the reaction.

Thereafter, the reaction rate increases because Mn^{2+} ions which act as autocatalyst provides an alternative route with lower activation energy.

Finally, near the end of the reaction, the reaction rate decreases because the concentration (amount) of reactants has been decreased.

20. Due to very high activation energy of reactants (H_2 and O_2), room temperature does not exert enough kinetic energy to the gases' molecules and hence collision energy between the two gases is insufficient to overcome the activation energy.

21. The average rate (which is the mean of several instantaneous rates taken over a period of time) after 60minutes is smaller than after 30minutes. This is due to the fact that instantaneous rates of a reaction decreases as time progresses due to decrease in concentrations of reactants. Hence the average rate taken over a longer period (60 minutes) would have a smaller value compared to that taken over a shorter period (30min) after the reaction begins.

22. To achieve effective collision between reacting molecules, the collision must have both activation energy and proper orientation of colliding molecules. So the reaction whose most of its colliding reactant molecules have improper orientation will be slow even if those colliding molecules have attained activation energy.

23. Hint: Draw well labelled energy profile diagram suiting given data; from which you can easily deduce the energy values which are asked in the question.

(a) 25 kJ (b) 16 kJ (c) 6 kJ

24. (a) 0.15g/s (b) 13.3g
Hint: mass of flask and contents decrease due the loss of oxygen gas as the flask was open. So $(150 - 145)$ g or 4.5g is the mass of oxygen produced in 30s.

25. 0.55min

EXERCISE 10

1. Zero order: Half-life is directly proportional to the initial concentration of reactant.

First order: Half-life remains constant even after varying initial concentration of reactant**.**

Second order: Half-life is inversely proportional to the initial concentration of reactant.

2. Zero order

Explanation

The rate of reaction did not change even after decreasing the concentration of reactant. This implies that, the reaction rate is independent to the concentration and hence it must be of zero order.

3. Any reaction including zero order reactions needs concentration of reactants for the reaction to take place (a reaction cannot continue if the concentration of the reactant(s) is zero). It is the **rate** of reaction that is independent and not the reaction itself.

4.

(i) **Catalytic decomposition of HI over the surface of gold metal at high pressure (**to give hydrogen gas and iodine gas) and **photochemical combination of hydrogen gas and chlorine gas** to give hydrogen chloride gas.
(ii) **Decomposition of hydrogen peroxide** (to give water and oxygen gas) and **radioactive decay**.
(iii) **Thermal decomposition of hydrogen iodide** (to give hydrogen gas and iodine gas) and **thermal decomposition of nitrogen dioxide (**to give nitrogen monoxide gas and oxygen gas).
(iv) **Acid hydrolysis of ester** (to give carboxylic acid and alcohol) and **acid hydrolysis of sucrose** (to give glucose and fructose).

5. 444s

6.

(i) Third order.
(ii) The reaction rate will increase by a factor of 8.

7. First order $(\text{order} = 1)$

8. 144 minutes

9. $1.15 \times 10^{-6}\%$

10. 8.3s

11.

(i) First order with respect to A, third order with respect to B.

(ii) $7.4 \times 10^{13} L^3 mol^{-3} sec^{-1}$

12.

(a) $5.17 \times 10^{-3}\ s^{-1}$.

(b) $t_{3/4}$ does not depend on the initial concentration because this is a first order reaction, which means that the time required for given fraction of reactant to react is only related to the rate constant.

13. The order with respect to BrO_3^- is 1; The order with respect to Br^- is 1**;** The order with respect to H^+ is 2

The overall order of reaction is 4; The value of k is $8 dm^3 mol^{-3} s^{-1}$

14. 5.68g

Assumption: the reaction is of the first order since it is decomposition reaction (Recall: most of the decomposition reactions are first order reactions).

15. A reaction takes place due to collision of reacting molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are very few.

16. Disagree

Explanation

Her statement only holds with reactions with order of one and above in which reaction rate is continuously decreasing as the reaction proceeds due to decrease in concentration of reactants. However, for zero order reactions, the reaction rate does not depend on concentration of reactants and therefore the reaction rate remains constant despite the decrease in concentration.

17. For decomposition of ammonia (or hydrogen iodide) gas, the gas must be adsorbed over the metal which catalyses the reaction. Only ammonia molecules which have been adsorbed by the metal surface are capable of undergoing decomposition. If the entire metal surface has been covered by the gas (at high pressure), the rate of decomposition will remain constant regardless of concentration of the gas because for every adsorbed gas molecule which get decomposed, another unadsorbed gas molecule over the metal surface replace it, get adsorbed and thus keeping number of adsorbed gas molecules constant and the reaction rate as well.

18. Hint: Radioactive decay is the first order reaction.

The percentage that remains is 0.454%.

19. 116.3days

20. Don't agree.

Hint: The order of reaction can be deduced from units of rate constant. Show from units ($M^{-1}s^{-1}$) of given rate constant ($1.83 \times 10^{-3} M^{-1}s^{-1}$) that the reaction is of the second order. Then solve the question by using the integral equation of second order reaction to get the final answer which is 3.8×10^{-5}s.

21. With sufficient PH_3, all of the catalytic sites on the tungsten surface are occupied. Thus, further increase in the amount of phosphine will not affect the reaction rate and hence the rate is independent of $[PH_3]$.

22. 16 minutes

23. First order

24. The rate would decrease to 1/8 of the initial rate.

25. First order

26. 161 minutes

27. Second order

28. 34.2 minutes

29. (a) 2

(b)**(i)**

The order of reaction with respect to A is 2

The order of reaction with respect to B is 0

(ii) Rate equation: $R = K[A]^2$

Units of rate constant: $mol^{-1} dm^3 s^{-1}$

30.

(a) $R = K[HgCl_2][C_2O_4^{2-}]^2$

(b) $7.62 \times 10^{-3} M^{-2} min^{-1}$ (or $7.62 \times 10^{-3} L^6\ mol^{-2} min^{-1}$)

(c) $2.6 \times 10^{-5}\ M min^{-1}$

(d) 0.514M

31.(a) The order of the reaction with respect to $A = 1$

The order of the reaction with respect to $NaOH = 1$

The initial rate in the experiment $4 = 2.4 \times 10^{-3} M/s$

(b)

(i) $R = K[A]$ (or $R = K[A][NaOH]^0$)

(ii) The value is 0.45. Its unit is s^{-1}

(iii) NaOH is so much in excess that more addition of it has no effect on the rate of the reaction.

EXERCISE 11

1.

1) Temperature.
2) Catalyst.
3) Chemical identity of reactants (or nature of reactants).

2. Activation energy (E_a)

3. On increasing the temperature, both collision frequency and collision energy are increased and hence the reaction rate is increased by large extent.

4. Zero activation energy means that both reaction rate and rate constant remains the same even after changing the temperature.

5. Arrhenius constant (A) and activation energy (E_a).

6.

(a) $H-H$ and $Cl-Cl$ bonds are so stable that high energy is required to break the bonds and hence the activation energy for the reaction is very high.
(b) According to Boyle's law increases in pressure (at constant temperature) decrease the volume of gases. This leads to more frequent collisions between hydrogen and chlorine molecules.
(c) According the kinetic theory of gases: increase in temperature increase kinetic energy of hydrogen and chlorine gas. Thus more molecules of hydrogen and chlorine will attain sufficient energy to overcome activation energy.
(d) To increase surface area

7.(i)

Collision energy factor.
When temperature is increased kinetic energy of reacting particles is increased. This makes more reacting particles to attain activation energy and therefore the collisions between the particles become more energetic resulting to the formation of activated complex.
Collision frequency factor.
When temperature is increased, speed of reacting particles is increased thus making the particles to collide more frequently and hence the possibility of reaction between the reacting particles become higher.
(ii) Collision energy factor is more important.
8. $35.9\ \mathrm{kcal/mol}$

Warning!

On your working don't insert simplified Arrhenius equation directly. Because in the question we are already given with the Arrhenius equation in the form of $k = Ae^{-Ea/RT}$, all of your working must start with this form of equation. So in this question, the simplified Arrhenius equation must be applied after showing its derivation from the given equation in the question.

9. (a) 39.4 kJ/mol (b) $2.5 \times 10^{-4} s^{-1}$

10. 390.6K

11. $9.25 \times 10^{14} sec^{-1}$

12. $1715 J/mol (or 1.715 kJ/mol)$

13.

1) Enzymes in the body to help metabolic activities.
2) Catalytic converters in exhaust system of cars to ensure proper combustion of fuel.

14.

1) Milk gets sour faster when it is kept at room temperature instead of being kept in the refrigerator.
2) Eggs tend to hard boil faster when they are at sea level in comparison to mountains or elevated levels.

15. Disagree.

Explanation

Apart from temperature and activation energy, the value of rate constant is also affected by the value of Arrhenius constant which in turn depends on a chance of having proper orientation between reacting molecules. Two reactions with identical activation energy at the same temperature, will have different rate constant even if their reactants have different chances of having proper orientation whereby the reaction whose reactants have greater chance of having proper orientation for the reaction to take place will possess greater value of Arrhenius constant and hence greater value of rate constant.

16. Rate constant increases as temperature increases. So the value of rate constant at 127°C must be greater than that of rate constant at 27°C in contrary to what she got where the rate constant at 127°C is smaller.

17. This can be done by calculating the ratio of reaction rate (which is equal to the ratio of rate constant) by using the calculated activation energy she found and then comparing it with the given ratio as follows:

Using $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.30R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

Since reaction rate varies directly proportional to the rate constant; $\frac{k_2}{k_1} = \frac{R_2}{R_1} = 3$ where R_2 and R_1 is the reaction rate at 20°C and 50°C respectively.

Then $\log\left(\frac{R_2}{R_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

Substituting $\log\left(\frac{R_2}{R_1}\right) = \frac{284.24}{2.303\times8.314}\left(\frac{323-293}{293\times323}\right) = 4.7\times10^{-3}$

From which; $\frac{R_2}{R_1} = \log^{-1}(4.7\times10^{-3}) = 1.01 \neq 3$

Since the calculated ratio (1.01) is not equal to the given ratio (3), Kipute got the wrong answer.

18. From $\log\left(\frac{R_2}{R_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$; $E_a = \frac{2.303\mathbf{R}T_1T_2}{T_2-T_1}\log\left(\frac{R_2}{R_1}\right)$

Thus the wrong value of E_a (284.24J/mol) was found after multiplying incompatible value of R (0.082) to other parameters.

So we have to eliminate it by dividing the incompatible R from the wrong answer and then the compatible R is included through multiplication.

That is; correct $E_a = \frac{284.24\text{J/mol}}{0.082}\times 8.314 = 28819\text{J/mol or } 28.82\text{kJ/mol}$

Hence the correct value of activation energy is 28.82kJ/mol.

19. When temperature is increased by 10℃, kinetic energy of molecules increases, number of molecules possessing activation energy become double, therefore number of effective collision double and hence the rate of reaction double even if the kinetic energy did not double (to double reaction rate, you need **number of particles** which have attained activation energy to be doubled and not kinetic energy).

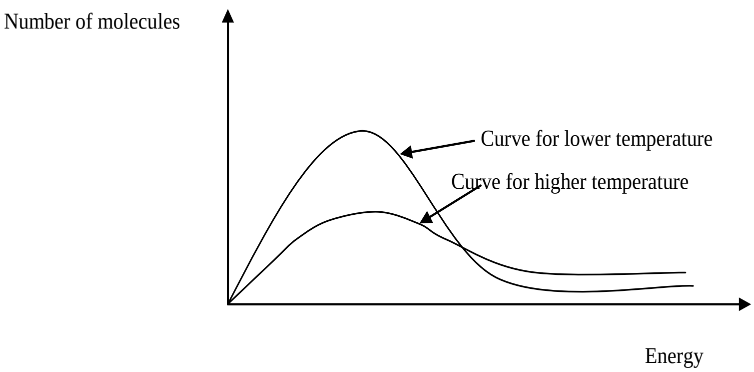
20.

(a) Collision process

Explanation:

Collision process causes some molecules to slow down and therefore loosing 'Kinetic energy'.

(b)



(c)

(i) Very few collisions have energy which is greater than activation energy

(ii) By addition of catalyst

Explanation

Catalyst lower activation energy and therefore more collisions will possess energy which is greater than activation energy.

21. (a) $1.76\times10^2\text{kJ/mol}$ (b) $2.31\times10^{10}\text{Lmol}^{-1}\text{s}^{-1}$

Hint for calculating the value of A in (b)

Select any pair of related rate constant and temperature, and then with the value of E_a obtained in (a) substitute in the Arrhenius equation($k = Ae^{-E_a/RT}$ or $\ln k = \ln A - \frac{E_a}{RT}$) to get the value of A.

22. 24.206 kJ/mol

23. Activation energy, $E_a = 44.027\text{kJ/mol}$**;** Arrhenius factor, $A = 1.13\times10^4\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$

24. 123.5kJ/mol

Hint:

Substitute the rate in place of the rate constant in the equation $\log\left(\frac{K_1}{K_2}\right) = \frac{E_a}{2.303R}\left(\frac{T_1-T_2}{T_1T_2}\right)$ because of the direct relationship between the rate and the rate constant.

25. 108.83kJ/mol

EXERCISE 12

1. (i) 2 (ii) 1

2. The chances that three or more particles are colliding at the same time, with proper orientation and sufficient energy, are extremely small. This makes difficult to have reactions with high molecularity.

3. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, the molecularity will be at least one (cannot be zero or negative).

4.

(a) An **activated complex** is the structure along the reaction pathway of the highest energy, which determines the activation energy for the reaction. An **intermediate** can be any structure found in the reaction path.
(b) The rate-determining step is the elementary reaction that controls the mathematical form of the overall rate law. The rate-determining step is usually the slowest elementary reaction.
(c) The slowest elementary reaction.

5.

(i) A reaction mechanism must meet two criteria.

1) The summation if all steps in the reaction mechanism must agree with the stoichiometry of the overall reaction.
2) The suggested mechanism must agree with the experimental rate law of the overall reaction.

(ii) Reaction mechanisms are considered "plausible" rather than "correct" because different sequences of elementary reactions may meet the two requirements.

6.

(a) $HOOH + 2I^- + 2H_3O^+ \longrightarrow I_2 + 4H_2O$
(b) OH^- and HOI
(c) $R = K[HOOH][I^-]$
(d) Second order (or 2)

7.

(a) $R = k[XY]$
(b) $(\text{unit of time})^{-1}$
(c)

$$XY \longrightarrow X + Y \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{slow}$$
$$XY + X \longrightarrow X_2 + Y \ldots\ldots\ldots\ldots\ldots\text{fast}$$
$$Y + Y \longrightarrow Y_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{fast}$$

Note:

Any other possible mechanism is accepted provided that it satisfies the following conditions:

- Steps in the mechanism add up to the overall reaction
- One step in the mechanism must start with XY
- Rate determining step (slow step) must involve one molecule of XY

As an example, another possible mechanism is;

$$XY \longrightarrow X + Y \quad \text{(slow)}$$
$$XY + Y \longrightarrow Y_2 + X \quad \text{(fast)}$$
$$X + X \longrightarrow X_2 \quad \text{(fast)}$$

8. Reaction mechanism is only a logical explanation of how reaction progresses. It cannot be proven to be true. There may be more than one proposed mechanism, in which the slow elementary step is considered the rate determining step.

9. Reaction mechanism enables understanding of chemical reactions at the molecular level. This is important in the following manner:

1. Chemical reactions optimisation in industries
Through understanding of elementary reactions in the reaction mechanism, reaction rate can be understood. Good understanding of the reaction rate helps in designing and optimising chemical reactions in industrial processes where reaction speed is critical.

2. Designing new compounds
Through knowledge of reaction mechanisms products that will be formed in a reaction can be predicted. This is useful for designing new compounds with specific properties fitting daily life purposes.

3. Development of new drugs and therapeutic agents
Understanding the mechanisms of enzyme-catalysed reactions provides insights into how biological systems function, and thus can lead to the development of new drugs and therapeutic agents.

4. Development of new chemical reactions and catalyst
Understanding the reaction mechanism can provide insight into the underlying factors that govern chemical reactivity, such as bond strengths, steric effects, and electronic properties. This information can be used to design new chemical reactions and develop new catalysts which may be crucial in daily life.

10.

(i) **Mechanism:**
Step 1: $\text{Hot water } + \text{ tea bag} \longrightarrow \text{Hot water} - \text{tea bag mixture}$
Step 2: $\text{Hot water} - \text{tea bag mixture} + \text{sugar} \longrightarrow \text{tea}$
(ii) Taking step 1 + step 2 gives;
Overall equation: $\text{Hot water } + \text{ tea bag} + \text{sugar} \longrightarrow \text{tea}$
(iii) **The intermediate** is $\text{Hot water} - \text{tea bag mixture}$
11. Overall reaction equation: $2O_3 + \text{sunlight} \longrightarrow 3O_2$**;** Catalyst: **No** catalyst.

12.

(a) $O_3 + O \longrightarrow 2O_2$ (Hint: take step 1 + step 2)
(b) Cl

Justification

Cl is used in the step 1 and regenerated in step 2 thus its amount at the end of the reaction is the same as its amount the beginning of the reaction.

(c) ClO

ClO is the product of the step 1 which is consumed as the reactant in the step 2 and therefore it does not appear in the overall reaction equation.

13. Raising the temperature will drive the fast equilibrium step (step 1) towards the left, decreasing the concentration of B which is required for step 2. The decrease in concentration of B will in turn decrease the rate of the second reaction (step 2), and hence the rate of the overall reaction (A $\longrightarrow$ products) will decrease as the temperature rises.

14.

(a) $R = k[NO_2][CO]$
(b)

Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$; (Slow)

Step 2: $NO_3 + CO \longrightarrow CO_2 + NO_2$; (Fast)

15. (a)

(i) **Kinetic energy of particles.** To be effective, the colliding particles must have certain minimum energy which is known as activation energy.
(ii) **The orientation of particles.** To be effective, the colliding particles must have good orientation relative to one another. Even very energetic collision (collisions with kinetic energy greater than activation energy) may not lead to reaction if the particles are not oriented properly.

(b) Decrease in temperature, would decrease the rate of reaction
Explanation

Decrease in temperature lowers the kinetic energy of molecules and therefore:

- Collisions between particles become less energetic (fewer colliding particles will attain activation energy)
- Frequency of collision will be decreased (due to decrease of the speed).

(c) Slowest step, is the rate determining step in the reaction mechanism.
In the given mechanism, the slowest step is: $AB + B \longrightarrow C + D$
Thus the rate law of the above step, is the rate law of the overall reaction

That is; $R = K[AB][B]$…………………. (i)

But the overall reaction equation of the overall mechanism is;

$A + 2B \longrightarrow C + D$ (Obtained by adding the two given steps in the mechanism)

And the equation has no AB; so AB in $R = K[AB][B]$ must be eliminated by using the fact that:

In $A + B \rightleftharpoons AB$

$R_f = K_f[A][B]$ and $R_b = K_b[AB]$

But at equilibrium: $R_f = R_b$

That is $K_f[A][B] = K_b[AB]$

From which $[AB] = \frac{K_f}{K_b}[A][B]$ ………………. (ii)

Substituting (ii) in (i) gives;

$R = \frac{K \times K_f}{K_b}[A][B][B] = \frac{K \times K_f}{K_b}[A][B]^2$

But $\frac{K \times K_f}{K_b}$ gives another constant, say k'

Thus $R = k[A][B]^2$

Hence the rate law expression for the reaction is $R = K[A][B]^2$

(d) Catalyst lower activation energy by providing alternative route for the reaction.

The value of k increases with temperature due to increasing number of collisions between reactants are occurring with sufficient energy to form activated complex as the temperature increases.

16.

(a) $R = k[A]^2[B]$

(b) $K = 0.12$, units: $L^2mol^{-2}min^{-1}$

(c)

$A + B \rightleftharpoons AB \ldots\ldots\ldots\ldots\ldots\ldots\ldots fast$

$AB + A \longrightarrow C + P \ldots\ldots\ldots\ldots\ldots slow$

$P + B \longrightarrow D \ldots\ldots\ldots\ldots\ldots\ldots\ldots fast$

Alternative possible mechanism

$A + A \rightleftharpoons A_2 \ldots\ldots\ldots\ldots\ldots\ldots fast$

$A_2 + B \longrightarrow C + P \ldots\ldots\ldots\ldots slow$

$P + B \longrightarrow D \ldots\ldots\ldots\ldots\ldots\ldots fast$

17.

(a) Step 2

(b) From step 2: $R = k[N_2O_2]\,[H_2]$

Eliminating $[NO_2O_2]$ by assumption that step 1 forms rapid equilibrium;

That is $k_f\,[NO]^2 = k_b[N_2O_2]$

From which $[N_2O_2] = \frac{K_f}{K_b}\,[NO]^2$

Then $R = \frac{k\times k_f}{k_b}[NO]^2[H_2]$

But $\frac{k\times k_f}{k_b} = k'$ (It gives modified another constant)

Thus $R = k'\,[NO]^2\,[H_2]$ and hence the given mechanism is constant with observed rate law

Given that:

$NO + NO \longrightarrow N_2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$

$N_2O_2 + H_2 \longrightarrow H_2O + N_2O \ldots\ldots\ldots\ldots (ii)$

$N_2O + H_2 \longrightarrow N_2 + H_2O \ldots\ldots\ldots\ldots\ldots (iii)$

Taking (i) + (ii) + (iii)

$NO + NO + N_2O_2 + H_2 + N_2O + H_2 \longrightarrow N_2O_2 + H_2O + N_2O + N_2 + H_2O$

Cancelling like terms in opposite sides of the equation gives;

$NO + NO + H_2 + H_2 \longrightarrow N_2 + H_2O + H_2O$

Or (by combining like terms)

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ and hence the given mechanism is consistent with the overall stoichiometry of the reaction.

18.

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

Step 2: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$ (fast)

Intermediate is IO^-

19.

(i) Three

(ii) Two

(iii) Second step (has highest activation energy)

(iv) Third step (has lowest activation energy

(v) Endothermic

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

(a) Because the chances that three particles colliding at the same time, with proper orientation and sufficient energy, are extremely small.

(b) $R = k[A]^x[B]^y$

$R_1 = 5.02 \times 10^{-4} = k[0.1]^x[0.1]^y$

$R_2 = 2.51 \times 10^{-4} = k[0.1]^x[0.05]^y$

$R_3 = 1.251 \times 10^{-4} = k[0.05]^x[0.05]^y$

$$\frac{R_1}{R_2} = \frac{5.02 \times 10^{-4}}{2.51 \times 10^{-4}} = \left(\frac{0.1}{0.05}\right)^y$$

$2^1 = 2^y$ or $y = 1$

$$\frac{R_2}{R_3} = \frac{5.02 \times 10^{-4}}{2.51 \times 10^{-4}} = \left(\frac{0.1}{0.05}\right)^2$$

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

(i) So the order of reaction with respect to A is 1 and the order of reaction with respect to B is 1

(ii) Substituting obtained values for x and y in R_1
$5.02 \times 10^{-4}Ms^{-1} = k \times 0.1M \times 0.1M$ from which $k = 0.0502M^{-1}s^{-1}$

(iii) From the simplified Arrhenius equation:

$\log k_1 = -\frac{E_a}{2.303RT_1} + \log A$…………………………….. (i)

And $\log k_2 = -\frac{E_a}{2.303RT_2} + \log A$……………………….. (ii)

Take (ii) − (i) give $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

Where $k_2 = 6.71\ M^{-1}\ sec^{-1}, k_1 = 0.0502M^{-1}sec^{-1}$

$T_2 = 342K, T_1 = 298K$ and $R = 8.314$

Then $\log\left(\frac{6.71}{0.0502}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{342-298}{342 \times 298}\right)$ or $E_a = 94289J/mol$ or $94.289kJ/mol$

Hence the activation energy of the reaction is $94.289kJ/mol$

(iv) From $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

Then $\log\left(\frac{k_2}{0.0502}\right) = \frac{94289}{2.303 \times 8.314}\left(\frac{310-298}{310 \times 298}\right)$

From which $k_2 = 0.219M^{-1}\ Sec^{-1}$

Question 2

(a)

(i) **True:** Increase in temperature tends to increase frequency of collision between reacting particles and make the collision more energetic. It also increases the value of rate constant. These facts make increase number of reacting particles which attain activation energy and hence the rate of reaction is increased.

(ii) **False:** Most of the reactions are positively catalysed thus leading to increase the rate of reaction by lowering the activation energy. However, for negative catalysed reactions the rate of reaction is decreased by increasing activation energy thus making the statement true in few cases.

(iii) **False:** The rate of zero order chemical reaction is independent to concentration.

(b) Using: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

Where $k = 2.2 \times 10^{-5}sec^{-1}$

$t = 1hour = 3600sec$

$$\text{Then } \log\left(\frac{a}{a-x}\right) = \frac{2.2 \times 10^{-5} \times 3600}{2.303} = 0.034$$

It follows that; $\frac{a}{a-x} = \log^{-1}(0.034) = 1.08$

Then $\frac{a-x}{a} = \frac{1}{1.08} = 0.92 =$ Fraction of undecomposed sample

Thus undecomposed percentage of the sample is $0.92 \times 100\% = 92\%$

Hence the percentage decomposition of the sample after 1hour $= (100 - 92)\% = 8\%$

Question 3

(a)

1. Unimolecular elementary reactions.
2. Bimolecular elementary reactions.
3. Termolecular elementary reactions.

(b) $R = k[A]^x[B]^y$

Then

$R_1 = 5.02 \times 10^{-4} = k[0.1]^x[1]^y$ ………………..………………………….. (i)

$R_2 = 1.004 \times 10^{-3} = k[0.2]^x[1]^y$ ……………….……………………… (ii)

$R_3 = 2.000 \times 10^{-3} = k[0.2]^x[2]^y$ ………………………………………… (iii)

$$\frac{R_2}{R_1} = \frac{1.004 \times 10^{-3}}{5.02 \times 10^{-4}} = \left(\frac{0.2}{0.1}\right)^x$$

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

$$\frac{R_3}{R_2} = \frac{2.008 \times 10^{-3}}{1.004 \times 10^{-3}} = \left(\frac{2}{1}\right)^y$$

$2^1 = 2^y$ or $y = 1$

Overall order is $(x + y) = 1 + 1 = 2$

Hence the reaction is of the second order

Question 4

(a) Activation energy minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy.
That is; Activation energy = Threshold energy – Average energy

(b) $R = k[HgI_2]^x[C_2O_4^{2-}]^y$

$R_1 = 0.502 \times 10^4 = k[0.0836]^x[10.202]^y$ ………………..……….………….. (i)

$R_2 = 2.08 \times 10^4 = k[0.0836]^x[0.404]^y$ ……………….……………………… (ii)

$R_3 = 1.06 \times 10^4 = k[0.0418]^x[0.404]^y$ ………………………………………… (iii)

$$\frac{R_2}{R_1} = \frac{2.08 \times 10^4}{0.502 \times 10^4} = \left(\frac{0.404}{0.202}\right)^y$$

$4 = 2^y$

$2^2 = 2^y$ or $y = 2$

$$\frac{R_2}{R_3} = \frac{2.08 \times 10^4}{1.06 \times 10^4} = \left(\frac{0.0836}{0.0418}\right)^x;\ 2^1 = 2^x \text{ or } x = 1$$

(i) The order of the reaction with respect to $C_2O_4^{2-}$ is 2 and the order of the reaction with respect to HgI_2 is 1.

(ii) Rate law expression for the reaction is obtained by substituting obtained values of x and y in $R = k[HgI_2]^x[C_2O_4^{2-}]^y$
So the rate law expression for this reaction is $R = k\,[HgI_2]\,[C_2O_4^{2-}]^2$

(iii) Substituting values for *x* and y in R_1

$0.52 \times 104\text{mol dm}^{-3}\text{ min}^{-1} = k\,(0.0836\text{moldm}^{-3})\,(0.202\text{moldm}^{-3})^2$

From which $k = 1524384\text{dm}^6\text{ mol}^{-2}\text{min}^{-1}$

The value of rate constant is 1524384 $\text{dm}^6\text{ mol}^{-2}\text{ min}^{-1}$

(iv) Overall order of the reaction $= x + y = 1 + 2 = 3$

Thus the reaction is of the third order

Question 5

(a) It increases frequency of collision between reacting particles.

(b) Checking whether the reaction is of first order or not by calculation of rate constants:

From the equation of first order chemical reaction: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

From which $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

And initial concentration, $a = 1.0023\text{M}$

Time/Min	(a – x) or $[C_{12}H_{12}O_{11}]/M$	$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$
30.00	0.9022	3.51×10^{-3}
60.00	0.8077	3.59×10^{-3}
90.00	0.7253	3.59×10^{-3}
130.00	0.6300	3.57×10^{-3}
160.00	0.5010	3.47×10^{-3}
200.00	0.5020	3.47×10^{-3}

(i) From the above it has been shown that the rate constant at different time in the reaction course is the same. Thus the reaction obeys the first order equation and hence the reaction is of the first order.

$$k = \frac{k_1 + k_2 + k_3 + k_4 + k_5 + k_6}{6}$$

$$k = \frac{(3.51 + 3.59 + 3.57 + 3.47 + 3.59 + 3.47) \times 10^{-3}}{6} = 3.53 \times 10^{-3}\text{min}^{-1}$$

Thus the rate constant, $k = 3.53 \times 10^{-3}\text{min}^{-3}$

For first order chemical reaction, $t_{1/2} = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{3.53 \times 10^{-3}} = 196.3 \text{ minutes}$$

Hence the half-life for the reaction is 196.3 minutes

(ii) Substituting $t = 4\text{hours} = 240\text{minutes}$ and $a = 1.0023\text{M}$ to $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

$$\log\left(\frac{1.0023}{a-x}\right) = \frac{3.53 \times 10^{-3} \times 240t}{2.303}$$

From which $(a - x) = 0.43\text{M}$

So concentration of $C_{12}H_{12}O_{11}$ after 4hours is 0.43M

Question 6

(a) The spark initiates combustion of coal by providing heat required for overcoming activation energy of the reaction. The reaction being exothermic, once initiated it produces more heat to enable more combustion of unreacted coal. Adding the fact that the coal is in the form of dust which has large surface area, the reaction is very fast, and as consequence of these facts, an explosion results.

(b) Half-life for first order chemical reaction is given by: $t_{1/2} = \frac{0.693}{k}$ or $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1590\text{yr}} = 4.35849 \times 10^{-4}\text{yr}^{-1}$

Using $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

From which $t = \frac{2.303}{k}\log\left(\frac{a}{a-x}\right)$ where $a = 100$ and $a - x = 25$

Then $t = \frac{2.303}{4.3589 \times 10^{-4}}\log\left(\frac{100}{25}\right) = 3181.25$

Hence it will take about 3180years for given sample to decay to 25%

Question 7

(a) Activation energy of combustion of coal is too high to be achieved at room temperature.

(b) For first order chemical reaction: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{300\text{sec}} = 2.31 \times 10^{-3}\text{sec}^{-1}$

Using first order equation: $t = \frac{2.303}{k}\log\left(\frac{a}{a-x}\right)$

With t = 1200seconds, a = 100 (initially was 100% of the isotope)

It follows that: $\log\left(\frac{100}{a-x}\right) = \frac{2.31 \times 10^{-3} \times 1200}{2.303}$

From which $(a - x) = 6.25$

Thus 6.25% of the isotope will remain after 1200seconds

Question 8

(a) This may occur if:

1. The collision has insufficient energy to overcome activation energy of the reaction.
2. Particles in the collision have improper orientation for the reaction to take place.

(b) Using $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Where $k_1 = 4.46 \times 10^{-5}\ /s, k_2 = 1.5 \times 10^{-3}/s$

$T_1 = 293K, T_2 = 328K, R = 8.314$

$$\log\left(\frac{1.5 \times 10^{-3}}{4.46 \times 10^{-5}}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{328 - 293}{293 \times 328}\right)$$

From which $E_a = 80269 J/mol$ or $80.269 kJ/mol$

Activation for the reaction is $80.269 kJ/mol$

Question 9

(a) No;

Explanation:

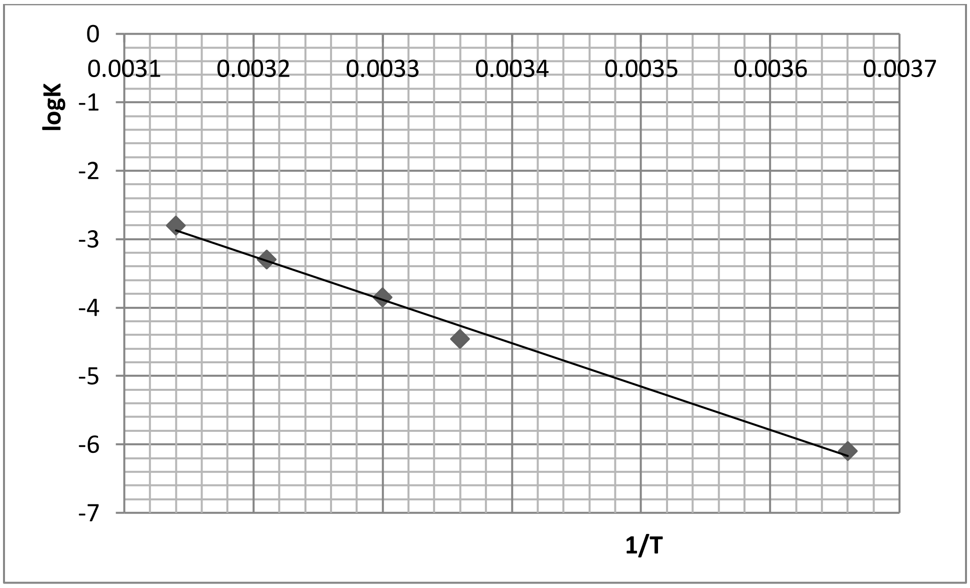
Reaction rates are compared in moles (not mass). Although the same mass of two elements is formed over the same time, the number of moles of aluminium is greater than that of iron because aluminium has smaller atomic mass. Hence, the rate of formation of aluminium is greater than that of iron.

(b)

TABLE OF RESULTS

Temperature (k)	K (sec^{-1})	Log k	$\frac{1}{T}(K^{-1})$
273	7.9×10^{-7}	- 6.1	3.66×10^{-3}
298	3.5×10^{-5}	- 4.46	3.36×10^{-3}
303	1.41×10^{-4}	- 3. 85	3.3×10^{-3}
312	5×10^{-4}	- 3.3	3.21×10^{-3}
318	1.5×10^{-3}	- 2.8	3.14×10^{-3}
320	4.9×10^{-3}	- 2.3	3.125×10^{-3}

Graph of log k against $\frac{1}{T}$



Hints:

(i) To find activation energy:

- Firstly, find the slope of the graph, (m) by taking any two points from the graph (not given specific given points). In finding the slope don't forget to multiply the factor of 10^{-3} on denominator
- Then take $m = -\frac{E_a}{2.303R}$ where $R = 8.314J\ mol\ K^{-1}$

(ii) To find Arrhenius factor

With obtained value of activation energy (E_a) and any one point on the graph; substitute them on simplified Arrhenius equation $\log k = -\frac{E_a}{2.303RT} + \log A$ to get A

Question 10

(a) Half-life of zero order reaction varies inversely proportional to initial concentration of reactant while that of second order varies directly proportional to the initial concentration.

(b) $T_1 = 317°C = 590K;\ T_2 = 427°C = 700K$

$K_1 = 1.4 \times 10^{-3}\ dm^3\ mol^{-1}\ sec^{-1}, K_2 = 6.4 \times 10^{-2}\ dm^3\ mol^{-1}\ sec^{-1}$

Using $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

$$\log\left(\frac{6.4 \times 10^{-2}}{1.4 \times 10^{-3}}\right) = \frac{E_a}{2.303 \times 8{,}314}\left(\frac{700-590}{700 \times 590}\right)$$

From which $E_a = 119339J/mol$ or $119.339kJ/mol$

The activation energy of the reaction is $119.339kJ/mol$

Question 11

(a) There are various method which can be used to deduce order of chemical reaction from the kinetic data. This includes:

- Graphical method,
- Half-life method,
- Integral method and
- Initial rate method

(b) $R = k[Z]^x[Y]^y$

Then:

$R_1 = 0.002 = k[0.1]^x[0.1]^y$…………………..…………...……………….. (i)

$R_2 = 0.00798 = k[0.1]^x[0.2]^y$…………………….…………………………. (ii)

$R_5 = 0.00601 = k[0.3]^x[0.1]^y$…………………………………………. (iii)

$$\frac{R_2}{R_1} = \frac{0.00798}{0.002} = \left(\frac{0.2}{0.1}\right)^y$$

$2^2 = 2^y$ or $y = 2$

$$\frac{R_5}{R_1} = \frac{0.00601}{0.002} = \left(\frac{0.3}{0.1}\right)^x$$

$3^1 = 3^x$ or $x = 1$

(c) Hence:

(i) The order of reaction with respect to Z is 1
(ii) The order of reaction with respect to Y is 2
(iii) The overall order $= x + y = 1 + 2 = 3$

Thus the reaction is of the third order

(d) Substituting values of *x* and *y* to (i) $0.002mol/dm^{-3}\ min^{-1} = k \times 0.1mol/dm^{-3} \times (0.1moldm^{-3})^2$

$$k = \frac{0.002}{0.001} = 2dm^6mol^{-2}min^{-1}$$

Hence:

(i) Rate constant is $2dm^6mol^{-2}min^{-1}$
(ii) Units of rate constant is $dm^6mol^{-2}min^{-1}$

Question 12

(a) For reaction (i):

- **Disappearance of purple colouration of $KMnO_4$** (*by noting the rate the change of the colour intensity*).
- **Formation of carbon dioxide ga**s (*by measuring the rate of increase of volume of the gas*)

For reaction (ii):

- **Formation of white precipitate of AgCl** (*by noting the rate of intensity of the colour formation*).
- **Disappearance of green colouration of $CuCl_2$** (*by noting the rate of the change of the colour intensity*).

(b) So using $t_{1/2} = \frac{0.683}{k}$ (half-life for first order chemical reaction)

From which $k = \frac{0.683}{t_{1/2}}$

Then rate constant at 27°C $= \frac{0.693}{5000}\,sec^{-1} = 1.386 \times 10^{-4}sec^{-1}$

Given that at 37°C: $t_{1/2} = 1000seconds$

Then rate constant at 37°C: $= \frac{0.693}{1000}sec^{-1} = 6.93 \times 10^{-4}sec^{-1}$

Using: $\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

From which $E_a = \frac{2.303RT_1T_2}{(T_1-T_2)}\log\left(\frac{k_1}{k_2}\right)$

Then $E_a = \frac{2.303\times 8.314\times 300\times 310}{(300-310)}\log\left(\frac{1.386\times 10^{-4}}{6.93\times 10^{-4}}\right) = 124464J/mol$

Hence the activation energy of the reaction is $124.464kJ/mol$

Question 13

(a)
(i) By increasing frequency of collision between reactants.
(ii) Not true.

Explanation

The extent of which reaction rate will increase after increasing the reactant concentration is determined by order of chemical reaction; it is not the same for all reactions. For example; zero order reaction, the reaction rate will remain the same even after doubling the concentration of reactant. Or in the second order reaction, doubling the concentration of reactant will make the reaction rate quadruple. The given statement holds for the first order reactions only.

(b) An equation for first order chemical reaction is $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

But volume of $KMnO_4$ used varies directly proportional to the concentration of undecomposed hydrogen peroxide

Thus if V_o is the volume of $KMnO_4$ used before decomposition of hydrogen peroxide and V_t is the volume of the manganate used after time, t then $\frac{a}{a-x} = \frac{V_o}{V_t}$

So in terms of volume of $KMnO_4$;

The equation: $k = \frac{2.303}{t}\log\left(\frac{V_o}{V_t}\right)$

Where $V_o = 75cm^3$

Volume of $KMnO_4$ used in cm^3	47	30	13	7.2
Time (minutes)	06	09	20	29
$k = \frac{2.303}{t}\log\left(\frac{V_o}{V_t}\right)$	0.0779	0.1018	0.0876	0.0808

If obtained values are written to one decimal place, they all give the same value of 0.1. That is the values are almost the same and hence the reaction is of the first order as it obeys first order equation.

The rate constant, $k = \frac{k_1+k_2+k_3+k_4}{4} = \frac{0.0779+0.1018+0.0876+0.0808}{4} = 0.0870min^{-1}$

The rate constant is $0.0870min^{-1}$

Question 14

(a)
(i) High activation energy means low reaction rate and vice-versa.
(ii) There are two factors which affect activation energy as explained below:
1. **Nature of reactants:** Usually ionic reactants have low activation energy while covalent reactants have high activation energy.
2. **Catalyst:** Positive catalysts decreases the activation energy while negative catalyst increases activation energy.

(b) $R = k[A]^x[B]^y$……………………………………………… (i)

$2R = k(2[A])^x[B]^y$……………………………………………… (ii)

(When concentration of B was kept constant while that of A doubled, the rate of reaction doubled)

$3R = k[A]^x(3[B])^y$…………………………………………… (iii)

(When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled).

(ii)÷ (i) Gives: $2^1 = 2^x$ or $x = 1$

(iii) ÷ (i) gives: $3^1 = 3^y$ or $y = 1$

Thus the reaction of first order with respect to both reactants A and B which can be deduced from the molecularity of reaction (1)

(i) Hence reaction (1) is rate determining step and
(ii) The rate law for the reaction is $R = k[A]\,[B]$

Question 15

(a) For a change in total pressure to affect the reaction rate, it must affect partial pressure of reactants. The addition of helium which is noble gas does not affect partial pressure of reactants (nitrogen and hydrogen gas) and thus the reaction rate remains unchanged keeping the rate of formation the same.
(b) Let rate law of the reaction to be: $R = k[G]^x[F]^y$

Then $3.1 \times 10^{-3} = 3.44 \times 10^{-4} \times 2^x \times 3^y$

$9 = (2^x)(3^y)$……………..……………………….. (i)

And $7.75 \times 10^{-4} = 3.44 \times 10^{-4} \times 1^x \times 1.5^y$

But $1^x = 1$

Then $1.5^y = \dfrac{7.75}{3.44}$ … … … … … … … … … … … … … … . (ii)

Then $y = \dfrac{\log\left(\frac{7.75}{3.44}\right)}{\log 1.5} = 2$

Substituting y = 2 to (i)

$9 = (2^x)3^2$ or $x = 0$

Then reaction is of the second order with respect to F and zero order with respect to G Overall order

$= x + y = 0 + 2 = 2$

Hence the overall order for the reaction is 2

Question 16

(a) Yes, it is possible.

Explanation

Activation energy may be altered by adding (or removing) catalyst. Adding positive catalyst to the chemical system of chemical reaction, decreases activation energy while adding negative catalyst, increases activation energy.

(b) (i) Reaction mechanism:

Initially; $OH + O_2 \rightarrow OOH + O$…………………………………………… (i)

Then; $O + NO \rightarrow NO_2$ ……………………………………………….….. (ii)

Finally; $OOH + CO \rightarrow CO_2 + OH$…………………………………………. (iii)

Adding (i),(ii) and (iii) and then cancelling like terms:

$\cancel{OH} + O_2 + \cancel{O} + NO + \cancel{OOH} + CO \rightarrow \cancel{OOH} + \cancel{O} + NO_2 + CO2 + \cancel{OH}$

Hence the overall reaction is $NO + CO + O_2 \rightarrow NO_2 + CO_2$

(ii) *Intermediates are molecular entities which are formed from reactants (or another intermediates) and react further to give product either directly or indirectly*

Thus from above reaction, intermediates are OOH and O

(iii) OH is catalyst because initially participated in converting oxygen molecule into more reactive oxygen atom and finally it was regenerated (remain unchanged)

Question 17

(a) Zinc powder has greater surface area and thus it enables to achieve faster reaction than zinc wire.
(b) Disintegration of an isotope as result of its decomposition is the first order chemical reaction.

For first order chemical reaction, $t_{1/2} = \frac{0.693}{k}$ or $k = \frac{0.693}{3\text{days}}$

But $1\text{day} = 60 \times 60 \times 24\text{seconds}$

So $3\text{days} = 3 \times 60 \times 60 \times 24\text{seconds}$

Then k in $\sec^{-1} = \frac{0.693}{3 \times 60 \times 60 \times 24} = 2.6736 \times 10^{-6}\sec^{-1}$

(i) The rate constant is $2.6736 \times 10^{-6}\sec^{-1}$

From $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

$t = \dfrac{2.303}{2.6736 \times 10^{-6}}\log\left(\dfrac{0.031}{0.001}\right)$ seconds or 14.87 days

(ii) Thus 14.87days are required to x – 210 to disintegrate from 0.031mg to 0.001mg

Question 18

(a) As the reaction proceeds, concentration of reactants decreases while concentration products are increases. Hence like velocity, reaction rate may take both negative values (for reactants) and positive values (for products) unlike speed which takes positive values only.

(b)

(i) Rate equation is deduced from stoichiometric coefficients of reactants of the slowest step which is the rate determining step whereby concentration of each reactant in the equation is raised to the coefficient.
Rate equation is $R = k[Z][W]$

(ii) In the slow step, **two** molecules react (collide);

Hence the molecularity of the slow step is 2.

Question 19

(a) By providing alternative mechanism with lower activation energy.

(b) From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

Thus the slope of the graph logk against $\frac{1}{T}$, m is given by: $m = -\frac{E_a}{2.303R}$

Or $E_a = -2.303mR$

But $m = -9.8 \times 10^3 K$

And $R = 8.314 Jmol^{-1}K^{-1}$

So $E_a = -2.303 \times 9.8 \times 10^3 \times \frac{8.314J}{mol} = 187.6kJ/mol$

The value of activation energy is 187.6kJ/mol

(ii) Using $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

With $T_1 = 409K, T_2 = 389K$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{187.6 \times 10^3}{2.303 \times 8.314}\left(\frac{389 - 409}{409 \times 389}\right)$$

From which $\frac{k_2}{k_1} = 0.0587$

Thus the new rate constant is 5.87% of the original rate constant and hence the rate constant is decreased by 94.13% when the temperature is lowered from 409K to 389K

Question 20

(a) From given data:

- When concentration of B is doubled while that of A is kept constant, the rate of reaction is doubled and hence the reaction is of the first order with respect to B.
- When concentration of A is doubled while that of B is kept constant, the rate of reaction is doubled and hence the reaction is of the first order with respect to A.

(i) Hence the rate equation for the reaction is: $R = k[A][B]$

(ii) From (i) above $R = k[A][B]$

So using data of first row in a given table:

$1 \times 10^2 Msec^{-1} = k(2 \times 10^{-2}M)(1 \times 10^{-2}M)$

From which $k = 5 \times 10^5 M^{-1} sec^{-1}$

(b) $\Delta H^\theta = E_{af} - E_{ab}$

Where ΔH^θ is the standard heat of reaction

E_{af} is the activation energy for forward reaction

E_{ab} is the activation energy for backward reaction

Then $50 = 200 - E_{ab}$

$E_{ab} = (200 - 50)kJ/mol = 150kJ/mol$

Activation energy of backward reaction is 150kJ/mol

Question 21

(a) An increase in concentration of that reactant, decreases rate of the chemical reaction.

(b) $R = k[X]^m[Y]^n$ ………………………………………………….. (i)

When [X] is increased to 3 [X] the rate of reaction, R become 9R

That is $9R = k(3[X]^m[Y]^n$ ……………………………… (ii)

Taking (ii) $\div$ (i) gives; $9 = 3^2 = 3^m$ or $m = 2$

Hence the reaction is of the second order with respect to X.

Question 22

(a) The initial rate will decrease to one-third.
(b) $R = k[A][B]$ (Second order chemical reaction)

Substituting given values:

$8 \times 10^{-3}\,\text{moldm}^{-3}\,\text{sec}^{-1} = k \times 0.2\,\text{moldm}^{-3} \times 0.2\text{moldm}^{-3}$

$k = 0.2\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$

Question 23

(a) The evidences are:
1. Exothermic reactions may be slow. Example, rusting of iron.
2. Exothermic reaction may not start without suitable initiating conditions. Example, wood does not burn (combust) at room temperature unless it is ignited.

(b) $R = k[CH_3\,CHO]^x$

$R_1 = 1.04 = k(0.46)^x$

$R_2 = 2.05 \times 10^{-4} = k(0.2)^x$

Then $\frac{R_1}{R_2} = \frac{1.04}{2.05\times10^{-4}} = \left(\frac{0.46}{0.2}\right)^x$

$5073.17 = 2.3^x$

Introducing logarithms to base ten both sides gives; $x = \frac{\log(5073.17)}{\log(2.3)} = 10$

Thus the reaction is of tenth order and its rate law is: $R = k[CH_3\,CHO]^{10}$

From which $k = \frac{R}{[CH_3\,CHO]^{10}}$

When $[CH_3\,CHO]$ is equivalent to pressure of 0.46atm, $R = 1.04\text{atmsec}^{-1}$

Then $k = \frac{1.04\text{atmsec}^{-1}}{(0.46\text{atm})^{10}} = 2451.63\text{atm}^{-9}\text{sec}^{-1}$

The rate constant for the reaction is $2451.63\text{atm}^{-9}\text{sec}^{-1}$

Question 24

(a)

Substance added to an excess of zinc and 100 cm^3 of 0.2M HCl	Volume of hydrogen $/cm^3$	Effect on initial rate of reaction
100 cm^3 water	240	Decreased
10g zinc	240	No change
50 cm^3 0.2M hydrochloric acid	360	No change

If you have not got how the above table has been filled, the explanation below will be of big help to you!

- $100cm^3$ water decrease concentration of HCl but does not change number of moles of it. So because number of mole of HCl remain unchanged ($240cm^3$). Also because concentration of HCl is decrease (after dilution of $100cm^3$ water), the rate of reaction will be decreased.
- 10g zinc has no effect on both volume of H_2 produced and rate of chemical reaction because zinc is already present in excess. More addition of it (10g zinc) is just increasing amount of unreacted zinc.
- $50Cm^3$ 0.2MHCl (1×10^{-2} mol of HCl) is the half amount of $100cm^3$0.2MHCl (2×10^{-2} mol of HCl) originally used in the reaction mixture which produced $240cm^3$ of H_2. So this extra amount of HCl will produce extra $1/2 \times 240cm^3$ or 120 cm^3 of hydrogen gas making a total of $360cm^3$ ($240cm^3 + 120cm^3$) produced. However the concentration of HCl remain unchanged (it is still 0.2MHcl) and therefore the rate of chemical reaction remain unchanged too.

(b) If $R = K[A]^m[B]^n = 5 \times 10^{-5}$

$R_1 = K(0.16)^m\,(0.2)^n = 5 \times 10^{-5}$

$R_2 = K(0.24)^m\,(0.2)^n = 7.5 \times 10^{-5}$

$R_3 = K(0.32)^m\,(0.1)^n = 5 \times 10^{-5}$

$\frac{R_2}{R_1} = \frac{(0.24)^m\,(0.2)^n}{(0.16)^m\,(0.2)^n} = \left(\frac{0.24}{0.16}\right)^m = \frac{7.5\times10^{-5}}{5\times10^{-5}}$

From which $\left(\frac{3}{2}\right)^m = \left(\frac{3}{2}\right)^1$ or $m = 1$

Hence the order of reaction with respect to A is 1

$\frac{R_3}{R_2} = \frac{K(0.32)^m\,(0.1)^n}{(0.26)^m\,(0.2)^n} = \frac{5}{7.5}\left(\frac{0.32}{0.24}\right)^m\left(\frac{0.1}{0.2}\right)^n = \frac{5\times10^{-5}}{7.5\times10^{-5}}$

From which $\left(4/3\right)^1\left(\frac{1}{2}\right)^n = 2/3$

Then $\left(\frac{1}{2}\right)^n = {}^2/_3 \times {}^3/_4 = {}^1/_2$ or n = 1

Hence the order of reaction with respect to B is 1

Thus the rate equation is $R = k[A][B]$

Then $R_4 = k(0.12)(0.15)$

And $R_3 = k(0.32)(0.1) = 5 \times 10^{-5}$

So $\frac{R_4}{R_3} = \frac{0.12\times0.15}{0.32\times0.1} = \frac{R_4}{5\times10^{-5}}$: $R_4 = 2.8 \times 10^{-5}$

Hence the rate of the fourth experiment is $2.8 \times 10^{-5} Ms^{-1}$

Question 25

(i) The intermediate, firstly is formed as product and then is consumed as reactant while the catalyst, firstly is used as reactant and then is regenerated as product.

(ii) Using $R = k[N]^n$ where n is the overall order of reaction

From which $k = \frac{R}{[N]^n}$

Thus units of $k = \frac{\text{units of R}}{(\text{units of}[N]^n)} = \frac{Ms^{-1}}{M^n} = s^{-1}$

Then $M^{1-n}\ s^{-1} = s^{-1}$ or $M^{1-n} = 1$ or M°

Then $1 - n = 0$ or $n = 1$

Hence the overall of the reaction is 1

T is greater than 700K because the rate constant at T is greater than rate constant at 700K and the value of rate constant increase with the increase in temperature.

Question 26

(a) Does not affect.

Explanation

Titration experiments involve reactions between liquid solutions. Since liquids are incompressible, pressure has no effect in such reactions and hence the time taken to observe end-point is not affected by pressure.

(b) Five times the average molecular energy $5 \times 1.3kJ/mol = 6.5KJ/mol = 6500J/mol$

Fraction of miles with energy equal to or greater than 6500J/mol

$$e^{-E/RT} = e^{\frac{-6500}{8.314\times298}} = 0.0725$$

But total number of molecules $= nN_A = 1mol \times 6.02 \times 10^{23}$ molecule/mol $= 6.02 \times 10^{23}$ molecules

Thus number of moles with energy equal to or greater than 6500J/mol

$$= 0.0725 \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 4.3645\times 10^{22} \text{molecules}$$

Hence the number of molecules is 4.3645×10^{22} molecules

Question 27

(a) The initial rate will increases

Explanation:

Addition of hydrogen gas increases its concentration thus increasing the frequency of collision between hydrogen and iodine molecules.

(b) The initial rate will decrease

Explanation

Increase in volume of reaction vessel decreases concentration of the reactants ($H_2(g)$ and $I_2(g)$) and thus the frequency of collisions between them is decreased.

(c) The initial rate will increase

Explanation

The catalyst provides the alternative route of the reaction which has lower activation energy.

Refer to the text for the diagram.

(d) The initial rate will increase

Explanation

Increase in temperature:

- Increases number of molecules with kinetic energy greater than activation energy (In other words it makes collisions between reactant more energetic).
- Increases frequency of collisions between reactants (because the speed of particles increases with increase in temperature).

Refer to the text for the diagram.

Question 28

(a)

(i) The reaction is second order with respect to Cl^-

Justification:

Tripling $[Cl^-]$ between trials 1 and 2 with no change in $[MnO_4^-]$ or $[H^+]$ results in a nine-fold increase in the rate. (Alternatively you may justify by using calculation –just show the calculation of deducing the order of the reaction).

(ii) The reaction is first order with respect to $[MnO_4^-]$

Justification;

Doubling $[MnO_4^-]$ between trials 3 and 2 with no change in $[Cl^-]$ or $[H^+]$ results in a doubling of the rate.

(b)

(i) $\text{Rate} = K[Cl^-]^2\,[Mno_4^-]\,[H^+]^3$

(ii) $1.93 \times 10^{-3}\ M^{-5}s^{-1}$

(c) It is not single step reaction

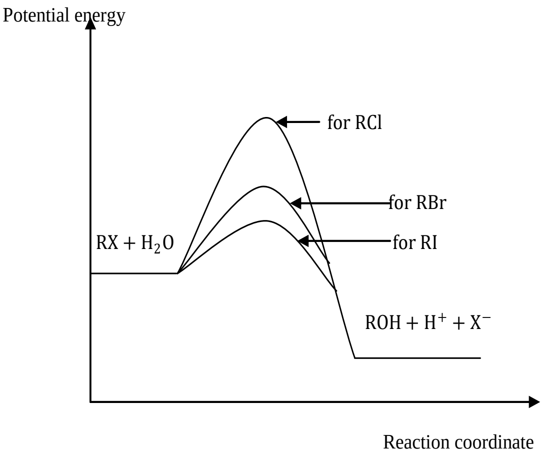
Justification

- The orders of the reaction with respect to reactants do not correspond to the coefficients in the balanced equation
- The reaction requires the simultaneous collision of many reactant particles which is practically impossible

Question 29

(a) $R = k[RX]$

(b)



Note:

The overall reaction equation which is $RX + H_2O \longrightarrow ROH + H^+ + X^-$ is obtained by combining (through addition) the given two steps in the question.

Question 30

(a) Increase in pressure; decrease the volume of gaseous reactants (($C_2H_4$and H_2) thus increasing their concentrations. The increase in concentration leads to more frequent collisions between C_2H_4 and H_2 and hence the reaction rate is increased

(b) Increase in temperature increase frequency of collision between C_2H_4 and H_2 through increasing their speed. It also increases the number of molecules (collisions) with activation energy through increasing their kinetic energy. As result, number of molecules with activation energy is increased making more collisions between C_2H_4 and H_2 result in the formation of activated complex and hence the rate of reaction is increased.

(c) Nickel is the catalyst for the reaction. It provides alternative route for the reaction with lower action and thus number of molecules with kinetic energy equal to or greater than activation energy is increased and hence the rate of reaction is increased.

(d) Powdered nickel has greater surface area than a single piece of nickel of the same mass. Greater surface area of catalyst means more catalytic sites and hence greater rate of the reaction.