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 / moldm^{-3}s^{-1}

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

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

(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 → cC + dD, the rate equation could = k $[A]^a[B]^b[E]^e$

(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 1.0moldm^{-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

(1) $2H^+(aq) + H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(s) + 2H_2O(l)$

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

(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/time

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

(1) $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$

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