

CHEMISTRY

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry

1) How fast? – Rates

a) *Demonstrate an understanding of the terms 'rate of reaction', 'rate equation', 'order of reaction', 'rate constant', 'half-life', 'rate-determining step', 'activation energy', 'heterogeneous and homogenous catalyst'*

i) Rate of (a chemical) reaction – the rate of change of concentration of a reactant or product with time / $\text{mol dm}^{-3} \text{s}^{-1}$

(1) Rate of reaction cannot be measured directly – can only be determined from concentration and time data

(2) Average rate of reaction =
$$\frac{\Delta \text{concentration (of reactant (decreases with time) or product)}}{\Delta \text{time}}$$

(3) This is only a reasonable assumption if the concentration of a reactant has fallen by less than 10% during the time elapsed

(4) For a reaction to take place, reactant molecules must collide with kinetic energy greater than or equal to the activation energy and with the correct orientation

ii) Rate equation – comes from experiments, showing us how rate depends on the concentration of each species

(1) For a reaction: $aA + bB \rightarrow cC + dD$, the rate equation could be $k[A]^a[B]^b$

(2) The subscripts are the stoichiometries in the chemical equation

(3) The superscripts are the partial orders of reaction

(4) E could be a catalyst (to be involved in the rate equation of a reaction, the species does not have to be a reactant or product necessarily)

iii) Overall order of reaction – sum of the powers to which the concentrations of reactants are raised in the experimentally determined rate equation (the total of the superscripts)

(1) Partial order of one reactant – the power to which the concentration of that reactant/species is raised in the experimentally determined rate equation

(2) Cannot be predicted from the chemical equation, depending on both the stoichiometry and the mechanism of the reaction – have to be found experimentally

iv) Rate constant – 'k' is the rate constant, which varies with...

(1) Orientation factor – the complexity of the geometry of the molecules eg. If only 1 in 10 collisions occurs with the correct orientation, constant orientation factor = 0.1

(2) The activation energy of the reaction – a large activation energy results in a large, negative exponent and therefore a small value for the rate constant

(3) The temperature – rise in temperature increases the 'RT' so the value for the exponential term is less negative and k gets larger, so the rate of reaction increases

(4) The presence of any catalyst – lowers the activation energy so the exponent becomes less negative and k gets larger, so the rate of reaction increases

v) Half-life – time taken for the concentration of a reactant to halve

vi) Rate-determining step – the slow step that is so slow compared to the subsequent fast step(s)

- (7) Angle of rotation of the plane of polarisation of the plane-polarised light gradually decreases as the single chiral isomer of 2-iodobutane is hydrolysed
- (8) Eg2. Rate of hydrolysis of sucrose by invertase to produce fructose and glucose – sucrose is dextrorotatory (rotates the plane clockwise) and the final mixture is laevorotatory (rotates the plane counter clockwise)

viii) Conductimetric analysis

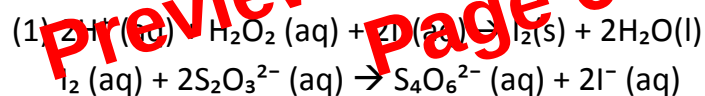
- (1) Measuring the conductivity changes in a reaction mixture over time
- (2) Reflect the changes in the ions present in the solution
- (3) Can be used to measure the changes in concentration of the various components of the mixture

ix) pH measurements

- (1) If one of the products in a reaction is an acid or an alkali and the reaction takes place in aqueous solution, the change in pH with time can be measured
- (2) Problem – pH is a logarithmic quantity
- (3) If the reactant is a strong acid and the starting concentration is 1.0mol dm^{-3} , the pH only changes by 1 unit (from 0 to 1) when 90% of the acid has reacted
- (4) The pH rises to 2 when 99% of the acid has reacted
- (5) This method requires a very accurate, and hence expensive, pH meter to monitor the change in acid concentration – unsuitable for school laboratory use

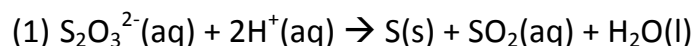
c) Investigate reactions, which produce data that can be used to calculate the rate of the reaction, its half-life from concentration or volume against time graphs, eg. A clock reaction

i) Iodine 'clock' reaction – monitor colour change to find the time taken to produce a fixed amount of product



- (2) Can compare the effect of altering the concentration of hydrogen peroxide – the reaction is repeated with consistent volumes of KI and sodium thiosulphate
- (3) A solution of hydrogen peroxide and sulphuric acid is added to a solution of iodide ions, thiosulphate ions and starch to oxidise the iodide ions
- (4) Iodine, formed slowly, reacts rapidly with thiosulphate until all of the thiosulphate is used up
- (5) The excess iodine then reacts with the starch to form a blue-black complex
- (6) Measure the time from the mixing of the solutions until the solution turns blue-black
- (7) The amount of iodine produced in the measured time is proportional to the volume of sodium thiosulphate solution taken
- (8) The average rate of reaction for each experiment is proportional to $1/\text{time}$

ii) Sulphur 'clock' reaction – sodium thiosulphate is decomposed by acid, producing a precipitate of sulphur



- (2) Can repeat the experiment with different relative amounts of sodium thiosulphate and water to vary the concentration of sodium thiosulphate

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